Chemical manipulation and analysis : qualitative and quantitative, with an introduction of the general principles of chemical nomenclature, the construction and use of formulæ, the doctrine of equivalent proportions, and on the preparation and management of gases / by Henry M. Noad.

Contributors

Noad, Henry Minchin, 1815-1877.

Publication/Creation

London : R. Baldwin, 1852.

Persistent URL

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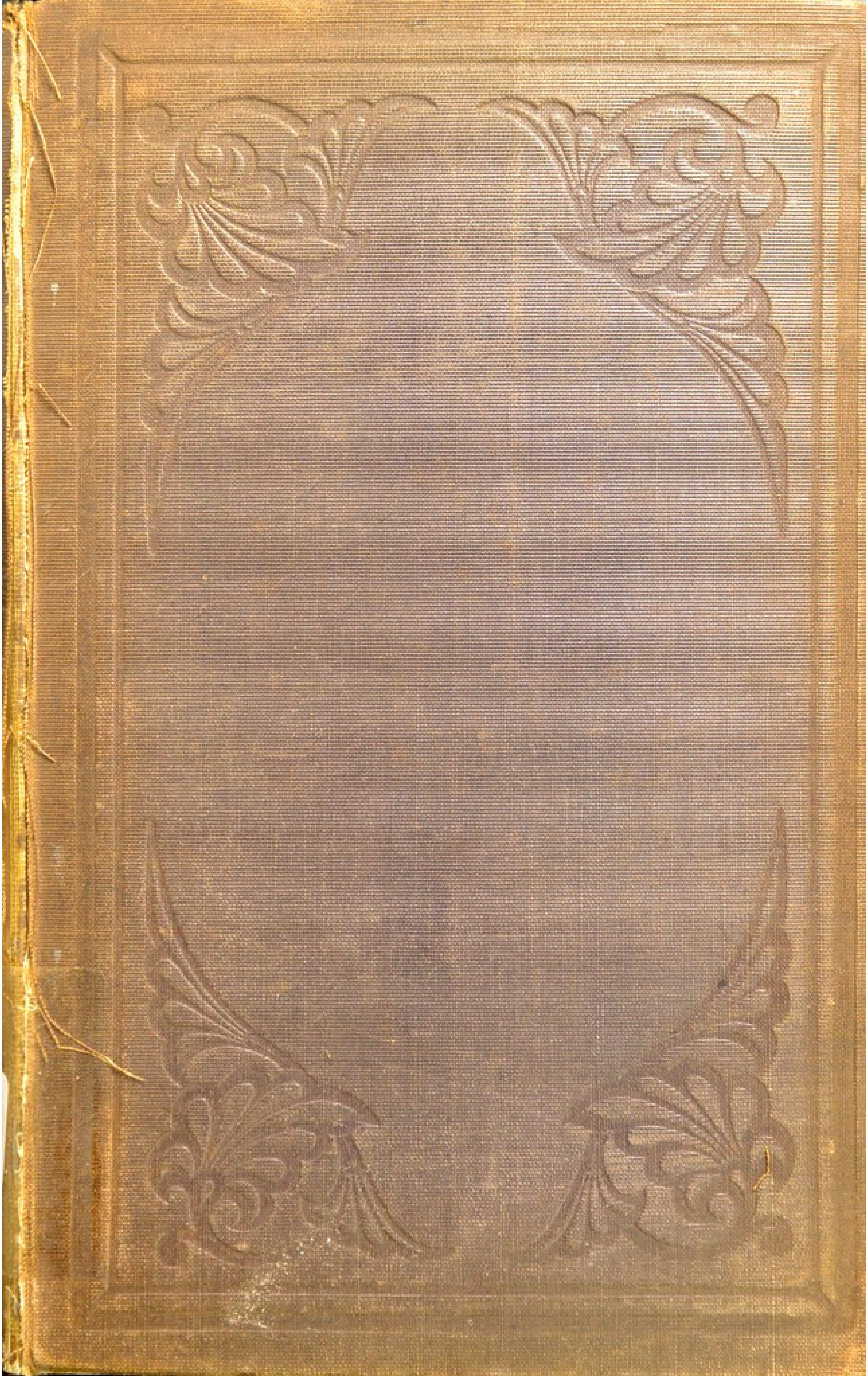

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CHEMICAL
MANIPULATION AND ANALYSIS,

QUALITATIVE AND QUANTITATIVE.

WITH
AN INTRODUCTION
EXPLANATORY OF
THE GENERAL PRINCIPLES OF CHEMICAL NOMENCLATURE;
THE CONSTRUCTION AND USE OF FORMULÆ;
THE DOCTRINE OF EQUIVALENT PROPORTIONS:
AND ON THE
PREPARATION AND MANAGEMENT OF GASES.

BY HENRY M. NOAD, PH. D.
LECTURER ON CHEMISTRY AT ST. GEORGE'S HOSPITAL;
AUTHOR OF "LECTURES ON ELECTRICITY," "LECTURES ON CHEMISTRY," ETC.

A New Edition, considerably enlarged.

LONDON:—ROBERT BALDWIN,
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1852.

LONDON:
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TO

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In the present Edition I have added to the Introduction a Chapter on the "Preparation and Management of Gases," and have described a series of Experiments, by the performance of which the Student may become practically acquainted with the properties of each of this interesting class of substances. I have also re-arranged the Analytical Tables on what, I hope, will be found a more convenient principle. Much additional matter relating to the quantitative determination of substances and their separation from each other, has also been added, bringing this portion of the work down to the latest possible period.

These additions and improvements, together with a copious Index which is also subjoined, will, I trust render the work an acceptable addition to Chemical Literature.

St. George's Hospital Medical School,
March 25th, 1852.

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OF THE IMPORTANT DOCTRINE OF EQUIVALENT PROPORTIONS;

OF CHEMICAL NOTATION AND THE CONSTRUCTION AND USE OF FORMULÆ; AND

OF THE GENERAL PRINCIPLES OF CHEMICAL NOMENCLATURE.

IN the course of this Work (page 139) will be found a Table containing the names of all those substances which are at present regarded by Chemists as Elementary. There are fifty-nine of these bodies, all of which have resisted every effort to resolve them into simpler forms of matter. Among them are found bodies of the most diverse characters, both physical and chemical; and out of them, as far as we yet know, everything solid, liquid, and gaseous, in and about the globe which we inhabit, is composed.

The names of these fifty-nine substances have not been assigned to them in accordance with any prescribed rule, the discoverer of each particular body following his own fancy in this respect, and being generally guided in his selection either by some marked peculiarity in the new substance, or by some circumstance connected with its discovery. Thus, *Mosander* having found in *oxide of cerium* a large proportion of the oxide of a hitherto unnoticed metal, he named the newly discovered body *Lantanium* or *Lanthanum*, from the Greek word λανθάνω, *I lurk*, it having lain concealed in the ores of cerium; and the name *osmium* was given to a peculiar metal found in the ores of platinum, from ὀσμὴ, *smell*, having reference to the disagreeable and pungent character of its vapour.

The names selected by their discoverers for some substances are indeed sufficiently eccentric; thus *Berzelius* derived the title of *Selenium*, which he conferred on a certain brittle opaque solid discovered by him in the sulphur of *Fahlun*, from Σελήνη, *the Moon*, in consequence of his having at first mistaken it for *Tellurium*, which derived *its* name from *tellus*, *the Earth*. But, whatever may be thought of the propriety of such names, they can lead neither to mistakes nor to confusion, and are in this respect far better than words more significantly chosen, and bearing reference to certain characteristic properties possessed, or supposed to be possessed by the substance. This method has rarely been successful: thus the name *oxygen*, proposed by *Lavoisier* for the *Dephlogisticated air* of *Priestley*, though at the time well chosen, has not stood the test of time. In *Lavoisier's* day this substance was supposed to be the sole cause of acidity, hence its name, from ὀξὺς, acid, and γεννᾷν, to generate; we now know, however, that this property of generating acidity is not peculiar to oxygen. Again, the same celebrated French Chemist proposed the name *azote* for that gas first noticed by *Rutherford*, and which we now call *nitrogen*—the word "azote" is derived from α, privative, and ζωὴ, life, and was suggested by the inability of the gas to support respiration; the term, however, was very unfortunate, there being several other gases in the same predicament, and equally fatal to animal life. The name *azote* is now abolished, that of *oxygen* is still retained, not because a better might not probably be found, but because it is inexpedient to make any change whatever in an old-established nomenclature, without cogent and well-considered reasons.

These fifty-nine elementary substances have been differently classified by different chemists; some divide them into two great classes, viz., *Electro-positive*, including all those bodies which, by their union with oxygen, form compounds the electro-chemical relations of which are decidedly *positive;* and *Electro-negative*, including those bodies which, by their union with oxygen, form compounds, the electrical characters of which are either decidedly *not* positive, or which may be regarded either as positive or negative. Other chemists arrange the elements into certain small groups or natural families, the members of each group being connected together by certain analogies, and the several groups shading into each other through the medium of certain links, like the classes created by the naturalist for the objects of the organic world; for a full exposition of this system of classification the reader may consult *Mr. Graham's* "Elements of Chemistry." Another division sometimes adopted is that into *combustibles* and *supporters of combustion;* but the most convenient is that founded on the physical properties of the elements in a free state—the division into *metalloids* and *metals*, the former comprising *oxygen*, *hydrogen*, *nitrogen*, *chlorine*, *bromine*, *iodine*, *fluorine*, *sulphur*, *selenium*, *tellurium*, *phosphorus*, *arsenic*, *carbon*, *boron*, and *silicon*, are, without exception, electro-negative; the metals, on the other hand, are nearly all electro-positive; those that are not so ought, according to *Berzelius*, to be ranked among the metalloids.

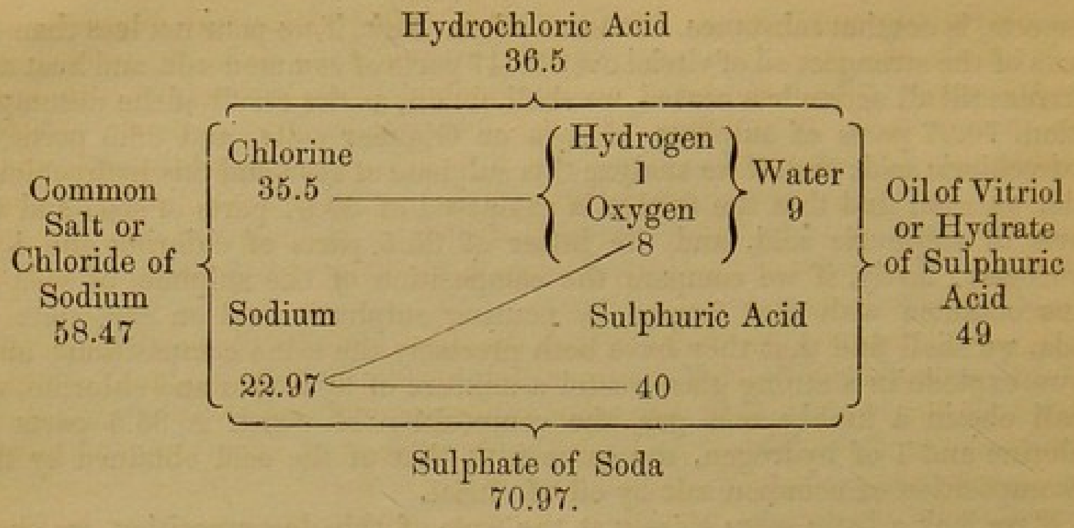
In the Table above referred to there will be seen, opposite to each element, certain letters and figures; these constitute its *symbol* and its *chemical equivalent:* the former is a very convenient method of representing a substance, and the constitution of the compound into which it enters; it is formed from the first letter or letters of the Latin name of the body, thus the metal *Tin* is written *Sn*, an abbreviation of the Latin word *Stannum; Mercury*, *Hg*, from the Latin *Hydrargyrum; Antimony*, *Sb*, from *Stibium*. When there is only one elementary substance with the same initial letter, that letter usually serves as its symbol, thus *F* suffices for *Fluorine*, and *H* for *Hydrogen;* but where there are several elements, the name of each of which commences with the same letter, then other letters are added to the initial letter in order to keep each substance distinct; thus there are no less than eight substances commencing with the letter *C*, viz., Carbon, Cadmium, Chlorine, Cerium, Chromium, Cobalt, Copper, and Calcium, the respective symbols for which are C, Cd, Cl, Ce, Cr, Co, Cu (*Cuprum*), and Ca.

The meaning of the term "equivalent," as applied to the numbers in the third and fourth columns of the Table, may be illustrated by the following:—Common culinary salt, wherever or however procured, whether by evaporation from the waters of the ocean or excavated from the mines of *Salzburg*, or formed artificially in the laboratory by pouring hydrochloric acid on carbonate of soda, has always the same composition, viz., 35.5 parts of chlorine and 22.97 parts of the metal sodium; and a substance not having this precise composition, however similar it may be to common salt in other respects, is not that substance, but some other. Now, if we pour not less than 49 parts of the strongest oil of vitriol over 58.47 parts of common salt, and heat the mixture till all action has ceased, we shall obtain, as the result of the decomposition, 70.97 parts of sulphate of soda or Glauber salts, and 36.5 parts of hydrochloric acid; and, if we analyze this sulphate of soda and this hydrochloric acid, we shall find that the former is composed of 30.97 parts of soda and 40 parts of sulphuric acid, and the latter of 35.5 parts of chlorine and 1 of hydrogen; lastly, if we compare the composition of the sulphate of soda as thus obtained with that formed by pouring sulphuric acid on carbonate of soda, we shall find that they have both precisely the same composition; and, if we explode in a strong glass vessel a mixture of hydrogen and chlorine, we shall obtain a highly acid gas, the composition of which is 35.5 parts of chlorine and 1 of hydrogen, the same with that of the acid obtained by the decomposition of common salt by oil of vitriol.

If we look a little more closely at the facts of this decomposition, we shall get a clear idea of what is meant by the term " equivalent." We have seen that 58.47 parts of common salt, when treated with 49 parts of oil of vitriol, yield 70.97 parts of sulphate of soda, a *perfectly neutral substance*, containing 40 parts of sulphuric acid, but not a trace of chlorine; it is easy, therefore, to understand that in this reaction 40 parts of sulphuric acid must have removed 35.5 parts of chlorine, and the term *equivalents*, as applied to these two numbers, cannot be misunderstood: 40 parts of sulphuric acid are *equivalent* to 35.5 parts of chlorine, and whenever chlorine replaces sulphuric acid, or sulphuric acid chlorine, in a compound, it is always in proportions indicated by these numbers.

Again, the oil of vitriol which we have employed in effecting the above decomposition of common salt contained a certain quantity of *water;* none of this compound is, however, found in dry sulphate of soda. What, then, has become of it? The sulphate of soda, though it contains no water, contains an element which is not found in common salt, viz., *oxygen;* and the acid gas which is evolved during the decomposition contains also an element which is not found in common salt, viz., *hydrogen;* but these two substances, when chemically combined, constitute water, and the analysis of this fluid shows its composition to be 8 parts by weight of oxygen to 1 part by weight of hydrogen; but these are the *very proportions* in which the former is found in the sulphate of soda combined with the 22.97 parts of *sodium*, and the latter in the hydrochloric acid gas combined with the 35.5 of chlorine. What do we deduce from these facts? Obviously this:—that, as 8 parts of oxygen are equally required by 22.97 parts of sodium, and by 1 part of hydrogen, 22.97 parts of *sodium* must be *equivalent* to 1 part of *hydrogen;* and, whenever sodium replaces hydrogen, or hydrogen sodium, the change must be effected in accordance with these proportions. Similarly as 22.97 parts of sodium and 1 part of hydrogen are equally saturated by 35.5 parts of chlorine, so 35.5 must be the proportion in which chlorine replaces 22.97 of sodium and 1 of hydrogen; in other words, 35.5 must be the " equivalent " of chlorine, and, on the same principles, 8 must be the " combining equivalent " of oxygen, that being the proportion in which it equally satisfies 22.97 of sodium and 1 of hydrogen; and whenever, in any compound, oxygen replaces hydrogen, it must do so in the proportion of 8 to 1: when chlorine, in the proportion of 8 to 35.5; and when sodium, in the proportion of 8 to 22.97.

This reaction between common salt and oil of vitriol may perhaps be more clearly shown by means of the following diagram:—



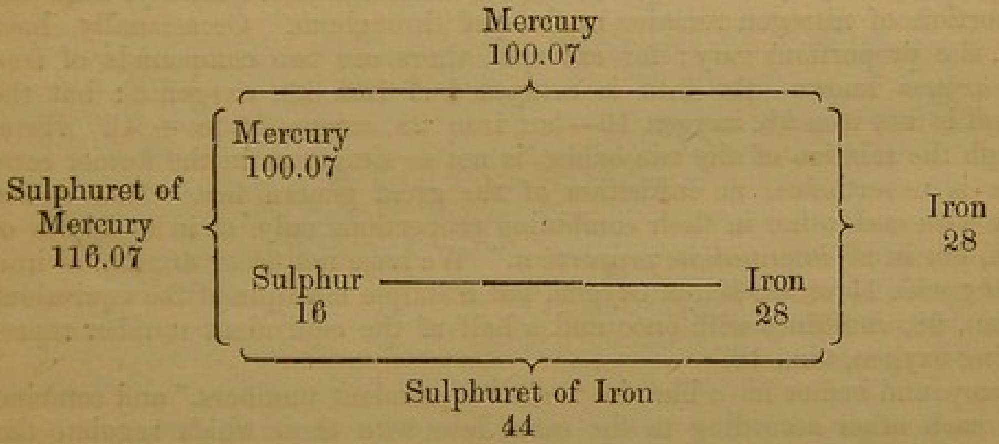
The two compounds which react on each other are placed outside the two side brackets—their composition is shown inside the same; the products of the decomposition are placed at the top and bottom of the diagram, and the nature of the reaction is shown by the lines between the four brackets, connecting together the different constituents of the new compounds. On referring to the Table at page 139, the figures in the third column, opposite chlorine, sodium, hydrogen, and oxygen, will be found the same with those attached to these elements in the diagram: in this list, sulphuric acid, being a compound body, will not be found. The composition of this important acid has, however, been correctly ascertained; it is known to be composed of 16 parts, by weight, of sulphur, and 24 of oxygen; but opposite the element *sulphur* we find the number 16 as its equivalent, and from this we easily deduce the equivalent of sulphuric acid, thus: $16 + 24\,(8 \times 3) = 40$.

But why these particular numbers in preference to any other? Why select 22.97 as the equivalent for sodium, and 35.5 as that for chlorine? It will be evident, on a little reflection, that any other set of numbers will do equally well, provided they bear to each other the same proportion as 22.97 does to 35.5. The real experimental import of the equivalent numbers is the expression of the *proportional* and *relative* weights of bodies, in which they produce analogous effects in chemical combinations, and the selection of these numbers is, therefore, a matter of indifference, provided they all bear to each other the true relations. The numbers selected in the above illustration are those which are now pretty generally adopted by chemists in all parts of Europe. The principle on which they are constructed assumes as its starting point the *composition of water*. This fluid is found on analysis to be composed of 8 parts, by weight, of oxygen, and 1 part, by weight, of hydrogen; hence 8 is employed to express the *equivalent* of oxygen, and 1 that of hydrogen.

The other system of numbers, forming the fourth column of the Table in page 139, and which, till lately, seems to have had the preference at least in Germany and France, was constructed on the assumption of 100 as the equivalent of oxygen. The numbers in this series are obtained by multiplying those in the former by $12\frac{1}{2}$, which gives us 12.5 for hydrogen and 100 for oxygen, and the equivalent proportions of all the other substances represent the quantities of those substances which combine with 100 parts of oxygen to form a protoxide; thus 395.70 parts of copper, 350 parts of iron, 406.59 parts of zinc, and 735.29 parts of tin, each combine with 100 parts of oxygen to form the first stage of oxygenation of those metals: hence these numbers are taken as their respective equivalents, and dividing each by $12\frac{1}{2}$

we obtain the numbers 31.66, 28, 32.52, and 58.52, which represent the equivalents of copper, iron, zinc, and tin, on that scale which assumes hydrogen as unity. There can be no doubt as to which series of numbers deserves the preference on the grounds of convenience, particularly since the progress of discovery is continually adding to the list of those elements, the equivalents of which, being exact multiples of that of hydrogen, may be expressed by whole numbers, and thus far more readily retained in the memory than numbers with the appendages of fractions, or than those longer ones found in the list on the oxygen scale.

Every elementary substance is thus provided with its *chemical equivalent;*—with a number indicating the proportion in which it enters into combination with the equivalent of any other substance with which it is capable of combining, and in which it replaces the equivalent of every other substance in cases of decomposition. Do we wish to know, for example, how much *iron* is required to decompose thoroughly a certain quantity of *cinnabar* or *sulphuret of mercury?* We simply refer to the Table of Equivalents, where we find opposite the metals *mercury* and *iron* the numbers 100.07 and 28. Now cinnabar is known to be a compound of 100.07 of mercury and 16 of sulphur; it is known also that iron is capable of forming a definite compound with sulphur, and the law of equivalents teaches us, that as 28 and 100.07 are respectively the equivalents of *iron* and *mercury*, so the same quantity of sulphur that will satisfy 28 parts of the first will likewise satisfy 100.07 parts of the last, and that therefore, to remove the whole of the sulphur from 116.07 (100.07 + 16) parts of cinnabar, we require at least 28 parts of iron, the reaction by which the decomposition is brought about being simply a substitution of 28 of iron for 100.07 of mercury: thus—



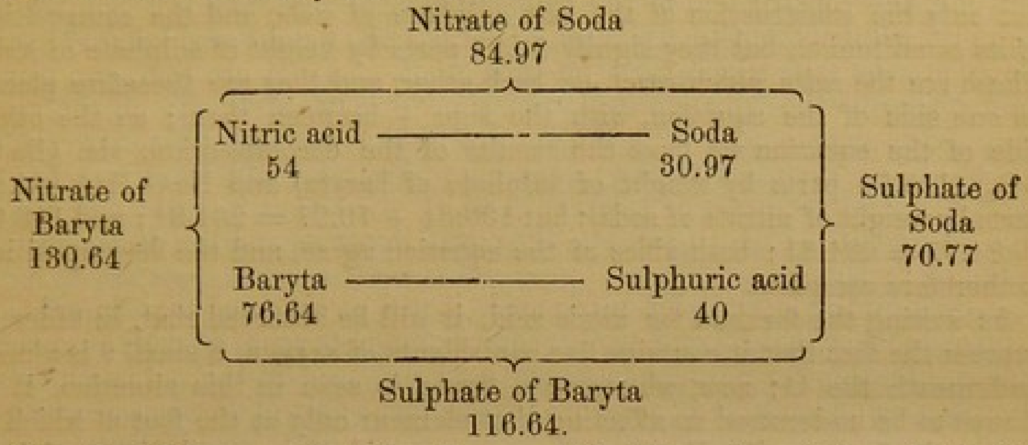
and this is not only true with regard to the compounds of these two metals with sulphur, for it has been fully proved that the same quantity of any substance whatever, which combines with 100.07 of mercury, will also combine with exactly 28 of iron, provided this latter metal be capable of entering into chemical combination with that substance.

To give another example. If a rod of *zinc* be suspended in a clear solution of acetate of lead, the latter metal will be deposited on the zinc in a beautiful arborescent form. Now if this lead deposit be collected and weighed, and if also the loss sustained by the rod of zinc be carefully determined, it will be found that, for every 103.56 grains of metallic lead precipitated, there are 32.52 grains of zinc dissolved; these 32.52 grains of zinc may be obtained from the solution in the state of oxide, combined with 8 grains of oxygen; but it is known also that 103.56 grains of lead combine with 8 of oxygen to form litharge: hence it is clear, that as 32.52 grains of zinc and

103.56 grains of lead each combine with 8 grains of oxygen to form their respective oxides, these numbers must represent the equivalents of these metals, and the experiment itself proves that these are actually the proportions in which they replace each other in their union with acetic acid.

But some substances enter into combination with each other in more than one proportion, forming several distinct compounds—how are these proportions regulated? It is an important and well-established law, and one which of all others gives the most beautiful harmony to the science, "that when one body, A, unites with another body, B, in two or more proportions, the quantities of the latter united with the same quantity of the former bear to each other a very simple ratio." For example, there are five compounds of nitrogen and oxygen known; the equivalent number of nitrogen, as lately deduced from the analyses of *sal-ammoniac*, *nitrate of silver*, and *nitrate of lead*, is 14. The simplest compound of nitrogen and oxygen known is *nitrous oxide*, or "laughing gas," it is therefore considered as a *protoxide*, and to be composed of nitrogen 14, oxygen 8. The next compound, *nitric oxide*, is the gas obtained by the action of nitric acid on metallic copper, or mercury; and analysis shows that it contains just *twice as much* oxygen as nitrous oxide: it is, therefore, composed of nitrogen 14, oxygen 16 (8 × 2). The third compound, viz., *nitrous acid*, is formed by adding 50 measures of oxygen gas to 200 measures of nitric oxide; its composition is, nitrogen 14, oxygen 24 (8 × 3). The fourth compound, viz., *hyponitric acid*, is formed by mixing together 4 volumes of nitric oxide and 2 volumes of oxygen, both perfectly dry; its composition is, nitrogen 14, oxygen 32 (8 × 4); and the fifth compound, viz., *nitric acid*, is composed of nitrogen 14, oxygen 40 (8 × 5). Here the most simple relation is observed between the quantities of oxygen in the different compounds; they are all simple multiples of the smallest quantity, while the proportion of nitrogen remains unchanged throughout. Occasionally, however, the proportions vary; for example, there are two compounds of *iron* and *oxygen* known—the first is composed of iron 28, oxygen 8; but the second is not iron 28, oxygen 16—but iron 28, oxygen 12 (8 + 4). Here, though the relation of the two oxides is not so simple as in the former case, there is nevertheless no infraction of the great general law, "that bodies unite with each other in their combining proportions only, or in multiples of them, but in no *intermediate proportion*." We have not 30 or 40, &c., of iron uniting with 15 or 20, &c., of oxygen, but a simple multiple of the equivalent of iron, 28, combines with once and a half of the equivalent number representing oxygen, viz., 12.

Compound bodies have likewise their "equivalent numbers," and combine with each other according to the same laws with those which regulate the union of simple substances. The equivalent number of a compound body is always the sum of the equivalent numbers of its constituents; thus the combining equivalent of nitric acid is 54, being composed of nitrogen 14 and oxygen 40 (8 × 5); that of *baryta* is 76.64, being composed of barium 68.64, and oxygen 8; but nitric acid and baryta combine together, forming a neutral salt called nitrate of baryta, the equivalent of which is 130.64 (nitric acid 54 + baryta, 76.64). Again, the equivalent number of sulphuric acid is 40 (sulphur 16 + oxygen 24 (8 × 3)), and that of soda is 30.97 (sodium, 22.97 + oxygen, 8); but sulphuric acid and soda combine together, forming likewise a neutral salt, sulphate of soda, the equivalent of which is 70.97, the sum of the combining numbers of its constituents. Now, on bringing a solution of nitrate of baryta into contact with a solution of sulphate of soda, mutual decomposition of the two salts takes place; the solution, however, remains neutral, there is no redundancy either of acid or of base. This fact, which appears to have been first noticed by the Saxon Chemist, *Wenzel*, as far back as 1777, is easily explained. The salts resulting from the decomposition are each composed of a single equivalent of acid and of base, like the salts from which they are formed. Thus



Here it will be seen that the change which takes place is the substitution of *equivalent* quantities of the different bodies for each other; the two bases exchange acids, and the neutrality of the liquid is preserved, because each base meets with its precise equivalent of the new acid with which it enters into combination. It also follows, as a consequence of the same law, that the neutrality of the liquid will still be preserved, whatever may be the proportions in which the salts may be mixed; the decomposition will go on to the extent of the equivalents present and no further, the excess of either salt remaining unaffected.

SYMBOLS AND FORMULÆ.

Having thus briefly explained the meaning and use of the figures in the third and fourth columns of the Table (page 139), we may return to the consideration of the use of the letters in the second column, which constitute the symbols of the elements. These symbols afford a means of exhibiting in a concise and comprehensible form the composition of a compound; the mode in which its elements may be supposed to be arranged; and the changes which occur in its constitution by the substitution of one element for another. We will take the reaction between nitrate of baryta and sulphate of soda, which we have just been considering, by way of illustrating the application of these symbols, and the great advantages attending their use. This reaction would be written thus, in the form of an equation:—

$$BaO, NO_5 + NaO, SO_3 = BaO, SO_3 + NaO, NO_5.$$

Here we have a most comprehensive view, not only of the whole reaction, but likewise of the composition of the different compounds therein concerned. The collocation of letters, BaO, NO_5 shows at once that nitrate of baryta is composed of nitric acid and baryta; it shows further that baryta is a compound of barium and oxygen, and nitric acid a compound of nitrogen and oxygen, that in baryta one *equivalent* of barium is combined with one *equivalent* of oxygen, and that in nitric acid one *equivalent* of nitrogen is combined with *five equivalents* of oxygen: but the formula has a still more significant meaning. BaO, NO_5 expresses, not an indefinite quantity of nitrate of baryta, but 130.64 parts by weight of that salt. The equivalent number of a compound is, as we have stated above, the sum of the equivalent numbers of its constituents. On referring to the Table, the equivalent number of barium will be found to be 68.64; that of oxygen, 8; and that of nitrogen, 14. BaO stands, then, for 76.64 parts by weight of baryta (68.64 + 8,) and

NO_5 stands for 54 parts by weight of nitric acid (14 + (8 × 5); BaO, NO_5 consequently represents 130.64 parts by weight of nitrate of baryta. The same observations apply to the collocation of letters NaO, SO_3; they express not only the construction of the salt sulphate of soda, and the composition of its constituents, but they signify 70.97 parts by weight of sulphate of soda. These are the salts which react on each other, and they are therefore placed on one side of the equation, with the sign + between them; on the other side of the equation we have the results of the decomposition, viz. (BaO, SO_3) (116.64 parts by weight of sulphate of baryta) and NaO, NO_5 (84.97 parts by weight of nitrate of soda); but $130.64 + 70.97 = 201.61$; and $116.64 + 84.97 = 201.61$; both sides of the equation agree, and the decomposition is therefore complete.

In writing the formula for nitric acid, it will be observed that, in order to express the fact that it contains five equivalents of oxygen, a small 5 is placed underneath the O; now, whenever a figure is seen in this situation, it is always to be understood as affecting that element only at the foot of which it is placed; for example, Fe_2O_3 means a compound of *two* equivalents of *iron* and *three* equivalents of oxygen: S_2O_2 a compound of *two* equivalents of sulphur and *two* equivalents of oxygen; when, however, a large figure is placed *before* a collocation of letters, it affects the whole compound expressed by those letters; thus $3\ NO_5$ means *three* equivalents of nitric acid; $3\ Fe_2O_3$ represents *three* equivalents of sesquioxide of iron, and $3\ S_2O_2$, *three* equivalents of hyposulphurous acid. When formulæ representing a reaction are thrown into the form of an equation, certain other signs are sometimes necessary. For example, when terchloride of gold and protosulphate of iron, both in solution, are brought into contact in certain proportions, the whole of the gold is precipitated in the metallic form. The reaction is concisely expressed thus:

$$AuCl_3 + 6\ (FeO, SO_3) = 2\ (Fe_2O_3, 3\ SO_3) + Fe_2Cl_3 + Au$$

one equivalent of terchloride of gold, and *six* equivalents of protosulphate of iron, give rise to *two* equivalents of persulphate of iron, *one* of sesquichloride of iron, and *one* of metallic gold. Now, here, as *six* equivalents of protosulphate of iron are required, the entire formula of that salt is placed within brackets, the figure 6 being prefixed; had the brackets been omitted *, the formula would only have been affected by the 6 as far as the comma, and it would have been read *six equivalents of protoxide of iron, and one equivalent of* sulphuric acid. Again, one of the products of this reaction is two equivalents of persulphate of iron; the whole formula of persulphate of iron is therefore placed within brackets, the figure 2 being prefixed: had this been omitted, it would have been interpreted *two* equivalents of sesquioxide of iron, and *three* of sulphuric acid, and thus the equation would no longer be intelligible.

Some chemists employ certain other abbreviations. Thus, in writing down the composition of certain minerals, instead of using the symbol for oxygen they express the number of equivalents of that element by dots or points placed over the symbol of the element with which it is associated; thus $\dot{\mathrm{Fe}}$ signifies protoxide of iron, and $2\ \dot{\mathrm{Fe}}$ or $\dot{\mathrm{Fe}}$ signifies two equivalents of the same oxide; $\dddot{\mathrm{S}}$ expresses sulphuric acid, and $\dddot{\mathrm{S}}_3$ or $3\ \dddot{\mathrm{S}}$, *three* equivalents of that acid. When there are two equivalents of the *electro-positive* element, they are sometimes written by simply placing a dash underneath the symbol, thus $\underline{\dddot{\mathrm{Fe}}}$ signifies sesquioxide of iron: $\underline{\dddot{\mathrm{Al}}}$ means alumina; sometimes however the symbol itself is repeated instead thus, $\mathrm{Al}\dddot{\mathrm{Al}}$, $\mathrm{Fe}\dddot{\mathrm{Fe}}$. Compounds of sulphur

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* Which they accidentally are in page 203, from which this reaction is taken.

are in like manner occasionally expressed by placing commas over the element with which the sulphur is associated; thus $\overset{''}{A}s$, $\overset{'''}{A}s$, $\overset{''}{\overset{'''}{A}}s$ are sometimes written for the three sulphurets of arsenic, and $\overset{'}{S}n$, $\underline{\overset{'''}{S}n}$, and $\overset{''}{S}n$, for the three sulphurets of Tin. The formulæ of certain organic acids are, likewise, often abbreviated; thus $\overline{A}$, $\overline{T}$, $\overline{C}$, are written for acetic, tartaric, and citric acids, instead of the formulæ representing their composition as $C_4H_3O_3$; $C_3H_4O_{10}$; $C_{12}H_5O_{11}$.

The great advantages of this system of notation are particularly appreciated in the organic department of Chemistry; besides the immense assistance it offers to the memory, it enables Chemists to represent their theoretical views respecting the arrangement of the elements of certain compounds which would be wholly impossible from a mere statement of their per-centage composition as determined by analysis. We not unfrequently meet with two or more compounds which, though wholly unlike in their physical and chemical properties, yield nevertheless upon analysis the *same* elements in the *same* proportion; without the use of formulæ it would be quite impossible to give an intelligible representation of the constitution of such compounds, but with the aid of the symbolic language we can do so with the utmost perspicuity. The following may serve as an illustration.

By distilling benzoic acid with sulphuric acid and pyroxylic spirit, an oily, fragrant liquid is obtained, which yields on analysis a per-centage composition answering to the formula $C_{16}H_8O_4$. An oil of the same composition, but possessing totally different properties, is obtained by acting on oil of anise with dilute nitric acid. Lastly, by the action of dilute nitric acid on *cymol* (a hydrocarbon obtained from *oil of cummin*) a crystalline substance having acid properties is obtained, the composition of which is likewise $C_{16}H_8O_4$. In the language of chemistry these bodies are said to be *isomeric;* but it is evident that even the *empirical* formula, $C_{16}H_8O_4$, does not point out the true constitution of each substance. The symbolic language, nevertheless, enables the chemist to exhibit, at a glance, his theoretical ideas respecting them. Thus the first of these oily compounds is considered to be a salt of the oxide of the hypothetical radical *methyle* (C_4H_3) viz., the benzoate, and its composition is written thus:—

$$(C_4H_3)\,O + C_{14}H_5O_3 = C_{16}H_8O_4.$$

The second is regarded as the hydride of another hypothetical radical *anisyle* ($C_{16}H_7O_4$), and is thus expressed:—

$$(C_{16}H_7O_4)\,H = C_{16}H_8O_4.$$

The third, from the circumstances of its derivation, and from its great analogy to benzoic acid, may be considered as the hydrated oxide of another hypothetical radical ($C_{16}H_7O_2$), corresponding to benzoyl, and be written thus:—

$$(C_{16}H_7O_2)\,O + HO = C_{16}H_8O_4.$$

NOMENCLATURE.

We have already mentioned that the 59 elementary substances may be very conveniently arranged into two grand classes, viz., the *metalloids* and the *metals.* It has also been stated that, in giving names to these different bodies, no rule has, generally speaking, been observed, each particular discoverer following his own fancy in his selection. The names of compound bodies, however, *are* constructed in accordance with certain rules, and the system of nomenclature still followed is that of *Lavoisier*, which was constructed as far back as the year 1787, and which, though in some of its details it does not exactly accord with the views of the chemists of our day, is retained from the confusion and inconvenience which it has been felt would be introduced into the science, by making any alterations which might not meet the absolute approval of the chemical philosophers of all countries.

Of all the simple substances, the one which is the most plentifully diffused is *oxygen*; it is, moreover, the element, the combinations of which are, on the whole, the most important. The founders of the chemical nomenclature naturally, therefore, directed their especial attention to the compounds of oxygen, and made them the basis of their system.

Oxygen forms, with other simple bodies, three classes of compounds. I. Acids. II. Bases. III. Neutral or indifferent substances. The members of the two latter classes have received the name of *oxides; oxide* of potassium, *oxide* of iron, and *oxide* of lead furnish examples of *basic oxides*, and *oxide of carbon* may be quoted as an instance of an *indifferent oxide*. At the time the nomenclature was constructed, it was supposed that there could not exist more than two compounds of oxygen and the same body possessing *acid* characters; hence names were only provided for two acids with the same radical.

To express the acid containing the smallest proportion of oxygen, the termination *ous* was given to the element forming the radical of the acid, and the termination *ic* was appended to signify the acid containing the largest proportion of oxygen. Thus two compounds of sulphur and oxygen were known, the first was called sulphur*ous* and the latter sulphur*ic* acid. But the progress of science has pointed out the existence of other acid compounds of sulphur and oxygen. One of these acids contains less oxygen than sulphurous acid; another contains more than sulphurous, but less than sulphuric acid. To give names to these new substances, without disturbing the general principles of the nomenclature, the term *hypo* (from the Greek ὑπὸ, under) was introduced. Thus *hypo*sulphur*ous* acid expresses very conveniently the acid containing less oxygen than sulphurous acid, and *hypo*sulphur*ic* acid, that containing less oxygen than sulphuric, but more than sulphurous acid. In other cases acids were discovered containing more oxygen than the *ic* compound, and to meet such cases the term *hyper* (from the Greek ὑπὲρ, over) was introduced, thus an acid compound of chlorine and oxygen is known which contains more oxygen than chlor*ic* acid, the name *hyper*chloric acid was given to this substance; it is now, however, more generally called *per*chloric acid.

It frequently happens that the same body forms several compounds with oxygen which are either *basic* or *indifferent*. The Greek language is again resorted to for furnishing a means of distinguishing these different oxides. Thus there are three oxides of manganese and oxygen known, the first written symbolically is $Mn\,O$, and is called the *protoxide;* the second is written $Mn_2\,O_3$*, and, as it contains once and a half as much oxygen as the protoxide, it is called the *sesquioxide;* these two oxides are *bases*, that is, they combine with oxygen acids forming definite salts; the formula of the third is $Mn\,O_2$,

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* It is written Mn_2O_3 instead of $Mn\,O\,1\tfrac{1}{2}$, in order to avoid the inconvenience of introducing fractions, and to obviate the necessity of dividing the *atom* of oxygen, on the supposition that the equivalent numbers are actually expressive of the absolute weights of the individual atoms.

and, as it contains *twice* as much oxygen as the protoxide, it is called the *deutoxide*: this oxide is *indifferent*, that is, it does not form salts with oxygen acids, it is generally called *peroxide* of manganese, because it contains the largest proportion of oxygen with which the metal can combine to constitute an oxide; there are other compounds of manganese and oxygen, but these are distinct *acids*.

Salts are named according to a very simple rule, the names of acid and base being so combined that the name of the acid shall determine the *genus*, that of the base the *species*. When the name of the acid terminates in *ic*, the generic name of the salt terminates in *ate*, thus salts of sulphur*ic* acid are called sulph*ates*: when the name of the acid terminates in *ous*, the generic name of the salt terminates in *ite*, thus salts of sulphur*ous* acids are called sulph*ites*: in the same manner we have *hypo*sulph*ates* and *hypo*sulph*ites*. The same acid sometimes combines with the same base in more than one proportion: thus we have two compounds of chromic acid and potassa, the symbols for which are KO,CrO_3 and $KO, 2CrO_3$, and they are called respectively the chrom*ate* and the *bi*chrom*ate* of potassa. Salts also exist in which the quantity of acid is less than that which exists in the *neutral* salt, these compounds are designated *sub*-salts; and, lastly, we are furnished in common alum with an instance of what is called a double salt, where a new and characteristic compound is formed by the union of two distinct salts. The formula for dry alum is $KO,SO_3 + Al_2O_3, 3SO_3$, which shows it to be composed of sulphate of potash and sulphate of alumina.

The names given to the compounds formed by chlorine, iodine, and the other metalloids, either with the metals or with each other, are in strict accordance with the rule adopted for the oxygen compounds: thus we have chlor*ides*, *bi*chlor*ides*, *sesqui*chlor*ides*, and *per*chlor*ides*; iod*ides*, brom*ides*, fluor*ides*, sulph*ides* (sometimes called sulphurets), carb*ides* (or carburets), phosph*ides* (or phosphurets), hydr*ides* (hydrurets), &c. Water is remarkable as acting sometimes the part of an acid and sometimes that of a base: when in the former capacity, the compound is called a *hydrate*, as the *hydrate of potassa;* when in the latter, the compound ought in strictness to be named by adding the word *water* to that of the acid, though this rule is often infringed; thus the strongest sulphuric acid of commerce is known to have the composition $SO_3 + HO$, it ought therefore to be called *sulphate of water*, though it is generally termed *hydrated sulphuric* acid, or *hydrate* of sulphuric acid.

Certain of the metalloids form amongst each other energetic acids, as *chlorine* and *hydrogen*, *iodine* and *hydrogen*, *fluorine* and *hydrogen*, &c.; these are called hydrogen acids, and are named respectively *hydrochloric*, *hydriodic*, and *hydrofluoric* acids: it is here that the present nomenclature seems most defective, though it has not yet been thought advisable to make any important change, for the reasons already alluded to.

We have lastly to remark that, from the great analogy subsisting between certain compounds of sulphur with the metalloids and metals, and the corresponding compounds with oxygen, the terms *sulphur acids* and *sulphur bases* have been introduced to designate two classes of compounds, which act towards each other precisely as oxygen acids and oxygen bases, giving rise to a series of true salts called sulphur salts. Sulphur and carbon, for example, combine together and form a compound which corresponds in its properties so completely with carbonic acid that it is called *sulphocarbonic* acid: it enters into combination with *monosulphuret of potassium*, forming a compound analogous to carbonate of potassa, and which has received the name of *sulphocarbonate of monosulphuret of potassium*.

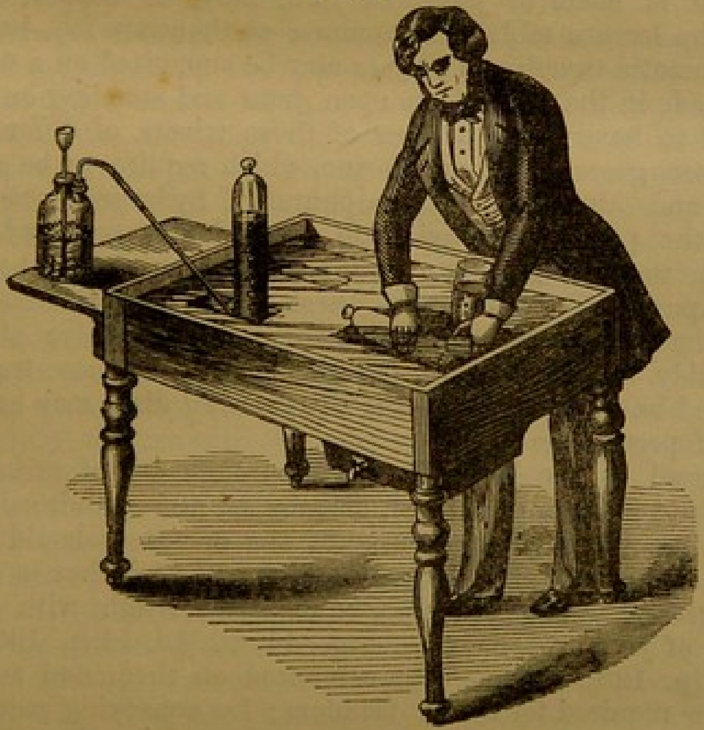
ON THE

PREPARATION AND MANAGEMENT OF GASES.

APPARATUS AND MANIPULATION.

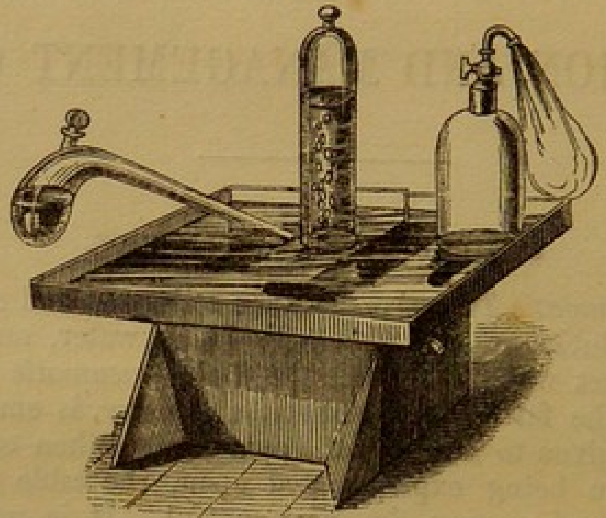
The Hydro-Pneumatic Trough.—For the collection and retention of gases which are not soluble, or only sparingly so, in water, and which are not alterable by contact with that fluid, the *hydro-pneumatic trough*, invented by Dr. Priestley, the father of pneumatic chemistry, is employed. Various forms have been given to this useful apparatus. When considerable quantities of gases are being experimented upon, the table trough shown in Fig. 1 will be found among the most useful. It is made of japanned copper fixed in a framework of wood, standing about 32 inches from the ground. The size of the trough may be as follows:—Length, 30 inches; breadth, 21 inches; depth of well, 12 inches; length, 14 inches; breadth, 10 inches.* For the convenience of collecting gases, two slits or small wells are cut in the shelf, the length of which may be 7 inches, and the breadth and depth 2 inches. The use of these minor wells will be readily understood by reference to the figure, where a gas is represented as being collected over one of them. The well is provided with a stop-cock for the purpose of drawing off the water when it becomes foul, and a movable

Fig. 1.



cover may be adapted to the frame so that the apparatus may serve the general purposes of a table when not otherwise employed. A smaller portable trough is shown in Fig. 2; its dimensions are :—length, 18 inches;

Fig. 2.

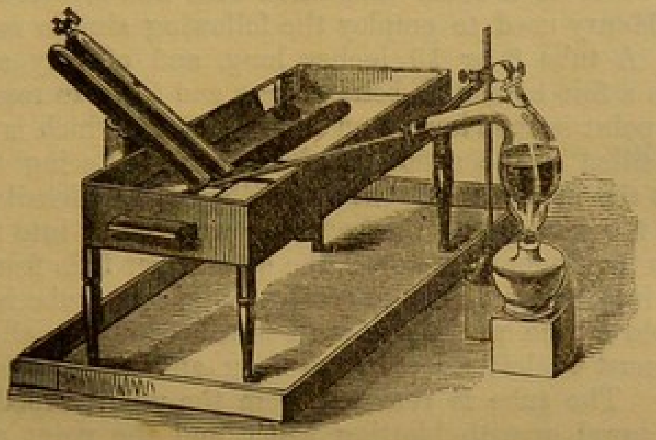


breadth, 14 inches; length of well, 12 inches; breadth, 7½ inches; depth, 8 inches. It is made of japanned iron, zinc, or copper, and is well adapted for the lecture table. A common earthenware foot-bath makes an excellent pneumatic trough. The jars may be supported on a well-varnished iron trivet, made in the form of an open grate and standing on four feet; it is convenient to have three or four of these trivets, of different sizes and heights. Those gases, such as chlorine, which require to be collected over warm water, and others, such as sulphuretted hydrogen, which cannot be received in the principal trough, are conveniently prepared in Griffin's circular brown ware troughs, two or three of which should be at hand for these special purposes. The size of these troughs is, diameter 10 inches, depth 4½ inches; they are provided with movable beehive shelves, which add considerably to their utility. In the absence of these troughs a common wash-hand basin, or even a large evaporating dish, may be used for the preparation of peculiar gases.

The jars used in the hydro-pneumatic trough are of various sizes and shapes; they are plain or graduated, bell-shaped and cylindrical, and with or without stoppers. For general purposes the operator should have at hand half a dozen bell-jars, about 12 inches high and 2¾ inches in diameter, the edges being ground so that they may be covered air-tight with a glass plate. Other forms of jars are shown in Figs. 11, 12, 13, 14 (p. 133). Transfer jars, Fig. 6 (p. 128), having caps cemented on them and surmounted by stop-cocks, are required for filling bladders; for conveying gases into globes for the determination of their specific gravities; and for observing the effects of the mixture of various gases. There should be three or four of these jars of different sizes; one large and one small one being graduated. Chlorine, and such gases as cannot be retained for any length of time over water, should be collected in wide-mouthed bottles; care should be taken that they are completely filled with the gas, and the stoppers should be greased before they are introduced.

The Mercurio-Pneumatic Trough.—Dr. Priestley was the first to suggest the employment of mercury for the reception and retention of those gases which are absorbed by water, and although the student may in most cases dispense with the mercurial-pneumatic trough, and collect and examine such gases by the method of displacement presently to be described, it may be useful to give a brief description of a portable form of this apparatus, and to offer a few observations on the precautions to be observed in manipulating with it. As mercury is both expensive and heavy, the trough is constructed in such a manner as to economize the metal as much as possible. The dimensions of the apparatus shown in Fig. 3, which is made of cast iron well

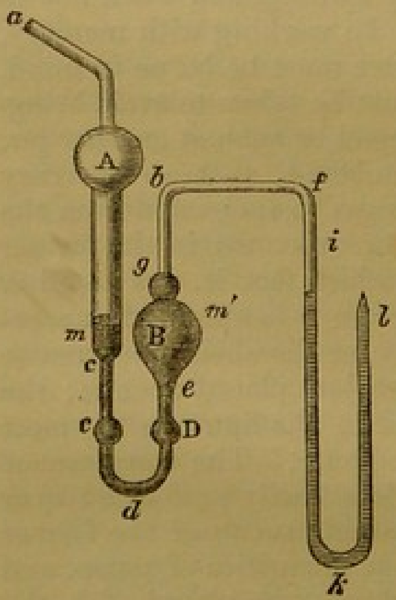
Fig. 3.



painted and varnished, are as follows:—Height, 7½ inches; length, 13½ inches; width, 5½ inches; depth of well, 5½ inches; length of channel for mercury, 10 inches; width, 1 inch; depth, 2 inches. It requires about 22 lbs. of mercury to work it; including the filling of two jars 6 inches long, and ¾ inch in diameter, and one graduated stoppered jar the same height, and 1½ inch in diameter. The jars used at the mercurial trough should not be less than ⅛ inch thick; they are supported while filling with gas by a sort of iron frame, as seen in the figure. The trough should always stand in a tray, in order to avoid any loss of mercury by spilling, and when not in use it should be covered, to exclude dirt and dust. In working with mercury, the great weight of that fluid as compared with water must be borne in mind, and in moving a wholly or partly filled jar, care must be taken to avoid bringing it suddenly in contact with the sides of the vessel or against another jar. In filling the jars with gas, it must be remembered, that as mercury is nearly fourteen times heavier than water, so the gas in its escape from the delivering tube has fourteen times the resistance to overcome in the former than in the latter; the practical application of which fact is, not to allow the extremity of the delivering tube to dip further than is absolutely necessary beneath the surface of the metal, and not to cover the shelf to a greater depth than is required to secure the mouths of the jars placed upon it; the slanting position in which the jars are represented in the figure is the most favourable one for securing the least amount of pressure. The transference of gas from one jar to another is an operation less easily performed over mercury than over water, on account of the density and opacity of the former fluid; but as the operator is never dealing with large quantities of gases, and as these are in general contained in tubes which may be closed with the finger, careful manipulation is alone required to conduct the operation successfully. *Faraday*, in his minute instructions in pneumato-chemical operations, puts the student on his guard against an "insidious emission" of gas, which sometimes takes place imperceptibly, and without any observable disturbance of the mercury, and which is occasioned by the circumstance that, unlike water, mercury has not the property of *wetting* and *adhering* to the surface of the jar. In consequence of the absence of this property, the gas frequently does not rise in bubbles, but suddenly returns round the edge of the jar, and passes up in a stream between the vessel and the mercury. The best remedy against this inconvenience is to keep the mercury clean, and frequently to wipe the beak of the retort or the end of the delivering tube, which should be slightly curved, so as to turn up underneath the mouth of the jar. It is sometimes required to transfer a portion of gas from a wide jar standing over water to a small tube filled with and inverted over mercury. The late Dr. Henry used to employ the following simple contrivance * for this purpose. A tube 8 or 10 inches long, and of very small diameter, is drawn out to a fine bore, and bent at one end so as to resemble the italic letter *l*. The point is then immersed in quicksilver, which is drawn into the tube till it is filled by the action of the mouth. Placing the finger over the aperture at the straight end, the tube filled with quicksilver is next conveyed through the water, with the bent end uppermost, into the inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. The whole of the quicksilver must not, however, be allowed to escape, but a column must be left a few inches long, and must be kept in its place by the finger. The tube is removed from the water, wiped dry by an assistant with a towel or with blotting paper, and the point of the bent end introduced into the aperture of the tube standing over quicksilver. On withdrawing the finger from that aperture which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough.

A more useful apparatus, and one particularly convenient when gases are to be submitted to the action of a reagent, is the *decanting pipette of M. Ettling*, shown in Fig. 4. It is mounted on a wooden support. The bulbs A and B have a diameter of about 2 inches; and the smaller ones, C D, of about $\frac{1}{2}$ inch. *g f k l* is a capillary tube. Let us suppose the apparatus to be arranged for the purpose of submitting a known volume of gas to the action of caustic potash, to remove and estimate carbonic acid. The reagent is introduced into the upper part of B; the capillary tube *g f b i* being likewise filled with it. The tube is then filled with mercury between the marks *m d m′* and *i k l*, and the beak *k l* being passed into the tube holding the gas to be analyzed, and standing on the mercurial trough, suction is applied at *a*, the gas thereupon passes into the bulb B, driving forward the mercurial column, *i k l*, which passes into the second branch of the capillary tube, a fresh quantity of mercury entering the beak of the pipette and sustaining the equilibrium of the mercury forced upwards into A. The pipette may now be removed and agitated, if necessary, without fear of losing any of the gaseous mixture contained in B. The absorption being terminated, the gas is retransferred to the original tube

Fig. 4.



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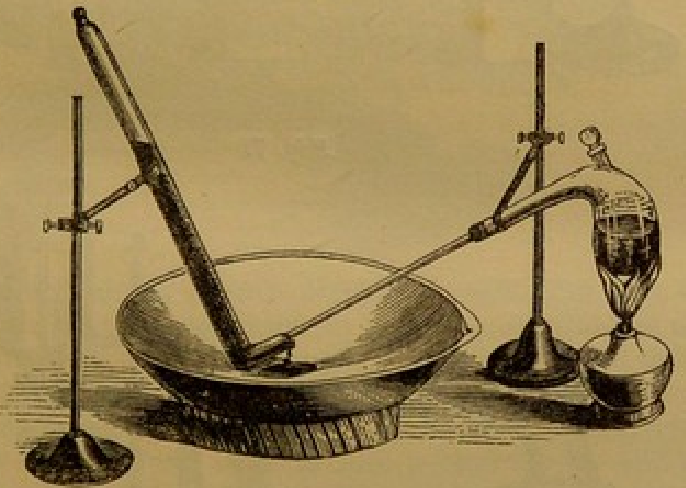
* Elements of Experimental Chemistry, vol. i. p. 21.

by an operation the reverse of the preceding one. The beak of the pipette is introduced into the tube (filled with mercury), and the pipette and tube being simultaneously raised to a certain height above the mercury in the trough, the gas is driven from B into the tube by the pressure of the mercurial column $m\,m'$, its velocity being regulated by management, and the pipette withdrawn the moment the reagent reaches the summit of the capillary tube.

During a long course of experiments with the mercurial trough the surface of the metal will often require cleaning and drying; indeed, after any acid gas has been prepared over it, it should be washed with water, and after having dried it as much as possible with blotting paper, the last traces of moisture may be removed by holding a red-hot poker in it for a short time.

It is possible to collect and examine qualitatively small quantities of gases over mercury, without the use of the mercurial trough, by employing the little apparatus shown in Fig. 5, which was first suggested by Mr. Cooper. It is made of a tube from $\frac{1}{2}$ to $\frac{3}{4}$ inch in diameter, and from 5 to 10 inches high, closed at the top, but open at the lower end, and bent as shown in the sketch; it may be either graduated or not. When about to be used, it is filled with mercury by holding it in an inclined position and pouring the metal in at the mouth; it is then secured by a tube-holder over a basin in the position represented in the figure, and the beak of the retort or delivery tube introduced at the mouth, so as to cause the gas to ascend and displace the mercury: the operation must be stopped when the tube is filled with gas nearly to the bend. Various experiments relating to inflammability, smell, absorbability by water, density, &c., may be made on the gas thus collected, by removing the tube from its support, closing the aperture with the finger, and allowing a bubble or two of the gas for each experiment to pass round the bend towards the finger, which is easily done, and all communication between the bubbles so detached and the residual portion cut off, by first inclining the tube and then restoring it to its upright position.

Fig. 5.



Collection of Gases by Displacement.—This method is often resorted to with great convenience for the extemporaneous preparation of gases for immediate use, when no very great degree of purity is necessary. The accompanying sketches (Figs. 6 and 7) will convey all the information required relative to the mode of manipulation. If the gas is heavier than atmospheric air, such as chlorine, hydrochloric acid gas, &c., the tube proceeding from the generating flask is bent twice at right angles, and introduced to the bottom of the clean dry jar, into which the gas is to be received; the heavier air displaces the lighter, and when the bottle is full, which in the case of chlorine is easily seen by the colour, and in that of hydrochloric acid gas by the fumes which make their appearance immediately that gas comes into contact with *moist* air, it is carefully removed and stopped. If the gas is lighter than atmospheric air, such as ammonia, the reverse operatin is to be performed; the bottle is supported on the ring of the retort stand, with its open end downwards; and the straight tube proceeding from the evolution flask is passed upwards till it nearly touches the bottom of the bottle; here the lighter gas displaces the heavier, and when the jar is full (which in the case of ammonia is easily learned by holding a piece of moistened turmeric or red litmus paper to its mouth, those test papers turning respectively brown and blue on coming into contact with the alkaline gas) it is removed and closed with its greased stopper.

Fig. 6.

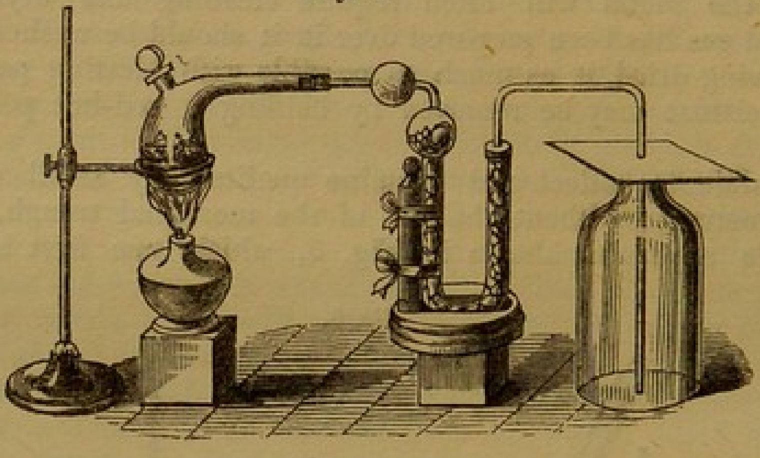
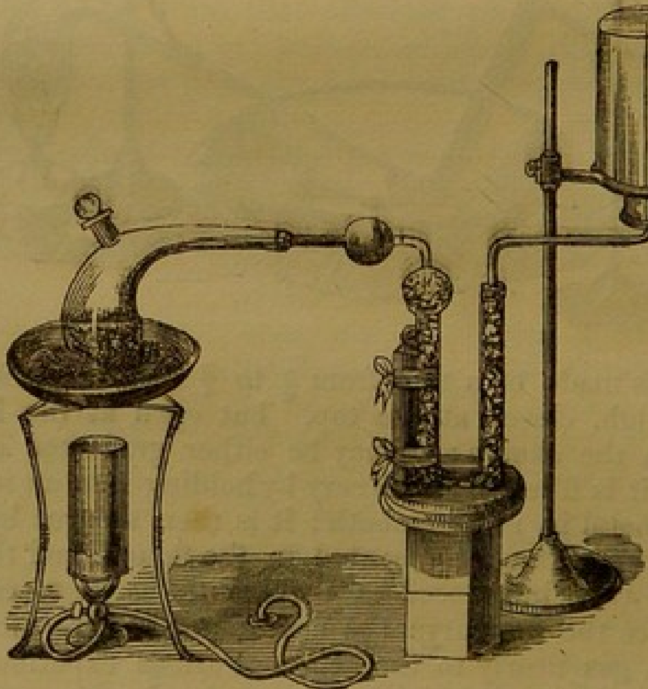
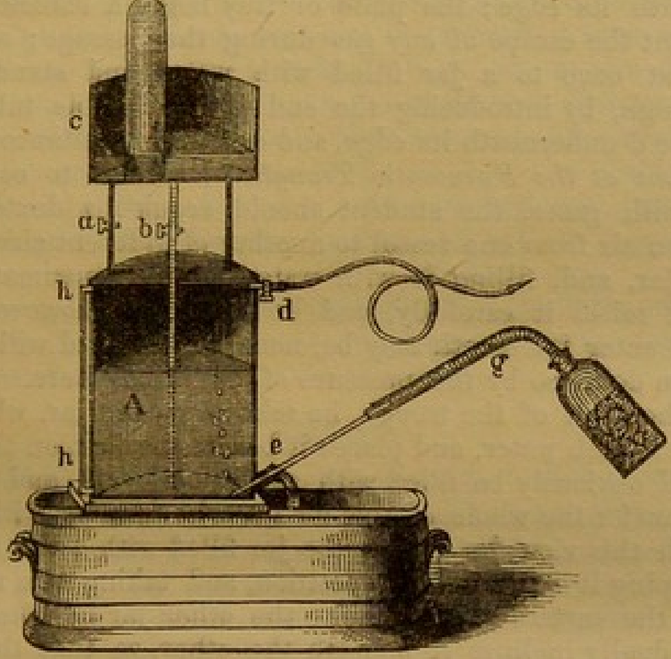


Fig. 7.



The Gas-holder.—When a series of experiments with the same gas is about to be performed, large vessels called gas-holders are employed for its collection and retention. Fig. 8 exhibits the method of filling one of these receivers with oxygen gas. The gas-holder is composed of a cylindrical vessel, A, of japanned copper or iron, capable of containing from one to three cubic feet of gas. It is surmounted by a trough, C, which is supported on three or four pillars; two of which, *a* and *b*, are hollow and furnished with stop-cocks. The tube *a* opens immediately below the upper part of the lower cylinder; the tube *b*, on the other hand, descends nearly to the bottom, as shown by the dotted lines; there is also a lateral tube and stop-cock *d*, to which a length of vulcanized India-rubber tubing may be attached, for the purpose of conveying the gas in any required direction; and, lastly, a large curved tube *e*, provided with a good sound cork, is inserted at the bottom of A. The apparatus is first filled with water thus: the stop cock *d* is opened, and the lower tube *e* is closed with its cork, the stop-cocks *a* and *b* are opened, and the trough C is filled with water, which runs into the lower vessel through the long tube *b*, the air escaping through the tubes *a* and *d*; the supply of water in C is kept up till the gas-holder is completely filled, which is ascertained by the glass gauge-tube *h h*.

Fig. 8.



To fill the apparatus with gas, all the stop-cocks are shut, and the cork is removed from the lower aperture; under these circumstances the water is prevented from escaping by the pressure of the atmosphere. The beak of the retort, or the end of the delivering tube, is then introduced, through *e*, into the interior of the cylinder; the gas, as it enters, rises to the upper part of the vessel, displacing the water, which flows out through the same aperture into a tub or trough placed underneath for the purpose; the progress of the filling is ascertained by observing the level of the water in the gauge-tube *h h*, which, of course, corresponds exactly with that in the gas-holder. When the cylinder is nearly, but not quite, full of gas, the delivering tube is removed from *e*, and the aperture again closed with its cork; the gas may thus be preserved for any length of time. To fill a jar with gas, it is first filled with water, and transferred to the trough c, where it is placed immediately over the aperture of *a*; the stop-cocks of both *a* and *b* are then simultaneously opened; the gas rises in the form of bubbles through the water in the jar, a corresponding quantity of water passing from c into A, through *b*; the jar being full, both stop-cocks are again closed; the jar may now be removed to the working pneumatic trough, by placing a plate underneath its edge; the plate or tray holds a sufficient quantity of water to prevent the escape of any gas during the passage; or the gas may be conveyed at once to a jar filled with water, and standing over the pneumatic trough, by introducing the end of the flexible tube attached to the lateral tube *d* underneath its edge, and opening simultaneously *a* and *d*.

Manipulations at the Pneumatic Trough.—Previous to commencing his experiments with gases, the student should acquire a dexterity in transferring common air from one vessel to another of different sizes. He begins by taking a jar, and, filling it with water at the pneumatic trough, he inverts it, and raises it carefully, and he finds that, however near to the surface of the water its mouth may be, none of the fluid will escape, being prevented from doing so by the pressure of the atmosphere. The filled jar being set on the shelf of the trough, he takes a second jar, which he inverts without filling it with water, and places it beside the first on the shelf. The second jar will obviously be filled with atmospheric air, and the operator's object is to transfer the whole of this air into the first jar without wasting a bubble. With this view, he grasps the jar filled with water firmly with his left hand, keeping it in an upright position, and taking care not to raise its mouth above the surface of the water; the other jar he takes in his right hand and gradually inclines it beneath the other, so that the air may rise slowly in bubbles, displacing the water from the first, and expelling it into the trough; in this manner, with a little care, the whole of the gas may be transferred from one vessel to the other by a sort of inverted pouring. There is not the slightest difficulty in this operation when both jars are of the same size; but when gas has to be transferred from a vessel with a wide mouth to one with a narrow one, careful manipulation is required to avoid loss. The object is best attained by introducing the beak of a pretty wide funnel into the opening of the narrow jar, and retaining it there by the hand while the gas is being transferred, in the manner shown in Fig. 1. The movable shelf of the pneumatic trough (Fig. 2) is provided with funnels underneath; but it is always safer to employ a glass funnel, in which all that is going on is seen, and, consequently, the flow of gas more easily regulated. When stoppered jars are used, they are filled with water by simply removing the stopper, plunging the jar downwards completely underneath the water, and then replacing the stopper, previously touched with a little tallow, and again raising it. If, while standing full on the shelf, the stopper be again removed, the water will immediately sink in the jar to the same level as the water outside, being pressed equally upwards and downwards by the atmosphere, and falling, therefore, in consequence of its own gravity. The same remarks apply to the jar provided with brass cap and stop-cock. It is sometimes required to transfer a gas from a jar to a bladder: for this purpose the bladder is provided with a stop-cock and connecting piece, corresponding exactly with that on the capped jar. The bladder, from which all air has been expelled by squeezing, is attached to the previously filled jar, and the communication between them being established by turning both stop-cocks, the jar is pressed into the water, upon which the gas passes into the bladder till it is filled; it is then removed. Bags made of Mackintosh cloth are excellent substitutes for bladders, and constitute gas-holders for many purposes much more convenient than the copper gas-holders above described. When a portion of the contained gas is required, the operator has only to screw a pipe upon the bag, and transfer it into a jar inverted in water.

In filling jars with water in the well of the pneumatic trough, they should be gradually and slowly immersed, so that the air may escape smoothly without causing much disturbance, and care must be taken that none of the escaping air find its way into other jars standing full of gas on the shelf; to avoid this, the latter are placed so far upon the shelf, that their mouths are completely closed. Another thing to be observed, is not to allow the water to accumulate to too great a height above the level of the shelf, or jars of gas may fall over, owing to their buoyancy. As a general rule, jars should not be quite filled with gas; but the water within and without preserved at about the same level.

We now proceed to describe the methods of preparing some of the most important gases, and to detail a series of experiments by which the student may make himself familiar with their properties.

OXYGEN.

Equivalent, 8 *or* 100; *Symbol*, *O*; *Density*, 1105·6 (*Air* = 1000).

Preparation 1. *By heating Red Precipitate or Peroxide of Mercury*, $Hg\,O_2$.—This method which, though not a practically useful one, is interesting as being that by which oxygen gas was first procured by Priestley in 1774, may be conducted thus:—108 grains of the substance are introduced into a test-tube of hard German glass, to which is adapted a cork and bent tube passing underneath the funnel of the shelf of the pneumatic trough; heat is applied to the tube, the first effect of which is to expand the air, and to drive a portion of it out in the form of bubbles; this first portion is not to be collected, being merely common air. The oxide gradually reaches the temperature at which it suffers decomposition; it is then resolved into two elements—*mercury*, which condenses in the upper part of the tube; and *oxygen*, which escapes abundantly in a gaseous form, and which may now be collected for examination. The decomposition proceeds till nothing is left in the tube but metallic mercury, and the gas collected (provided all atmospheric air has been previously expelled from the tube) is very pure. The reaction is simply this:—

$$Hg\,O_2 = Hg + O_2;$$

and, taking 100 as the equivalent number for mercury, and 8 as that for oxygen, it follows that every 108 grains of oxide of mercury should yield 8 grains of oxygen. Now, as 100 cubic inches of oxygen gas weigh 34·19 grains, the result of the decomposition of 108 grains of oxide of mercury should be the production of about 24 cubic inches of oxygen gas and 100 grains of mercury; and if a small globular flask be interposed between the tube and the receiver to catch the mercury as it distils over, and if the receiver be graduated, it will be found that a tolerably correct analysis of the red precipitate has been made*.

2. *By heating to redness Peroxide of Manganese*, $Mn\,O_2$.—This oxide

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* Red precipitate is usually made by heating nitrate of mercury till all the nitric acid is expelled, and then calcining the mass almost at a red heat. It occasionally happens that this calcination has not been carried to a sufficient extent, in which case the first application of heat to the tube will occasion the formation of nitrous fumes, and a yellow sublimate of subnitrate will appear.

requires for its decomposition a higher temperature than oxide of mercury, and must consequently be heated in a vessel of iron; the malleable iron bottles in which mercury is imported form excellent retorts for the purpose. A quantity of peroxide of manganese, previously washed with very dilute hydrochloric acid to decompose any carbonate of lime which may have become mixed with it, and subsequently well dried, is introduced into one of these bottles, to the aperture of which is screwed an iron pipe; the bottle is then heated to strong redness in an open fire or furnace, when oxygen gas in the proportion of about five gallons to each pound of oxide is liberated. Unlike oxide of mercury, the peroxide of manganese does not lose the whole of its oxygen by ignition. Its composition is—

Manganese	63·36
Oxygen	36·64
	100·00

By ignition it becomes—

Manganese	63·36
Oxygen	24·42
	87·78

it loses, therefore, 12·22 parts, or one-third, of its oxygen. Expressed in formulæ, the decomposition is—

$$3\ Mn\,O_2 = (Mn_2\,O_3 + Mn\,O) + O_2;$$

or three equivalents of peroxide of manganese are resolved into a compound of one equivalent of sesquioxide and one of protoxide of manganese and two of oxygen.

By heating peroxide of manganese with oil of vitriol, one-half of its oxygen may be obtained in a gaseous state, and the operation may be conducted in a common Florence oil flask over an argand lamp. The peroxide in this process is reduced to protoxide, which combines with the sulphuric acid, forming sulphate of protoxide of manganese, thus:—

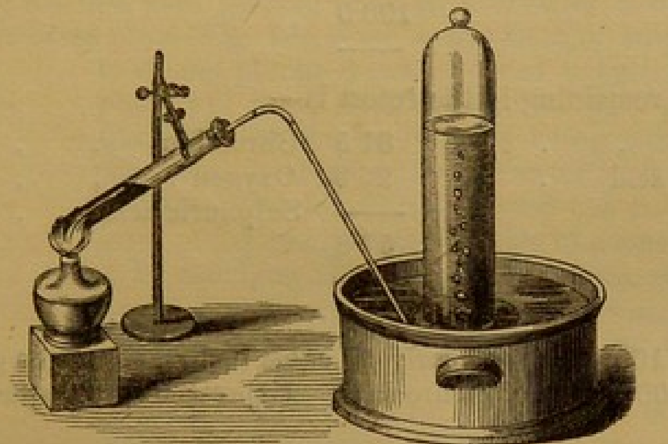
$$Mn\ O_2 + HO\ SO_3 = Mn\ O\ SO_3 + HO + O.$$

The former process, is, however, much to be preferred, and is the one always resorted to for preparing the gas in large quantities, and where very great purity is not required.

3. *By heating Chlorate of Potash, with about one-third of its weight of Oxide of Manganese or Oxide of Copper.*—When small quantities only of the gas are required, the decomposition may be conveniently conducted in a common test tube of German glass, to which is adapted a bent tube, as shown in Fig. 9, and the heat of a spirit lamp is quite sufficient; if chlorate of potash *without* oxide of manganese or oxide of copper be employed, nearly a red heat is required, and then the gas is disengaged with such violence, that the delivery tube can scarcely carry it off fast enough, and the end of the tube, being softened by the heat, frequently blows out: there is no danger of this when the salt has been previously mixed with the metallic oxides above mentioned. The decomposition proceeds regularly and quietly at a much

lower temperature. No chemical action is exercised by these oxides; they appear to act mechanically by separating the particles of chlorate of potash from each other, and thus exposing them more readily to the influence of heat. Test tubes, containing a small quantity of "oxygen mixture," may be usefully kept on hand as convenient extemporaneous means of procuring small supplies of pure oxygen.

Fig. 9.



When a gas-holder has to be supplied with a charge of pure oxygen, the "oxygen mixture" may be decomposed in an iron mercury bottle, as shown in Fig. 8; the bent gun-barrel *g* is screwed into the mouth of the bottle, and made air-tight by a little lute. With regard to the theory of this process, the composition of chlorate of potash is—

Chloric acid	61·51	Chlorine	28·88
		Oxygen	32·63
Oxide of potassium	38·49	Oxygen	6·53
		Potassium	31·96
	100·00		100·00

The salt remaining in the retort is chloride of potassium, the composition of which is—

Chlorine	28·88
Potassium	31·96
	60·84

Thus the salt loses the whole of its oxygen; every 100 grains yielding 39·16 grains, or 114·5 cubic inches. Expressed in formulæ, the decomposition is—

$$\mathrm{KO,\ ClO_5 = KCl + O_6}.$$

4. *By heating Bichromate of Potash with strong Sulphuric Acid.*—Three parts of the bichromate in powder are heated in a retort, with four parts of strong oil of vitriol; one-half of the oxygen contained in the chromic acid is given off, and there remains in the retort a mixture of sulphate of potash

and sulphate of sesquioxide of chromium; the reaction is as follows. The composition of bichromate of potash is—

Chromic acid	68·5	Chromium	36·8
		Oxygen	31·7
Potash	31·5	Potash	31·5
	100·0		100·0

The mixture remaining in the retort is—

Potash	31·5	Chromium	36·8
Sulphuric acid	26·3	Oxygen	15·7
		Sulphuric acid	78·4
	57·8		
			130·9

Therefore 16 grains, or nearly 47 cubic inches, of oxygen gas are liberated from every 100 grains of bichromate. Expressed in an equation, the decomposition is—

$$KO, 2\,CrO_3 + 4\,SO_3 = KO, SO_3 + Cr_2O_3, 3\,SO_3 + 3\,O.$$

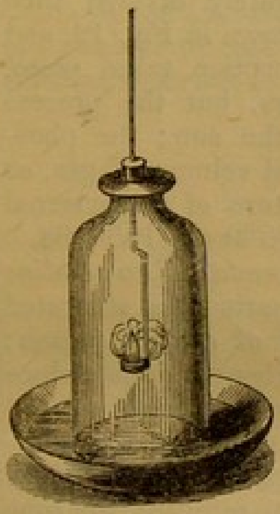
Properties of Oxygen Gas.—In appearance it is not to be distinguished from atmospheric air, being colourless, and destitute of taste and smell. It is, however, heavier than air in the proportion of 1·10563 to 1·00000; one cubic inch weighs about one-third of a grain. It is slightly soluble in water, which at ordinary temperatures dissolves $\frac{46}{1000}$ of its volume. It supports in an eminent degree the combustion of burning bodies, as the subjoined experiments will testify. It is absolutely essential to animal life. An animal dies almost instantly when introduced into a vessel deprived of oxygen; on the other hand, it will live in an atmosphere of pure oxygen four or five times longer than in an equal volume of common air. It enters into combination with all the elementary substances with the exception of fluorine, no compound of which with oxygen is at present known. The compounds which it forms with the elements are either acids, bases, or neutral substances, $As\,O_3$ and $As\,O_5$ (arsenious and arsenic acids) are examples of the first; PbO, KO (oxides of lead and of potassium), are examples of the second; and CO, $Mn\,O_2$ (carbonic oxide and binoxide of manganese), may be quoted as instances of the third. The union of oxygen with other substances is attended with the evolution of heat. It is therefore the true agent of ordinary combustion; in common language, a combustible body, combining with oxygen, is said to *burn*. Oxygen gas is continually entering the lungs from the atmosphere, and as the same amount of heat is evolved whether the body suffering oxidation unite slowly or rapidly with oxygen, the heat of the body is mainly, if not altogether, preserved by the chemical combinations which are constantly taking place in the body between oxygen and the elements constituting the organism. The most striking properties of oxygen gas may be demonstrated by the following experiments.

Experiment 1.—Fill a test tube with oxygen gas, and having lighted a piece of green wax taper attached to a bent wire, blow out the flame, and before the last spark has become extinguished, plunge it into the tube of gas; the taper will be rekindled with a sort of explosion, and will continue to burn with great brilliancy till the whole of the gas is consumed.

Experiment 2.—Attach a piece of the bark of charcoal to a stout iron wire by means of brass binding wire, hold it in the flame of a spirit lamp till it begins to burn, then immerse it in a two-pint jar of oxygen gas; the charcoal will burn rapidly and with brilliant scintillations. The result of the combustion is carbonic acid gas.

Experiment 3.—Into a little capsule of copper or porcelain fastened to the extremity of an iron wire passing through a cork, or better through a hole in a circular brass plate (Fig. 10), place a fragment of sulphur, set fire to it, and plunge it into a jar of oxygen gas; the sulphur will burn with a beautiful pale purple flame, the result of the combustion being sulphurous acid gas, which is absorbed by the water in the dish.

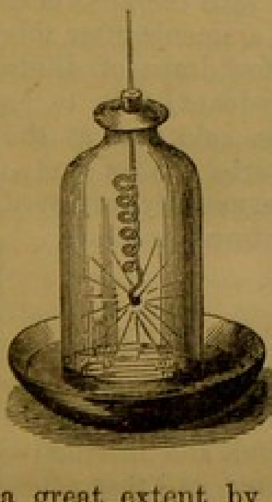
Fig. 10.



Experiment 4.—Substitute for the sulphur a fragment of *dry* phosphorus the size of a small pea, ignite it by touching it with a red-hot wire, and plunge it into a jar of oxygen; it will burn with a brilliancy scarcely endurable by the eye, evolving intense heat, and the jar will become filled with white fumes, chiefly consisting of phosphoric acid, which will gradually disappear, becoming dissolved by the water in the dish. The phosphorus should be dried between two pieces of blotting paper previous to igniting it, as, should it be wet, it is apt to spirt and cause the destruction of the jar by the projection of ignited particles against its sides.

Experiment 5.—Coil a piece of clean annealed watch spring into a helix, as shown in Fig. 11, attach its upper extremity to the brass plate, and affix to the lower end the sulphur tip of a match, ignite the sulphur and plunge the whole into a two-pint jar of oxygen; the heat of the burning sulphur speedily causes the end of the spring to become red hot, when it immediately enters into vivid combustion, throwing off brilliant sparks. The fused globules of oxide of iron frequently remain for some time red hot on, and fused into, the plate, even though covered with water.

Fig. 11.



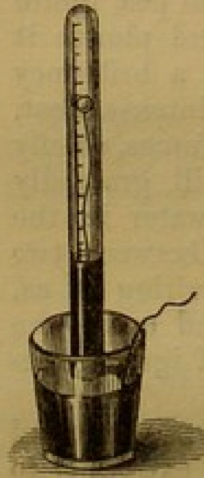
Experiment 6.—Make some turnings of zinc into a ball, in the centre of which insert a minute piece of phosphorus, fix the ball to a copper wire, and, having set fire to the phosphorus, introduce it into a jar of oxygen, the zinc will take fire and burn with a beautiful green flame surrounded by a white one.

These experiments may be multiplied and varied to a great extent by those desirous of witnessing the beautiful phenomena attending the combustion of different substances in oxygen gas, thus:—a mixture of nitrate of strontia and charcoal powder burns with a *rose-coloured* flame; a mixture of boracic acid (one part) and charcoal powder (three parts) with a *green* flame; of nitrate of baryta (one part) and charcoal powder (four parts) with a *yellow* flame; of nitrate of lime and charcoal powder (equal parts) with an *orange-red* flame, &c. The great heat attending the combustion of imflammable substances in pure oxygen may be well illustrated by passing a stream from the gas-holder through the flame of a spirit lamp; not only may iron and steel be fused in the blowpipe jet thus produced, but even platinum yields to it. Oxygen gas thus becomes in the laboratory a very convenient and manageable source of intense heat.

QUANTITATIVE ESTIMATION OF OXYGEN.

1. *By Phosphorus.*—Phosphorus is melted under water at about 104° Fahr., and cast into a bullet-mould. While in a liquid state, a platinum wire, bent into a ring at its extremity, is introduced through the cavity of the mould, which is then cooled by plunging it into cold water; a ball of phosphorus with a platinum wire firmly attached to it is thus obtained. The air to be deprived of oxygen is carefully measured in an accurately divided tube standing over mercury; the ball is then introduced as shown in Fig. 12, and allowed to remain till no further absorption takes place, which usually requires about 24 hours, but the process is quickened by placing the tube in the sun; the phosphorus is then removed, and the residual volume of gas, as soon as it has arrived at the temperature of the external air, is read off, with the precautions given at pp. 128–133.

Fig. 12.



2. *By Hydrated Protoxide of Iron suspended in an alkaline solution.*—A mixture is made of equal parts of a saturated solution of protosulphate of iron and of caustic potash; the best method of employing this absorbent is to introduce into the tube containing the gas to be analyzed several small tubes open at both ends, and then the alkaline solution. The gas is thus exposed to a large absorbing surface. After being well agitated for eight or ten minutes, the tube is allowed to remain at rest till the froth has subsided, and the residual gas then measured.

3. *By an ammoniacal solution of Protochloride of Copper.*—The decanting pipette is employed, and the gas is frequently agitated with the absorbing liquor; but since the gas necessarily contains a portion of ammonia after this process, it must be agitated in a second pipette with a few drops of dilute sulphuric acid before it is passed back again into the graduated tube to be measured. *M. Doyere* regards the ammoniacal cupreous solutions as the most unexceptionable of all absorbents of oxygen. It absorbs ten or twelve times its volume of the gas, and so completely, that it may be usefully employed as a means of obtaining perfectly pure *nitrogen* gas from atmospheric air.

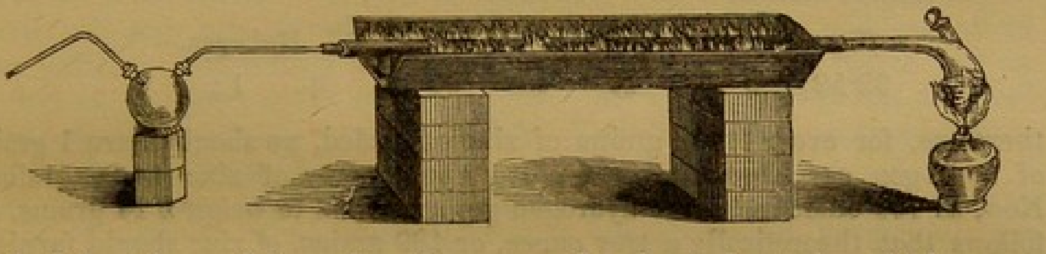
HYDROGEN.

Equivalent, 1 or 12·5; *Symbol*, H; *Density*, 69·26 (*Air* = 1000).

Preparation 1. *By the Decomposition of Water at common temperatures by Potassium or Sodium.*—Though by no means a practically useful method of preparing hydrogen gas, this experiment is a beautiful and instructive one, as demonstrating that hydrogen is a constituent of water, and that potassium and sodium are the metallic bases of the alkalies potash and soda. It may be made as follows:—Fill a test tube with mercury, close the mouth with the finger, and invert it over the mercury trough, or over a small evaporating dish containing the requisite quantity of the fluid metal; throw up into the tube by means of a pipette a few drops of water, which, from their superior lightness, will rise to the upper part of the tube, displacing a corresponding volume of mercury. Next, introduce a fragment of potassium. The moment the metal comes into contact with the water, bubbles of gas will be seen to form and occupy the upper part of the tube, the metal itself gradually disappearing. When all action is over, pass the thumb underneath the mouth of the tube, and invert it so as to bring the gas into contact with the thumb; have ready a lighted taper, and apply it to the mouth of the tube, the gas will be found to be inflammable, burning with a pale yellow flame. The water may next be tested; it will be found to have all the properties of an alkali, restoring the blue colour of reddened litmus paper, and changing yellow turmeric paper reddish brown; further, on supersaturating the alkaline liquor with hydrochloric acid, and adding a few drops of bichloride of platinum (see p. 32), a bright yellow crystalline precipitate of double chloride of platinum and potassium will be formed.

2. *By the Decomposition of Water at a high temperature by Iron.*—A tube of porcelain or iron filled with iron turnings is arranged along a combustion furnace, as shown in Fig. 13, a small retort containing water is adapted to one end of the tube, and from the other proceeds a bent glass tube, which passes air-tight through a cork into one of the apertures of a two-necked flask, whence from the other neck the gas is conveyed to a large receiver standing on the hydro-pneumatic trough, or to a gas-holder. The water in the retort is made to boil, and the steam passing over the red-hot iron is decomposed, its oxygen entering into combination with the metal, and its hydrogen passing off in the form of gas. The use of the small two-necked flask between the red-hot tube and the receiver, is to retain any water that may rush backwards from the trough in the event of the sudden condensation of the steam in the retort.

Fig. 13.



3. *By the Decomposition of Water at common temperatures by Iron or Zinc and an acid.*—It is by this process that hydrogen gas is invariably prepared in the laboratory, zinc being generally preferred to iron. The ordinary zinc of commerce is fused in a stone-ware crucible, and the melted metal poured from a height into a pan of cold water. It thus becomes resolved into small irregular grains presenting a large surface, and consequently more rapidly acted upon by the acid. Zinc cuttings may also be used.

A sufficient quantity of the metal being introduced into the evolution flask, and the funnel and delivering tubes being properly arranged, as shown in Fig. 1, water is poured in through the funnel till the gas-bottle is about half full, concentrated sulphuric acid is next added in small quantities at a time. The moment the acid comes into contact with the zinc the action commences, and as the temperature rises hydrogen gas is given off in great abundance, and may be received either into a gas-holder or into jars. When the action slackens it may be renewed by the addition of a fresh quantity of acid, till the requisite quantity of gas is obtained.

In this operation the decomposition of the water by the zinc *in the cold* is brought about by the strong affinity which exists between oxide of zinc and sulphuric acid, as in the preceding section we saw that a similar affinity between protoxide of manganese and sulphuric acid caused the binoxide of manganese to yield more oxygen when heated with that acid than when exposed to a red heat alone. Expressed in symbols the reaction is—

$$\mathrm{Zn + HO, SO_3 = Zn\,O, SO_3 + H.}$$

The hydrogen gas is thus seen to come from the water of the oil of vitriol, and the change really consists in the substitution of zinc for hydrogen, *sulphate of oxide of hydrogen* becoming *sulphate of oxide of zinc.* The use of the large quantity of water which it is found necessary to add is to dissolve the sulphate of zinc, which would otherwise speedily put a stop to the action, by covering, and so protecting, the zinc from the attack of the acid.

With regard to the quantity of gas evolved during the conversion of a certain quantity of zinc into sulphate, the following statement will show what we have a right to expect. The combining proportions of zinc, sulphuric acid, and water are respectively 32·52, 40, and 9, and, substituting these numbers for the symbols in the above equation, we have—

$$\overset{\text{Zinc.}}{32{\cdot}52} + \overset{\text{Water.}}{9} + \overset{\text{Sulphuric acid.}}{40} = \overset{\text{Sulphate of oxide of zinc.}}{80{\cdot}52} + \overset{\text{Hydrogen.}}{1}\,;$$

therefore, for every 32·52 grains of zinc expended, we should have 1 grain of hydrogen gas liberated, or for every ounce troy of zinc 14·76 grains. Now, as 100 cubic inches of hydrogen gas are found to weigh 2·14 grains, it follows that theoretically a troy ounce, or 480 grains, of zinc should furnish 690 cubic inches of hydrogen, and in a carefully-conducted experiment, nearly this quantity will be actually obtained.

Properties of Hydrogen Gas.—It is colourless, and, when perfectly pure, without taste or smell. The peculiar and somewhat disagreeable odour which the gas, when prepared by the last process, always possesses, arises from the impurity of the zinc, which, as met with in commerce, contains a small quantity of *carbon,* and not unfrequently *arsenic* and *sulphur;* the smell of the gas arises from an oily substance formed by the union of the carbon with a small quantity of the hydrogen. If arsenic and sulphur are present, they also combine with a portion of hydrogen, giving birth to two highly-poisonous compounds, viz., arseniuretted and sulphuretted hydrogen. The gas may be thoroughly freed from all these impurities by allowing it to remain for some time in contact first with a strong solution of caustic potash, which removes the oily matter and the sulphuretted hydrogen, and then with a solution of corrosive sublimate, which absorbs the arseniuretted hydrogen. The hydrogen gas after this treatment is left perfectly pure, or mixed only with watery vapour. Like oxygen, hydrogen gas has never been liquefied. It is the lightest substance known, its density (air=1000) being only 69·26. It is therefore 14½ times lighter than atmospheric air; hence its employment for filling balloons. The principle by which a balloon rises in the atmosphere is precisely the same as that which causes the ascent of a cork from the bottom of a vessel filled with water. The weight of the volume of air which it displaces must exceed the weight of the balloon and all that it carries with it. "Knowing the specific gravities of atmospheric air and of the gas with which the balloon is to be filled, and the weight of the envelope in which it is confined, it is not difficult to compute the size the balloon must have, in order to rise from the ground or to carry a given weight to a given height in the atmosphere. A globe of air one foot in diameter at the level of the sea, and under ordinary pressure, weighs about $\frac{1}{25}$ lb. avoirdupois. An equal globe of hydrogen gas obtained in the usual way, may be assumed (making every allowance for imperfect preparation) to be about six times lighter than atmospheric air; consequently, $\frac{5}{6}$ths of its whole buoyant force will act in impelling it upwards; that is to say, the force with which a sphere of such gas one foot in diameter will tend to rise in the atmosphere will be $\frac{5}{6} \times \frac{1}{25} = \frac{1}{30}$ of a pound avoirdupois. The ascensional forces of different spheres will be proportional to their magnitudes, that is to the cubes of their diameters; therefore a sphere 12 feet in diameter would rise with a force of 57 lbs., and one of 24 feet in diameter with a force of $8 \times 57 = 456$ lbs. But these determinations must be diminished by the weight of the envelope. The best material for the purpose at present known is thin silk varnished with elastic gum or India-rubber. The quantity of this material required to cover a globe one foot in diameter, weighs about $\frac{1}{20}$th of a pound. Now for a globe of greater size, the quantity required will increase with the square of the diameter: hence the covering of a balloon 12 feet in diameter must weigh about 7 lbs., and one of 24 feet in diameter about 28 lbs. It follows, therefore, that a balloon 12 feet in diameter, will only raise from the ground a weight of 50 lbs., and one of 24 feet, 428 lbs. Computing in the same manner, it is found that a balloon 60 feet in diameter would raise a weight equal to about 6950 lbs, and that one $1\frac{1}{2}$ feet would barely float, the weight of the bag being just equal to that of the imprisoned gas."*

Hydrogen gas is eminently combustible, burning, when pure, with a flame so feebly luminous, that by daylight it is scarcely visible, but producing a heat so intense that a thin platinum wire may be actually fused in it. If a cold body be held against the flame, moisture is deposited on it—water being the sole result of the combustion. When mixed with air it burns rapidly, and with explosion, the most explosive mixture being that of two volumes of hydrogen with five of common air. This property of hydrogen gas must be remembered while experimenting on its inflammability, and a sufficient time allowed for the escape of all the atmospheric air from the gas-bottle before applying a light to the exit tube, otherwise an explosion attended with very disagreeable consequences might ensue. With pure oxygen, hydrogen gas forms a far more explosive compound than with atmospheric air, the most formidable mixture being one volume of the former to two volumes of the latter gas. The two gases may, however, be made to burn together silently; the luminosity of the flame thus produced is very feeble, but the heat is the most intense that can be produced by combustion—determining the fusion of certain substances which undergo no alteration by the strongest heat that can be produced in furnaces of the best construction. When the hydro-oxygen flame is directed against a cylinder of pure lime, a light of exceeding brilliancy is produced; it is well known under the name of the Drummond light, and is the illuminating agent in the gas-microscope. Hydrogen gas, though itself inflammable, cannot maintain the combustion of another burning body. A lighted taper is immediately extinguished on being introduced into a jar full of the gas. Neither is it fitted for respiration, speedily causing the death of an animal confined in it, by suffocation, though when mixed with a large quantity of common air it may be received into the lungs without inconvenience.

The following experiments may serve to impress on the student's mind the properties of hydrogen gas.

Experiment 1.—Having filled two or three jars with the gas, close the mouth of one with a glass plate, and remove it, mouth upwards, from the

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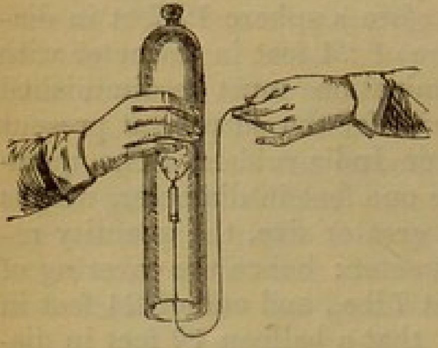
* Brande's Dictionary of Science, Literature, and Art; Article, *Balloon.*

pneumatic trough; have ready a lighted taper, and apply it to the mouth of the jar—observe that the gas will burn with a very feeble flame.

Experiment 2.—Remove another jar from the trough, mouth downwards, pass the lighted taper rapidly upwards into the gas, as shown in Fig. 14, and observe that it will be immediately extinguished. The unfitness of hydrogen gas for supporting combustion may be more strikingly shown by filling a large test tube with the gas over the mercurio-pneumatic trough, and passing up into it a piece of phosphorus; then, on touching the phosphorus with a bent red-hot wire, it will be observed to melt but not to take fire.

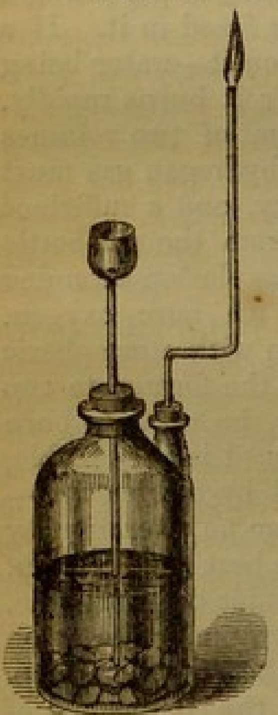
Fig. 14.



Experiment 3.—Close the mouth of one of the jars with a glass plate, then invert the jar and remove the plate; after a few seconds apply a light, and observe that no combustion will ensue, all the gas having escaped.

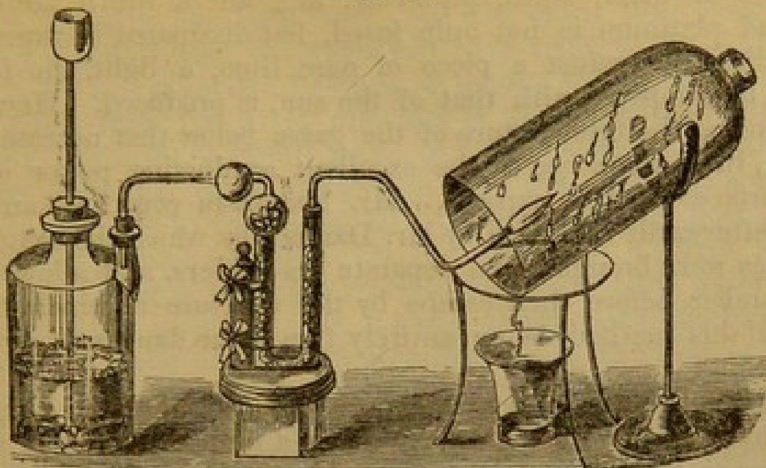
Experiment 4.—Adapt to one of the tubulares of a gas-bottle containing the materials for generating hydrogen gas, a tube bent twice at right angles and drawn out to a point, as shown in Fig. 15: having seen that both corks are tight, pour oil of vitriol through the funnel; allow the action to go on for some time, that all the atmospheric air may be thoroughly expelled, then apply a light to the point of the tube; the gas will take fire, and burn with a pale colourless flame not easily extinguished by blowing. This apparatus has received the name of the "Philosophical Lamp." Hold a dry glass jar over the flame, and notice that it becomes moist. That this moisture is really water will be demonstrated by the next experiment. After the philosophical lamp has been burning for some time, and when the flame has got small, hold over it a glass tube, about 18 inches long and ¾ths of an inch in diameter, open at both ends; notice that the flame becomes elongated and flickering, and that at the same time a musical note of higher or lower pitch, according to the length and diameter of the tube, is produced. This sound is occasioned by the rapid succession of detonations arising from the gas being carried up and mixed with the air in the tube.

Fig. 15.



Experiment 5.—To obtain a satisfactory proof that water is the result of the combustion of hydrogen, the gas must be *dried* before it is burnt; it may otherwise be supposed that the water deposited on a cold surface is merely water dissolved by the gas during its evolution from moist materials. The experiment is made as shown in Fig. 16. The gas is prepared as usual from zinc, water, and sulphuric acid, and is allowed to flow through a U-shaped tube filled with fragments of fused chloride of calcium, before it makes its escape through the aperture of the exit tube; here it is lighted and allowed to burn underneath a large open receiver supported in a slanting position over a small dish, into which the water is received. The experiment may be allowed to go on as long as the materials in the flask will furnish the gas, or till a quantity of water, sufficient for examination, has been collected. The

Fig. 16.



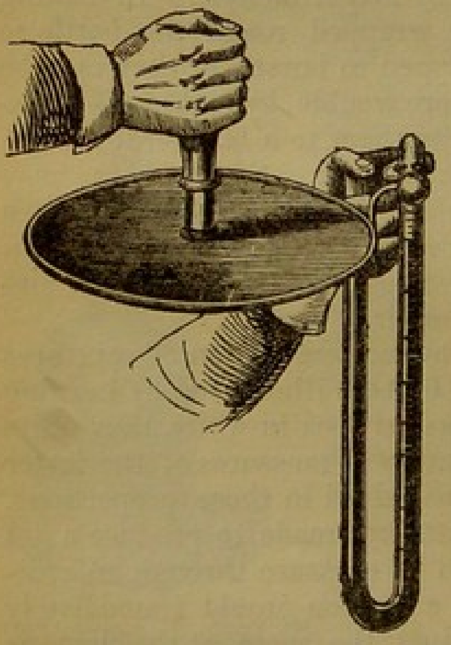
chloride of calcium having, in this arrangement, completely deprived the hydrogen of moisture, no other conclusion can be arrived at than that water is the result of its combustion in atmospheric air.

Experiment 6.—Introduce into a stout four-ounce glass bottle different mixtures of hydrogen gas and atmospheric air, and notice the proportions which occasion the loudest explosion on being inflamed. They will be found to be two measures of hydrogen and five of atmospheric air. Next burn a mixture of two measures of hydrogen and one of oxygen; the explosion will be far louder. These are the exact proportions in which the two gases combine to form water, as will be demonstrated by Experiment 8. In making these experiments, a handkerchief should be wrapped round the bottle to protect the person from injury if it should happen to burst; or they may be made with perfect safety, though with a little more trouble, by making the mixtures in a capped bell receiver, and transferring them to a bladder, to which a brass tobacco-pipe-shaped tube is afterwards screwed. Soap-bubbles may then be made and exploded, taking care to remove the bladder from the dish before applying the light. The great lightness of hydrogen gas may be shown by filling the soap-bubbles with pure hydrogen gas from the bladder, and noticing the rapidity with which they rise in the air.

Experiment 7.—The intense heat produced by the combustion of mixtures of oxygen and hydrogen gases may, obviously, be best illustrated by burning them together as nearly as possible in the proportions in which they unite to form water. These proportions are two volumes or measures of the latter to one of the former gas. Now, if the gases be mixed in these proportions, the mixture transferred to a bladder, and an attempt made to produce a jet of flame by igniting the mixture as it is forced by pressure through an ordinary tube with a narrow aperture, a violent explosion would immediately ensue, the gas in the bladder becoming ignited the moment the flame is applied to the orifice of the tube. The experiment may, however, be made with perfect safety by employing the safety-tube invented by Mr. Hemming. This consists of a brass cylinder, about 6 inches long and ¾ths of an inch wide, filled with pieces of fine brass wire of the same length, packed lightly together by forcing a pointed rod of metal into the centre of the bundle. To this cylinder a jet is adapted, and it is screwed on the bladder or Macintosh bag containing the gaseous mixture. The bladder or bag may now be placed under the arm, and the gases inflamed as they rush out of the jet under the pressure thus applied; a narrow colourless pencil of flame is produced, having wonderful heating powers, as may be shown by introducing into it fragments of glass, silica, pipe-clay, &c., all of which substances are melted; and platinum is not only fused, but dissipated in vapour. If the flame be directed against a piece of pure lime, a light, the brilliancy of which may be compared with that of the sun, is produced. Hemming's jet acts by reducing the temperature of the gases below that necessary for their combustion, in consequence of the excellent conducting power of the large metallic surface which it exposes. Mr. Maugham contrived an apparatus, which was afterwards improved by Mr. Daniell, by which the oxygen and hydrogen gases were brought from separate gas-holders, and allowed to mix in a small chamber before their escape by the aperture at which they are inflamed, and this method, being entirely free from danger, is now generally adopted.

Experiment 8.—The important experiment by which the composition of water is proved, may be made by exploding a proper mixture of oxygen and hydrogen gases by the electric spark. The instrument used for this purpose is called a *Eudiometer*. Many forms have been given to it, but that known as the "Syphon Eudiometer" is on the whole the most convenient for the experiment about to be described. This apparatus consists of a moderately stout glass tube, from 18 to 20 inches in length, and of about $\frac{3}{8}$ths of an inch internal diameter. Two platinum wires are hermetically sealed into the opposite sides of the closed end, so as to approach within $\frac{1}{10}$th of an inch of each other; and the tube, after being accurately graduated through one half of its length into tenths and hundredths of a cubic inch, is bent into a syphon form, as shown in Fig. 17. The tube is filled either with water or mercury in the usual manner, and the gases to be exploded, consisting of two measures of the purest hydrogen and one of the purest oxygen, are passed into it by means of a funnel. A sufficient quantity having been introduced, the aperture of the eudiometer is closed with the thumb, and it is brought into a vertical position. By a little dexterity a portion of the mixture may be transferred to the sealed limb of the syphon, and being thus secured, the thumb may be removed, and the quantity read off, taking care first to bring the water or mercury in each limb to the same level. If water has been used, the tube is now to be carefully wiped; it is then grasped firmly in the hand, in the manner shown in the figure, the fore-finger of the left hand touching the inner platinum wire. The charged disc of an electrophorus is next brought into contact with the outside platinum wire, upon which a spark passes between the wires, and the gases are fired. At the moment of explosion great heat is evolved, by which a considerable dilatation of the gases is produced, so that if too great a quantity has been operated upon, the water or mercury may be driven beyond the bend into the open limb of the instrument, and the accuracy of the experiment destroyed. The quantity exploded should not occupy more than two inches of the tube, and the thumb should be held firmly on the open end. The column of air between the thumb and the surface of the fluid acts as a spring, and

Fig. 17.



counteracts the elastic force of the heated gases. The apparatus is allowed to cool, and if water has been used, and the gases were pure, they will have entirely vanished, and the water will have risen in the sealed limb, so as entirely to fill it; generally, however, a minute bubble of air will still be left, which arises from the great difficulty of obtaining either of the gases, especially the hydrogen, perfectly pure, or from a portion of the air, which water always contains, being carried up into the eudiometer with the explosive mixture. The hydrogen gas for this experiment is best prepared by the voltaic decomposition of water. In the absence of a voltaic battery, this may be done by filling a platinum crucible with well-boiled water acidulated with sulphuric acid; inverting it in a basin of the same, placing on the top of the crucible a piece of zinc: in accordance with the laws of electrolytic decomposition, the hydrogen from the decomposed water will be liberated from the electro-negative metal (the platinum), and the crucible will gradually become filled with very pure gas. If the eudiometer has been filled with mercury, the experiment will be more instructive, as the water generated by the explosion will be seen to form, as the tube cools, in minute drops on its sides, occupying a volume some 2000 times less than that of the gaseous mixture.

Water, then, results from the combination of two volumes of hydrogen with one volume of oxygen; and, knowing the densities of these two gases, the composition of water by weight is ascertained thus:

1 volume of oxygen weighs	1·1056
2 ,, of hydrogen ,, . . $2 \times 0{\cdot}0692 =$	0·1384
	1·2440

we have therefore the proportion:—

$$\begin{array}{l} 1{\cdot}2440 : 1{\cdot}1056 :: 100 : x; \quad x = 88{\cdot}87 \\ 1{\cdot}2440 : 0{\cdot}1384 :: 100 : y; \quad y = \underline{11{\cdot}13} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad 100{\cdot}00 \end{array}$$

therefore 100 parts of water are composed of

Oxygen	88·87
Hydrogen	11·13
	100·00

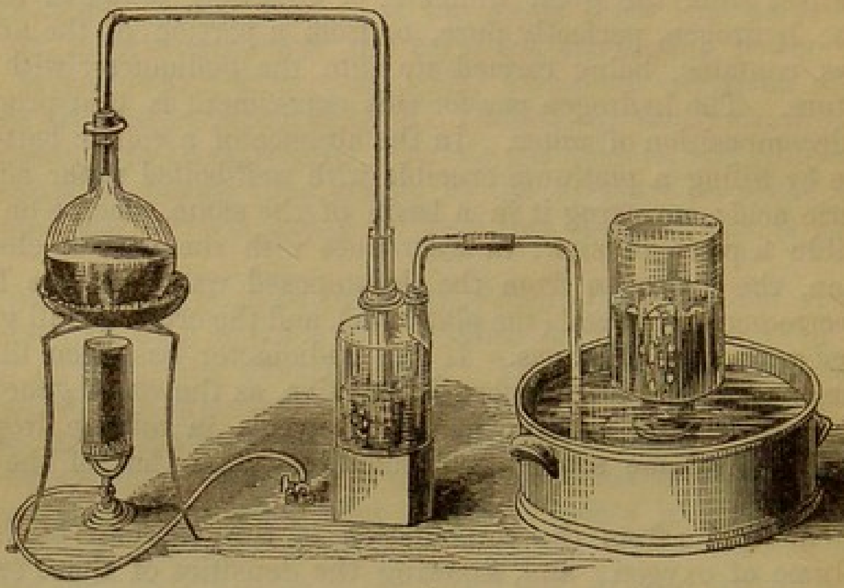
NITROGEN.

Equivalent, 14 *or* 175; *Symbol*, *N*; *Density*, 971·37 (*Air* = 1000).

Preparation 1. *By absorbing the Oxygen from a certain quantity of common Air by burning Phosphorus.*—A small porcelain capsule is made to float on the surface of a dish of water by means of a cork; a piece of dry phosphorus the size of a pea is placed in the capsule and ignited; the whole is immediately covered with a large bell glass receiver. The combustion of the phosphorus goes on in the limited quantity of air till the oxygen is entirely absorbed, and there remains in the jar nitrogen gas, and vapours of phosphoric acid, which are gradually absorbed by the water. When the receiver is cold, the water will be found to have risen in the jar so as to fill about one-fifth. The oxygen from a small quantity of air may be absorbed by phosphorus at ordinary temperatures, by leaving a ball of it in contact with the air in a graduated tube for twenty-four hours.

2. *By the Decomposition of Ammonia by Chlorine.*—Into the flask (Fig. 18) is introduced some peroxide of manganese in powder, and on it is poured hydrochloric acid; chlorine gas is formed, and is conveyed into a two-necked flask, containing a diluted solution of ammonia. The yellow colour of the chlorine disappears, but abundance of gas is disengaged, which is received in the usual manner in a receiver standing in the hydro-pneumatic trough. This gas is pure nitrogen, and is produced by the following reaction. Ammonia is a compound of nitrogen and hydrogen, and chlorine has a powerful affinity for the latter element, with which it forms hydrochloric acid; the moment, therefore, that the chlorine enters the ammoniacal solution, it decomposes it, and hydrochlorate of ammonia is formed, the other constituent of the ammonia, viz., nitrogen, being liberated as gas. In making this experiment, care must be taken to keep the ammonia in excess; for if the chlorine be allowed to pass through the solution after the ammonia is entirely converted into hydrochlorate, another kind of decomposition will take place, giving birth to an extremely explosive compound, viz., the *chloride of nitrogen*; there is no danger of this happening as long as the liquor in the two-necked flask smells strongly of free ammonia.

Fig. 18.



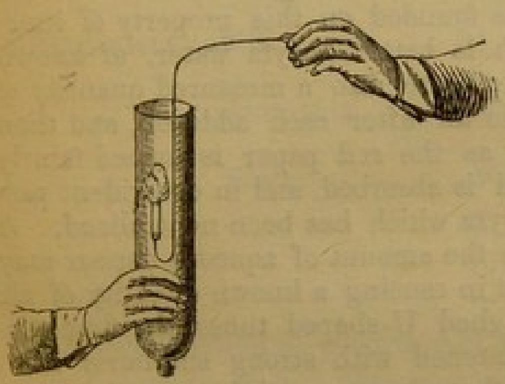
3. *By boiling a concentrated solution of Nitrite of Ammonia.*—The solution is simply poured into a retort and boiled; the gas comes over quite pure, according to the following reaction, from which it will be seen that nitrite of ammonia contains the elements of *four* equivalents of water, and *two* of nitrogen, into which it is entirely resolved.

$$NH_3\,HO,\,NO_3 = 4\,HO \times 2\,N.$$

For the nitrite of ammonia may be conveniently substituted a mixture of alkaline *nitrite* of potash and hydrochlorate of ammonia. The former salt is prepared in a suitable state, by passing the nitrous gas derived from the decomposition of 1 part of starch by 10 parts of nitric acid into a strong solution of caustic potash, until the product is decidedly acid, and then adding a little more caustic potash in order to render it perceptibly alkaline. When 1 volume of this salt is boiled with 3 of a highly concentrated solution of hydrochlorate of ammonia, nitrogen gas is given off with perfect regularity and of great purity, provided it be passed through a flask containing a little dilute sulphuric acid, in order to remove any ammonia that may be disengaged at the same time.

Properties of Nitrogen Gas.—It is colourless and without taste or smell, and has never been liquefied. It is a little lighter than atmospheric air, 100 cubic inches, at 60° F., weighing 29·95 grains, the same bulk of common air weighing 30·829 grains. It is not combustible, neither does it support the combustion of a burning body, as the simple experiment of plunging a piece of burning phosphorus or a lighted taper (Fig. 19) into a jar of it, will show. It is fatal to animal life; not that it exercises any specific injurious effect on the organs, seeing that it forms no less than $\frac{4}{5}$ths of the bulk of atmospheric air, but because it does not contain that gas which is essential to respiration, namely, oxygen. Its use in the atmosphere is supposed to be principally to check the activity of oxygen. It is absorbed by water at ordinary temperatures, in the proportion of about 25 parts to 1000.

Fig. 19.



Analysis of Atmospheric Air. By absorption of the Oxygen.—To the absorbents of this principle mentioned (page xxxiv), may be added an alkaline solution of pyrogallic acid*, which appears to have a capacity for absorbing oxygen not inferior to that of potash for carbonic acid. The air to be analyzed is measured in a graduated tube over mercury, a solution of caustic potash, made by dissolving 1 part of dry hydrate of potash in 2 parts of water, is introduced, in the proportion of from $\frac{1}{40}$th to $\frac{1}{30}$th of the volume of the air, by means of a common pipette with a curved point; the tube is moved quickly up and down in the mercury, so that the alkaline solution may be spread uniformly over the inner surface, and when no further decrease of space is perceptible, the diminution of volume is read off; this gives the amount of carbonic acid.

A strong solution of pyrogallic acid, amounting in volume to about one-half that of the solution of potash, is next introduced into the tube, which is well shaken as before; and when no further absorption is perceptible, the amount of nitrogen remaining is measured off. The rapidity with which pyrogallic acid absorbs oxygen is very remarkable; by means of it half a dozen analyses of air, of sufficient accuracy for most cases, may be made in the course of an hour. Ordinary gallic acid may be employed instead of pyrogallic, but the absorption is much slower, requiring from 1½ to 2 hours instead of as many minutes.

By detonation with Hydrogen.—The principle of this method will readily be understood from the details given in the last section respecting the management of the syphon eudiometer. A certain volume of air is introduced and accurately measured†; a volume of hydrogen a little less than

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* Prepared by distilling fragments of Chinese galls in small retorts. The aqueous distillate is evaporated on the water-bath and sublimed, by which from 10 to 15 per cent. of brown crystalline pyrogallic acid is obtained.

† In all quantitative experiments with gases, the proper corrections must be made for *temperature, pressure,* and *aqueous vapour,* for which the reader is referred to pp. 128–131 –256; and I may here make the remark, that the *correct* analysis of a gaseous mixture is only to be made with the aid of the most accurate instruments, and by adopting a great many

that of the air is then added, and the volume again accurately determined. The spark is then passed through the mixture. After cooling, the volume of the residual gas is read off. Now, since oxygen consumes an amount of hydrogen exactly double its own volume, it is clear that one-third of the diminution which the total volume has sustained must be oxygen, the water resulting from the combustion being so small that it may be neglected.

Determination of Carbonic Acid and Aqueous Vapour.—The constant presence of carbonic acid in the atmosphere is proved by the pellicle of carbonate of lime, which invariably forms over the surface of lime-water exposed in an open vessel. One method of determining the amount of carbonic acid in a given quantity of air is founded on this property of lime-water to condense it. Lime, or, which is better, baryta water, of known strength, is dropped from a graduated pipette into a measured quantity of air; the liquid is well agitated with the air after each addition, and then tested with red litmus paper. As soon as the red paper is turned faintly but distinctly blue, all the carbonic acid is absorbed, and in equivalent proportion by weight to the quantity of baryta which has been neutralized. A more accurate method, and one by which the amount of aqueous vapour may be determined at the same time, consists in causing a known quantity of air to pass through a series of carefully weighed U-shaped tubes, the first containing fragments of pumice-stone moistened with strong sulphuric acid, which retains the watery vapour, and the others containing pumice-stone moistened with caustic potash, which retains the carbonic acid; by weighing the U-shaped tubes again, after the passage of the air through them, a direct determination of the water and carbonic acid absorbed is obtained.

Besides oxygen, nitrogen, carbonic acid, and aqueous vapour, the only other compounds that have been detected in atmospheric air, are *ammonia* and *carburetted hydrogen;* the former seems an essential constituent, it being the present opinion that it is through it plants obtain their supply of nitrogen. By volume, the composition of 10,000 parts of dry air may be represented as follows:—

Nitrogen	7912
Oxygen	2080
Carbonic Acid	4
Carburetted Hydrogen, C_2H	4
Ammonia	traces
	10,000

(*Graham.*)

PROTOXIDE OF NITROGEN.

Equivalent, 22 or 275, *Symbol,* NO; *Density,* 1520·4 (*Air* = 1000).

Preparation. By heating Nitrate of Ammonia.—Carbonate of ammonia is dissolved in pure and dilute nitric acid till effervescence ceases; the filtered solution (to which a small quantity of carbonate of ammonia may be added to insure the absence of free nitric acid) is concentrated till a drop taken out on a glass rod solidifies on cooling. The evaporating-dish is now removed from the fire, and the white cake which forms as it cools is broken

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precautions which it would be quite out of place to go into here, but for which the reader is referred to *Regnault's* admirable "Cours Elémentaire de Chimie," tome ii. p. 493, et seq., and to a paper entitled "Etudes sur la Respiration," by M. Doyere, "Annales de Chimie et de Physique," vol. xxxiii. pp. 1–55.

up and transferred to a well-stoppered bottle. About 6 oz. of the nitrate thus prepared are placed in a tolerably capacious retort and heated; the salt first fuses, and when the temperature rises to 340° F., it boils and evolves a large quantity of gas; the heat may be now somewhat slackened; the decomposition goes on till the salt entirely disappears, being resolved into protoxide of nitrogen and water, according to the subjoined reaction; and the gas may be received over the pneumatic trough in jars, or in the gas-holder, but the water should be warm, as cold water absorbs considerable quantities of protoxide of nitrogen.

The composition of nitrate of ammonia is—

1 Equivalent.	Nitric acid	54	67·50	Nitrogen Oxygen	17·50 50·00
1 „	Ammonia	17	21·25	Nitrogen Hydrogen	17·50 3·75
1 „	Water	9	11·25	Oxygen Hydrogen	10·00 1·25
		80	100·00		100·00

The composition of protoxide of nitrogen is—

1 Equivalent.	Nitrogen	14	63·64
1 „	Oxygen	8	36·36
		22	100·00

That of water—

1 Equivalent.	Oxygen	8	88·89
1 „	Hydrogen	1	11·11
		9	100·00

from which it appears that the 35 parts of nitrogen, contained in 100 parts of nitrate of ammonia, combine with 20 of the oxygen to produce 55 parts of protoxide of nitrogen, whilst the remaining 40 parts of oxygen combine with the 5 of hydrogen to form 45 parts of water; consequently, 100 grains of nitrate of ammonia yield 55 grains of protoxide of nitrogen, and from 6 oz. (troy) 1584 grains, or 3356 cubic inches, or nearly 2 cubic feet, should be obtained. Expressed in an equation the reaction is:—

$$NH_3\,HO\,NO_5 = 2\,NO + 4\,HO.$$

Properties.—It is colourless, and possesses a faint agreeable smell. It is considerably heavier than atmospheric air, 100 cubic inches weighing 47·2 grains. At 32°, and under a pressure of 30 atmospheres, it becomes a liquid; and at 150° below zero solidifies. Water dissolves about $\frac{3}{4}$ths of its volume, and acquires a sweetish taste. It maintains the combustion of burning bodies with greater brilliancy than atmospheric air. When taken into the lungs, it produces in some persons a sort of intoxication, accompanied by peculiarly agreeable sensations, a property which has procured for it the name of "The Laughing Gas." The following is Sir H. Davy's account of the experiment in which this remarkable property was discovered. "On the 17th of April, 1799, having previously closed my nostrils and exhausted my lungs, I breathed four quarts of nitrous oxide from and into a silk bag. The first feelings were those of giddiness and fulness of the head, but in less than half a minute, the respiration being continued, they diminished gradually, and were succeeded by a sensation analogous to gentle pressure on all the muscles, attended by a highly pleasurable thrilling, particularly in the chest and in the extremities. The objects around me became dazzling, and my hearing more acute. Towards the last inspirations, the thrilling increased, the sense of muscular power became greater, and at last an irresistible propensity to action was indulged in. I recollect but indistinctly what followed; I know my motions were various and violent. These effects very soon ceased after respiration, and in ten minutes I had recovered my natural state of mind." In making this experiment, great care should be taken to employ pure gas. There may be two sources of impurity. 1st. If the temperature of the decomposing salt should rise much above 450°, the protoxide may be contaminated with deutoxide, and so rendered quite unfit for breathing. 2nd. If the nitrate of ammonia should be contaminated with hydrochlorate, chlorine may become mixed with it, which is equally objectionable. Both these impurities are easily avoided, the first by checking the heat the moment dense white fumes begin to appear in the retort, and the second by using pure nitric acid in the preparation of the nitrate. With these precautions, the gas from about two ounces of the salt may be breathed from and into a silk bag or bladder, through a pretty wide glass tube, with perfect safety. When protoxide of nitrogen is mixed with hydrogen and inflamed, it is decomposed with a loud explosion, water being formed and nitrogen set free. In this manner its composition has been determined.

The following experiments may be made with this gas:—

Experiment 1.—Fill a wide test tube or small jar with the gas, and plunge into it a taper with a glowing wick; the taper will be lighted, and will burn nearly as brilliantly as in oxygen.

Experiment 2.—Make a similar experiment with phosphorus; the light will be insupportably vivid.

Experiment 3.—Make a corresponding experiment with sulphur, using the metal cup and sliding wire (Fig. 10), and notice that if the sulphur is only burning feebly when it is introduced, it will probably be extinguished; but if in a state of active inflammation, it will burn with a considerably increased degree of brilliancy.

The extinction of the feebly burning sulphur, in a gas containing one half of its volume of oxygen, while it continues to burn in atmospheric air which contains only one-fifth of its volume, becomes intelligible when it is considered that in atmospheric air the oxygen and nitrogen gases are in a state of *simple mixture*, while in protoxide of nitrogen they are *chemically combined*. The combustible body must, therefore, break down this chemical union before it can itself combine with the oxygen; to do this a high temperature is required.

Experiment 4.—Introduce into the syphon eudiometer 10 divisions of protoxide of nitrogen, and 15 divisions of pure hydrogen; pass the electric spark, and, when the tube is cool, measure the volume of the residual gas; it will be found to occupy 15 divisions. Now, if protoxide of nitrogen were, like atmospheric air, a mere mechanical mixture of its constituent gases, its composition might be deduced from the volume which has disappeared, one-third of the diminution being oxygen; but this not being the case, it is necessary to determine the exact quantity of hydrogen that has been consumed. With this view, pass up into the eudiometer 5 divisions of pure oxygen gas, making, in the whole, 20 divisions*; now pass the spark again, and, after waiting a few minutes for the tube to cool, measure the residual gas: the 20 divisions will be found to be reduced to 12·5; consequently 7·5 have disappeared. These 7·5 divisions represent the quantity of water formed, and, therefore, consisted of 5 of hydrogen and 2·5 of oxygen. We now have the data necessary for calculating the composition of protoxide of nitrogen, it being evident that of the 15 divisions that were left after the first explosion, 5 consisted of hydrogen and 10 of nitrogen. Now the quantity of hydrogen added in the first place amounted to 15 divisions, of which 5 were left unconsumed by the oxygen of the protoxide of nitrogen; 10 divisions of hydrogen were, therefore, consumed, and as these must have combined with 5 of oxygen, the 10 parts of protoxide which were introduced into the eudiometer must have consisted of 10 parts of nitrogen and 5 parts of oxygen, or 100 parts of nitrogen and 50 of oxygen, from which its specific gravity is deduced, thus:—

1 volume of nitrogen	0·972
½ do. of oxygen	0·552
	1·524

a number which agrees very closely with that obtained by actually weighing the gas.

Experiment 5.—A direct proof that this gas contains exactly its own volume of nitrogen may be obtained by the following experiment:—

Measure a certain quantity of the gas in a graduated tube over mercury, and transfer it to a curved tube likewise filled with, and inverted over, mercury. Next attach a piece of potassium to the end of an iron wire and introduce it into the curve of the tube, as shown in Fig. 20; apply the flame of a spirit lamp to the tube immediately underneath the potassium, at the same time grasping the tube firmly with the hand. The metal will take fire and burn brilliantly, decomposing the gas, absorbing its oxygen, and setting free its nitrogen. When the tube is cold, transfer the residual gas to the tube in which it was originally measured; its volume will be found unaltered, but it will be found to consist of pure nitrogen.

Fig. 20.

DEUTOXIDE OF NITROGEN.

Equivalent, 30 *or* 375; *Symbol*, NO_2; *Density*, 1038·8 (*Air* = 1000).

Preparation 1. *By the action of dilute Nitric Acid upon Mercury, Copper, or Iron.*—Clippings of copper are placed in a two-necked gas-bottle, similar to that used in the preparation of hydrogen, and on them is poured through the funnel a mixture of equal parts of common nitric acid and water. Copious red fumes are evolved, and the gas may be collected in the usual way over water, as soon as the gas occupying the upper part of the generating flask is nearly colourless. The reaction is as follows:—A portion of the nitric acid gives up three-fifths of its oxygen to the copper; which, thus becoming oxide of copper, is dissolved by the remaining nitric acid, producing a rich blue solution. The nitrogen of the decomposed nitric acid is set free

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* It is better to measure the gases in a separate tube, graduated on precisely the same scale as the eudiometer tube, and then to transfer them to the latter.

in combination with the remaining two-fifths of oxygen, forming deutoxide of nitrogen. For complete decomposition four equivalents of nitric acid and three of copper are required. Thus:—

$$3\,Cu + 4\,NO_5 = 3\,(Cu\,O, NO_5) + NO_2.$$

2. *By the action of Nitrate of Potash on a solution of Protochloride of Iron in Hydrochloric Acid.*—Two equal portions of hydrochloric acid are measured out; one portion is heated with iron turnings; protochloride of iron is formed, which is mixed with the other portion of acid, and nitrate of potash added, and the mixture exposed to heat in a retort or gas-bottle. The reaction is as follows:—

Six equivalents of protochloride of iron, *four* of hydrochloric acid, and *one* of nitrate of potash, produce *one* equivalent of deutoxide of nitrogen, *three* of sesquichloride of iron, *one* of chloride of potassium, and *four* of water; or in symbols:—

$$6\,FeCl + 4\,HCl + KO, NO_5 = NO_2 + 3\,(Fe_2\,Cl_3) + KCl + 4\,HO.$$

Properties.—It is colourless and transparent, sparingly soluble in water, which dissolves only $\frac{1}{20}$th of its volume; rather heavier than common air, 100 cubic inches weighing 32·137 grains, and quite irrespirable. Its most remarkable property is that of forming deep red fumes when mixed with atmospheric air. This is occasioned by the absorption of oxygen; hence this gas has been used to detect that principle, and to separate it from other gases. Combustibles that do not evolve much heat in burning, such as a taper or sulphur, are extinguished on being plunged into this gas; but a mass of red-hot charcoal, or a piece of burning phosphorus, effect the decomposition of the gas, and burn in it with almost as much brilliancy as in oxygen. The fact that deutoxide of nitrogen will not maintain the combustion of feebly burning bodies while the protoxide, which contains, relatively to the quantity of nitrogen, only one half as much oxygen, readily supports the flame of a taper, shows that in the deutoxide the nitrogen and oxygen are held together by a stronger bond of union than in the protoxide. Deutoxide of nitrogen is absorbed in large quantities by a solution of sulphate of iron, a reaction which serves to separate it from the protoxide; the iron solution acquires a deep brown colour. Nitric acid likewise absorbs a large quantity of this gas; mutual decomposition takes place; the gas takes oxygen from the acid, and both pass into the state of hyponitric acid. The colour of the liquid varies with the degree of concentration of the acid. With monohydrated nitric acid it is brown; with a somewhat weaker acid it is yellow; with nitric acid of the density of 1·35 the colour is green; with acid of the density of 1·25 it is clear blue; and, lastly, with an acid of the density of 1·15 it is colourless. Deutoxide of nitrogen has never been exhibited in a liquid state.

The following experiments may be made with this gas:—

Experiment 1.—Into a quantity of the gas contained in a tall jar, throw up a few bubbles of common air, or still better of oxygen; notice the red fumes produced, and observe the rapid absorption which takes place.

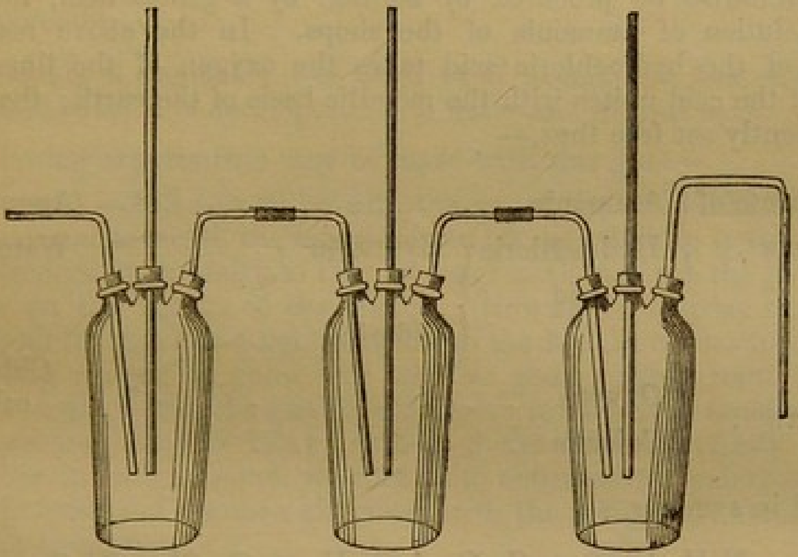
Experiment 2.—Fill a tall jar with blue litmus water; pass into it a quantity of well washed deutoxide of nitrogen; observe that the blue colour of the water remains unaltered; pass into the jar a few bubbles of oxygen, and notice that the colour of the litmus water immediately changes to red, in consequence of the formation of hyponitric acid. As deutoxide of nitrogen completely removes oxygen from a gaseous mixture, it was much used by Priestley, Dalton, and other chemists, in the analysis of atmospheric air; but the results are not found to be trustworthy, in consequence of the formation, in uncertain proportions, of different compounds of nitrogen and oxygen.

Experiment 3.—Introduce into a large test tube full of the gas a lighted taper; it will be immediately extinguished.

Experiment 4.—Into a large jar of the gas introduce a piece of dry burning phosphorus; it will burn with a brilliant light.

Experiment 5.—Adapt to a large gas-bottle, containing the materials for generating deutoxide of nitrogen, six bottles arranged as shown in Fig. 21.

Fig. 21.



Fill the first two bottles about one-third full of the most highly concentrated nitric acid; into the third pour an equal quantity of acid of the density of 1·45; into the fourth, acid of 1·35; into the fifth, acid of 1·25; and into the sixth, acid of 1·10. As the gas traverses each bottle, observe that the acid in the first bottle will assume different colours; that in the second will become permanently *brown;* that in the third *yellow;* that in the fourth *green;* that in the fifth *blue;* and, lastly, that in the sixth will remain colourless. The change of colour noticed in the acid in the first bottle, is caused by its gradual dilution by the water carried over from the generating-bottle by the gas.

Experiment 6.—Burn potassium in a measured volume of the gas, precisely in the manner described in the corresponding experiment with the protoxide; the residual volume will be found to be just one half that of the original; proving that deutoxide of nitrogen contains in one volume ½ a volume of nitrogen, whence its density is deduced, thus:—

½ volume of nitrogen	0·486
½ do. of oxygen	0·552
	1·038

and its percentage composition from the following proportion:—

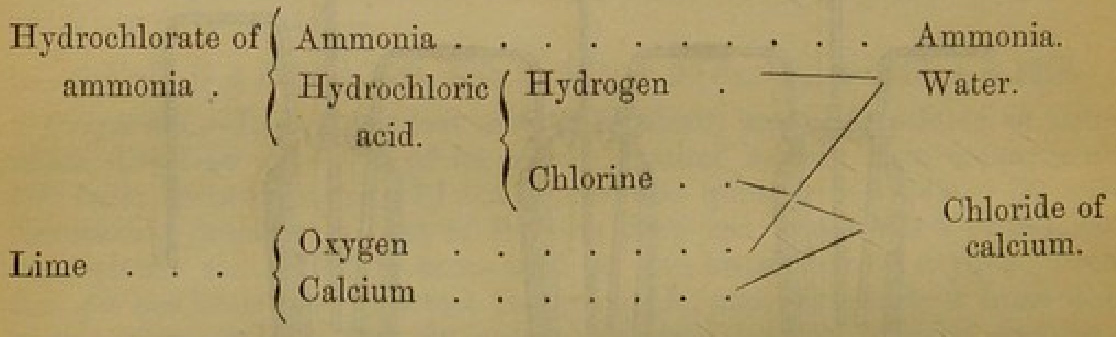
1·038 : 0·486 :: 100 : 46·66 nitrogen.
1.038 : 0·552 :: 100 : 53·34 oxygen.

100·00

AMMONIA.

Equivalent, 17 *or* 212·5 ; *Symbol*, NH_3; *Density*, 596·7 (*Air* =1000).

Preparation. By heating together Sal Ammoniac and Quick-lime.—One part of finely-pulverized sal ammoniac (hydroclorate of ammonia) is mixed with two of slaked lime ; the mixture is placed in a small retort and heated, the gas is received over mercury, or it may be collected by displacement, the apparatus being arranged as in Fig. 7 ; or, when small quantities only of the gas are required, in Cooper's mercurial tube receiver (Fig. 5.) Ammoniacal gas may likewise be procured by boiling, by a gentle heat, the common aqueous solution of ammonia of the shops. In the above reaction the hydrogen of the hydrochloric acid takes the oxygen of the lime, and the chlorine of the acid unites with the metallic basis of the earth ; the ammonia is consequently set free thus,—



Expressed in symbols,—

$$NH_3 HCl + CaO = NH_3 + CaCl + HO.$$

Properties.—It is colourless, of a strong pungent odour, occasioning a copious flow of tears. It is considerably lighter than atmospheric air, 100 cubic inches weighing only 18·19 grains. It possesses strong alkaline properties, and from its existing in the gaseous state, it has received the name of the *volatile alkali*. It restores the blue colour of reddened litmus paper, and neutralizes the strongest acids. It is exceedingly soluble in water, which in the cold absorbs no less than 500 times its volume of the gas, the whole of which may be expelled again by ebullition. The *liquor ammoniæ* of the Pharmacopœia is a solution of ammoniacal gas in water ; the absorption may be effected in Woulf's apparatus (Fig. 21), or the water and the gas may be distilled over together. When cooled to 40° below zero, ammoniacal gas becomes a liquid under ordinary atmospheric pressure ; under a pressure of 6½ atmospheres it liquefies at 50° *. By transmitting ammonia through a red-hot porcelain tube, filled with fragments of iron, copper, or platinum, it is decomposed into its constituent gases in the proportion of 2 volumes of nitrogen to 6 volumes of hydrogen. The metals in this experiment appear to act by increasing the heated surface over which the gas passes, as they take no part in the decomposition ; the platinum is entirely unaltered, but the copper and iron become brittle from their absorbing a small portion of nitrogen. Ammonia is feebly combustible ; not sufficiently so, however, to burn in common air ; a small jet of it may be burned in pure oxygen. By passing a series of electric sparks through a small quantity of ammonia, it suffers complete decomposition ; the volume of the gas becomes exactly doubled, 4 volumes of ammonia being composed of 2 volumes of nitrogen

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* Regnault.

and 6 of hydrogen. Ammonia and hydrochloric acid gas combine together volume for volume, both gases disappear, and the sides of the jar become covered with a white powder (hydrochlorate of ammonia). Solution of ammonia is likewise decomposed by chlorine. The experiment has already been described as a method of procuring nitrogen gas. The reaction is as follows:—

6 vols. chlorine . . . . } 6 vols. hydrochloric acid . . } Hydrochlorate of ammonia.
4 vols. ammonia { 2 vols. nitrogen
6 vols. hydrogen }
12 vols. ammonia . . . . }

When ammonia is conducted over peroxide of manganese, heated to redness in a porcelain tube, it is decomposed into water and nitrous acid.

The following experiments may be made with this gas:—

Experiment 1.—Fill a small jar with the gas at the mercurial trough, pass a small saucer underneath the mouth of the jar, and remove it to a trough of water; introduce it carefully so that no water shall get into the jar, and rest the saucer on the bottom of the trough. Now suddenly raise the jar, the mercury from its superior weight will fall to the bottom of the trough, and a corresponding volume of water will take its place; the instant the water comes into contact with the gas, it will absorb it with such rapidity that the jar will become instantly filled; indeed, if the gas is perfectly pure, the water rushes in with so much violence as to endanger the safety of the jar; but a single bubble of common air mixed with the gas greatly diminishes the force of the absorption.

Experiment 2.—Fill a bladder with ammoniacal gas, and substitute it for the retort in Fig. 13, the gun-barrel or porcelain tube having been previously filled with iron or copper turnings. When the tube is red-hot, force the gas from the bladder through it, receiving the gases from the other extremity underneath a jar standing over the hydro-pneumatic trough. Examine the gases thus collected: they will be found to consist of nitrogen and hydrogen, and their proportions may be ascertained by detonating a measured portion in the syphon eudiometer with pure oxygen (refer to Ex. 8, sect. Hydrogen). When the tube is cool, remove and examine the metal turnings, they will be found to have become brittle.

Experiment 3.—Fill a bladder with the gas and pass it through a tube heated to redness and filled with peroxide of manganese; let the gases from the opposite end of the tube be conducted into a large globular receiver, which will soon become filled with ruddy fumes, showing the production of nitrous acid.

Experiment 4.—Plunge a lighted taper into a jar of the gas; it will be immediately extinguished.

Experiment 5.—Endeavour to make a jet of the gas burn in atmospheric air; it will be found impossible to keep up a continuous flame.

Experiment 6.—Repeat the same experiment in oxygen; if the gas be not forced out in too rapid a stream, and if the aperture of the tube be fine, it will burn with a yellow flame.

Experiment 7.—Introduce a slip of red litmus paper into a jar of the gas; it will become blue, thus showing the alkaline nature of the gas.—N.B. If the gas be *perfectly dry*, it has no action on vegetable colouring matters.

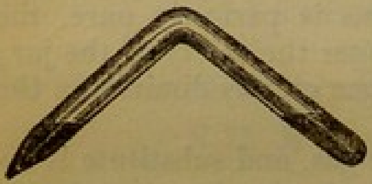
Experiment 8.—Provide two pint wide-mouth stoppered bottles, the edges of which are ground so that they may be closed air-tight with glass plates;

Fig. 22.

fill one with ammoniacal gas by displacement (Fig. 7), and return its stopper. Fill the other also by displacement with hydrochloric acid gas, for which purpose put 300 grains of common salt into a stoppered retort, and pour upon it about double its weight of concentrated sulphuric acid, receiving the gas as shown in Fig. 6. When the bottle is full, which is known by the fumes rolling over the mouth, remove the delivering tube and close the bottle with its glass plate. Next remove the stopper from the bottle containing the ammonia and cover it with the glass plate, then invert the bottle containing the acid gas over that containing the alkaline gas, as shown in Fig. 22, and remove both glass plates; the gases will rush together, dense white fumes will be produced, and the interiors of both bottles will be found lined with a white crust (sal-ammoniac). If *chlorine* be substituted by hydrochloric acid gas in this experiment, the two gases unite with a flash of flame.

Experiment 9.—The liquefaction of ammonia may be effected as follows:—Expose chloride of silver in the pulverulent form to a current of dry ammonia—a very large quantity will be absorbed. Introduce a portion of the saturated chloride into a stout green glass tube, bent as shown at Fig 23, and then seal up the open extremity. Having surrounded this sealed extremity with ice, place the other end containing the chloride into a vessel of water, the temperature of which is to be slowly raised by a spirit lamp; at about 100° it enters into ebullition, and gives off the whole of the ammonia it had absorbed, which liquefies under its own pressure at the cold end of the tube into a clear, colourless, mobile fluid. On allowing the tube to cool, the liquid gradually disappears, being re-absorbed by the chloride, from which it may be again expelled and liquefied by heating it as before.

Fig. 23.



This experiment should only be undertaken by those conversant with glass-blowing, as an imperfect tube may occasion a serious accident.

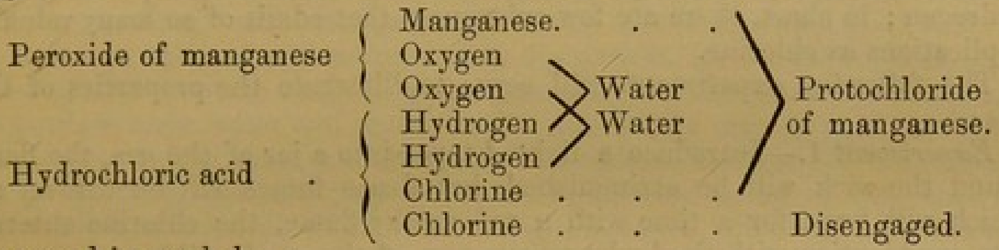
Experiment 10.—Introduce into the syphon eudiometer a quantity of ammonia, and note accurately its volume; pass electric sparks through the gas as long as the volume continues to increase, and note that it becomes at last exactly doubled.

Experiment 11.—Measure into the eudiometer 10 parts of the gaseous residue of the last experiment, and 5 of oxygen; pass the spark; when the tube has cooled, the 15 measures will be reduced to 3·75; consequently, 11·25 measures have disappeared, and must have consisted of 7·5 measures of hydrogen and 3·75 measures of oxygen; these being the proportions in which the gases unite to form water. The 10 measures of the gaseous residue consisted therefore of 7·5 measures of hydrogen and 2·5 of nitrogen, and as these 10 measures were produced originally from 5 measures of ammonia, it appears that 50 measures of ammoniacal gas contain 75 measures of hydrogen and 25 of nitrogen.

CHLORINE.

Equivalent, 35·5 *or* 443·75; *Symbol*, *Cl*; *Density*, 2440 (*Air* = 1000).

Preparation. 1st. *By heating Peroxide of Manganese with Hydrochloric Acid.*—A mixture of equal weights of black oxide of manganese, and common hydrochloric acid is heated in a flask (Fig. 18); the gas, which escapes copiously on the application of a gentle heat, is conducted first through a bottle containing a little water, to remove hydrochloric acid, and then to the hydro-pneumatic trough. It should be received over warm water, as cold water absorbs double its volume of chlorine. The bottles should be removed from the trough as fast as they are filled, and the stoppers greased a little before they are inserted. It may also be collected by displacement. In this reaction two equivalents of hydrochloric acid are required for one of peroxide of manganese, and half the chlorine contained in the acid is obtained as gas, thus—

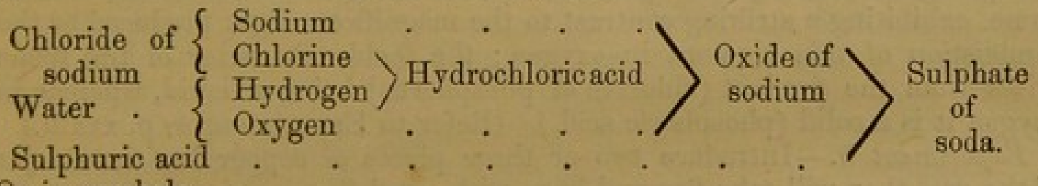


Expressed in symbols—

$$Mn\ O_2 + 2\ H\ Cl = Mn\ Cl + 2\ H\ O + Cl.$$

2. *By the action of Sulphuric Acid on a mixture of Peroxide of Manganese and common Salt.*—One part of peroxide of manganese in fine powder is mixed with 4 parts of common salt (chloride of sodium), the mixture is placed in a flask, and on it is poured 2 parts of strong oil of vitriol diluted with an equal bulk of water. Chlorine is set free by the following reactions:—

The chloride of sodium is first decomposed by the sulphuric acid into hydrochloric acid, and sulphate of soda, thus—



Or in symbols,—

$$Na\ Cl + H\ O,\ SO_3 = NaO,\ SO_3 + H\ Cl.$$

The hydrochloric acid reacting with the peroxide of manganese, as in the former process, gives rise to free chlorine and chloride of manganese. The final reaction may therefore be represented thus:—

$$Na\ Cl + Mn\ O_2 + 2\ SO_3 = Na\ O,\ SO_3 + Mn\ O,\ SO_3 + Cl.$$

Properties.—It is a gas of a yellowish-green colour, whence its name, from the Greek χλωρὸς. It is considerably heavier than atmospheric air, 100 cubic inches weighing 76·59 grains. It is absolutely irrespirable, the smallest quantity producing coughing and great irritation in the trachea. It is soluble in water, which at 60° takes up double its volume, and acquires the colour, smell, and properties of the gas. With water, chlorine forms a crystalline hydrate, composed of 28 parts of chlorine to 72 of water; this hydrate is decomposed at a temperature a few degrees above the freezing-point, and from it chlorine may be obtained in a liquid state. Some of the crystals dried between folds of filtering paper are placed in a stout glass tube, which is then bent into the form of a syphon, and the extremity sealed. On heating the end of the tube containing the crystals in a water bath at 95°, the crystals resolve themselves into two strata of liquid, the lower of a deep yellow colour, consisting of the liquefied gas, and the upper of a lighter colour, of a saturated solution of chlorine in water. Chlorine possesses energetic affinities; with hydrogen it combines both with and without explosion, and several metals take fire spontaneously in it. It combines with oxygen, forming compounds remarkable for their instability, and with nitrogen, it forms one of the most formidably-explosive compounds known. Chlorine is largely employed in the arts as a bleaching agent; it destroys vegetable colouring principles by entering into combination with their hydrogen. It is equally valuable as a disinfectant, destroying the putrid exhalations from decomposing organic matters, which it does by separating their hydrogen; in short, there are few substances that admit of so many valuable applications as chlorine.

The following experiments will serve to illustrate the properties of this gas:—

Experiment 1.—Introduce a lighted taper into a jar of the gas, the flame round the wick will be extinguished, but dense fumes will be thrown off, which will burn for a time with a red smoky flame, the chlorine entering into combination with the hydrogenous part of the combustible.

Experiment 2.—Dip a piece of paper into oil of turpentine, and immerse it in a jar of chlorine, it will spontaneously take fire and the jar become filled with carbonaceous fumes; here, again, the chlorine seizes the hydrogen of the combustible, and rejects the carbon, the other constituent of the turpentine.

Experiment 3.—Sprinkle into a jar of chlorine some powdered antimony or arsenic, the metals will fall to the bottom of the jar in a brilliant shower of fire.

Experiment 4.—Place a piece of phosphorus in the metallic cup (Fig. 10), and plunge it into a jar of chlorine, it will take fire and burn with a feeble flame, exhibiting a striking contrast to the magnificent light produced by the combustion of this element in oxygen; the feeble character of the flame arises from the product (chloride of phosphorus) being a liquid, whereas in oxygen it is a solid (phosphoric acid.) (Refer to Experiment 4, p. xxxiii.)

Experiment 5.—Introduce two or three pieces of copper leaf into a jar of the gas, they will take fire and burn with a red flame.

These experiments succeed best if the jars of chlorine are slightly warmed. The jars must not be closed with their stoppers at the conclusion of the experiments, unless the precaution be taken of inserting a piece of paper, or they will infallibly become permanently fixed. To avoid as much as possible the escape of the irritating gas into the room, it is well to place the jar upon a soup plate containing a little water, and to have at hand a large bell jar, with which it may be immediately covered.

Experiment 6.—Into a stout bottle introduce equal measures of hydrogen and chlorine, and inflame the mixture; an explosion will take place, the two gases combining to form hydrochloric acid.

Experiment 7.—Provide a glass balloon and a glass flask, both of precisely the same capacity; the neck of the globe must be adapted air-tight by grinding to that of the flask; fill the flask with perfectly dry chlorine by displacement and the globe with dry hydrogen; put the two vessels together, and invert them for a few minutes to allow the heavy chlorine to mix freely with the light hydrogen; expose the apparatus to a strong light, but not to the direct rays of the sun. The yellow colour of the chlorine will rapidly diminish, and when it has disappeared, expose the bottles to the sun's rays for a few minutes; this insures the perfect union of the gases, without, however, risking an explosion. Now take the two glasses apart under mercury, and notice that the fluid metal does not rise in either the flask or the globe, showing that the volume of the gases remains unaltered. Chlorine acts upon mercury, but the absence of action in this case proves that no free chlorine is present. To demonstrate that the hydrogen is not in excess, throw a little water into the flask while standing over the mercury, and notice that the gas is entirely absorbed, and that the water has become strongly acid. The whole experiment proves that chlorine and hydrogen combine volume to volume without condensation to form hydrochloric acid gas.

Experiment 8.—Prepare a strong aqueous solution of chlorine thus:—Fill a stout bottle with the gas, and having closed it with a good cork, remove it to a basin of cold water, mouth downwards, loosen the cork so as to allow a little water to rush in, agitate the gas with this water; as absorption takes place more water will enter, and at last, if the gas is pure, the bottle will become full of water containing its own volume of chlorine. The bleaching property of chlorine may be shown by pouring some of this chlorine water into a solution of sulphate of indigo, the blue colour of which it will discharge; and its deodorizing property may be illustrated by pouring some of the solution into a jar of water impregnated with sulphuretted hydrogen, the abominable smell of which it destroys.

CARBONIC ACID.

Equivalent, 22 *or* 275; *Symbol,* CO_2; *Density* 1529 (*Air* = 1000).

Preparation. By acting on Carbonate of Lime with a strong Acid.—Fragments of marble are placed in a two-necked gas bottle, and on them is poured sufficient water to fill the bottle one-third; it is then agitated, so as to expel the bubbles of air which adhere to the marble. Hydrochloric acid is poured into the bottle through the funnel, active effervescence immediately takes place, and carbonic acid gas is disengaged in large quantities. The reaction is as under—

Carbonate of lime	Carbonic acid		Carbonic acid gas disengaged.
	Calcium		Chloride of calcium.
	Oxygen	water	
Hydrochloric acid	Hydrogen		
	Chlorine		

In symbols—

$$CaO, CO_2 + H\,Cl = Ca\,Cl + HO + CO_2.$$

After the action has continued for some minutes, the gas may be received over water or mercury, or by displacement (Fig 6). It may be considered pure when it is completely absorbed by caustic potash.

Properties.—It is colourless and nearly odourless, but possessing a slightly sour taste. It is considerably heavier than atmospheric air, 100 cubic inches weighing, at 60° Fahr., 47·339 grains. It is soluble in water, which at common temperatures dissolves its own volume of the gas, acquires an agreeable acidulous taste, and sparkles when agitated. The quantity of carbonic acid gas which water is capable of dissolving increases with the pressure to which it is subjected; when the pressure is removed the gas escapes with effervescence; it is the basis of effervescing drinks. Under a pressure of 36 atmospheres, and at the temperature of 32°, carbonic acid gas becomes an extremely mobile colourless liquid, remarkable for its extraordinary dilatability by heat, being more expansible than air itself. At 14° it liquefies under a pressure of 27 atmospheres, and at — 22° under a pressure of 18 atmospheres. Below — 72° liquid carbonic acid becomes a clear, transparent, colourless solid, like ice. When solid carbonic acid is mixed with ether, it forms a semi-fluid mass, like half-melted snow, and produces a cold as low as — 135°. Pure carbonic acid gas is instantly fatal to animal life; and air containing not more than 1 or 2 per cent. of it has been known to produce serious effects; it acts as a narcotic poison. Neither will it support combustion; a candle will not burn in air containing one-fourth of its volume of carbonic acid. This gas is formed in a great number of natural processes; in all ordinary combustions; in respiration; and in fermentation; it is also poured into the atmosphere in enormous quantities from active, and from fissures in the neighbourhood of extinct, volcanoes. Many mineral waters, such as those of Pyrmont and Tunbridge, are highly charged with it, and it exists in greater or less quantities in all kinds of well and spring water.

Some of the most striking properties of carbonic acid gas may be demonstrated by the following experiment:—

Experiment 1.—Fill a tall jar with the gas by displacement (Fig. 6), let down a lighted taper to the bottom of another jar containing common air, and pour the gas from the first jar upon it, just as you would pour a liquid; the heavy carbonic acid gas will displace the common air, and the moment it comes into contact with the flame, will put it out. By the aid of a lighted taper the progress of the filling of a jar with this gas by displacement may be traced.

Experiment 2.—The opposite properties of carbonic acid gas and oxygen, the one to extinguish flame, and the other to support it with brilliancy, are well illustrated by the following experiment. Provide two wide-necked bottles, the mouths exactly fitting each other; one bottle must be open at both ends, and the edges ground so as to admit of being closed air-tight with a glass plate, the other bottle must be closed at one end. Fill the latter bottle with carbonic acid gas, and the other with oxygen; now invert the oxygen bottle over the carbonic acid bottle precisely as directed in Experiment 8, section "Ammonia." You thus have an atmosphere of pure oxygen floating on one of carbonic acid. Now light a green wax taper with a wide-spreading wick, and plunge it into the oxygen, and while it is burning brilliantly, depress it into the carbonic acid; before the last spark is extinguished raise it again into the oxygen; with a little address the taper may be extinguished and relighted several times.

Experiment 3.—Fill a bottle half full of carbonic acid gas at the water trough, insert a cork, remove it from the trough, and agitate it well, notice that the water will absorb the gas and acquire sparkling properties; notice also that the water will communicate a wine-red tint to blue litmus paper, but that the blue colour is restored when the paper becomes dry.

Experiment 4.—Pass a stream of the gas from the evolution bottle into a small jar containing lime-water, notice that a white flaky precipitate is first formed, but that as the gas continues to pass the precipitate is dissolved, and a perfectly clear solution obtained. Here carbonate of lime was first formed and precipitated, but carbonate of lime being soluble in free carbonic acid, the precipitate was redissolved as soon as the gas was present in sufficient excess.

Experiment 5.—Burn a spirit lamp underneath a large funnel, to the beak of which a long tube bent twice at right angles is adapted, the free end passing to the bottom of a tall jar; after the lamp has been burning for some time, test the air in the jar for carbonic acid by a lighted taper, and notice the progress of the accumulation. This experiment proves that carbonic acid is a product of ordinary combustion. (Refer to Experiment 2, section "Oxygen.")

Experiment 6.—Expel the air from the lungs through a glass tube into a jar containing lime-water until the liquid becomes very turbid, a precipitate will gradually form; after it has collected, draw off the supernatant clear liquid with a pipette, and pour on a few drops of hydrochloric acid, notice that effervescence takes place, and that the liquid becomes clear. Here carbonic acid from the lungs (a product of respiration) forms carbonate of lime with the lime-water; the carbonate of lime is again decomposed by the hydrochloric acid, and the gas expelled.

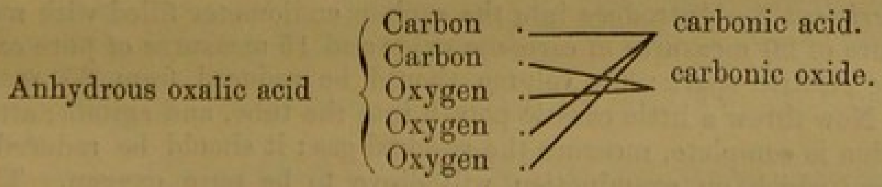
Experiment 7.—Fill a clean and dry Florence flask with carbonic acid gas by displacement, introduce a little ball of potassium, and heat it strongly by a spirit lamp, the metal will burn with a brilliant violet flame and become converted into potash, while carbon in the form of a black film will be deposited on the sides of the flask; carbonic acid is thus shown to be composed of carbon and oxygen.

CARBONIC OXIDE.

Equivalent, 14 *or* 175; *Symbol*, *CO*; *Density*, 967·8 (*Air* = 1000).

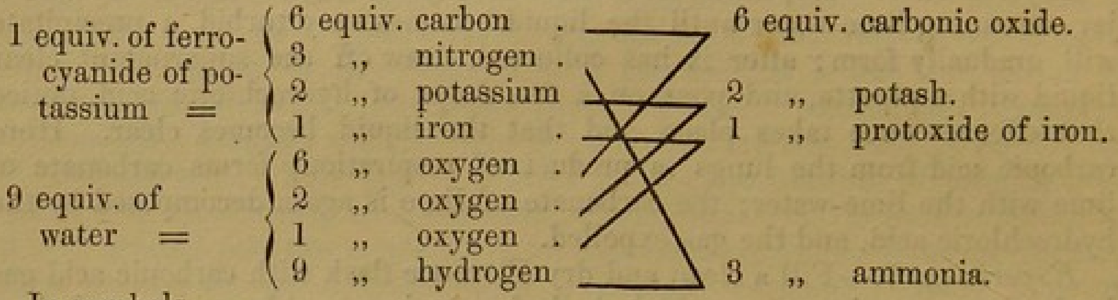
Preparation 1. *By decomposing Carbonic Acid by red-hot Charcoal.*—An intimate mixture of finely-powdered chalk and charcoal is strongly heated in an iron retort in a reverberatory furnace. The carbonate of lime is decomposed, and carbonic acid is set free, which in its turn is decomposed by the red-hot charcoal, which takes away half its oxygen, the carbonic acid is thus converted into carbonic oxide.

2. *By decomposing crystallized Oxalic Acid by concentrated Sulphuric Acid.*—To one part of crystallized oxalic acid in a stoppered retort or gas flask is added five or six parts of concentrated oil of vitriol, and heat applied; the oxalic acid first dissolves in the sulphuric acid, and is then decomposed into two gases, carbonic acid and carbonic oxide; the former gas is absorbed by allowing the gaseous mixture to bubble through a two-necked Woulfe's bottle containing a strong solution of caustic potash, the carbonic oxide is thus obtained pure, and may be received in the usual manner over water. The reaction is as under: 1 equivalent of crystallized oxalic acid is composed of 2 equivalents of carbon and 3 of oxygen, plus 3 equivalents of water; the peculiarity of this acid is, that it cannot exist save in combination with water or some base, the sulphuric acid unites with the water of the crystallized acid, and the anhydrous acid is set free and immediately resolved into carbonic acid and carbonic oxide, thus—



3. *By decomposing Ferrocyanide of Potassium by Sulphuric Acid.*—To one part of crystallized ferrocyanide of potassium (yellow prussiate of potash) is added 4 or 5 parts of concentrated oil of vitriol, the mixture is heated in a flask, and the gas, after passing through a wash bottle containing a little water, is collected over the hydro-pneumatic trough. In this reaction the

elements of one equivalent of ferrocyanide of potassium and nine equivalents of water (partly from the oil of vitriol, and partly from the crystallized salt), are rearranged into 6 equivalents of carbonic oxide, 2 of potash, 3 of ammonia, and 1 of peroxide of iron, thus—



In symbols—

$$K_2 Fe C_6 N_3 + 9 HO = 6 CO + 2 KO + Fe O + 3 H_3 N.$$

Half an ounce of the salt yields upwards of 300 cubic inches of carbonic oxide perfectly pure. This beautiful reaction was discovered by the late *Dr. Fownes.*

Properties.—It is colourless, and without smell; it has never been liquefied. It burns in the air when set on fire with a characteristic blue flame. It is rather lighter than atmospheric air, 100 cubic inches weighing 30·2 grains. Water dissolves about $\frac{1}{16}$th of its volume of it; neither the solution nor the gas itself has acid or basic properties. The bluish flame sometimes seen on the surface of coke furnaces is caused by the combustion of this gas; the carbonic acid produced by the combustion of the fuel in the lower part of the furnace giving up part of its oxygen to the red-hot embers through which it passes. Carbonic oxide acts on the system as a true poison. In its pure state it is instantly fatal to animal life, and air containing but a small percentage of it exercises a very prejudicial action on the economy. It is probably to its presence that the oppression and headache frequently experienced in badly-ventilated rooms in which coke or charcoal furnaces are burning are to be attributed. Carbonic oxide is absorbed by potassium, which is the reagent employed to remove it in the analysis of gaseous mixtures.

The following experiments may be made with this gas:—

Experiment 1.—Having filled a tall jar with the gas, remove it from the pneumatic trough by covering the mouth of the jar with a glass plate, set down the jar mouth upwards, remove the glass plate and inflame the gas, observe that it burns with a blue flame; when the flame is extinguished, pour some lime-water into the jar and agitate it, notice that the lime-water becomes turbid, indicating the formation of carbonic acid.

Experiment 2.—Introduce into the syphon eudiometer filled with mercury a mixture of 20 measures of carbonic oxide and 15 measures of pure oxygen; pass the electric spark; the volume should be reduced from 35 measures to 25. Now throw a little caustic potash into the tube, and agitate; after the absorption is complete, measure the residual gas; it should be reduced to 5 measures, which on examination will prove to be pure oxygen. The 20 measures absorbed by the caustic potash are carbonic acid, and are exactly equal to the quantity of carbonic oxide originally introduced into the tube; carbonic oxide, therefore, in burning, passes into carbonic acid without undergoing any alteration of volume. The quantity of oxygen consumed is 10 measures, for, of the original 15 measures, 5 were left unused. From these data it is learned that 100 measures of carbonic oxide combine with 50 measures of oxygen to form 100 measures of carbonic acid. Now carbonic acid gas contains its own volume of oxygen; it is evident, therefore, that carbonic oxide can only contain one-half its volume of that principle.

PROTOCARBURETTED HYDROGEN.

Equivalent, 16 *or* 200; *Symbol*, $C_2 H_4$; *Density*, 559·6 (*Air* = 1000).

Preparation. By strongly heating a mixture of Acetate of Soda, Hydrate of Potash, and Quick-lime.—Three parts of pulverized quick-lime are moistened with a solution of 2 parts of caustic potash in a small quantity of water, the paste thus formed is dried at a low red heat; a mixture of 10 parts of this alkaline powder, and 4 of crystallized acetate of soda, is strongly heated over a charcoal furnace in a Florence oil flask, coated with a mortar composed of plaster of Paris, and half its weight of sand and coal ashes. The flask is provided with a good cork and delivering tube. The gas, which is disengaged in abundance, is collected over water in the usual manner. The reaction is represented in the following equation—

$$NaO, C_4 H_3 O_3 + KO, HO = NaO, CO_2 + KO, CO_2 + C_2 H_4,$$

by which it is seen that the elements of one equivalent of dry acetic acid, and one equivalent of water, rearrange themselves into 2 equivalents of carbonic acid, which remain in the flask in combination with the potash and soda, and 1 equivalent of light carburetted hydrogen, which passes off as gas.

This gas is identical with that terrible enemy of the coal miner, *fire-damp;* it is also the most considerable constituent of coal gas; it is constantly produced during the putrefaction of vegetable substances under water; the bubbles of gas frequently seen rising from the bottoms of pools consist principally of this variety of carburetted hydrogen, and by stirring the mud at the bottom of such pools, the gas may be collected in bottles. It always contains a large quantity of carbonic acid, and likewise some nitrogen. By the subjoined equation it will be seen that a mixture of protocarburetted hydrogen and carbonic acid may be supposed to be formed by the reaction of 4 equivalents of carbon with 4 equivalents of water, thus—

$$4\ C + 4\ HO = 2\ CO_2 + C_2 H_4.$$

Properties.—It is colourless and without taste or smell; it is lighter than atmospheric air, 100 cubic inches weighing between 16 and 17 grains. It has never been liquefied, and is only very sparingly soluble in water. Although instantly kindled by a light, and burning with a pale bluish flame, it requires a high temperature to ignite it, on which peculiarity the safety lamp is founded. When it burns in the air the results of the combustion are water and carbonic acid.

The properties and composition of this gas are evinced by the following experiments:—

Experiment 1.—Having filled a capped bell jar with the gas, screw a jet on the stopcock; depress the jar steadily underneath the water of the trough so as to force a stream of gas through the jet, and endeavour to inflame the gas by holding a red-hot iron wire or glass rod over it; it will be found impossible to kindle it by such a heat; make a corresponding experiment with hydrogen and carbonic oxide, and observe that both these gases will readily inflame. Now apply a lighted taper to the jet, and notice that the gas will burn with a pale blue flame.

Experiment 2.—Introduce into the syphon eudiometer filled with mercury 40 measures of a mixture of 30 measures of protocarburetted hydrogen and 10 measures of pure oxygen; pass the spark. The 40 measures should be reduced to 20; absorb the carbonic acid formed by the combustion, by a globule of hydrate of potash; after the absorption is complete, 10 measures only should remain, which consist of oxygen. Now the 10 parts of carbonic acid absorbed consist of 5 parts of carbon vapour and 10 of oxygen; the other 10 measures of oxygen, therefore, which have disappeared, must have combined with 20 measures of the hydrogen contained in the protocarburetted hydrogen to form water, and the 10 measures of this gas originally introduced into the eudiometer must have consisted of 20 measures of hydrogen and 5 of carbon vapour, or 100 measures, of 200 measures of hydrogen and 50 of carbon vapour. Now

			Grains.
50	cubic inches	of carbon vapour weigh	12·70
200	,,	hydrogen ,, ...	4·23
100	,,	protocarburetted hydrogen should weigh	16·93

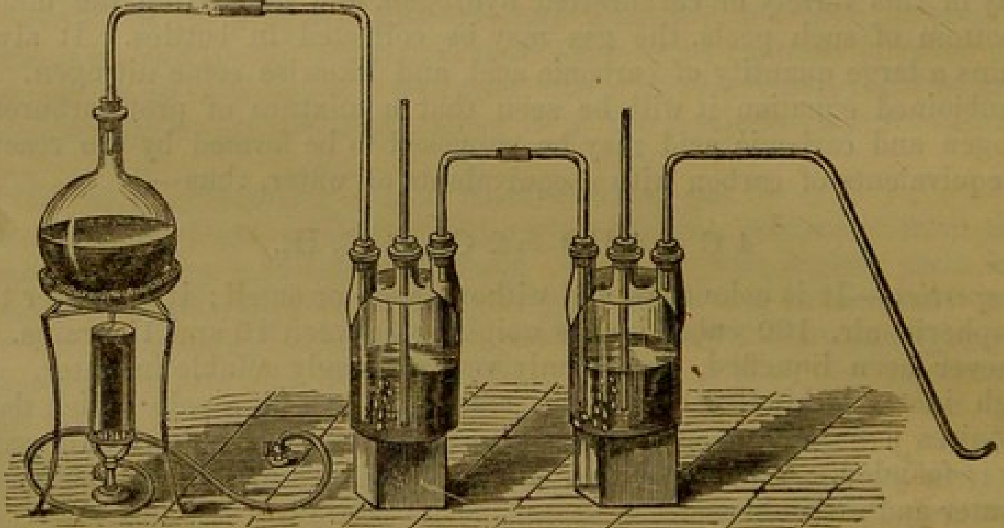
a number which agrees closely with that obtained by actually weighing the gas.

Bicarburetted Hydrogen.

Equivalent, 28 *or* 350; *Symbol*, $C_4 H_4$; *Density*, 985·2 (*Air*=1000).

Preparation. By the action of concentrated Sulphuric Acid on Alcohol.—One part by weight of alcohol is heated in a capacious flask (Fig. 24) with 5 or 6 parts of concentrated sulphuric acid. The gaseous products are bearburetted hydrogen, or *olefiant gas*, and carbonic and sulphurous acids. The mixture is passed through two Woulfe's bottles, the first containing a little water to condense any alcohol and ether which may distil over, and the second a strong solution of caustic potash, by which the carbonic and sulphurous acids are absorbed. By comparing the formula of bicarburetted hydrogen with that of alcohol, the action of sulphuric acid on the latter would

Fig. 24.



seem to be very simple, consisting merely in the removal of the elements of two equivalents of water, thus—

$$C_4\ H_6\ O_2 = C_4\ H_4 + 2\ HO\ ;$$

but the action is in reality by no means so simple, for if the vapour of absolute alcohol be caused to traverse a mixture of 100 parts of concentrated sulphuric acid and 30 of water kept at its boiling temperature (about 330° Fahr.), abundance of olefiant gas is disengaged, while at the same time a quantity of water distils over from the acid, exactly corresponding with that which the alcohol should have lost in becoming converted into bicarburetted hydrogen. The composition of the acid mixture remains unaltered, and it is capable of transforming an almost unlimited quantity of alcohol into bicarburetted hydrogen; the formation of olefiant gas in this reaction cannot, therefore, be owing to the mere affinity of sulphuric acid for water. In the preparation of bicarburetted hydrogen by heating together alcohol and sulphuric acid, the disengagement of gas is at first tolerably regular; after awhile, however, it becomes tumultuous, and is given off in jerks, the mixtures become black and viscous, swelling up considerably, so that it is necessary to employ a capacious flask; at the end of the operation a black solid mass remains in the flask, the composition of which is very complicated.

Properties.—Olefiant gas is a colourless gas, burning with a brilliant white flame, which deposits abundance of carbon on cold bodies with which it comes into contact. It is somewhat lighter than atmospheric air, 100 cubic inches weighing about 30 grains. By exposing it under pressure to a cold 166° below 0°, it was condensed by *Faraday* into a transparent colourless liquid. Water absorbs about $\frac{1}{8}$th of its volume of it, and it is likewise absorbed by, and forms peculiar compounds with, fuming sulphuric acid and perchloride of antimony; the latter substance is employed to effect its separation in the analysis of gaseous mixtures. It is decomposed when passed through a porcelain tube at a white heat, depositing its carbon, and giving off twice its volume of hydrogen gas; at a red heat it is decomposed into carbon and protocarburetted hydrogen. It is condensed also by chlorine, with which it forms an oily liquid, from which it derives its names, "Olefiant" (oil making) and Elayle (ἔλαιον and ὕλη), the source of an oil. The oily compound of olefiant gas and chlorine results from the union of equal volumes of each gas. It has long been known under the name of Dutch liquid, having been discovered by some Dutch chemists. Its formula is $C_4\ H_4\ Cl_2$. It is a colourless liquid, possessed of a very agreeable smell. When burnt with chlorine, olefiant gas undergoes complete decomposition, hydrochloric acid being formed and carbon deposited. Some of these properties of the gas are exhibited in the following experiments.

Experiment 1.—Collect a quantity of the gas in a capped bell jar, endeavour, as in the corresponding experiment with protocarburetted hydrogen, to inflame it with a red-hot poker, observe that it will readily take fire and burn with a remarkably-brilliant white flame. Hold a white plate in the flame, and notice that carbon is deposited on it.

Experiment 2.—Hold over the jet a sheet of iron wire trellis containing about 500 apertures in the square inch, inflame the gas above the jet, then raise the trellis, and observe that the flame will not pass through the gauze though the gas continues to burn above it. Notice the difference in the character of the flame; instead of being white and brilliant, it will be pale blue, giving very little light; hold a white plate in this altered flame, and observe that no carbon is deposited upon it; hold a coil of platinum wire in it, and notice that it is raised to a white heat, showing that the flame, though it has lost its brilliancy, is not diminished in its heating powers. Now inflame the gas as it issues from the jet, and bring the trellis down upon it, observe that no flame will pass through, but that a black smoke will rise through the meshes. Look down upon the flame through the gauze and observe its hollow structure.

The phenomena observed in this experiment are thus explained:—The flame cannot pass through the trellis because the metallic tissue conducts the heat so rapidly away that the temperature falls below that which is necessary to support it. The flame becomes blue because the combustion is perfect, sufficient air becoming mixed with the gas before it is inflamed thoroughly to oxidize both the carbon and the hydrogen, no soot is therefore deposited on a cold surface. On the other hand, soot *is* deposited on a cold body held in the white flame, because the combustion there is not perfect, sufficient oxygen not being present to combine with both the hydrogen and the carbon; a portion of the latter is therefore unburned, though it is heated to whiteness by the intense heat produced by the combustion of the hydrogen, and hence the brilliant light.

Experiment 3.—Divide a tall jar 2 feet high and 4 inches in diameter into three equal parts, pasting a slip of paper outside to mark each division. Fill the jar one-third full of olefiant gas, and then the remaining two-thirds with chlorine; remove the jar quickly from the trough by slipping a glass plate under its mouth, invert it, remove the plate, and apply a light. Observe that the gaseous mixture burns slowly, with a red flame, throwing off a dense smoke, smelling strongly of naphthaline, and depositing a thick coating of carbon on its sides. In this experiment the hydrogen of the olefiant gas passes to the chlorine, and forms with it hydrochloric acid gas, while the carbon, being left uncombined, makes its appearance in its natural form.

Experiment 4.—Instead of burning the mixture of chlorine and olefiant gases, allow them to act on each other in the cold. With this view throw into the tall jar equal volumes of each, and observe that almost complete absorption will gradually take place, and that an oily-looking liquid (Dutch liquid, $C_4\ H_4\ Cl_2$) will float on the surface of the water.

N.B.—Olefiant gas may be completely separated from a mixture containing protocarburetted hydrogen, hydrogen, carbonic oxide, and nitrogen, by chlorine; as, though this principle exerts an action on all the combustible gases with phenomena peculiar to each, olefiant gas is the only inflammable gas condensed by it in the absence of light. Suppose in a gaseous mixture containing the gases before enumerated, it is desired to know the quantity of olefiant gas, the following experiment may be made.

Experiment 5.—Into a graduated tube about $\frac{3}{10}$ inch in diameter, pass a certain quantity, say 30 measures, of chlorine, observe its exact volume, and then shade it from the light by a pasteboard case. Now throw up a certain quantity, say 50 measures, of the gaseous mixture, and allow it to remain at rest for a quarter of an hour or so, then gradually raise the cover till the surface of the water within the tube appears. Note the diminution, and divide its amount by 2, which will give the quantity of olefiant gas.

Experiment 6.—Introduce into the syphon eudiometer filled with mercury 50 measures of a mixture of 10 measures of bicarburetted hydrogen and 40 of oxygen; pass the spark; 30 measures should remain, of which 20 should be absorbed by caustic potash, the remaining 10 being oxygen; the 10 measures of olefiant gas have therefore consumed 30 measures of oxygen. Now in the 20 measures of carbonic acid formed, there are 20 measures of oxygen, and 10 measures of gaseous carbon; 10 measures of oxygen have therefore been consumed by the hydrogen of the olefiant gas; these 10 measures must have taken 20 measures of hydrogen; hence the composition of the 10 measures of olefiant gas is 20 measures of hydrogen, *plus* 10 of vapour of carbon, or 100 volumes contain 200 volumes of hydrogen and 100 volumes of carbon vapour. Now

	Grains.
100 cubic inches of carbon vapour weigh	25·4
200 ,, hydrogen gas weigh	4·2
100 ,, olefiant gas should weigh . . .	29·6

which agrees very closely with the number obtained by actually weighing the gas.

N.B.—The explosion of oxygen and olefiant gas being very violent, this experiment should only be attempted in a very stout tube.

CYANOGEN.

Equivalent, 26 *or* 325; *Symbol*, C_2, *N*; *Density*, 18·19 (*Air* =1000).

Preparation. By heating Cyanide of Mercury.—A portion of the salt is heated to dull redness in a small glass retort. It is decomposed into metallic mercury, which condenses in the cold part of the retort, and cyanogen, which is evolved as gas, and which may be collected in Cooper's mercurial tube receiver. A black mass remains in the retort, having the same composition as the gas, and is in consequence termed *paracyanogen*.

Properties.—It is a colourless gas, of a peculiar and penetrating smell, resembling that of bitter almonds. It is considerably heavier than atmospheric air, 100 cubic inches weighing 55·5 grains. It is one of the most easily liquefied of the gases, becoming a colourless very mobile liquid, under a pressure of 4 or 5 atmospheres at ordinary temperatures. Its liquefaction may be accomplished without the slightest danger by sealing some cyanide of mercury hermetically in a long syphon-shaped tube, and heating it while the empty limb is plunged into a mixture of ice and salt. Cyanogen burns with a splendid purple flame, the result of its combustion being carbonic acid and nitrogen. It is soluble in water, which takes up four or five times its volume of the gas in the cold, but abandons it again when heated. The aqueous solution undergoes spontaneous decomposition, and gradually deposits a brown powder. Cyanogen forms numerous combinations with other bodies, the most important being that with hydrogen, viz., the well-known poison hydrocyanic, or prussic acid. The analysis of cyanogen cannot be accomplished by detonating it in the eudiometer with oxygen *alone*, the combustion being always incomplete; but by adding to the mixture an indefinite quantity of pure oxygen and hydrogen gases in the exact proportions in which they unite to form water (the gaseous mixture obtained by decomposing acidulated water by the voltaic battery is best adapted to the purpose), its decomposition may be affected thus:—

Experiment 7.—Pass into the syphon eudiometer 35 measures of a mixture of 10 measures of cyanogen and 25 of oxygen, and then an indefinite quantity of the detonating oxyhydrogen mixture. Wait a few minutes to allow the gases to become thoroughly mixed, and then pass the electric spark, the result of the explosion is water, carbonic acid, and nitrogen, together with excess of oxygen; its volume should be 35 measures. Agitate the mixture with a small quantity of caustic potash; the carbonic acid is absorbed, and 15 measures of a mixture of oxygen and nitrogen should remain. The 10 measures of cyanogen, therefore, having yielded 20 measures of carbonic acid, must have contained 10 measures of carbon vapour.

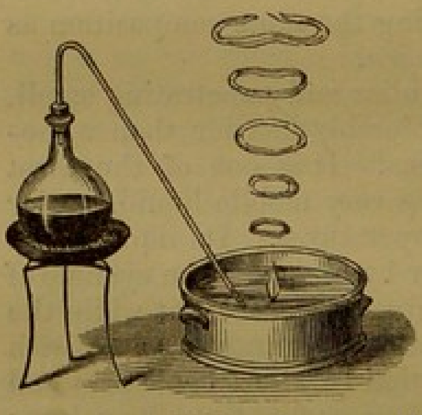
It still remains to analyze the 15 measures of oxygen and nitrogen. Throw into the eudiometer an equal volume of pure hydrogen, and pass the spark. On cooling, 15 measures should remain; 15 measures have, therefore, disappeared, which, being water, must have consisted of 10 measures of hydrogen and 5 of oxygen. In the 15 measures of oxygen and nitrogen left after the absorption by caustic potash, there must, therefore, have been 5 measures of oxygen and 10 of nitrogen. We thus get the data for ascertaining the composition of the 10 measures of cyanogen submitted to analysis. They must have consisted of 10 measures of nitrogen, *plus* 10 measures of carbon vapour; or, in other words, 1 volume of cyanogen contains 1 volume of carbon vapour and 1 volume of nitrogen condensed into 1 volume.

Phosphuretted Hydrogen.

Equivalent, 19 *or* 237·5; *Symbol*, PH_3.

Preparation. By boiling Phosphorus in a strong Solution of Caustic Potash.—A small flask (Fig. 25) is three-fourths filled with a concentrated solution of caustic potash; small fragments of phosphorus are added, and heat applied. Before adapting the delivering tube to the flask, a small quantity of the gas evolved should be allowed to escape. This precaution is necessary, for as this form of phosphuretted hydrogen takes fire on coming into contact with air, if all atmospheric air be not expelled from the flask before it is closed, the first liberation of the inflammable gas may occasion an explosion. The delivering tube is placed under the surface of the water in the pneumatic trough; as the gas rises it bursts into flame, producing a series of beautiful white wreaths of smoke, which enlarge as they rise in the air, and are very regular in form if the air be perfectly tranquil. If the bubbles of gas are allowed to pass into a jar containing oxygen, the combustion is exceedingly brilliant; but this experiment requires great care; the gas must only be allowed to rise in small bubbles, or an explosion may take place.

Fig. 25.



The theory of the action is this. Phosphorus alone does not decompose water, but in the presence of potash the affinity of this base for hypophosphorous acid, which is one of the products of the reaction, determines the decomposition of water precisely in the same manner as in the preparation of hydrogen from zinc, water, and sulphuric acid, the latter substance enables the zinc to decompose water at ordinary temperatures. One part of the phosphorus combines with oxygen to form hypophosphorous acid, which, with potash, forms the salt hypophosphite of potash; another part of the phosphorus unites with hydrogen to form phosphuretted hydrogen. The reaction may be expressed in formula, as under, but the phosphuretted hydrogen is always mixed with more or less free hydrogen.

$$4\ P + 3\ KO, HO = PH_3 + 3\ KO, 3\ PO.$$

CHEMICAL MANIPULATION
AND
ANALYSIS,
QUALITATIVE AND QUANTITATIVE.

PART I.—QUALITATIVE.

In commencing this Treatise on Chemical Analysis, it may be well to explain briefly the circumstances which induced its appearance in its present detached form. Some time since the publisher of the "Library of Useful Knowledge" put into the writer's hands the Treatise on Chemistry, compiled some years ago for that publication by the late Professor Daniell, with a request that he would revise it, and prepare a Supplement bringing down the science to its present condition, in accordance with the plan adopted with regard to other scientific treatises comprised in the "Library."

The writer undertook the task; but, on carefully reading through the work, he found that the progress of Chemistry, during the last ten years, would require such numerous and material alterations to be made in it, to suit it in any way to his own views, that after much deliberation he was induced to suggest that a new work should be written, which should include also the important subjects of "Organic Chemistry" and "Chemical Manipulation and Analysis;" in short, that in the new publication the whole subject of Chemistry should be treated in a complete and popular manner, according to the original views of the projectors of the "Library of Useful Knowledge." This proposition being assented to, the writer of this small treatise has undertaken to draw up a general work on Chemistry, embodying such of the results of recent investigation as shall be suitable to the occasion, and not losing sight of the important fact, that the work is intended for the general as well as for the scientific reader.

A considerable time being necessarily required to perform this task in an efficient manner, it has been thought advisable to issue the present Treatise at once, as an *earnest* of what is intended, and to enable those parties who are in possession of the former work to give it something of a character of completeness.

This present work will, then, be devoted to a detail of the methods of conducting the analyses of inorganic and organic substances, a description of the apparatus required, and the methods of manipulation. It is hoped that the student, whose pursuits may place him out of the reach of oral instruction, will find it sufficiently explicit to enable him to pursue successfully this fascinating recreation, whilst others, more fortunately situated, may not find it useless as an auxiliary to their laboratory labours.

CHAPTER I.

General Remarks on Chemical Analysis.

Chemistry is distinguished from most other sciences by being essentially experimental; its object is the investigation of the material constituents of the globe, and the study of their different properties and relations; the student is, therefore, constantly engaged in observing the phenomena presented on submitting the different substances that come under his notice to the action of various agents, and in the accumulation of facts derived from experimental inquiry. It is, indeed, this circumstance which gives to Chemistry its principal charm; the tyro no sooner begins to read than he begins to experimentalise, and being thus enabled, to a certain extent, to verify for himself the facts brought before him, he acquires an interest in his pursuit which attaches him daily more and more to it.

In order to pursue analytical Chemistry with any chance of success, the student must possess certain qualifications; these may be stated to be—habits of strict order and scrupulous neatness; a dexterity of manipulation which practice alone can give; a firm conviction that the laws of Nature are unchangeable, and that variations in experimental results must consequently imply either a non-fulfilment of certain necessary conditions, or some error in manipulation; and a rigorous *honesty*, not only in recording results, but in experimenting, and in interpreting the phenomena which present themselves in the course of an investigation.

The determination of the constituent parts of a compound body is termed its *analysis;* and this may be either of two kinds, according to the object which the operator has in view. If he merely seek a knowledge of the general nature of the substance, he is satisfied, when by the application of certain tests, and by the performance of certain operations, he has obtained evidence of the presence of those elements of which the compound is made up, and the analysis he performs is called *qualitative;* but if he desire to appeal to the balance, and to ascertain not only the *nature,* but the actual *amount* of the elements present, he must shape his analysis in such a manner as to separate the constituents of the compound completely from each other, and obtain them either pure or in some other well-known form of combination: he then performs a *quantitative* analysis. For example, if on the addition of a few drops of solution of ferrocyanide of potassium to a neutral and clear liquid a beautiful blue precipitate be obtained, the operator is at once satisfied of the presence of iron; and if he is working *qualitatively* only, this experiment is, with regard to that particular element conclusive, it requires no additional confirmation; but if he desire to estimate the exact amount of iron present, he must conduct his analysis in such a manner as to separate every particle of the metal in the state of sesquioxide, in which state it is weighed, and the amount of metal deduced by calculation. Now, before the chemist can proceed to estimate the proportions of the constituents of a compound body, he must know exactly how many elements are present, and what those elements are. The qualitative analysis always, therefore, precedes the quantitative; and it will be necessary to separate the two courses of study, and to treat each individually.

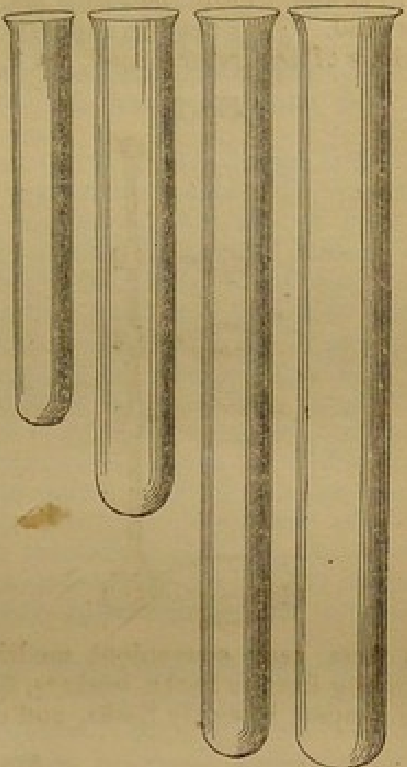
Qualitative Analysis — Operations to be performed and Apparatus required.

1. *Solution.*—To prepare a substance for the exertion of chemical action, and to suit it for the reception of the various tests and reagents to which we may wish to submit it, recourse is always, if possible, had to solution. Now solution is of two kinds, being effected either by fluids which exert no chemical action on the body dissolved, as when sugar is dissolved in water, or camphor in spirits of wine; or by fluids which do exert a chemical action on the substance, as when chalk is dissolved in vinegar, or iron in dilute sulphuric acid. Whenever it is practicable, the substance under examination is dissolved in water; but, if that menstruum fail, recourse is then had to other fluids, the selection of which requires care and judgment.

A compound may be made up of constituents, some of which are soluble in water, and some insoluble. In order to ascertain this point, a small quantity of the substance, brought into a fine state of division by pulverization, is introduced into a test tube covered with distilled water and submitted to heat; the liquid is filtered, while hot, into a small platinum capsule and evaporated carefully and slowly; if a residue remain, it of course indicates that a substance soluble in water existed in the compound. Should there be reason to suspect the presence of a volatile body soluble in water, heat should not be applied in the first instance, but the substance under examination repeatedly agitated with cold distilled water, and the clear solution allowed to evaporate spontaneously. Bodies, however, capable of assuming the gaseous state by the heat of boiling water, may in most cases be recognised by their odour, or by the application of certain tests which will hereafter be described.

Alcohols, ether, pyroxilic spirit, and certain oils, are occasionally successfully employed to dissolve substances on which water has no action, sometimes also a mixture of alcohol and water is found very useful. For example, if the object be to separate sulphate of lime (gypsum) from chloride of sodium (common salt), this cannot be effected by water alone, sulphate of lime being partially soluble in that fluid; but by employing a mixture of one part of alcohol and two or three parts of water the two substances are easily separated, sulphate of lime being entirely insoluble in diluted spirit. Acids, again, sometimes act as mere solvents, and may be conveniently employed as such; thus oxalate of lime dissolves in hydrochloric acid without decomposition, as does also phosphate of lime, and both of these salts may be obtained again from their acid solution, unaltered by supersaturation with ammonia.

Fig. 1.*



The apparatus required for the purpose of solution is in general very simple. For qualitative experiments there is nothing so convenient as the Test Tube, *fig.* 1. It should be made of hard German glass, and the bottom blown round and tolerably thin. The student should possess a good stock of these useful implements: they should be of various sizes, from three to six inches long, and of such a diameter that they may readily be closed with the thumb, for the purpose of agitation. They should be kept ready for use in a rack, to which it is advisable that there should be attached a series of pegs on which the tubes may be inverted, to drain after being washed. If the tube-rack stand be provided with a couple of drawers, they will be found to add to its convenience: they serve to hold the blowpipe, platinum foil and wire, charcoal supports, fluxes, &c., &c. The Spring-Holder, *fig.* 2, is a useful accompaniment to the Test Tube apparatus; it serves to grasp the tube while its contents are under the influence of heat. When larger quantities of liquid have to be operated upon, flasks of various sizes may be substituted for test tubes. The common Florence oil flask forms an admirable vessel for this purpose. The edge of the mouth should be carefully rounded in the blowpipe flame, whereby it is rendered less likely to crack by the insertion of a cork. It is, generally speaking, of very uniform thickness throughout, and will bear the direct application of heat without cracking. As a general rule, however, the naked flame of the oil, gas, or spirit lamp should not be allowed to come into actual contact with the bottoms of glass vessels, but the heat communicated through the medium of sand; for this

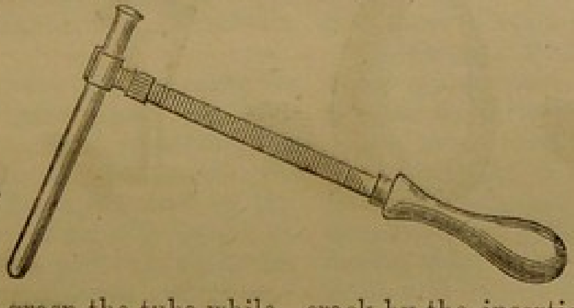


Fig. 2.

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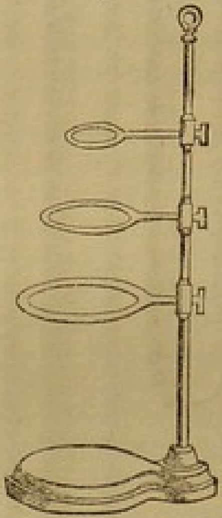
* The publisher is indebted to Mr. Button, of Holborn Bars, for having permitted him to take copies from several of the engravings in his "Catalogue" for illustrating the present work: the majority of the woodcuts are, however, new.

purpose a series of thin shallow iron dishes should be provided, from three to six or eight inches in diameter, which should be about half filled with fine silicious sand. They may be supported on the rings of the retort stand, *fig*. 3, and thus form very convenient media for conveying heat to flasks, beakers, &c.

Fig. 3.



To support Florence flasks, and other round-bottomed vessels, rings of thin sheet-iron or copper, covered with list, will be found very serviceable; they should be of different diameters and heights; they are likewise of great use for supporting evaporating basins, and the laboratory should therefore be plentifully supplied with them.

Besides Florence flasks, vessels, shaped as in the accompanying figures, are occasionally found very convenient. *Figs*. 8 and 10, called Phillips's Precipitating Jars, are particularly useful for precipitations; the sloping shape allowing the precipitate to descend without any obstructions from the sides of the glass. The flasks, *figs*. 4 and 5, should be of hard white glass, with thin bottoms, and bordered mouths, ground smooth for the reception of corks, and to admit of being closed air-tight by ground glass plates. The form, *fig*. 9, having a thin bottom, and shaped like an inverted bell, is called the Beaker. It is a vessel of very extensive use in the laboratory, being particularly adapted for heating solutions, which require stirring with a glass rod. The laboratory should

Fig. 4.

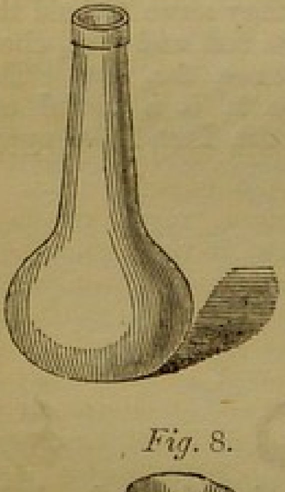


Fig. 5.

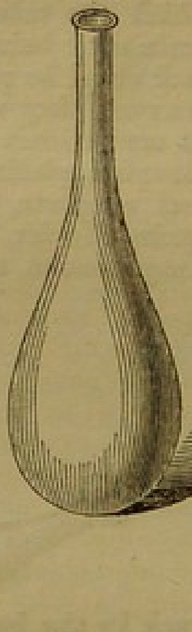


Fig. 6.

Fig. 7.

Fig. 8.

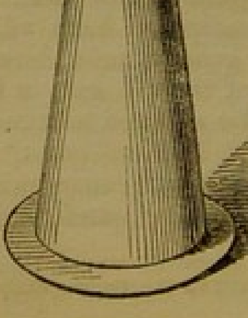
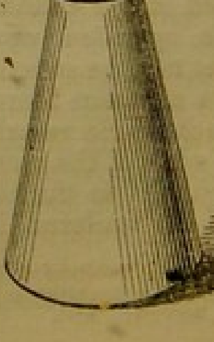


Fig. 9.

Fig. 10.



be liberally supplied with these vessels, which should be of various sizes, from two or three ounces to two or three pints, and some of them should be ground on the edge, so as to admit of being closed air-tight by a glass plate, as shown in *fig.* 10.

2. *Precipitation.*—The term precipitation does not necessarily imply the subsidence of a solid substance to the bottom of a vessel, inasmuch as the body rendered insoluble may either float on the surface of the liquid, or remain suspended in it. When the chemist speaks of a body being precipitated, he means that it has, by the action of certain agents, passed from a soluble to an insoluble state. The body separated is called the precipitate, and the substance occasioning the separation is called the precipitant. The vessels employed for effecting precipitations may be the same as those already described for solutions. For small quantities the test tube is always employed; when the quantity is large, the beaker is, on the whole, the most convenient, from the admirable manner in which it bears sudden elevations of temperature; the Phillips's jar is also very useful. Precipitates make their appearance in very different forms, and under very different circumstances. The student must, therefore, be careful not to draw too hasty conclusions with regard to the action which bodies exert on each other; and if, on bringing two substances into contact, he observe no immediate effect, he must not, on that account, conclude that no action has taken or will take place. A few examples will serve to illustrate this.

1st. The precipitate may not make its appearance until after the lapse of a considerable time. Thus, in testing for *magnesia*, by means of *phosphate* of *soda* and *ammonia*, if the earth exist in the solution only in very minute quantity, no precipitate will perhaps make its appearance for several hours; days may even elapse ere the minute stellar crystals of the double phosphate of magnesia and ammonia can be distinctly recognised.

2nd. Decomposition may have taken place, and yet, from the solubility of the educt in the fluid menstruum, no precipitate makes its appearance. Thus, on adding oxalic acid to a solution of lime in hydrochloric acid containing free acid, no precipitate appears, oxalate of lime being soluble in hydrochloric acid; but, on neutralizing the liquid by ammonia, oxalate of lime is immediately precipitated. Again, on adding to an aqueous solution of *malate of soda* a few drops of chloride of calcium, the fluid still remains clear, malate of lime being soluble in water, but on the addition of alcohol it instantly separates as a white powder.

3rd. Occasionally (though this is rare) the precipitate makes its appearance only on the application of heat, the newly formed compound being more soluble in cold than in hot water. Thus, on adding *lime water* to a cold solution of *citric acid*, or a *citrate*, no precipitate takes place till the solution is heated, when *basic citrate of lime* appears as a white powder, which redissolves as the solution cools: again, on adding a cold dilute solution of caustic potassa to newly precipitated *tartrate of lime*, a clear solution is obtained, but on heating a gelatinous precipitate separates, which is again dissolved as the solution cools.

4th. The precipitated substance is frequently redissolved by an excess of the precipitant: thus, hydrated oxide of chromium, hydrated oxide of zinc, and alumina, are each thrown down from solutions of their salts by potassa, but the precipitates are all completely and instantly redissolved by the addition of an excess of the alkali: again, on pouring iodide of potassium into a solution of bichloride of mercury, a beautiful scarlet precipitate immediately ensues; but, if excess of the iodide be added, the precipitate is dissolved, and a clear and colourless solution obtained.

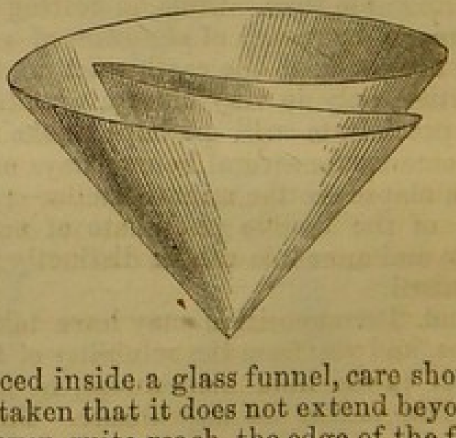
The forms in which precipitates make their appearance have been distinguished by various names, such as *crystalline*, examples of which are furnished by the acetate of silver, a salt formed on adding solution of a neutral acetate to solution of nitrate of silver; by the double chloride of platinum and potassium, and by the bitartrate of potassa; *pulverulent*, as the oxalate and sulphate of lime; *flocculent*, as alumina; *curdy*, as chloride of silver; *gelatinous*, as when oxide of zinc is precipitated from its solution by potassa or ammonia, or as when chloride of calcium is added to an aqueous solution of hydrofluoric acid, or of the soluble fluorides, in which case the precipitate is so transparent that it may easily be supposed that no change whatever has occurred. Sometimes, again, a reaction is evinced by the mere turbidity of the liquid, as when nitrate of silver is added to a solution containing minute traces of chlorine, or when a solution of a protosalt of tin is diluted with water, in which case the neutral salt is decomposed into a soluble acid, and an insoluble basic salt; or as when solution of protochloride of tin is added to a very dilute solution of gold, when a purple red tint is produced without the formation of any precipitate. The subsidence of a precipitate is frequently greatly facilitated by agitation, the flasks, *figs.* 4 and 5, are very serviceable on such occasions, inasmuch as they can be closed with the thumb, and will bear heat: in cases where an elastic vapour is evolved by agitation, or where there is excess of ammonia present, the flask employed should not be too thin, or it will be liable to burst from the pressure of the vapour: the addition of acids and salts also occasionally greatly facilitates precipitation; chloride of silver and sulphate of baryta, for example, separate much more readily by the addition of nitric acid; and oxide of tin, formed by the action of nitric acid on the metal, has its precipitation hastened by the addition of common salt. Oxide of iron again is sometimes eliminated in so finely comminuted a form that it remains suspended in the liquid for days; an addition of a known quantity of nitrate of lead, and a corresponding quantity of sulphuric acid, may often be very advantageously made to the turbid liquid; a known quantity of sulphate of lead is thereby introduced, which in its precipitation seldom fails to carry with it the whole of the suspended oxide of iron. Lastly, prussian blue precipitates from a solution containing free hydrochloric acid much more readily and completely than from a neutral liquid.

In qualitative testing, where the object is generally merely to ascertain the colour and general chemical characters of a precipitate, a few drops of the precipitant generally suffice, and the operation may almost always be performed in a test tube: but in quantitative experiments, where every particle of the precipitate must be obtained, the precipitant is added drop by drop until no further effect is produced, and the operation is most conveniently conducted in a beaker.

3. *Filtration, decantation, and washing.*—The separation of a precipitate from the fluid in which it has been produced may be effected either by filtration or decantation. For the former purpose we use white unsized paper, the perfect purity of which in qualitative operations is not very often a matter of consequence: it should be sufficiently strong to bear the weight of a considerable quantity of fluid, and yet so porous as to admit the free and ready passage of liquids. There is no difficulty in procuring paper of this kind, though it is not easy to obtain unobjectionable paper for quantitative operations; for, as it frequently happens that the filter has to be ignited with the precipitate, it is of course necessary to take into account the quantity and quality of the ashes left by the paper. An excellent article is sometimes to be met with under the name of Swedish paper, a filter four inches in diameter of which does not leave more than a hundredth of a grain of ash. It is difficult, however, to procure it genuine, and it is therefore advisable to free paper intended for minute and delicate experiments as much as possible from inorganic matter by treating it with hydrochloric acid, and subsequently washing with distilled water, so as to remove every trace of the acid: after drying, it may be considered fit for use. The inorganic impurities in filtering paper are iron, lime, and sometimes magnesia.

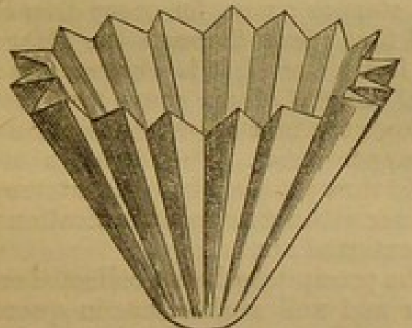
The paper is cut into a circular form of the required size and folded twice in opposite directions, so as to bring the four quadrants together; one quadrant is then opened from the other three so as to produce a conical cavity, as shown in *fig.* 11. The paper thus prepared is placed inside a glass funnel, care should be taken that it does not extend beyond, or even quite reach, the edge of the funnel; previous to pouring the fluid to be filtered on the paper, the latter should be moistened with distilled water, which

Fig. 11.



quickens the process and diminishes the chance of solid matter passing through the pores of the paper. In qualitative experiments where it is desirable to expedite the operation as much as possible, and in cases where a large quantity of a bulky precipitate has to be separated, the filtrate being the valuable part, as for example, in the separation of the alkaline earths by water of barytes in the process for estimating alkalies, the filter may be plaited so as to prevent its close adhesion to the glass. Ribbed funnels are sometimes employed for the same purpose, but they do not answer the purpose nearly so well as plaited paper. It is difficult to describe the method of making these plaited filters: an inspection of *fig.* 12, which shows the appearance the paper should present, will probably, however, convey all the requisite information. In cases where the precipitate has to be carefully collected, plain filters should invariably be used, as it is difficult to remove the solid matter effectually from the external and reentering angles of the plaited paper.

Fig. 12.



The funnel, during the operation of filtering, is placed on the ring of the retort stand, or in one of the holes of a filtering stand, and the fluid, if in a beaker, is carefully poured down a glass rod in the manner shown in *fig.* 13. The edge of the beaker is greased, by which the adhesion of particles of the liquid is prevented, and all loss from trickling down the outside of the glass obviated. The clear fluid as it drops from the funnel should not be allowed to fall directly into the receiving vessel, but caused to impinge on its side, as shown in the figure; by attending to this, we avoid all chance of loss by the splashing of the liquid. These minutiæ of course principally apply to quantitative experiments. The precipitate, being collected on the filter, has to be washed. This operation is best performed by means of the syringe bottle seen in *fig.* 13. The method of using which useful piece of apparatus is sufficiently obvious; it is filled with distilled water, and on forcing a stream of air from the lips through the short tube, a jet of water is propelled from the bent tube by the pressure of the air, and may be directed either in drops or in a pretty powerful stream wherever it is required. It is useful to have four of these bottles at hand: one stout one for cold water for general purposes; one made from a thin flat-bottomed flask, as in the figure, for hot water; and two smaller ones for alcohol and ether. The washing of the precipitate is to be continued until a few drops of the filtrate leave no residue when evaporated to dryness on a strip of platinum foil; occasionally, however, this indication would be fallacious in consequence of the partial solubility of the precipitate in water; in these cases special testing of the filtrate must from time to time be had recourse to. In washing a precipitate on a filter the solid matter should be washed from the sides of the paper and collected, as much as possible, in a thick stratum at the apex of the cone; the water will not in this case pass through so quickly, but under more favourable circumstances for exerting its solvent power on the substances to be removed. During the operation of filtering, the funnel should be covered with a glass plate, to protect its contents from the dust and dirt of the laboratory.

Fig. 13.

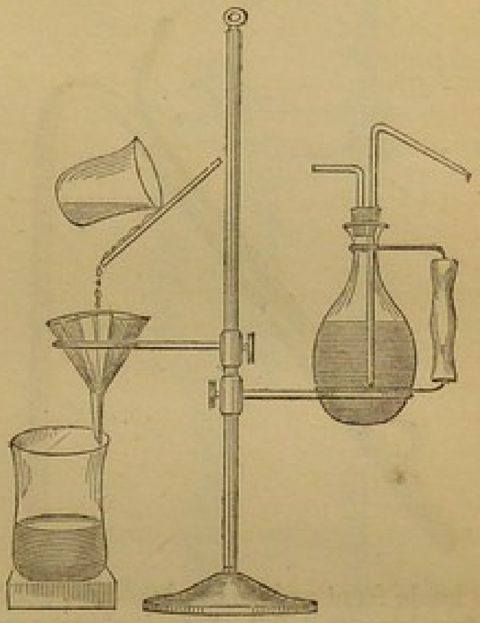


Fig. 14.

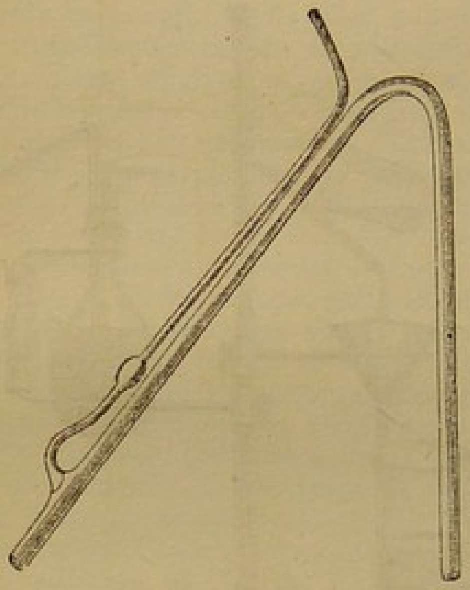


Fig. 15.

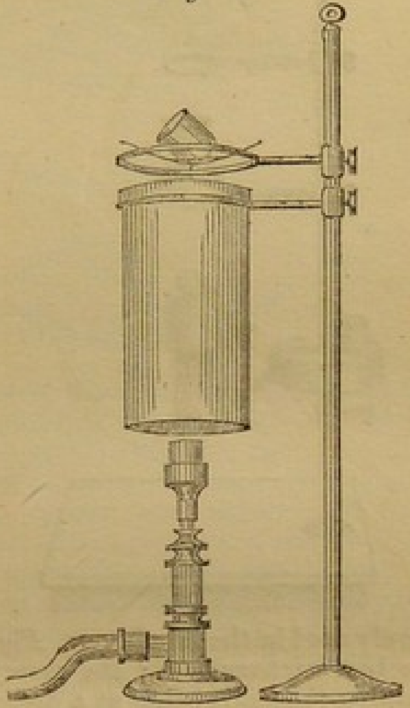
When the precipitate subsides rapidly and collects into a small space at the bottom of the vessel, the supernatant fluid may frequently be advantageously removed by a syphon, *fig.* 14, which may be made from a piece of glass tube about 2 feet long and 0.3 of an inch internal diameter. The extremities should be somewhat contracted. When this instrument is about to be used, it is filled with water from the syringe bottle, and, keeping the longer leg closed by a finger, the shorter leg is introduced into the fluid, taking care not to disturb the precipitate, and then, on removing the finger, the fluid is permitted to run out into a vessel placed to receive it: with care and by gradually inclining the vessel, nearly the whole of the clear fluid may be removed from a precipitate, the washing of which may either be consumed by decantation, or, which in most cases is preferable, it may be thrown on a filter and washed as usual. In cases where small quantities of fluid have to be removed from a precipitate, the *pipette*, *fig.* 15, is frequently found very serviceable. When the object is to remove finely divided matter from concentrated acids, filters of powdered glass are employed; coarse fragments of glass are first put into the neck of the funnel, these are successively covered with other portions more and more comminuted, the top being finished by a layer of small fragments, on this the acid is poured, and, on passing through, it becomes clear. It is sometimes of importance to prevent the access of air as much as possible during the filtration of certain liquids, as, for instance, in the separation of caustic soda or potass from carbonate of lime. An apparatus for this purpose has been described by Mr. Donovan: it consists of a vessel somewhat resembling in shape an hour-glass provided with a tube of communication between each bulb, in the narrow part of this vessel a small pellet of cotton or asbestos is somewhat loosely placed, the liquid being introduced through the neck of the upper vessel, which is closed by a stopper; now, for every drop of liquid that passes through the filter into the lower vessel, it is obvious that an equal volume of air must find its way through the tube of communication with the upper vessel. The filtration of the liquid thus proceeds in an uninterrupted manner without any communication with the external air.

The precipitate, being collected on the filter and well washed, has in quantitative experiments to be dried and weighed; its further treatment for this purpose depends on whether or not it may be ignited. If its nature be such that it will not bear a high temperature without decomposition, which is the case with all organic substances, the filter must have been previously dried at the same temperature to which it is subsequently to be submitted with the precipitate, and in that state carefully weighed. As filtering paper is a very hygroscopic substance, the filter must be weighed in a closed vessel (a small platinum crucible, with an accurately fitting cover, may be used for the purpose); it must be introduced while hot, and it is advisable to allow the whole to cool over a vessel of sulphuric acid underneath a bell jar. The weight of the filter and crucible being noted, the precipitate is collected, and, the rinsing water having been allowed to run off as much as possible, it is removed from the funnel, and placed upon two or three folds of bibulous paper, or, which is better, on a warm tile or brick, by which a great deal of the adhering water is removed; it is subsequently dried in the crucible until it ceases to lose weight, and by simply subtracting the weight of the filter and crucible from that of the filter, crucible, and precipitate, we have the exact weight of the latter.

When the precipitate may be ignited, it is not necessary to determine the weight of the filter, but the weight of the ash which a filter of an equal size leaves on ignition must have been ascertained by a previous experiment. The precipitate is allowed to get as dry as possible in the funnel, for which purpose it is well covered with a piece of bibulous paper, and placed for some hours in a warm situation; the contents of the filter are then transferred as completely as possible into the crucible in which it is to be ignited, and the filter itself burned, either by doubling it up, and, having applied a light to it, allowing it gradually to consume, holding it by a forceps over the crucible placed on a glazed sheet of paper; or, in the manner recommended by Fresenius, by cutting it in small pieces and incinerating it on the cover of the crucible, heated to redness over a gas or spirit lamp. The heat must be continued till every trace of blackness is removed from the ash, and this, in some cases, as for instance when the subject of the experiment is the basic phosphate of magnesia and ammonia, takes a considerable time. Care must be taken to conduct the operation of burning the filter in a spot entirely protected from draught. The ash of the filter is mixed with the precipitate in the crucible, and the whole is exposed to a heat gradually increasing until it gets red hot; it is then covered, allowed to cool, and weighed: from the gross weight, that of the crucible and filter ash have to be deducted to arrive at the weight of the precipitate itself. The operator must be careful not to heat the crucible too strongly at first, for, if the precipitate should not be perfectly dry, particles are apt to fly out.

With respect to the sources of heat, where gas can be commanded there is nothing so convenient or so cheap. When coal gas is allowed to mix with a sufficient quantity of air to effect the complete combustion of its carbon, it burns with a flame which, though having but little luminosity, possesses intense heat, and throws off no solid charcoal on cold bodies with which it is brought into contact; it is thus admirably adapted for the ignition of platinum crucibles. *Fig.* 16 represents the arrangement of the coal-gas jet for this purpose. The mixture of gas and air takes place in the chimney, and it is inflamed above the wire gauze fastened over the top.

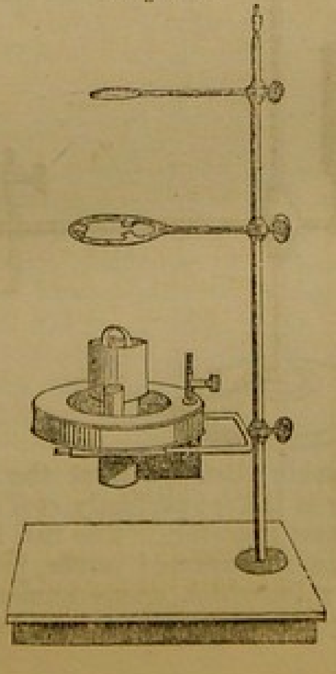
Fig. 16.



The crucible is supported in an inclined position on a triangular piece of iron wire, supported on a ring of the retort stand. Where a supply of gas cannot be commanded, the chemist must have recourse to lamps or furnaces for the ignition of his crucibles. In describing some of the most useful of these, we will take the opportunity to make a few remarks on the management of heat generally in chemical operations.

Lamps.—*Figs.* 17 and 18 represent

Fig. 17.



two forms of Berzelius's Argand pyroxylic spirit lamp, which are very extensively used in the laboratory. *Fig.* 18 is the best arrangement; the reservoir containing the spirit being at a distance from the burner, it escapes being heated during long operations; they are both mounted on stands with porcelain bases.

Fig. 18.

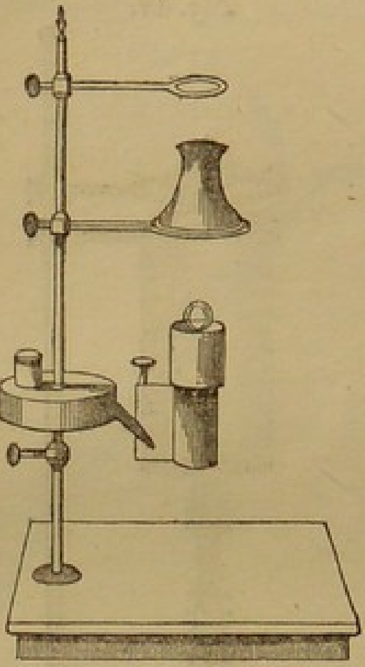
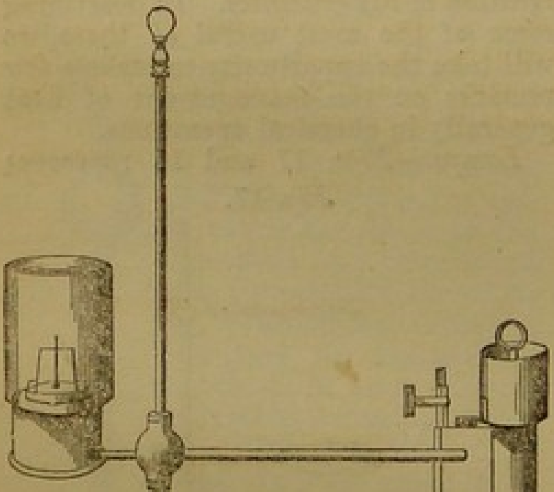


Fig. 19 is Mitscherlich's lamp, in which the reservoir of spirit is placed at a considerable distance from the flame, whereby it is kept perfectly cool during the longest operation. The fuel is contained in an inverted bottle provided with a valve which opens immediately over a gutter leading to a long horizontal tube, through which the spirit is conveyed to the burner; the flow of spirit is rendered perfectly regular by adapting a small piece of brass tube, about a quarter of an inch long, to the aperture through which it passes from the bottle. The brass caps are not provided with these small tubes as the lamps are procured from the instrument maker, but they will be found very great improvements, as the spirit is sometimes apt to run out too fast, occasioning sudden bursts of flame, and not unfrequently running over; while at other times it does not run out fast enough, occasioning irregularities in the flame.

Fig. 19.



The heating power of these lamps is greatly increased by inclosing the crucible in a jacket of iron plate as shown in *fig.* 20. The crucible rests on three knife edges, so placed as not to obstruct the action of the flame, which moves in the direction of the arrows, and all atmospheric air is excluded, except what passes up the chimney of the lamps.

Fig. 20.

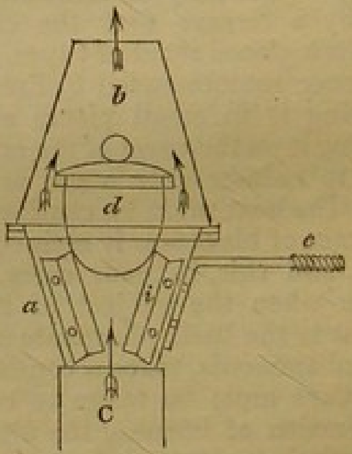
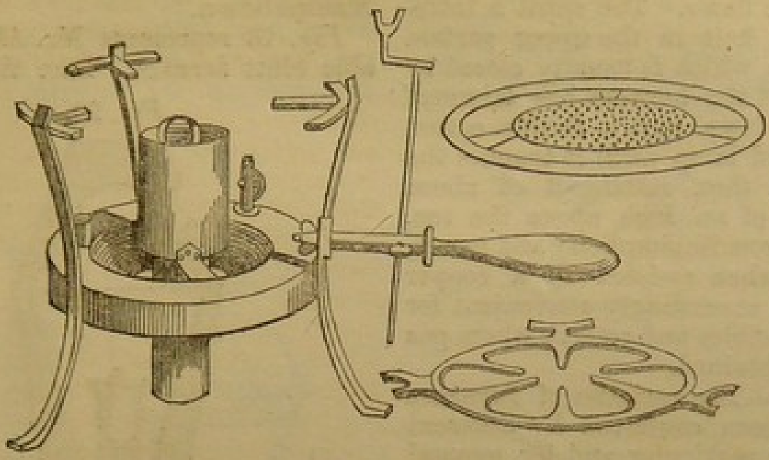


Fig. 21 is Luhme's universal lamp for boiling, &c.; it is supported on a solid brass stand with three feet, and is provided with a handle, stout brass ring for supporting round vessels, and a pierced iron plate for flat vessels: the crook attached to the handle is for the purpose of supporting the necks of retorts, flasks, &c.; it can be raised or lowered at pleasure. This is a very convenient and powerful form of lamp.

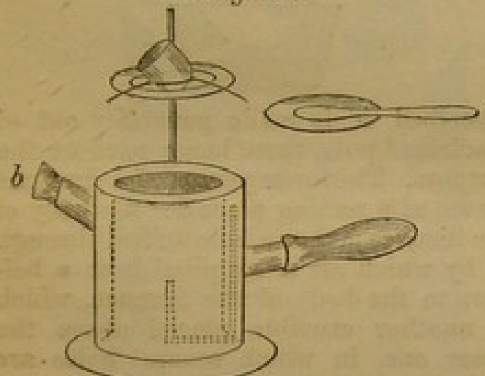
Fig. 22 represents a lamp of Russian invention, by which a very powerful heat may be obtained in a few minutes. It consists of a strong brass double cylinder or box, the dotted lines in the figure show the arrangement of the interior; a piece of tube terminating in a jet passes from the exterior to the interior chamber, rising nearly to the top of the former, the fuel (pyroxylic

Fig. 21.



spirit) is supplied through the aperture *b*, which should be closed with a good cork, and never with a brass cap screwed on as the instrument is sometimes sold. To give the lamp its maximum charge, the spirit should be poured in until it begin to flow out from the jet; a sufficient quantity should then be poured into the inner chamber, to reach within half an inch of the apex of the jet, the principle of the lamp will now become obvious. On inflaming the spirit in the inner chamber, that in the outer chamber gets heated and soon boils; the pressure of the vapour forces the boiling spirit through the jet in a powerful stream, which of course becomes immediately ignited, and thus acts as a powerful blowpipe, and so great is the heat produced, that a platinum crucible placed in the position shown in the figure, speedily becomes ignited to whiteness. A platinum triangle must be used to support the crucible, as an iron one would speedily become fused. The ring on which the triangle is supported should be of very stout iron wire. A lamp on this construction, about 3½ inches in height and 3¼ in diameter, will burn with a charge of 4 oz. of spirit for 30 minutes, which is long enough for most ordinary fluxions with carbonate of soda; it frequently therefore saves the necessity of lighting a furnace. In using this lamp certain precautions must be observed before giving it a charge of fuel. The operator must assure himself that the jet or pipe is not choked up by blowing through it; the cork at *b* should not be put in too tight, in order that it may be the part of least resistance, should a stoppage occur during an operation; and, lastly, the cork should be turned from the operator during an experiment, to secure him from accident should it get blown out by a stoppage.

Fig. 22.



Besides these different forms of lamp the common twisted cotton wick spirit lamp is a very useful instrument; a very considerable degree of heat may be obtained from it; and small platinum crucibles may be heated to redness in its flame. A very powerful lamp, frequently supplying the place of a furnace, is described by Faraday (see "Chem. Manipulation," p. 105); it is formed by making an aperture 0.8 or 0.9 of an inch by 1¼ inch through the body of the lamp, and fixing in it four burners upon Count Rumford's principle, each of a length equal to the width of the aperture, and one-eighth or one-tenth of an inch wide. These are placed parallel to each other, and at such distances as to have five spaces or airways, the two outer being half the width of the inner. These burners rise about a quarter of an inch above the lamp, and descend as low as the bottom of the body, being fastened in the aperture by their ridges, each burner is closed beneath, but has a small hole into the lamp as a passage for the alcohol; thus forming as it were a part of the lamp. The lamp is supported on four balls to allow of the access of air beneath, and up the apertures to the flame. The spirit is introduced by a hole in the upper surface of the lamp, which is usually closed by a screw, and the burners are trimmed by putting down each a double cotton of an Argand lamp until it touches the bottom, and then cutting it off about the length of an inch above the top. This lamp, from its simplicity and power, especially when assisted by a copper chimney, is exceedingly convenient for heating crucibles and retorts, where gas cannot be obtained.

Furnaces.—The varieties of furnaces that have been contrived by different chemists for particular and for general purposes are almost innumerable, and it would require an entire treatise to descant on their several uses and comparative merits. In the well-appointed laboratory, the wind, blast, and reverberatory furnaces, will of course find their proper places; but, as it is no part of our object in this treatise to give a minute description of the apparatus required in a large chemical establishment, we shall confine ourselves to the descriptions of a few of the furnaces, which seem best adapted to small private laboratories, and for the use of students in analytical chemistry.

A very useful furnace may be made out of a black lead or "blue" pot; one of those vessels, about a foot in height and seven or eight inches in width at the top, will make a furnace quite large enough for the ignition of small crucibles, and for operations on the small scale. It should have a series of round holes pierced in it at equal distances apart round the side for the admission of air, and it should be tightly bound round with stout iron or copper wire to strengthen and hold it together when it cracks. A small cast iron grate resting between the bottom and the second tier of holes, and a moveable hood or chimney complete the apparatus. "There is no difficulty," says Faraday, "in raising a crucible two inches and a half in diameter to a white heat by a furnace of this kind; and that in any situation which may be convenient upon the table or the floor, and with all the advantages of arranging or dismounting the apparatus with extreme facility." One of the greatest recommendations of this furnace is its extreme cheapness, the entire cost not exceeding a few shillings. Minute directions for constructing it and arranging it for different operations will be found in "Faraday's Chemical Manipulation."

Fig. 23 represents Mr. Aikin's portable blast furnace. Like the one last described, it is made generally out of black lead pots, three being used for the purpose. The lower part of the first one serves as a resting place for the body of the furnace; it has a hole drilled through it, by which air is supplied from a bellows to the body of the furnace, which is another crucible placed above the lower one, in which several holes are drilled to admit air; over the second crucible a third is inverted, with a large hole cut in the side for the escape of smoke and gaseous matters. Cast iron may be melted in this furnace, and moderate-sized crucibles brought to a full red heat in a few minutes. The fuel used is coke.

Fig. 23.

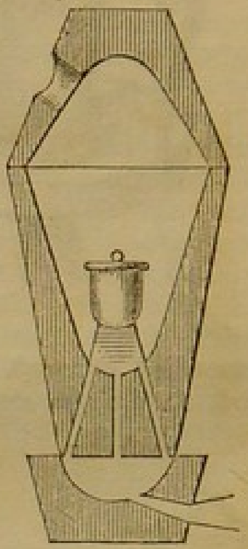
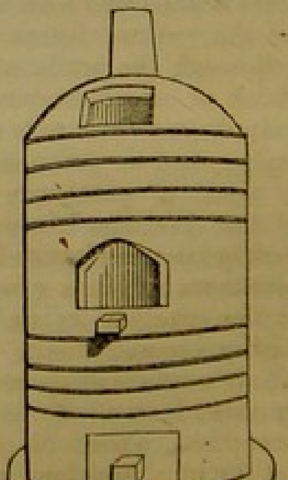


Fig. 24 is another useful form of table furnace; it is made in three pieces; the material being either the best refractory

Fig. 24.



fire clay or black lead; it is tightly bound with iron, and is usually made about twenty inches high and seven inches internal diameter. It is a very convenient furnace for evaporations, distillations, and crucible operations, where no great degree of heat is required.

Fig. 25.

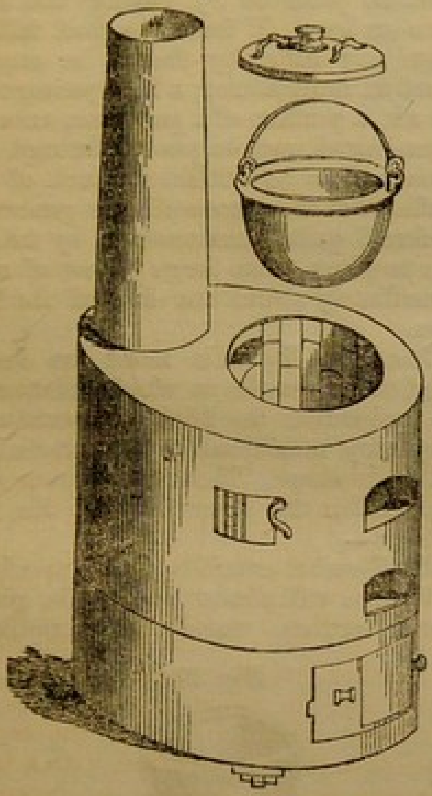


Fig. 26.

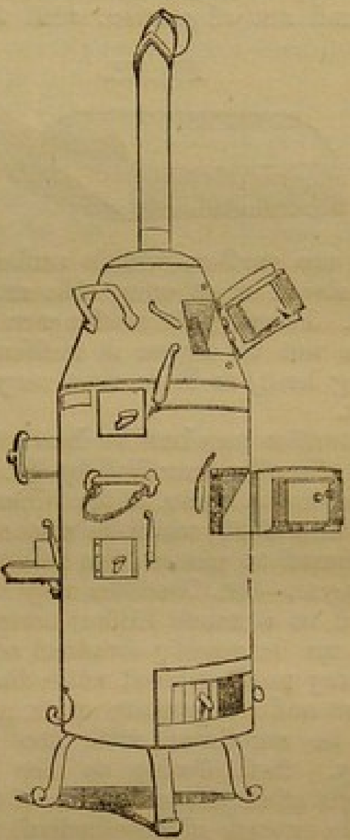
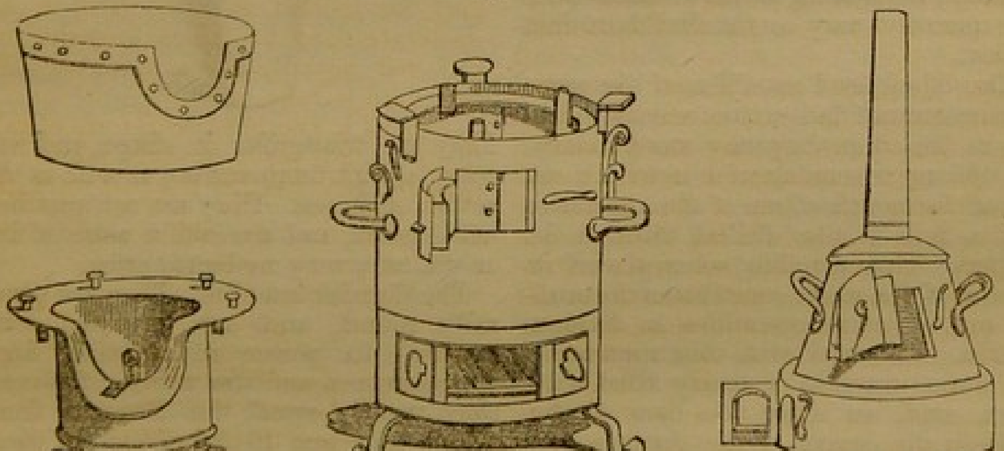


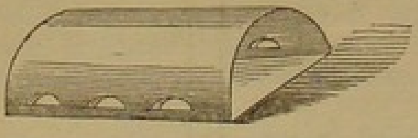
Fig. 27.



Figs. 25, 26, 27 represent three other forms of furnaces well adapted for the ordinary operations of the laboratory. *Fig.* 25 is known as Black's furnace, and is perhaps on the whole the most convenient where a stationary furnace is required. It consists of a case of strong sheet iron lined with refractory clay, the grate is fixed to the iron plate which supports the tube, and forms the top of the ash-pit, which is provided with a sliding door for the admission of air; there are various apertures in the front and sides of the furnace for the admission of tubes, crucibles, &c. The fuel used is coke. *Fig.* 26 is Knight's portable furnace; and *fig.* 27, Luhme's furnace, with sand bath jacket, &c. The diameter of the former is usually six inches, that of the latter about eight.

These furnaces are amply supplied with doors and apertures for the admission of muffles, *fig.* 28, which, besides their extensive uses in the operation of cupellation, are exceedingly convenient for the ignition of substances in small platinum capsules, or crucibles, in a draught of air and out of contact with the fuel.

Fig. 28.



They are earthen vessels arched above and closed in at every side except the front. In using the muffle care must be taken not to expose it suddenly to a strong heat, as it is then very apt to crack.

Attention may here be drawn to a new form of muffle described by Mr. Thomas Taylor in the Mems. of the "Chem. Soc." (vol. iii. p. 316), which he states that he has found to possess the following advantages:—1st. Crucibles may be maintained at a much higher temperature than can be readily obtained when the ordinary muffle is used, while the degree of heat and the quantity of air admitted may be regulated with the greatest nicety. 2nd. Owing to the greater draught of air, the oxidation of the lead (in the process of cupellation) is more quickly effected; and lastly, by looking through an opening in the furnace cover the operation may be watched from first to last.

Two black lead crucibles of the same size are ground flat, so that when applied one to the other they may stand steady. An oblong or semicircular notch is cut out of the mouth of one of the crucibles, and a hole is also drilled through its bottom. This crucible, when placed on the top of the other, constitutes the muffle, and of course resembles in shape a skittle. To cupel with this apparatus, the lower crucible is nearly filled with clean sand, set upon the bars of the grate in the centre of the furnace and brought to a low red heat. The cupel containing the lead of the alloy is then placed upon the sand and immediately covered by the crucible, taking care that the notch in its side shall be opposite to, and correspond with, the furnace door; more fuel is added, during which it is well to cover the hole in the top of the muffle with a crucible lid in order to prevent the admission of dirt. When the muffle has become throughout of a bright red heat the furnace door is thrown open, and the ignited fuel gently moved aside so as to permit a view of the side opening in the muffle. The current of air which is thus established through the muffle instantly causes rapid oxidation of the lead, and this may be regulated at pleasure by closing the door more or less. If from the fuel falling down any difficulty should be experienced in maintaining a free passage for the air, a portion of a porcelain tube, or a gun-barrel, may be passed through the furnace door to within an inch of the muffle; but this proceeding is generally rendered quite unnecessary, by taking care to place some large pieces of coke immediately round the door of the furnace.

Crucibles.—By this name are designated those vessels in which substances are subjected to high temperatures. They vary considerably in material as well as in shape. Those most commonly employed in the laboratory are the following:—

The Hessian crucible, *fig.* 29, to which preference will almost always be given where earthen vessels are required.

Fig. 29.

They are triangular in shape, and will resist a high temperature, as well as the action of fluxes. They are not provided with covers, and are sold in nests of five or six, at a very moderate price.

The Cornish crucible. They are generally round, and are provided with covers. In power of resisting high temperatures, and the action of fluxes, they nearly equal the Hessian, from which they are distinguished by their colour being white.

The blue pot, or black-lead crucibles. These vessels are made of a mixture of black lead and clay, and are generally of a large size, being principally used in the arts. They bear a very high temperature, and withstand the action of fluxes.

Crucibles made of Berlin ware, biscuit porcelain, and Meissen ware, are also much used. They are made very thin, and will stand a high temperature; the most convenient shapes are shown in *figs.* 30 and 31. Besides these, a crucible and cover of platinum is indispensable to the analytical chemist. This valuable vessel should be used with care; it should never be exposed unprotected to the fuel of a furnace. In almost every case a sufficient heat for all analytical operations may be obtained by the Russian blowpipe lamp, *fig.* 22; but when a very high temperature is required, and it is found necessary to resort to the furnace, the platinum crucible should be inserted into a Cornish one, the intervening space being filled up with magnesia. A pure silver crucible may in many cases be substituted for one of platinum; but it must be borne in mind that silver is far more fusible than platinum. Fusible metals, or compounds of metals likely to be reduced, must never be heated in vessels of silver or platinum, as the alloys formed greatly injure them: all compounds containing lead must also be particularly avoided. Our prescribed limits do not allow of our entering into the details of furnace operations. The student will find the subject fully treated in Faraday's valuable work on chemical manipulation.

Fig. 30.

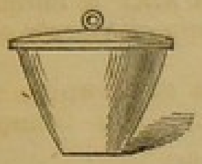
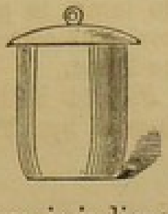


Fig. 31.



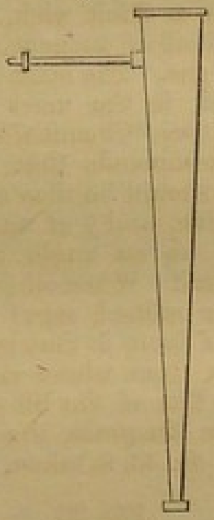
The Blowpipe.—For submitting small substances to high temperatures, and for obtaining a knowledge of the materials of which they are composed, the blowpipe is an invaluable instrument, and one with the use of which the chemical student should spare no pains to make himself thoroughly acquainted.

The blowpipe, though the forms which it has received are very numerous, is essentially a tube terminated by a small, round, smooth aperture, through which a current of air can be propelled by the mouth against the side of a flame. A miniature blast-furnace is thus set in action; and not only may an intense white heat be produced and directed against the subject of experiment, but several distinct operations may be performed on it, as will presently be shown.

The most simple form of blowpipe is a conical tube of japanned tin-plate or brass, about seven inches long, bent nearly at a right angle, about two inches from the narrow end; but as, during the operation of blowing from the mouth aqueous vapour condenses, and is driven through the jet with the stream of air, various contrivances have been devised for retaining the water.

Dr. Black's blowpipe, which is the cheapest, and, on the whole, perhaps the most useful of the numerous forms which have been given to this instrument, is shown in *fig.* 32. It is a conical japanned tin-plate tube, two-fifths of an inch wide at the broad end, which is closed, and one-third of an inch wide at the narrow end, which is open. A small brass pipe, terminated by a jet two inches long, and one-eighth of an inch in diameter, is adapted to the side of the tube near the broad end. The moisture from the breath is condensed and retained at the closed end, the conical form of which serves also, in some degree, to regulate the pressure of the air.

Fig. 32.



The principal point to be attended to in the construction of the blowpipe is the jet, of which there should be two, the calibre of the one being rather larger than that of the other; the aperture should be perfectly round and smooth, and the channel leading to it conical; and it should be made of platinum as being easier kept clean. In using the blowpipe, the air is supplied from the mouth, and not from the lungs; and during the blast the communication between these two organs is closed, respiration being carried on through the nostrils. The description of the method of blowing through the pipe is far more difficult than its acquisition. It is necessary, in the first place, to acquire the means of keeping the cheeks distended with air, whilst respiration goes on in an unimpeded manner through the nose; and to open and close the communication between the mouth and the lungs, and between the lungs and the air at pleasure. When this habit is gained, no difficulty is experienced in keeping up a strong and continuous stream of air without fatigue or injury to the health.

The fuel for supplying the flame for the blowpipe, may be either that of a candle with a thick wick, or oil, or a solution of oil of turpentine in spirits of wine, or gas. The latter, when it can be obtained, is the most convenient; and Griffin (see "Chemical Recreations," p. 114) recommends that the form of the burner should be that of a flat pipe, about 1½ wide, and ⅕ of an inch broad, cut aslant at an angle of 40° from the horizontal. When oil (which should be olive, or refined rape) is used, the best form of lamp is that recommended by Plattner, from whose valuable Treatise on the Use of the Blowpipe, translated by Dr. Muspratt, the accompanying sketch, *fig*. 33, is taken. It is mad of tinned iron plate, and varnished black; the socket inclosing the wick is made sufficiently slanting to admit of a considerable deflection of the flame, and there is adapted to it a tightly fitting screw, to prevent the leakage of the oil in travelling. The wick is folded together three or four times, and cut parallel with the oblique side of the socket, so as to allow the flame to be easily directed downwards. The lamp is adjusted by means of a screw to a brass pillar, as shown in the figure. The triangle with three bars of different lengths, seen in the drawing immediately above the lamp, is provided with a movable arm, and serves to support vessels over the flame.

Fig. 33.

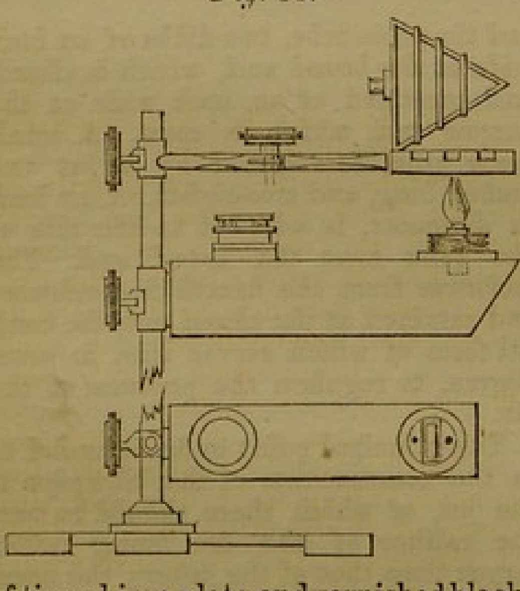
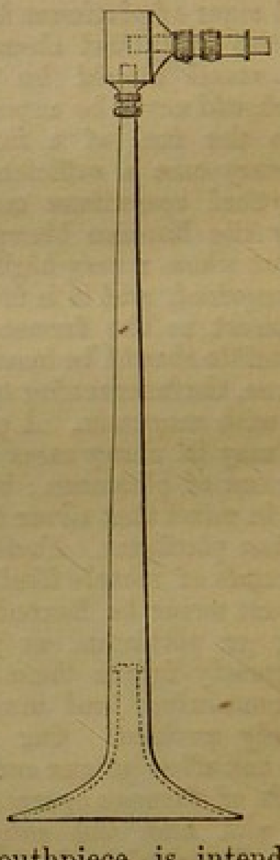


Fig. 34 is the form of blowpipe employed by Plattner. The trumpet-shaped mouthpiece is intended as a protection to the lips, and for increasing the force of the blast without fatigue to the operator. It should be made of horn, as being a substance of bad conducting power. If a candle be employed, it should be snuffed rather short, and the wick turned on one side towards the object, so that a part of it may lie horizontally; the stream of air from the blowpipe must be blown along the horizontal part as near as possible without striking the wick.

Fig. 34.



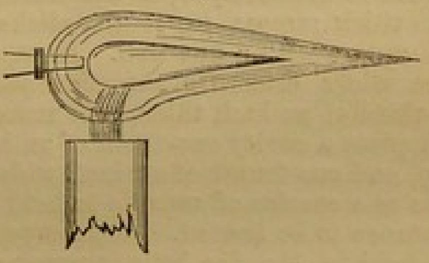
To understand the method of managing the blowpipe requires the knowledge of the properties of the different parts of a flame, which may best be studied in that of a steady-burning wax candle. *Fig*. 35 represents such a flame, which will be found, on examination, to consist of four distinct parts. The base, *a b*, is bright blue, it is here that oxygen enters the flame; the blue colour which is occasioned by the combustion of carbonic oxide disappears as the flame elongates, giving place to a thin, scarcely visible coating. Chemical action is here most intense, and this exterior mantle is the hottest part of the flame. In the very centre of the flame, surrounding the wick, is a dark, conical spot; this is the magazine, as it were, of the inflammable vapours, carburetted hydrogen, and olefiant gases, derived from the decomposition of the tallow; it is shut out from all communication with oxygen, and the combustible gases consequently remain unburned. Surrounding this dark portion is an intensely luminous envelope. It is here that the inflammable compounds of carbon and hydrogen are decomposed; the hydrogen burns into water, but the carbon, not meeting with a sufficient supply of oxygen to effect its oxidation, separates in a state of intense ignition. A few simple experiments will serve to elucidate the above description.

Fig. 35.

The hollow structure of the flame is proved by bringing down upon it a piece of thin glass or wire gauze, and viewing the section of the flame from above. That this hollow is filled with inflammable gases, is demonstrated by carefully introducing into its centre a piece of thin glass tube one-eighth of an inch in diameter, and six or eight inches long: the gases will escape through this tube, and may be inflamed at its exterior aperture. That the luminous part of the flame consists of intensely ignited charcoal is shown by introducing into it a cold body, such as a glass rod, which will become blackened from the deposition of carbonaceous matter. That the blue colour at the base of the flame is occasioned by the combustion of some form of carbon, is proved by holding close to it a glass rod, from the end of which a drop of lime water is suspended—the clear liquid speedily becomes milky, owing to the formation of carbonate of lime; and, lastly, that the hydrogen of the fuel is being converted into water at the exterior envelope is rendered evident by holding near it a large bright metallic surface, such as a polished snuffers, which speedily becomes bedewed with moisture. Of these four parts of the flame *two* are principally concerned in blowpipe operations—the blue part and the luminous part; and these two have totally different, and indeed opposite functions. From the first is produced the oxidating flame, and from the second the reducing flame. The oxidating flame may be considered as the blue oval base converted into a cone. To produce it the nozzle of the blowpipe is introduced about one-tenth of an inch within the flame, immediately above the wick, and a gentle and uniform current of air kept up from the mouth. The heat is greatest at the extremity of this flame; but to obtain the greatest oxidating power the subject of experiment should be kept as far from the apex of the flame as is consistent with a sufficiently elevated temperature. A too powerful blast must be avoided, as tending to cool the flame and to injure the process of oxidation: the aperture in the nozzle of the blowpipe must not be too small.

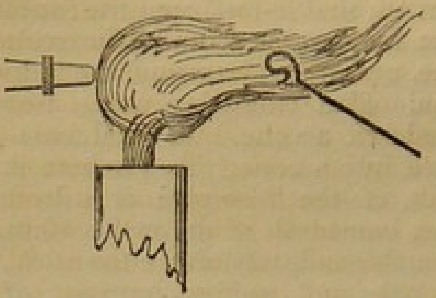
Fig. 36 shows the form which the flame should assume when oxidating effects are desired. The reducing flame is more difficult to obtain; the jet of the blowpipe must not be introduced into the flame, but kept just on its edge, and the stream of air, thrown higher over the wick than in the oxidating flame, the whole of the luminous portion thus becomes deflected, and appears as a long narrow cylinder surrounded by a feeble luminous mantle. It is in the luminous portion, consisting of partially consumed combustible matter, strongly disposed to combine with oxygen, that reductions are effected, and the assay must be entirely surrounded with it. *Fig.* 37 may serve to convey some idea of the general appearance of the reducing flame. If a lamp or candle be used as fuel, attention must be paid to the condition of the wick, which must be of moderate length, and very evenly and smoothly cut. The orifice in the jet of the blowpipe should be smaller than when oxidation is the

Fig. 36.



object, and the blast must be moderately strong and uninterrupted.

Fig. 37.



Objects are supported before the blowpipe either on charcoal or on platinum. When the subject of experiment has to be heated with free access of air, in order to see whether any volatile matters are given off, the operation is conducted in a glass tube open at both ends. The best charcoal for blowpipe operations is made from the wood of pine, willow, or alder; it should be well burned and free from bark. Griffin recommends that a supply of capsules of charcoal should be kept ready for use; he directs them to be made thus:—Take sticks of an inch in diameter, or, if the charcoal be in thick masses, cut it into sticks an inch square with a fine saw. Next, cut these sticks crosswise into flat pieces one-third of an inch thick, and make in each plate a cavity one-tenth of an inch deep, and one-fourth of an inch wide, to serve as a species of capsule to hold the substance to be heated. These capsules are held in the fire by a narrow and thin strip of tin plate.

As there is some difficulty in procuring unexceptionable charcoal for blowpipe experiments, Mr. Griffin has described and recommended the following simple methods of preparing supports for fusions, as well as for operations of *reduction*. Into a small boxwood mould there is first pressed a plastic mass made of fine pipe-clay and charcoal powder mixed in equal parts, by weight, with as much water slightly thickened with rice paste as is sufficient to form a stiff plastic mass. This forms a conical cup or crucible. On this is firmly pressed, by means of a suitable box-wood pestle, a round ball of either of the combustible compositions described underneath; the whole forms a small cylinder half an inch high, and half an inch in diameter at the top, and about two-fifths of an inch at the bottom: it weighs about 16 grains, consisting of 10 grains of clay, and 6 grains of combustible matter. The little cylinder is easily removed from the mould by means of the pestle, which, as well as the inside of the mould itself, should be oiled.

The combustible portion of the support for *fusions* is made of

Charcoal in fine powder .	12	parts.
Rice flour	$\frac{1}{2}$	"
Water, about	8	"

The rice is boiled with water to form a paste, with which the charcoal is afterwards mixed, into a mass of the consistence of dough.

The upper part of the support for *reductions* is made of

Charcoal in fine powder . .	9	parts.
Carbonate of soda, crystallized	2	"
Borax crystallized	1	"
Rice flour	$\frac{1}{2}$	"
Water about	8	"

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated, and the whole well kneaded into a stiff mass.

In using the support for fusions, it is heated before the blowpipe till it is red hot, and on removing it from the flame it continues to glow like a pastile, and would consume entirely away down to the clay mixture. A quantity of microcosmic salt is now added, which immediately melts into a small cavity bored in the centre of the support, forming a bead, which is heated in the blowpipe flame till it becomes transparent and colourless. It is now removed from the flame, and placed on a Berlin capsule; the subject of experiment is added, and, as in consequence of the glowing state of the support the flux remains in a pasty condition, the added substance is immediately absorbed. It is again fused before the blowpipe, and on removing it the pastile burns gradually away, leaving the bead on the clay support, where it may be conveniently examined.

In using the support for reductions it is first heated before the blowpipe; as the charcoal consumes, the fluxes fuse and become concentrated on the surface, and on heating a reducible metallic compound upon it, it becomes immediately exposed to a powerful reducing action.

These forms of support have certainly the merit of great portability, and are therefore well adapted to the travelling mineralogist. The whole of the apparatus may be purchased of Mr. Griffin, of Baker Street, for a few shillings.

The inventor chooses rice as being a strong, cheap, and convenient agglutinant, melting and binding the charcoal powder well together, and yielding itself by its decomposition a charcoal of difficult incineration. The supports are held before the blowpipe on a ring of iron wire thrust through a cork.

When charcoal is employed, for nearly all ordinary operations, the cavities may be bored in it by means of a simple conical tube of tin plate, the edges of which are sharpened by a file, the diameter of the small end may be one-fourth of an inch, that of the large one one-half. A very ingenious charcoal furnace for quantitative blowpipe operations will be found described, though not so clearly as could be desired, in the valuable manual of Plattner.

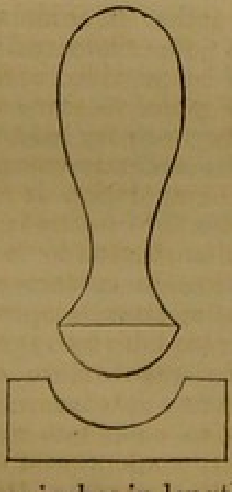
Charcoal is employed as a support when the subject of experiment has to be reduced; but when the object is to ascertain what coloured bead it produces when fused with borax or microcosmic salt, a platinum wire curved at one end may be advantageously employed. It should be about two inches long, and it may be fixed in a hilt, the handle of which is hollow, serving as a reservoir for extra wires. In using these wires the hook is moistened in the mouth, and then dipped into the pounded fused borax, which is melted in the flame into a clear bead; when cool it is again moistened, a minute quantity of the substance to be examined caused to adhere to it, and both fused together.

It is frequently required to heat the substance with nitre or bisulphate of potash; this is done in the small platinum spoon, *fig.* 38, of which it is convenient to have two sizes, one about nine-sixteenths of an inch in diameter, for melting substances with bisulphate of potassa, and the other about three-eighths of an inch in diameter for fusing substances with nitre. Stains on these spoons are, according to Dr. Muspratt, best removed by rubbing them with charcoal powder. In order to try the fusibility of specimen, it is held in the flame by means of the platinum forceps, *fig.* 39. The following simple method of preparing small thin clay basins for roasting ores and for the reduction of the lead and tin oxides contained in calcined and uncalcined minerals, &c., is given by Plattner. A fine proof clay is kneaded into a stiff paste with water, and having rubbed the surfaces of the box-wood press, *fig.* 40, with oil, a slip of paper three inches in length and one-fourth of an inch in breadth is placed on the middle of the concavity of the press, which is seven-eighths of an inch wide and 5-16ths of an inch deep, and upon this a small clay ball about half an inch in diameter; the upper surface of the press is then stamped horizontally on the clay mass as far as is required. This being done, the superfluous clay will have exuded, and the handle or upper part of the apparatus can be removed easily by careful turning; with a small knife the clay which is driven out may be cut away, and it can then be seen whether the basin is sufficiently thin and uniform; if so, the slip of paper is gently pulled and the dish extracted. After a few hours' drying the paper detaches itself from the little clay dish, which is then heated to redness in a platinum crucible. These basins should not exceed one thirty-second of an inch in thickness, and the proper consistence of the clay is soon ascertained: if the edges of two of these little vessels be ground with a file, one may serve as a cover to the other.

Fig. 38.

Fig. 39.

Fig. 40.



The steel mortar, *fig.* 41, is an apparatus of great use to the blowpipe analyst. It consists of three separate parts; the lower portion is a shallow dish of steel into which a massive hollow hemispherical cylinder, also of steel, is accurately fitted by grinding; the upper portion is a solid cylinder of the same metal, which exactly fills up the hollow cylinder. When a mineral has to be crushed, it is introduced into the bed of the mortar, the solid cylinder is then replaced and struck forcibly several times with a mallet, by which it is reduced to a coarse powder, and may afterwards be brought to an impalpable state by grinding in the agate mortar. *Fig.* 42.

Fig. 41.

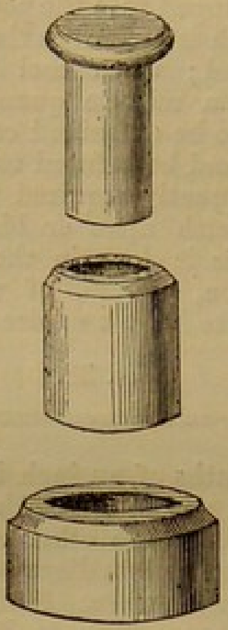
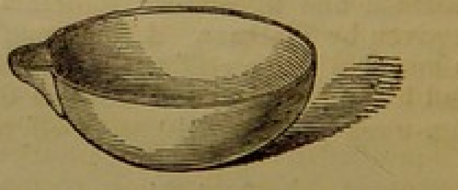


Fig. 42.

When a bead of gold or silver or other noble metal is obtained before the blowpipe, the operation of *cupellation* is resorted to in order to ascertain whether the metal is really pure or is contaminated with an inferior metal. The process consists in fusing the suspected alloy on charcoal with pure lead, and then heating the resulting bead in the oxidating flame upon a substance sufficiently porous to absorb the fused oxides produced by ignition. Griffin gives the following method of proceeding*:—Take a small quantity of very finely pounded bone ashes, mix it into a stiff paste with a few drops of water and a little carbonate of soda, and insert it into a small hole about one-fourth of an inch deep, bored in a piece of charcoal; smooth the surface with the end of a pestle, and slowly dry the mass over a lamp. Place the alloyed metal on this *cupel*, and heat for a considerable time in the oxidating flame. All the oxidizable metals present thus become oxidized, and form fusible compounds which sink into the cupel, while the gold, silver, and other noble metals remain in a brilliant globule on the surface. This method of assaying is so delicate, that it almost always produces a bead of silver when the common lead of commerce is submitted to trial.

Evaporation.—Evaporation is an operation to which the chemist is constantly resorting; he has recourse to it for concentrating liquids previous to the application of certain tests, for separating volatile fluids from fixed substances, for inducing crystallization, or for obtaining in a solid form substances held in solution by water or other liquids. When the object is to retain the fluid evaporated, as well as the solid residue, the process is called *distillation*. The ordinary operation of evaporation is conducted in basins of earthenware, silver or platinum: watch glasses also occasionally form very useful vessels. The earthenware basins, *Fig.* 43, should be as thin as is consistent with strength, and should resist the action of acids and alkalies in solution; the silver and platina vessels should be provided with a projecting slip of metal to serve as a handle, whereby they may be held by a pair of pincers. In ordinary cases the object sought by evaporation is attained by exposing the fluid to heat; sometimes, however, it is effected by leaving it for a certain time, in contact with the atmosphere at common temperatures or in confined air kept dry by hygroscopic substances. In quantitative experiments the evaporating substance should never be allowed to enter into actual ebullition, as a loss would almost unavoidably be sustained by bubbling. It is advisable, therefore, to apply heat through the

Fig. 43.



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* Chemical Recreations, p. 143.

medium of the water bath, which may be a copper basin about six inches in diameter and three inches deep, provided with a series of rings of different diameters to suit dishes of different sizes. While a liquid is evaporating, it is requisite carefully to protect it from dirt and dust: this is best done in the manner recommended by Fresenius, viz. by providing two small thin wooden hoops, one of which must be made to fit loosely in the other; a sheet of blotting paper is spread over the smaller, and the larger pushed over it: an excellent cover is thus formed, which, while it effectually guards the liquid, does not come into contact with it, and does not in the least impede or retard the process of evaporation. Sometimes it is necessary to evaporate fluids from solid substances contained in crucibles: in such cases the crucible should be supported in an inclined position, and the heat applied a little above the level of the liquid: an equal distribution of heat is thereby secured, and the loss of a portion of the sediment by spirting avoided. The same method may be adopted in the evaporation of solutions of those salts which have a tendency to effloresce and creep up the sides of the evaporating vessel: in the latter case the object may be also attained by slightly greasing the upper part of the sides of the dish. Very frequently in the course of an analysis large quantities of filtrates have to be evaporated down to perfect dryness: in such cases the fluids are first concentrated by evaporation over the naked fire, and afterwards transferred into smaller vessels, to be finished in the water bath. The process of transferring liquid from one basin to another, so as to avoid the smallest loss, requires care and a steady hand; the edge of the large dish should be slightly smeared with tallow, and the liquid poured down an inclined rod, as recommended above when treating of filtration. The evaporation of a mineral water from which carbonic acid or other elastic gases are expelled by heat, should always be commenced in a flask loosely covered with a piece of bibulous paper.

As the evaporation of a fluid in which a considerable sediment is formed draws to a conclusion, the thick mixture requires to be treated with great care; for, the circulation of the heat being now interrupted, the temperature frequently increases at the bottom of the vessel until above the boiling point of the solution, and then the sudden evolution of small quantities of steam occasions a projection of the portions of substance from the basin. Sometimes, indeed, when the solid residue dries hard, it forms a cake on the surface, underneath which steam accumulates, and suddenly explodes with a force not merely sufficient to disperse the contents of the vessel, but even to break it in pieces. In these cases the substance should be continually stirred with a glass rod, by which the loss by spirting is prevented.

Distillation.—This operation is performed when it is desired to collect the evaporating substance. It must obviously, therefore, be conducted in an apparatus in which the vapour as it rises may be refrigerated, again reduced to a liquid or solid state, and collected in a separate vessel: when the elastic fluid or vapour assumes on cooling the solid form, the process is called sublimation. The vessel in which almost every laboratory distillation is effected, is the glass retort: those made of hard green glass are the most serviceable, as they withstand the action of caustic alkalies: it is difficult, however, to get them stoppered. Retorts made of the hard German glass are now much used in this country; their high price, though lately much reduced, is the only objection to be raised against them: their shape differs somewhat from the retorts of English make. *Fig.* 44 shows one plain, and *fig.* 45 tubulated.

Fig. 44.

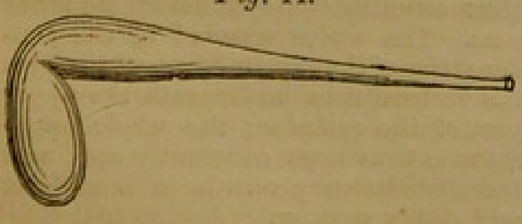
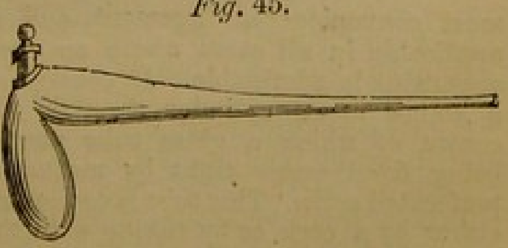


Fig. 45.



In applying heat to a retort, it should be communicated, as in the case of flasks, through the medium of sand; and the bend of the retort may be protected from the cooling influence of the air by a notched pasteboard or thin tin cone.

In the distillation of many liquids, particularly such as contain alcohol, the vapour is frequently evolved with such difficulty as not only to endanger the sudden expulsion of part of the substance, but the safety even of the whole apparatus. A tranquil and regular evolution of vapour may always be obtained by introducing into the retort certain angular solids on which the liquid has no chemical action, as slips of platinum; but care must be taken not to introduce these promoters of evaporation while the fluid is hot, or the burst of vapour might probably be so instantaneous as to do more harm than the previous irregular boiling. The same caution applies to the introduction of solids of whatever nature into liquids while boiling or near the boiling temperature. Sulphuric acid, which is the most difficult and dangerous of all substances to distil, may be drawn over quietly, regularly, and at a lower temperature by previously dropping into the retort a few pieces of platinum foil or wire. Various contrivances have been resorted to for the purpose of condensing the vapour in the process of distillation. In the common still this is well known to be accomplished by causing the vapour to pass through a long spiral tube called a worm, fixed in a tub, and surrounded by cold water. In the laboratory the receivers shown in *Figs.* 46 and 47 are frequently employed to collect and condense the products of distillation. The beak of the retort when charged is introduced into the aperture of the globe, which to keep it cool may be immersed in a basin of water in which some lumps of ice are floating. But Liebig's condenser, *fig.* 48, is by far the most convenient arrangement, and is applicable in all cases where an open apparatus is admissible. It consists of a hollow metal cylinder through the centre of which a glass tube passes, being fixed water tight by means of perforated corks. This tube is connected either by a cork or by tubing with the beak of the retort, a constant stream of cold water is caused to flow from a reservoir placed above, down the funnel, thus entering the cylinder at its lower part. The water warmed by the condensation of the vapour flows out through the vertical tube underneath the upper part of the cylinder; the whole apparatus is thus kept constantly cool, and the distillation proceeds in a uniform and steady manner.

Fig. 46.

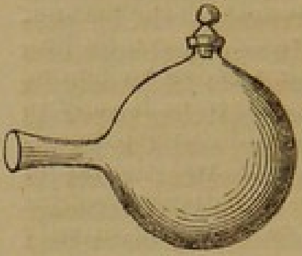


Fig. 47.

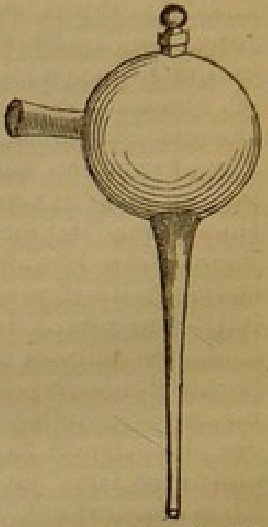
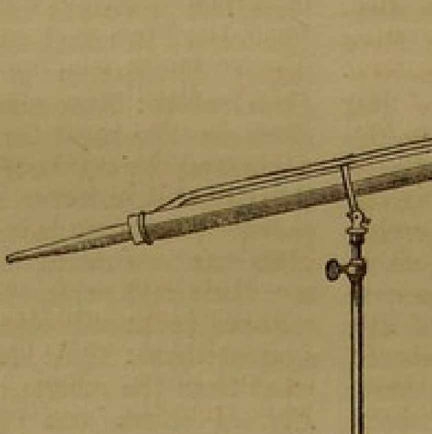
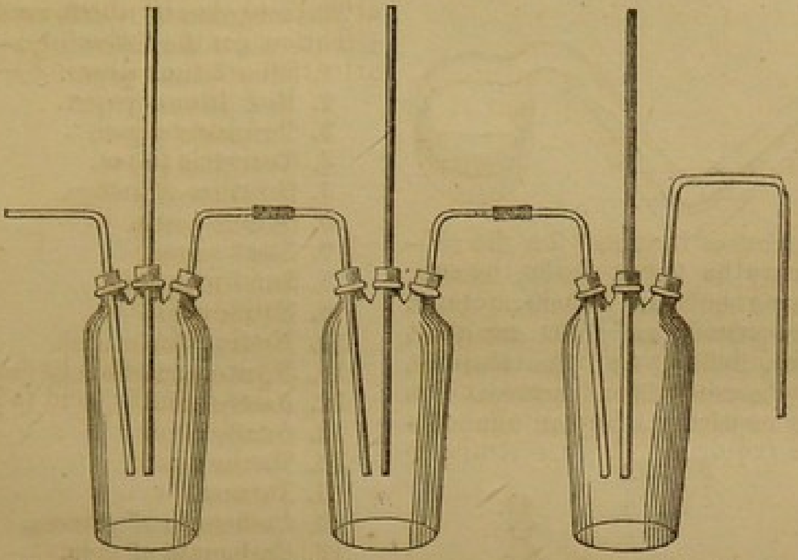


Fig. 48.



It is sometimes required to conduct the gaseous products of distillation into vessels containing water or other liquids,

Fig. 49.

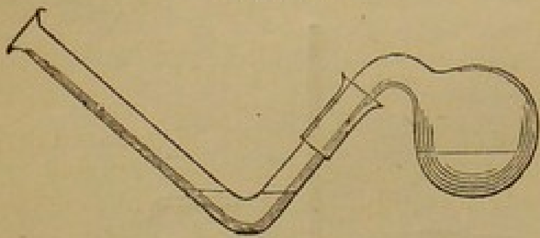


as in the preparation of hydrochloric and sulphurous acids, solution of ammonia, &c.; for such occasions the apparatus of Liebig would obviously be unfitted, and the arrangement shown in *fig.* 49 is best adapted to the purpose. It consists of a series of vessels placed side by side, and connected by tubes in such a manner that the tube originating in one vessel descends nearly to the bottom of the vessel which follows it. A simple inspection of the figure will show the direction in which the gas is supposed to be passing. After having acted on the water or solution in the first bottle, it passes through the bent tube into the second bottle, and from thence into the third. The junctions of the tubes with the bottles are made in various ways; sometimes they pass through corks as in the figure, at other times they are made tight by glazier's putty or linseed meal paste, or plaster of Paris. To prevent stiffness and rigidity, the tubes leading from bottle to bottle are not made of one continuous piece, but of separate pieces united air tight by tubes or collars of caoutchouc. This arrangement has received the name of Woulfe's apparatus; but it was first devised by Glauber. The upright tubes in the centre of each bottle are safety tubes, and are intended to admit air when from any cause the pressure within is so far diminished as to be considerably less than the atmosphere. Welter's safety tube, *fig.* 50, is also occasionally used for the same purpose: mercury is introduced until it fills about one-fourth of the little bulb, and the tube by its side to the same height: this closes a passage, but admits of a variable column of metal, according to the pressure within the retort and receiver. Whenever there is a condensation within, the external air has a tendency to enter by forcing the mercury into the ball, and will gain admittance when the fluids exert the least pressure. The delivering tubes in the bottles should have a height above the surface of the liquid more than fifteen times that from the bend of the safety tube to the level of the mercury when it is in the bulb. These tubes are also very conveniently inserted in the tubulature of retorts during distillation. Water may be used in the safety tube instead of mercury, provided no injury would result from a little entering the retort; but in this case the height from the bend to the top of the safety tube should be double or treble that by which the delivering tubes dip into the liquids in the bottles, otherwise the gases may force their way through the safety tube. It is sometimes required to collect for examination the uncondensable elastic fluids evolved during distillation, besides the liquid results; the object in such cases is easily attained by bending the delivering tube of the third bottle into a curve, and bringing it under the shelf of the hydro-pneumatic or the mercurio-pneumatic trough.

Fig. 50.

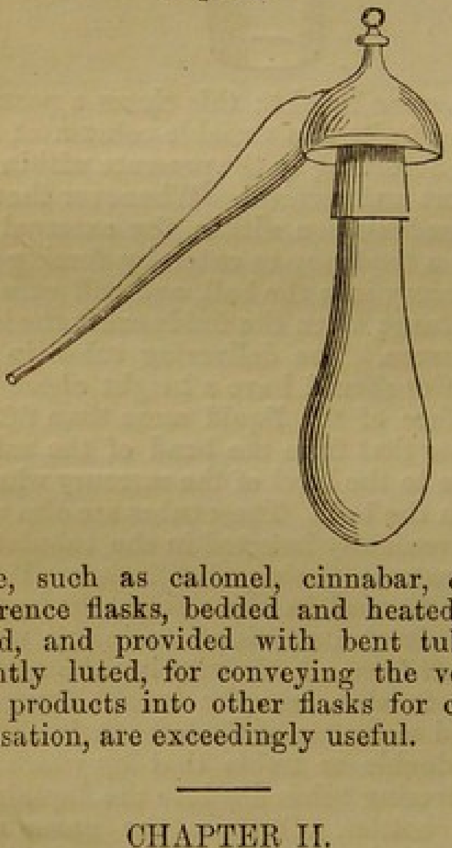
When the operation is conducted on a small scale, the receiver may be made out of a piece of tube bent in the manner shown in *fig.* 51, and a small tube retort employed: the distillation is conducted precisely in the same manner as with an ordinary retort and receiver.

Fig. 51.



The apparatus required for the sublimation may be tubes, flasks, retorts, capsules, or crucibles. When no great heat is required, as with camphor, naphthaline, iodine, &c., the alembic, *fig.* 52, may be used with advantage. For substances requiring a higher temperature, such as calomel, cinnabar, &c., Florence flasks, bedded and heated in sand, and provided with bent tubes, tightly luted, for conveying the volatile products into other flasks for condensation, are exceedingly useful.

Fig. 52



CHAPTER II.

On Reagents.

Those substances which are employed by the chemist to give him information as to the nature of the subject of his examination have received the general name of *Reagents;* though the manner in which they act, and the phenomena to which they give rise, are exceedingly varied. These bodies are of the highest importance to the analyst; indeed the judicious use of them, and the correct interpretation of the appearances presented by their action, constitute the skill of the analytical chemist. We shall here describe the preparation and uses of the most important of these substances, without, however, making any attempt to classify them.

The reagents to which we shall direct attention are the following:—

1. Blue litmus paper.
2. Red litmus paper.
3. Turmeric paper.
4. Georgina paper.
5. Solution of indigo.
6. Starch paste.
7. Lead paper.
8. Sulphuric acid.
9. Nitric acid.
10. Hydrochloric acid.
11. Nitro-muriatic acid (aqua regia).
12. Acetic acid.
13. Oxalic acid.
14. Tartaric acid.
15. Potassa.
16. Carbonate of potassa.
17. Carbonate of soda.
18. Ammonia.
19. Carbonate of ammonia.
20. Chloride of ammonium.
21. Hydrosulphuret of ammonia.
22. Sulphuret of potassium.
23. Oxalate of ammonia.
24. Sulphuretted hydrogen.
25. Ferrocyanide of potassium.
26. Ferricyanide of potassium.
27. Chromate of potassa.
28. Sulphate of potassa.
29. Bisulphate of potassa.
30. Cream of tartar.
31. Cyanide of potassium.
32. Antimoniate of potassa.
33. Baryta water.
34. Chloride of barium.
35. Nitrate of baryta.
36. Phosphate of soda.
37. Microcosmic salt.
38. Nitrate of potassa.
39. Borax.
40. Nitrate of silver.
41. Ammonia-nitrate of silver.
42. Sulphate of copper.
43. Iodide of potassium.
44. Acetate of lead.
45. Basic acetate of lead.
46. Sulphuret of iron.
47. Sulphate of lime.
48. Chloride of calcium.
49. Lime water.
50. Protochloride of tin.
51. Bichloride of platinum.
52. Sesquichloride of iron.
53. Sulphurous acid.
54. Chlorine water.
55. Chloride of mercury.

56. Protonitrate of mercury.
57. Protonitrate of cobalt.
58. Distilled water.
59. Alcohol.
60. Ether.

1. *Litmus Paper.*

This is an exceedingly delicate test of the presence of an acid; it is most conveniently prepared by dipping thin unsized paper into an infusion of the colouring principle in hot water until it acquires a full blue colour. The paper is dried by exposure to the air, and kept carefully protected from the light, which injures and finally destroys the colour. The blue colour of this paper is instantly changed red by contact with a fluid having an acid reaction.

2. *Red Litmus Paper.*

This is a valuable test of the presence of an alkali. To prepare it, a few drops of hydrochloric acid are mixed with a large quantity of water, and the blue paper immersed in it until it becomes slightly reddened: it is then removed and dried for use. The blue colour is restored by contact with an alkali.

3. *Turmeric Paper.*

This is prepared in the same manner as litmus paper; it should have a fine yellow colour; it indicates the presence of an alkali by changing to a red brown.

4. *Georgina Paper.*

This when properly prepared is an excellent test of both acids and alkalies; by the former it is coloured red, and by the latter green. It is prepared by dipping paper into the coloured infusion of the petals of the Georgina purpurea, and should have a fine violet colour.

5. *Solution of Indigo.*

Commercial indigo is digested in concentrated sulphuric acid, and the solution diluted with water till it is just distinctly blue. It is an excellent test for nitric acid, which, aided by heat, discharges the colour.

6. *Starch Paste.*

Common arrowroot starch is rubbed with cold water, and boiling water then added until a thin paste is formed. It is an invaluable test for free iodine; when brought into contact with which, an intense blue compound is formed.

7. *Lead Paper.*

Paper is saturated with a strong solution of basic acetate of lead, cut into strips and dried. It forms an extremely delicate test of the presence of sulphuretted hydrogen, which instantly communicates to it a deep brown black colour.

8. *Sulphuric Acid.* (SO_3.)

The commercial oil of vitriol always contains sulphate of lead, sometimes also nitric acid, arsenic, and tin. The first of these impurities is removed by diluting the acid with water; a turbidity indicates sulphate of lead, which is insoluble in the diluted acid. Nitric acid is indicated by the blue colour of solution of indigo being discharged when boiled with the acid. Arsenic is indicated by passing a stream of sulphuretted hydrogen through the clear diluted acid; a yellow precipitate is formed: if the precipitate be brown, it indicates tin. From all these impurities it may be freed by distillation; the first portions being rejected, and not more than three-fourths of the acid in the retort drawn over; for almost every qualitative operation the commercial acid may be employed. Sulphuric acid is of the most extensive use to the chemist, from its strong affinity for bases. It liberates most other acids from their combinations; and, from its powerful affinity for water, it effects remarkable changes in many substances in which the elements of that fluid exist. It is a powerful oxidizing agent, and in a diluted state it serves as a test for baryta, strontia, and lead.

9. *Nitric Acid.* (NO_5.)

This acid, the aquafortis of commerce, is prepared by distilling equal weights of oil of vitriol and nitre. It almost always contains sulphuric and hydrochloric acids, from which it may be freed, by adding nitrate of silver as long as a precipitation takes place, and then redistilling. This operation may, however, be avoided, if in the original preparation of the acid the first portions, about one-tenth or one-eighth of the whole, be collected in a separate receiver; these portions will contain all the impurities, and the remainder will be quite pure. Nitric acid is used as a solvent for metals, sulphurets, &c., and as a powerful oxidizing agent.

10. *Hydrochloric Acid.* (HCl.)

The muriatic acid of commerce is not sufficiently pure for analytical purposes. It contains sulphuric acid and iron, sometimes also sulphurous acid, chlorine, and arsenic. It is best prepared by the following process of Gregory. Six parts by weight of pure common salt are introduced into a flask, and gently heated with a cool mixture of ten parts by weight of oil of vitriol and four parts of water. The gas is conducted into a flask containing a quantity of distilled water, equal in weight to the salt, and surrounded with water in which lumps of ice are floating. The tube delivering the gas must dip about one-eighth of an inch into the water in the bottle; the process takes about two hours, and the acid obtained is quite pure and colourless.

Hydrochloric acid is very extensively used as a solvent, and for the detection of silver, mercury, lead, and ammonia.

11. *Nitromuriatic Acid, or aqua regia.*
($NO_4 + Cl.$)

This acid is prepared by adding nitric acid to twice or thrice its volume of strong hydrochloric acid; both acids undergo decomposition, hyponitric acid, chlorine, and water being formed. When the liquid is saturated with chlorine, this mutual decomposition ceases; but it recommences on the removal of the chlorine either by heat or by its combination with some other substance. Aqua regia is consequently the most powerful of solvents: its principal use in analytical chemistry is for dissolving gold and platinum, and for decomposing certain metallic sulphurets.

12. *Acetic Acid.* ($C_4\,H_3\,O_3$, or $\overline{A}$.)

The acetic acid of commerce frequently contains traces of sulphuric acid, but it may be obtained sufficiently pure for most analytical operations. If required quite free from all impurities, it is most conveniently prepared by distilling a mixture of ten parts of neutral acetate of lead with three of sulphate of soda, in a retort, with a cooled mixture of two and a half parts of sulphuric acid, and an equal weight of water: the distillation is continued to dryness. The acid thus obtained leaves no residue on evaporation. Acetic acid is employed as a solvent, and for acidifying liquids in the place of the mineral acids.

13. *Oxalic Acid.* ($C_2\,O_3$, or $\overline{O}$.)

The commercial acid is purified by two or three recrystallizations. It should leave no residue on ignition. It is employed as a precipitant of certain substances, particularly lime, for the detection of which it is a very valuable reagent. All the oxalates are soluble in the stronger acids.

14. *Tartaric Acid.* ($C_8\,H_4\,O_{10} = \overline{\overline{T}}$).

The commercial acid is sufficiently pure; well-defined crystals should be selected. It should be kept in powder, as its solution decomposes by keeping. It is employed to prevent the precipitation of certain metallic oxides by alkalies, and as a test for potassa.

15. *Potassa.* (KO.)

The best method of preparing this valuable reagent is to dissolve two parts of pure carbonate of potassa in twenty parts of boiling water in an iron pot, and to add in small portions at a time, to the boiling liquid, cream of lime, made by slaking one part of quicklime with boiling water; after boiling a few minutes the vessel is covered and allowed to stand for twenty-four hours; the clear liquid is then decanted. To obtain the potassa in the solid state, the liquid is evaporated to an oily consistence in a silver basin, poured out on a silver dish, and allowed to cool; it is then broken into fragments and preserved in well-stoppered bottles. Solutions of potassa, after being neutralized by nitric acid, should give no precipitate with chloride of barium, or nitrate of silver, nor should it effervesce on the addition of an acid. Silicic acid is a frequent impurity of potassa. It is detected by evaporating the alkali to perfect dryness, and adding water. Silicic acid, if present, remains undissolved.

The uses of potassa in analytical chemistry are very numerous; as a precipitant; as a solvent; as a means of separating certain oxides from others; and as a test for ammonia, which, aided by heat, it expels from all its salts.

16. *Carbonate of Potassa.* (KO, CO_2.)

This salt is best prepared by calcining pure cream of tartar: the incinerated mass is boiled in distilled water, filtered, and the clear liquid evaporated to dryness in a clean iron vessel, with constant stirring towards the end of the process; the dried mass must be kept in a well-stoppered bottle, and one part dissolved in five or six of distilled water for use. The carbonate of potassa of commerce usually contains alkaline sulphates and chlorides, alumina and silica. Carbonate of potassa is extensively employed as a precipitant, and for the decomposition of many insoluble salts, particularly organic, with metallic bases.

17. *Carbonate of Soda.* (NaO, CO_2.)

This salt is obtained pure by heating

the best bicarbonate of soda of commerce for some time to low redness: its uses are the same as those of carbonate of potassa. It is an indispensable reagent in blowpipe operations; as a flux; as a solvent; and as a decomposing agent.

18. *Ammonia.* (NH_3.)

Sal ammoniac is mixed with an equal weight of slaked lime, a little water added, and the mixture heated in a stoppered retort. The disengaged gas is first allowed to pass through a small quantity of water in a wash bottle, and from thence into another bottle nearly filled with distilled water immersed in a vessel containing ice-cold water; this bottle, for better security against sudden absorption, may be furnished with a safety tube. The water will absorb 670 times its bulk of the gas, and become possessed of all its chemical properties in a very high degree. It should be kept in small well-stoppered bottles, and not in one large one, as every time it is exposed to the air it absorbs a certain quantity of carbonic acid, its freedom from which is proved by its not rendering lime-water turbid. Ammonia is in constant use for neutralizing acids, its peculiar fitness for which consists in its not introducing any fixed matter; for precipitating insoluble bases; and for separating them from each other.

19. *Carbonate of Ammonia.*

(NH_4O, CO_2.)

The sesqui-carbonate of ammonia of commerce is dissolved in four parts of distilled water, and one of liquor of ammonia added. The solution when evaporated should leave no residue. This reagent is employed as a precipitant, and is very useful as a substitute for carbonate of potass, in cases where the introduction of a fixed base would be inconvenient. It is of special use in the separation of baryta, strontia, and lime, from magnesia, the latter of which earths is not precipitated in the presence of ammoniacal salts.

20. *Chloride of Ammonium.*

(NH_4 Cl.)

Sal-ammoniac of commerce is purified by two or three recrystallizations. Its solution in water should be neutral, and hydrosulphuret of ammonia should not discolour it: it should volatilize entirely when heated on platinum foil. The salt should be dissolved for use in eight parts of distilled water. It is of great use in analysis as a precipitant of various substances soluble in potassa, but insoluble in ammonia, and for keeping in solution certain oxides or salts when others are precipitated by ammonia or other reagents.

21. *Hydrosulphuret of Ammonia.*

(NH_4S, HS.)

This reagent is prepared by transmitting sulphuretted hydrogen gas through solution of ammonia, till the liquid gives no precipitate with sulphate of magnesia. It must be kept in well-stopped bottles free from lead. When first prepared it contains excess of sulphuretted hydrogen, is nearly colourless, and does not give a precipitate of sulphur when mixed with an acid; but by exposure to the air it gradually absorbs oxygen, and assumes a yellow tint from the presence of excess of sulphur, of which element it now yields a precipitate on the addition of an acid. It is necessary to bear in mind these facts. Hydrosulphuret of ammonia is of great use for subdividing into two groups those metals which are precipitated as sulphurets by sulphuretted hydrogen, from their acid solutions; some of these sulphurets being soluble, others insoluble in hydrosulphuret of ammonia. It also subdivides into groups those metals that are not precipitated by sulphuretted hydrogen from their acid solutions; some of these metals being precipitated by hydrosulphuret of ammonia, while others remain in solution: it likewise precipitates certain oxides as hydrates by the action of its ammonia alone, and certain salts that are dissolved only in free acids.

22. *Sulphuret of Potassima.* (KS_5.)

When sulphuret of copper is to be separated from sulphur combinations soluble in alkaline sulphurets, sulphuret of potassium prepared by boiling sulphur with solution of caustic potassa, is substituted for hydrosulphuret of ammonia, in which sulphuret of copper is partially soluble.

23. *Oxalate of Ammonia.*

(NH_4O, $\overline{O}$.)

This reagent is prepared by slightly supersaturating a solution of pure oxalic acid with carbonate of ammonia, and crystallizing: one part of the salt is dissolved in twenty or twenty-four parts of water for use; it is employed for the detection and precipitation of lime, and is more convenient than oxalic acid, as its solution does not decompose by keeping.

24. *Sulphuretted Hydrogen.* (HS.)

Fragments of protosulphuret of iron are covered with water in a gas evolution apparatus connected with a wash bottle; sulphuric or hydrochloric acid is poured into the bottle through a tube funnel, and the evolved gas received into a bottle containing cold distilled water as long as it continues to be absorbed. The solution must be preserved in well-stopped bottles. Sulphuretted hydrogen is a valuable reagent for separating metals into groups, and also as a means of reduction.

25. *Ferrocyanide of Potassium.*

(K_2, Cfy.)

The commercial yellow prussiate of potassa is sufficiently pure for analytical purposes; one part is dissolved for use in ten or twelve parts of water. It is of especial use for the detection of sesquioxide of iron and oxide of copper.

26. *Ferricyanide of Potassium.*

(K_3, Cfy_2.)

This reagent is prepared by transmitting a stream of chlorine gas through a solution of the above salt until it ceases to produce a blue precipitate, with a solution of sesquichloride of iron. Its crystals have a magnificent red colour; to procure them the solution is concentrated by evaporation, and rendered feebly alkaline by carbonate of potassa. This reagent serves to detect protoxide of iron by the formation of a characteristic blue precipitate.

27. *Chromate of Potassa.* (KO, CrO_3.)

Bichromate of potassa of commerce is dissolved in water, and carbonate of potassa added till the solution reacts slightly alkaline; from the concentrated liquid yellow crystals may be obtained. It is employed principally as a test for lead, with which it forms a pigment known as chrome yellow.

28. *Sulphate of Potassa.* (KO, SO_3.)

The salt of commerce is purified by two or three crystallizations, and dissolved for use in ten or twelve parts of water; it is used for the detection and separation of strontia and baryta.

29. *Bisulphate of Potassa.*

(KO, $2\,SO_3$.)

This is the fusible salt remaining when nitrate of potassa is decomposed by two equivalents of oil of vitriol in the process for making nitric acid; it is extensively employed in blowpipe operations; in solution it indicates lithia, boracic acid, nitric acid, hydrofluoric acid, bromine, and iodine, and separates baryta and strontia from other earths and metallic oxides.

30. *Bitartrate of Potassa.* (KO, HO, $\bar{T}$.)

The cream of tartar of commerce is sufficiently pure; it is useful in certain cases for separating metals from each other.

31. *Cyanide of Potassium.* (KCy.)

Eight parts of roasted ferrocyanide of potassium are fused at a bright red heat in a covered crucible with three parts of dry carbonate of potassa; the fused mass is poured carefully into a warm dish, and when cold broken into fragments, and kept in a well-closed bottle: it must not be kept in solution, but dissolved as required in four or five parts of water. In analysis its most important application is as a means of separating cobalt from nickel. As a blowpipe reagent mixed with an equal weight of carbonate of soda, it is exceedingly valuable from its powerful reducing action; and from its easy fusibility it is of special application in the reduction of arsenic.

32. *Antimoniate of Potassa.*

(KO, SbO_5.)

A mixture of one part of crude antimony with four parts of powdered nitre is thrown a little at a time into a crucible at a dull red heat; the mass is kept in a pasty state, with occasional stirring, for about half an hour, after which it is cooled, well washed, and heated to bright redness for half an hour, with two-thirds of its weight of pure carbonate of potassa. The cooled mass is digested with about fifty parts of warm water, and filtered for use when cold. It should not contain excess of alkali. Its use is as a test for soda, with which, provided no other base be present, it forms a very sparingly soluble crystalline precipitate.

33. *Caustic Baryta.* (BaO.)

Sulphuret of barium is boiled with excess of oxide of copper or oxide of lead, and filtered when the liquid gives a white precipitate, with acetate of lead: it is then diluted with water, and preserved in well-closed bottles. Its most important use is as a precipitant of magnesia.

34. *Chloride of Barium.* ($BaCl$.)

To prepare this useful reagent six parts of heavy spar (sulphate of baryta) are exposed to an intense red heat, with a mixture of one part of powdered charcoal and one and a half of fluor spar; the resulting sulphuret of barium is boiled with slight excess of hydrochloric acid filtered, and crystallized two or three times. The solution of these crystals must be neutral to test-papers, not affected by sulphuretted hydrogen, or hydrosulphuret of ammonia: it must, moreover, leave no residue when mixed with excess of sulphuric acid, filtered and evaporated. Its most important use is as a means of detecting and estimating sulphuric acid. From the property which baryta possesses of forming soluble salts with some acids, and insoluble salts with others, it is likewise a valuable reagent for distinguishing one group of acids from another.

35. *Nitrate of Baryta.* (BaO, NO_5.)

Native carbonate of baryta is digested with dilute nitric acid, the solution filtered and crystallized two or three times. Its uses and applications are the same as those of chloride of barium.

36. *Phosphate of Soda.*

($HO, 2\,NaO, PO_5$.)

The commercial salt is crystallized and dissolved for use in ten or twelve parts of water. It serves as a test for alkaline earths in general, but especially for the detection and estimation of magnesia, which it precipitates with the addition of ammonia as the basic phosphate of ammonia and magnesia.

37. *Phosphate of Soda and Ammonia.*

(NaO, NH_4O, PO_5.)

This salt (microcosmic salt) is prepared by boiling one hundred parts of crystallized phosphate of soda with sixteen of sal-ammoniac. Chloride of sodium separates, and the liquid, when filtered and evaporated, yields the double salt in fine crystals. When this salt is heated on charcoal or platinum wire, it loses water and ammonia, *meta-phosphate of soda* is formed, which, in consequence of its excess of acid, has the power of fusing almost every chemical compound. Hence its great use as a blowpipe reagent.

38. *Nitrate of Potassa.* (KO, NO_5.)

The nitre of commerce is purified by repeated crystallizations: its solution should give no precipitate with nitrate of silver, or chloride of barium: it is extensively employed as an oxidizing agent.

39. *Biborate of Soda.* ($NaO, 2\,BO_3$.)

The borax of commerce is purified by recrystallization. It should be exposed to a gentle heat in a platinum crucible till it no longer swells up; it is then powdered and kept for use. When heated on the ring of platinum wire, it should give a clear transparent glass. This glass possesses the property of dissolving most metallic oxides, the smallest portions of which communicate to it a colour; hence its important use as a blowpipe reagent.

40. *Nitrate of Silver.* (AgO, NO_5.)

Standard silver is dissolved in nitric acid, evaporated to dryness, and heated till all the copper present is converted into black oxide, which may be known by dissolving a portion of the fused salt in water and adding ammonia, which should not make the solution blue. The fused mass is dissolved in water, filtered and crystallized; the crystals are dissolved for use in fifteen or twenty parts of distilled water. It may be known to be pure by the filtrate from the precipitate, which it forms with excess of hydrochloric acid, leaving no residue when evaporated on a watch-glass. It is employed for arranging acids into groups, and is of special application in testing for, and estimating hydrochloric acid.

41. *Ammonia Nitrate of Silver.*

($AgO\ NO_5, + 2\,NH_3$.)

Ammonia is dropped into solution of nitrate of silver till the precipitate which first forms is nearly redissolved. It is employed for the detection of arsenic.

42. *Sulphate of Copper.* (CuO, SO_3.)

Blue vitriol is purified by two or three crystallizations. A solution of one part of this salt mixed with two and one quarter parts of protosulphate of iron is employed for the precipitation of hydriodic acid, as protiodide of copper. Ammonia-sulphate of copper prepared in the same manner as the corresponding silver salt is also employed as a test for arsenic.

43. *Iodide of Potassium.* (KI.)

The commercial salt is tested for carbonate of potassa by treating it with hot alcohol, in which the latter salt is insoluble. It is a reagent for certain metals, particularly for lead and mercury, with which it forms characteristic precipitates.

44. *Neutral Acetate of Lead.* ($PbO, \bar{A}$.)

The best sugar of lead of commerce is dissolved in ten or twelve parts of distilled water; it is useful for arranging acids into groups, and for the special detection of chromic acid.

45. *Basic Acetate of Lead.* ($3\,PbO, \bar{A}$.)

Seven parts of well-washed litharge and six of the best neutral acetate of lead are gently heated and agitated with thirty parts of water till the sediment has become perfectly white; the liquid is then decanted and preserved for use in a well-closed bottle. It has the same applications as the last described salt, but its chief use is as a test for sulphuretted hydrogen.

46. *Protosulphate of Iron.* (FeO, SO_3.)

Clean iron nails are digested with dilute sulphuric acid till hydrogen ceases to be evolved. The solution is filtered, and the crystals obtained washed with water slightly acidified with sulphuric acid and dried. This salt is a powerful deoxidizing agent, and is of especial application as a test for nitric acid. It also precipitates gold in the metallic state, and forms a blue compound with ferricyanide of potassium.

47. *Lime Water.* (CaO.)

Fresh slaked lime is agitated with cold water allowed to settle, and the clear fluid preserved in well-stopped bottles. It serves to detect carbonic acid, and as a means of distinguishing certain organic acids.

48. *Sulphate of Lime.* (CaO, SO_3.)

The precipitate formed on adding chloride of calcium to dilute sulphuric acid is well washed, digested, and agitated with water, and the fluid filtered for use. It is employed to distinguish between lime, strontia, and barytes.

49. *Chloride of Calcium.* ($CaCl$.)

Pure carbonate of lime is dissolved in dilute hydrochloric acid. The solution must be perfectly neutral. It is of great use for the classification of organic acids.

50. *Protochloride of Tin.* ($SnCl$.)

Granulated tin is boiled with concentrated hydrochloric acid, the metal being in excess; it is then diluted with four or five times its quantity of water, slightly acidulated with hydrochloric acid and filtered. It must be kept in well-closed bottles containing fragments of metallic tin to prevent the protochloride from passing into the state of perchloride. It is a powerful reducing agent. It also serves to detect mercury, and, when mixed with nitric acid, it indicates the presence of gold.

51. *Bichloride of Platinum.* ($PtCl_2$.)

The solution of the metal in aqua regia is evaporated to dryness in the water bath, and redissolved in 8 or 10 parts of water. It is of great use in analytical chemistry for the detection and estimation of potassa and ammonia.

52. *Sesquichloride of Iron.* ($Fe_2\,Cl_3$.)

Clean iron nails are digested with diluted hydrochloric acid; the decanted acid liquid is then boiled with successive additions of nitric acid, in a capacious vessel, till all effervescence ceases, and till it no longer tinges solution of red prussiate of potassa blue; it is then precipitated with excess of ammonia, and the well-washed hydrated peroxide of iron is heated with hydrochloric acid, care being taken that it is not all dissolved, it being necessary that the test should not contain excess of acid; it is then filtered for use. It is employed as a means of classifying organic acids, and is also of great use in the analysis of the phosphates of the alkaline earths.

53. *Sulphurous Acid.* (SO_2.)

This is prepared by transmitting the gases produced by the action of six parts of oil of vitriol on one part of charcoal (carbonic and sulphurous acid gases) through ice-cold water till no more is absorbed. It must be kept in well-closed bottles, and should always smell strongly of the acid. It is a powerful means of reduction; it precipitates mercury from its solution, converts chromic acid into oxide of chromium, arsenic acid into arsenious acid, &c.

54. *Hydrofluosilicic Acid.*
($3\,HF, + 2\,SiF_3$.)

Equal weights of a mixture of powdered fluor spar and quartz are gently heated, in a retort, with oil of vitriol, and the gas evolved passed into water, the extremity of the delivering tube dipping into mercury placed at the bottom of the jar in order to prevent the tube from becoming choked up with the silicic acid which is precipitated the instant the gas comes into contact with water. The gelatinous mass is filtered through linen, and the filtrate preserved for use. Hydrofluosilicic acid forms an insoluble compound with potassa, which base it is sometimes employed to separate from chloric acid. It is also used to discriminate between baryta and strontia, with the former of which it forms a crystalline deposit.

55. *Chlorine Water.* (Cl.)

The gas evolved by heating finely powdered peroxide of manganese with five or six times its weight of hydrochloric acid is conducted into ice-cold water, until the fluid is saturated. It must be kept in a well-closed bottle and preserved from the light. It is employed to expel iodine and bromine from their combinations.

56. *Chloride of Mercury.* ($HgCl$.)

The corrosive sublimate of commerce is purified by crystallization, and dissolved for use in 12 or 14 parts of water. It forms characteristic coloured precipitates with certain acids.

57. *Protonitrate of Mercury.*

(Hg_2O, NO_5.)

Mercury is gently heated with an equal weight of moderately strong nitric acid, till the formation of red fumes ceases; it is then boiled with the undissolved metal till a few drops of the solution are so completely precipitated by common salt, that no precipitate occurs in the filtered liquid on the addition of protochloride of zinc. The solution is then agitated till it is cold, and the crystals formed, shaken with 20 parts of cold water, to which a small quantity of nitric acid has been added. The bottle in which this reagent is kept should contain a small quantity of mercury. Its applications are the same as those of nitrate of silver. It is likewise employed to detect several substances of easy oxidation, formic acid, for instance, which it resolves into carbonic acid and water, a reduction of the metal at the same time taking place.

58. *Protonitrate of Cobalt.*

(CoO, NO_5.)

It is not easy to obtain this reagent quite pure, though for blowpipe experiments it is a matter of great consequence that it should be so. Fresenius gives the following directions for preparing it:—an intimate mixture of two parts of very finely powdered cobalt, four parts of saltpetre, one part of effloresced carbonate of soda, and one part of dry carbonate of potassa, is projected in small portions into a red-hot crucible, which is then exposed to the strongest possible heat till the mass is fusing; when cold, it is reduced to powder, boiled with water, and the well-washed mass dissolved in hydrochloric acid; the gelatinous mass is carefully evaporated to dryness; the residue boiled with water, filtered, and carbonate of ammonia (carbonate of potassa is better) added to the filtrate while kept at the boiling heat till all acid reaction ceases; the filtered solution is precipitated by carbonate of potassa, and the precipitate obtained washed and dissolved in nitric acid. The solution is evaporated to dryness at a gentle heat, and one part of the residue dissolved in ten parts of water for use. Solution of nitrate of cobalt is employed to distinguish certain metals in the oxidating flame of the blowpipe. This alumina acquires a beautiful pale blue colour, magnesia a rose-red tint, and zinc a bright green. A few drops of the solution are placed on the substance to be operated upon by means of a platinum wire or dropping tube.

59. *Distilled Water.* (HO.)

No other water should be employed in the laboratory. It should give no precipitate or even turbidity with chloride of barium, nitrate of silver, oxalate of ammonia or lime water, and should leave no residue on evaporation.

60. *Alcohol.* ($C_4 H_6 O_2$.)

Rectified spirits of wine, sp. gr. about .840, are sufficiently strong for most purposes. What is termed absolute alcohol, and which is sometimes required, is prepared by adding carbonate of potassa, that has recently been exposed to a red heat, to ordinary alcohol until it ceases to dissolve any more; the whole is allowed to digest for 24 hours; the liquid is then poured off, mixed with a sufficient quantity of quicklime to absorb the whole, and slowly distilled from a retort on a water bath at the temperature of about 180°; it is then obtained of a sp. gr. of .7947. It must not redden paper, and must volatilize without leaving any residue.

61. *Ether.* ($C_4H_5O.$)

Sulphuric ether of commerce is sufficiently strong and pure for all purposes. In inorganic analysis it is employed to detect and isolate bromine.

The student is recommended to prepare, as far as possible, his own reagents. He should at any rate assure himself by careful testing of their purity; by so doing he will not only save himself from much subsequent embarrassment, but he will be gaining much valuable experience in qualitative examinations.

CHAPTER III.

On the Comportment of Substances with Reagents.

1. Metallic Oxides.

By means of certain reagents this extensive class of compounds may be arranged into a series of groups; some of which, again, by other reagents may be subdivided into sections, the whole forming a very convenient classification.

First Group.—Metallic oxides not precipitated from their solutions by sulphuretted hydrogen, hydrosulphuret of ammonia, or alkaline carbonates.

The alkalies proper: *potassa, soda, lithia, ammonia.*

Second Group.—Metallic oxides not precipitated from their solutions by sulphuretted hydrogen, but precipitated by hydrosulphuret of ammonia under certain circumstances, as salts, and precipitated by alkaline carbonates.

The alkaline earths: *baryta, strontia, lime, magnesia.*

Third Group.—Metallic oxides not precipitated by sulphuretted hydrogen, but precipitated as oxides by hydrosulphuret of ammonia.

Alumina, glucina, oxide of chromium, thorina, yttria, oxides of cerium, zirconia, titanic acid, tantalic acid.

Fourth Group.—Metallic oxides not precipitated from their acid solutions by sulphuretted hydrogen, but completely precipitated by hydrosulphuret of ammonia as *sulphurets.*

Oxide of zinc, oxide of nickel, oxide of cobalt, protoxide of manganese, protoxide and sesquioxide of iron, and sesquioxide of uranium.

Fifth Group.—Metallic oxides completely precipitated from their solutions, whether acid, alkaline, or neutral, by sulphuretted hydrogen, their sulphurets being insoluble in alkaline hydrosulphurets. *Oxide of lead, oxide of silver, oxides of mercury, oxide of bismuth, oxide of cadmium, oxide of copper, oxide of palladium, sesquioxide of rhodium, oxide of osmium.*

Sixth Group.—Metallic oxides completely precipitated from their acid solutions by sulphuretted hydrogen, but not from their alkaline solutions, their sulphurets being soluble in alkaline sulphurets.

Oxide of antimony, oxide of arsenic, oxide of tin, oxide of platinum, oxide of iridium, oxide of gold, oxides of selenium, tellurium, tungsten, vanadium, and molybdenum.

Group 1st. — *The Alkalies Proper, Potassa, Soda, Lithia, Ammonia.*

Potassa, KO;—*General Characters:* When pure it is quite white, dissolving in water with the disengagement of heat, and attracting both water and carbonic acid from the atmosphere. It is highly caustic, and eminently alkaline; nearly all its salts are soluble in water; it is capable of being precipitated by very few reagents. Its presence is, however, evinced by the following.

Bichloride of platinum produces a bright yellow crystalline precipitate of double chloride of platinum and potassium ($KCl, + PtCl_2$) very sparingly soluble in water, and the formation of which is promoted by the presence of free hydrochloric acid. It is quite insoluble in strong alcohol. Previous to applying this test, the operator must be certain of the absence of ammonia, and the solution should be concentrated.

Tartaric acid added in excess produces a granular crystalline precipitate ($KO, HO, \overline{T}.$) soluble in strong acids and in carbonated and caustic alkalies, but insoluble in tartaric and acetic acids; the formation of the precipitate is facilitated by agitation.

Carbazotic acid dissolved in alcohol produces even in dilute solutions a bright yellow crystalline precipitate.

Perchloric acid produces a sparingly soluble white crystalline precipitate.

Before the blowpipe, potassa salts, if free from soda, heated on a platinum wire in the inner flame, tinge the outer flame *violet;* if soda salts be present, potassa may be detected by fusing a clear bead of borax with a small quantity of *oxide of nickel,* and then adding the mixture, the brown colour of the bead is changed to blue.

Soda (NaO). — *General Characters:* They are very similar to those of potassa; its solution or that of any of its salts affords no precipitates with any of the above reagents for potassa; but

Antimoniate of potassa, if properly prepared, produces in neutral and even in very diluted solution, if well agitated, and provided no other oxide but potassa be present, a crystalline precipitate (NaO, SbO_5).

Before the blowpipe, soda salts are distinguished by the strong yellow colour which they communicate to the outer flame, which reaction is not prevented by a very considerable excess of potassa. According to *Kobell*, one part of chloride of sodium may hereby be detected in 25 or 30 parts of chloride of potassium.

Lithia (LiO).—*General Characters:* When pure, this oxide is white; it is not so soluble in water as potassa or soda; its solution rapidly absorbs carbonic acid, when exposed to the air. Carbonate of lithia is very sparingly soluble in water. When a solution of a lithia salt is boiled with phosphate of soda, and ammonia added, a very sparingly soluble double phosphate of soda and lithia is deposited.

Before the blowpipe, salts of lithia are detected by the fine crimson tinge which they communicate to the outer flame, when heated in the inner flame on platina wire. Potassa salts do not interfere with this reaction; but soda salts destroy it, substituting for the crimson their own peculiar yellow colour.

Ammonia (NH_4O).—*General Characters:* The solution of pure ammonia in water is when concentrated highly caustic and alkaline; it has a powerful and penetrating smell, by which its presence can generally be detected. It attracts carbonic acid from the atmosphere. Most of its salts are soluble in water; and nearly all of them are totally volatilizable by heat. When present in an uncombined state in a quantity too small to be detected by the smell, its presence may be evinced by the production of white clouds, when a feather dipped in strong hydrochloric, or acetic acid (the latter is preferable), is held over the liquid.

Behaviour of Ammonia and Ammoniacal Salts with Reagents.

Bichloride of platinum produces a yellow crystalline precipitate ($NH_4Cl + PtCl_2$) having a great resemblance to the corresponding double salt of potassium.

Tartaric acid produces in concentrated solutions a crystalline bitartrate of ammonia much more soluble than the corresponding potassa salt.

When mixed and triturated with hydrate of lime, ammoniacal salts part with their ammonia, which may then be detected either by its smell or by strong acetic acid.

GROUP 2.

The Alkaline Earths, Baryta, Strontia, Lime, Magnesia.

Baryta (BaO).—*General Characters:* When pure it is of a grayish white colour; it combines with water with the evolution of great heat, and is completely dissolved. Its concentrated aqueous solution deposits crystals. It is powerfully caustic and alkaline; it combines greedily with carbonic acid, forming a white insoluble compound, which is poisonous.

Behaviour of Soluble Barytic Salts with Reagents.

Alkaline carbonates produce a white precipitate (BaO, CO_2) soluble with effervescence in free acids.

Ammonia, and caustic alkalies do not produce any precipitate, provided atmospheric air be excluded.

Sulphuric acid, or solution of any *soluble sulphate*, produces, even in the most dilute solutions, a white precipitate (BaO, SO_3) wholly insoluble in all acids and alkalies.

Hydrofluosilicic acid produces after awhile a colourless crystalline precipitate ($3\,BaFl, + 2\,S_2Fl_3$) silico fluoride of barium, almost completely insoluble in free nitric or muriatic acids.

Neutral phosphate of soda produces a white precipitate ($2\,BaO, HO, PO_5$) soluble in free acids.

Oxalic acid, or *binoxalate of potassa*, produces in concentrated solutions a white precipitate ($BaO, \bar{O} + aq.$) soluble in free acids; the formation of this precipitate is favoured by ammonia.

Chromate of potassa produces a yellow precipitate (BaO, CrO_3) insoluble in nitric and hydrochloric acids and in caustic alkalies.

Before the blowpipe, baryta cannot be detected; most of its salts impart a yellow colour to the flame of alcohol, but it is not characteristic.

Strontia (SrO).—*General Characters:* It greatly resembles baryta, but it is not so heavy, neither is its hydrate so soluble in water; its aqueous solution is consequently less caustic.

Behaviour of Soluble Strontia Salts with Reagents.

Alkaline carbonates, the caustic alkalies and phosphate of soda, behave towards solutions of strontia salts precisely as towards solutions of baryta salts.

Sulphuric acid produces a white precipitate (SrO,SO_3) insoluble in free acids, but not altogether insoluble in water: in very dilute solutions, therefore, sulphate of lime and other soluble sulphates do not occasion an immediate precipitate.

Hydrofluosilicic acid occasions no precipitate even in concentrated solutions.

Chromate of potassa in cold and dilute solutions produces no precipitate; but, by boiling, a copious yellow precipitate (SrO,CrO_3) is determined.

Oxalic acid produces a white precipitate $(SrO,\bar{O}+aq.)$ even in dilute neutral solutions: in very dilute solutions the precipitate is immediately determined by the addition of ammonia.

Before the blowpipe sulphate of strontia fuses to an opalescent mass, and colours the outer flame carmine red. Chloride of strontium, heated on the ring of platinum wire at the apex of the blue flame, tinges the whole flame immediately deep crimson; but as the assay fuses the colour disappears, by which it is distinguished from chloride of lithium. The presence of chloride of barium prevents the production of the coloured flame. Soluble salts of strontia, digested with alcohol, and inflamed, give rise to an intense and characteristic carmine red colour.

LIME (CaO). — *General Characters:* When pure, it is white and infusible. It has an acrid, caustic, alkaline taste. It has a powerful affinity for water, in combining with which it emits great heat, and falls into a bulky powder. The hydrate of lime is far less soluble in water than the hydrates of the two preceding oxides, one part requiring for a perfect solution from 450 to 500 parts of water. The solution is slightly caustic, and gradually absorbs carbonic acid from the atmosphere, until the whole of the lime is converted into carbonate.

Behaviour of Solutions of Salts of Lime with Reagents.

The *caustic and carbonated alkalies,* and *phosphate of soda,* behave with calcareous solutions precisely as with solutions of baryta and strontia.

Sulphuric acid and the *soluble sulphates* occasion no precipitate in very dilute solutions; but, on the addition of alcohol, a precipitate (CaO,SO_3) immediately takes place: in concentrated solutions a bulky precipitate is produced, soluble, though not remarkably so, in nitric and hydrochloric acids.

Hydrofluosilicic acid does not produce any precipitate in solutions of calcareous salts.

Oxalic acid and the *soluble oxalates* occasion an immediate precipitate $(CaO,\bar{O}+2\ aq.)$ in neutral solutions, soluble in the mineral acids, but insoluble in acetic acid. The formation of this precipitate is increased and quickened by the addition of ammonia.

Before the blowpipe, chloride of calcium, unless it has been fused, heated on the ring of the platinum wire tinges the outer flame red, but the colour is more feeble than with chloride of strontium. Pure lime and the carbonate emit a very strong light. Soluble lime salts impart a yellowish red tinge to the flame of alcohol.

MAGNESIA (MgO).—*General Characters:* It is a white infusible powder, possessed of a feeble but distinct alkaline reaction. Like lime, it is more soluble in cold than in hot water: 36,000 parts of boiling water, and 5,142 parts at 32°, being required to dissolve one part of the earth. Caustic magnesia does not emit any heat on being moistened with water.

Behaviour of Magnesian Salts with Reagents.

Ammonia, in neutral solutions, occasions a white bulky precipitate (MgO,HO). If the solution be acid, or if ammoniacal salts be present, no precipitate takes place, in consequence of the property possessed by magnesia of forming double salts with ammonia.

Caustic potassa produces a voluminous flocculent precipitate, which disappears on the addition of muriate of ammonia; but, on boiling with excess of potassa, the precipitate reappears, in consequence of the decomposition of the ammoniacal salt.

Carbonate of potassa produces in neutral solutions, and in the absence of ammoniacal salts, a white voluminous precipitate $2(HO,MgO,)+3(MgO,CO_2)$, which is increased by boiling, in consequence of the expulsion of the carbonic acid, which, in the cold, keeps a portion of magnesia in solution in the form of bicarbonate.

Carbonate of ammonia, by boiling, and in the absence of ammoniacal salts, occasions a slight precipitate.

Sulphuric acid produces no precipitate (MgO,SO_3), being very soluble in water.

Phosphate of soda alone does not produce any precipitate in very dilute solutions; but, if ammonia be added, a crystalline precipitate of basic phosphate of magnesia and ammonia ($2MgO, NH_4O,PO_5 + 2HO + 10HO$) is formed in highly diluted solutions. This precipitate is insoluble in ammoniacal salts, but soluble in free acids.

Oxalate of ammonia, in the absence of ammoniacal salts, forms a white precipitate ($MgO,\overline{O} + 2$ aq.).

Before the blowpipe, in the absence of other metallic oxides, salts of magnesia, when ignited on charcoal, then moistened with solution of protonitrate of cobalt, and again strongly *ignited*, acquire a feeble red tint.

General Remarks on the Oxides of the Second Group.

From the property of magnesia to form soluble double salts with ammonia, this earth may be kept in solution by the addition of sal-ammoniac and ammonia, while baryta, strontia, and lime are precipitated by carbonate of ammonia. The magnesia is detected in the filtered liquid by phosphate of soda. The immediate formation of a precipitate, on the addition of hydrofluosilicic acid, is characteristic of baryta. Strontia, in combination with baryta, is detected by converting both earths into chlorides, and digesting with absolute alcohol, in which chloride of barium is almost insoluble. Chloride of strontium is detected in the alcoholic solution by the carmine red flame it communicates to the alcohol when ignited; and lime is detected by oxalate of ammonia. To discover the alkalies in the presence of the oxides of the second group, the baryta, strontia, and lime are first removed by boiling with carbonate of ammonia and caustic ammonia, and from the filtered liquid the magnesia is precipitated by water of baryta; the excess of baryta is removed by adding sulphuric acid in slight excess, and boiling; the whole is then filtered, and the clear filtrate evaporated to dryness in a platinum dish, and ignited; the residue is redissolved in water, and the solution tested for potassa, soda, and lithia, by dividing it into three portions, and proceeding with each in the manner above directed for the discovery of the alkalies. A portion of the original solution is tested for ammonia, by heating with caustic potassa, and applying a feather moistened with strong acetic acid to the mouth of the tube.

GROUP 3.

Metallic Oxides not precipitated by sulphuretted hydrogen, but precipitated as oxides by hydrosulphuret of ammonia,—*Alumina, Yttria, Glucina, Thorina, Zirconia, Oxide of Chromium, Oxides of Cerium, Titanic Acid, Tantalic Acid.*

ALUMINA (Al_2O_3).—*General Characters:* When pure it is white, and in the state of powder it is light, and not at all compact. It has neither taste, nor smell, but it adheres to the tongue, thereby occasioning a slight sense of astringency. By the heat produced by a stream of oxygen gas directed against the flame of a spirit-lamp, it slowly melts, and gives a limpid and colourless globule, which on cooling becomes crystalline. It is quite insoluble in water, although it possesses a powerful affinity for that fluid, from which it can only be deprived by heating to redness. It condenses moisture from the atmosphere in a remarkable manner. The hydrate of alumina has a strong affinity for vegetable colouring principles.

Behaviour of Aluminous Solutions with Reagents.

Potassa produces in neutral solutions a bulky precipitate (Al_2O_3,HO), entirely soluble in excess of the precipitant, but redissolved by solution of sal-ammoniac, which destroys the solvent, $NH_4Cl + KO$ becoming $KCl + NH_4O$.

Ammonia occasions a bulky precipitate, not soluble in excess of the precipitant, and insoluble also in solution of sal-ammoniac.

The *alkaline carbonates* precipitate Al_2O_3,HO, with the evolution of carbonic acid.

Phosphate of soda produces a precipitate soluble in free acids, and in potassa.

Silicate of potassa (soluble glass) produces a precipitate of silicate of alumina in solutions of alumina in potassa.

Before the blowpipe, alumina, and many of its compounds, may be detected by heating the assay on charcoal, then moistening it with solution of protonitrate of cobalt; and again heating it strongly in the oxidating flame, a fine blue colour is produced.

GLUCINA (BeO) Oxide of Beryllium. —*General Characters:* This earth, when pure, has neither smell nor taste. It is insoluble in water, and infusible; but it does not harden in the fire like alumina, neither is the paste which it forms with water plastic.

Behaviour of Solutions of Glucina with Reagents.

Potassa precipitates and redissolves it; but, by continuous boiling in a dilute alkaline liquor, the earth is again completely precipitated. Solution of salammoniac likewise precipitates it from its solution in potassa.

Ammonia produces a voluminous precipitate, insoluble in excess of precipitant; the presence of chloride of ammonium does not prevent the formation of this precipitate.

The *carbonated alkalies* occasion a bulky precipitate, which is soluble in great excess of the precipitants, but more easily in carbonate of ammonia than in carbonate of potassa.

Phosphate of soda produces a voluminous precipitate.

Before the blowpipe, glucina and its salts cannot well be detected; they do not become blue when strongly heated with protonitrate of cobalt, like alumina.

YTTRIA (YO).—*General Characters:* This earth is of a pale yellow colour. Its specific gravity is 4.842, hence it is heavier than baryta, the specific gravity of which is 4.00. It is soluble in acids after ignition. It gradually absorbs carbonic acid from the atmosphere. Many of its salts have a faint amethyst red colour and a sweet taste.

Behaviour of Salts of Yttria with Reagents.

Potassa produces a white voluminous precipitate, insoluble in excess of the precipitant even by heat.

Ammonia behaves in the same manner.

The *carbonated alkalies* produce precipitates soluble in excess of the precipitants, particularly in carbonate of ammonia; from the latter solution crystals of double carbonate of ammonia and yttria may be obtained.

Sulphate of potassa produces, after a time, a precipitate which is completely redissolved by the addition of water, even if the water contain sulphate of potassa in solution.

Phosphate of soda produces a precipitate soluble in hydrochloric acid, from which it is again thrown down by boiling.

Ferrocyanide of potassium occasions a white precipitate.

Before the blowpipe, yttria cannot with certainty be detected. According to Plattner phosphate of yttria may be recognised by its giving a regulus of phosphuret of iron with boracic acid and iron, and from the difficulty with which it is dissolved by microcosmic salt.

THORINA (ThO).—*General Characters:* This rare earth is, when quite free from manganese, *white.* It is the heaviest of all the earths, its sp. gr. being 9.402. Its solutions have an astringent taste: it absorbs carbonic acid from the air. When moist, the hydrate dissolves readily in acids; but after having been dried it is acted on with difficulty. The calcined earth is only attacked by hot sulphuric acid. Sulphate of thorina is, according to Berzelius, distinguished from all other oxidized bodies known by its property of being precipitated by boiling, and slowly redissolving on cooling.

Behaviour of Solutions of Thorina with Reagents.

Potassa and ammonia produce a quickly subsiding precipitate insoluble in an excess of the precipitants.

The carbonated alkalies produce a precipitate dissolving readily in an excess of the precipitants.

Sulphate of potassa produces a double salt, insoluble in water containing sulphate of potassa.

Ferrocyanide of potassium occasions a heavy white precipitate soluble in acids.

Before the blowpipe, the reactions of thorina have not been studied.

ZIRCONIA (Zr_2O_3).—*General Characters:* When pure and calcined, glucina is a white infusible powder; when ignited, it becomes brilliantly incandescent; it is sufficiently hard to scratch glass. Its sp. gr. is 4.3. After having been ignited, it is soluble only in concentrated sulphuric acid. Its soluble salts have a purely astringent taste without any sweetness.

Behaviour of Solutions of Zirconia with Reagents.

Potassa and ammonia produce precipitates insoluble in an excess of the precipitants.

The *carbonated alkalies* produce precipitates slightly soluble in an excess of the precipitants; the hydrate of zirconia is soluble in carbonate of ammonia, but very sparingly so in the carbonates of the fixed alkalies.

Ferrocyanide of potassium occasions a white precipitate.

Sulphate of potash produces a white double salt almost insoluble in pure water.

Before the blowpipe, zirconia cannot be recognised except by the brilliant light it affords when ignited.

Oxide of Chromium (Cr_2O_3).—*General Characters:* After ignition it is of a fine green colour, and is only soluble in hot sulphuric acid: the hydrate is of a grayish green colour, and is readily soluble in acids, forming green solutions under reflected, and red by transmitted light; but if the hydrate has been strongly dried, but not ignited, it dissolves in acids with difficulty.

Behaviour of Solutions of Oxide of Chromium with Reagents.

Potassa produces a blueish green precipitate (Cr_2O_3, HO), readily soluble in an excess of the precipitant forming a green solution, from which the green anhydrous oxide is reprecipitated by boiling either alone or with chloride of ammonium.

Ammonia and carbonate of ammonia produce a blueish green precipitate, partially soluble in the precipitant, to which it imparts a red colour; but the precipitation is complete by boiling the ammoniacal solution.

Carbonate of potassa produces a blueish green precipitate, soluble completely in considerable excess of the precipitant, and not reprecipitated by boiling.

Phosphate of soda produces a light green precipitate.

Any compound of oxide of chromium when fused with nitre gives rise to the formation of chromate of potassa (KO, CrO_3), which is soluble in water, and to which it communicates a yellow colour.

Before the blowpipe, the presence of oxide of chromium is easily detected by the beautiful green bead obtained when it is heated with borax or microcosmic salt, both in the inner and outer flame: oxide of copper gives also a green bead, but only in the outer flame.

Oxides of Cerium (CeO, Ce_2O_3).—*General Characters:* The hydrated protoxide of cerium, when first precipitated, is white, but it gets rapidly yellow by exposure to the air by absorbing oxygen; it has never been obtained in a pure anhydrous state. Peroxide of cerium is a powder of a brick red colour; it is easily dissolved by acids: when heated with hydrochloric acid, chlorine is evolved.

Behaviour of Solutions of Oxide of Cerium with Reagents.

Potassa and ammonia produce bulky precipitates, insoluble in excess of the precipitants; the precipitate is first yellowish white, but by exposure to the air it becomes deep yellow.

The *alkaline carbonates* produce a precipitate soluble in a slight degree in an excess of the precipitants which thereby acquire a yellow colour.

Ferrocyanide of potassium occasions a white precipitate.

Sulphate of potassa forms a crystalline double salt very sparingly soluble in water, and not at all soluble in solution of sulphate of potassa.

Before the blowpipe, pure salts of cerium may be detected by fluxes. Red or dark yellow beads are obtained with borax or microcosmic salt in the oxidating flame, according to the quantity dissolved; these beads on cooling, or when subjected to the reducing flame, become quite colourless.

Titanic acid (TiO).—*General Characters:* It is a white, insipid, infusible powder: when heated, it assumes a fine yellow colour, but again becomes colourless on cooling. It reddens infusion of turnsole even after having been exposed to a red heat, though the calcination renders it insoluble in acids.

Behaviour of Solutions of Titanic Acid with Reagents.

Ammonia precipitates a white gelatinous hydrate (TiO, HO), soluble with great readiness in acids, and soluble also in small quantities in the carbonated alkalies: it is precipitated from its solution in carbonate of ammonia by long boiling: its solution in carbonate of potassa or soda is precipitated by boiling with sal-ammoniac.

Titanic acid is precipitated as a heavy white powder from its acid solutions by continued boiling: this precipitate cannot, however, be washed on a filter with pure water (Rosé): according to Berzelius it can be completely precipitated from its solution in sulphuric acid by long-continued boiling.

The *caustic alkalies and hydrosulphuret of ammonia* do not precipitate titanic acid in the presence of a sufficient quantity of tartaric acid.

Ferrocyanide of potassium produces a red brown precipitate. A bar of *metallic zinc* or *iron* placed in a solution of an alkaline titanate in hydrochloric acid, effects a reduction of the acid by the nascent hydrogen: and a blue or violet coloured oxide of titanium gradually subsides slowly, becoming white. Titanic acid precipitated by boiling is likewise reduced by zinc or iron in an acid liquid.

Sulphite of ammonia (NH_4O,SO_2), aided by a gentle heat, completely precipitates titanic acid.

Before the blowpipe, pure titanic gives with microcosmic salt a violet bead; the reaction is observed better on adding metallic tin; in the presence of peroxide of iron the glass appears, when strongly heated in the reducing flame, yellow, and on cooling, red; with borax no alteration is produced by the presence of iron.

TANTALIC ACID (Ta_2O_3).—*General Characters:* The hydrated acid is a powder of a milky white colour, insipid and inodorous. It reddens moistened turnsole paper. It dissolves easily in hydrochloric and other acids, but is precipitated by sulphuric acid, a circumstance which may be regarded as characteristic of tantalic acid. The hydrochloric solution of tantalic acid is precipitated of an orange yellow colour, by infusion of galls. It is not precipitated by sulphuretted hydrogen; but alkaline hydrosulphurets throw it down unaltered, with the disengagement of sulphuretted hydrogen.

Behaviour of Solution of Tantalic Acid with Reagents.

Ferrocyanide of potassium occasions a yellow precipitate.

The *hydrate of tantalic acid* is easily soluble in *caustic alkalies*, and at a boiling temperature it is soluble also in alkaline carbonates with the evolution of carbonic acid; it is soluble also in *hydrofluoric acid*, and in *binoxalate of potassa.*

At a certain temperature hydrated tantalic acid loses water and becomes anhydrous. When hot it is yellow, but in cooling it regains its white appearance: in this state it is soluble only with great difficulty in acids and alkalies. When a solution of tantalic acid is precipitated by sulphuric acid and brought into contact with zinc and hydrochloric acid, it dissolves, forming a fine blue liquid, which subsequently turns brown.

General Remarks on the Oxides of the Third Group.

Alumina and glucina are both dissolved readily by caustic potassa; but the two earths are distinguished from each other by the latter being precipitated from its alkaline solution by boiling, and by its hydrate being soluble in carbonate of ammonia. *Yttria, thorina,* and *zirconia* are not soluble in caustic potassa: *yttria* is distinguished from the other two earths by the double salt which it forms with sulphate of potassa being soluble in solution of sulphate of potassa; whereas the double salts formed by thorina and zirconia are not soluble in sulphate of potassa. These two latter earths are not very easily distinguished from each other; but the precipitate produced by carbonated alkalies in solutions of *thorina* is much more soluble in carbonate of potassa than the corresponding precipitate in solution of *zirconia. Thorina* is, moreover, more than double the density of *zirconia*, which is distinguished again by the glaring white light which it produces when strongly ignited. The colour of the salts of *oxide of chromium*, and their behaviour before the blowpipe, is quite sufficient to distinguish this oxide from all the other members of the group. *Oxide of cerium* is characterised by the deep yellow colour which it acquires by exposure to the air. *Titanic* and *tantalic* acids are distinguished by the blue colour produced on bringing a rod of zinc or iron into contact with their acid solutions; and *tantalic* acid is distinguished from *titanic* acid by the ready solubility of its hydrate in caustic potassa, and by its precipitation from its hydrochloric solution by sulphuric acid.

This group may be conveniently subdivided into two sections by the comportment of its members with caustic potassa: thus *alumina, glaucina, oxide of chromium,* and *hydrated tantalic acid* are soluble in caustic potassa: the other members are insoluble.

GROUP 4.

Metallic Oxides not precipitated from their acid solutions by sulphuretted hydrogen, but completely precipitated by hydrosulphuret of ammonia as sulphurets—*Oxides of Zinc, Nickel, Cobalt, Protoxide of Manganese, Prot-*

oxide and Sesquioxide of Iron, Sesquioxide of Uranium.

OXIDE OF ZINC (ZnO).—*General Characters:* When pure it is white; it becomes yellow when heated, but on cooling its whiteness usually returns, though sometimes it retains its yellow tinge. It is sometimes obtained crystalline, and is then always yellow. When the metal is burned in the air, the oxide is obtained of snowy whiteness, and in light flocks. In this state it is known as "philosophical wool." It has a remarkable affinity for alumina; a combination of the two oxides in atomic proportions is met with in the mineral kingdom crystallised in regular octohedrons, and is known under the name of *Gahnite.*

Behaviour of Solutions of Oxide of Zinc with Reagents.

Potassa and ammonia produce in neutral solutions a white gelatinous precipitate (ZnO,HO), readily soluble in an excess of the precipitants.

Sulphuretted hydrogen produces in neutral solutions a white precipitate (ZnS): in acid solutions no precipitate is formed.

Hydrosulphuret of ammonia completely precipitates salts of oxide of zinc, as ZnS, insoluble in an excess of the precipitant, as well as in *potassa* and *ammonia.*

The carbonates of the fixed alkalies precipitate basic carbonate of zinc ($3\,HO, ZnO + 2\,ZnO,CO_2$), quite insoluble in an excess of the precipitants, but soluble in *potassa* and in *ammonia.* The presence of any salt of the latter prevents the formation of this basic salt, a soluble double salt of zinc and ammonia being formed.

Carbonate of ammonia produces a white precipitate, soluble in an excess of the precipitant.

Phosphate of soda produces a precipitate soluble in acids, and in *potassa* and in *ammonia.*

Oxalic acid and binoxalate of potassa occasion precipitates which are soluble in acids and in fixed alkalies, but the formation of which is not prevented by sal-ammoniac.

Ferrocyanide of potassium produces a white gelatinous precipitate, insoluble in free hydrochloric acid.

Ferricyanide of potassium produces a yellowish red precipitate, soluble in hydrochloric acid.

Before the blowpipe, zinc salts are easily detected. Heated with carbonate of soda on charcoal in the reducing flame metallic zinc is produced, which volatilizes, and on coming into contact with the air is again oxidized, and the charcoal becomes covered with a sublimate, which when hot is yellow, and on cooling white, and gives when heated in the oxidating flame with a few drops of protonitrate of cobalt a beautiful and characteristic green colour.

OXIDE OF NICKEL (NiO).—*General Characters:* The pure oxide is of a deep ash gray colour; it is not magnetic; it dissolves readily in acids; its hydrate is of an apple-green colour.

Behaviour of Solutions of Oxide of Nickel with Reagents.

Potassa produces a bright green precipitate, insoluble in an excess of the precipitant, but soluble in carbonate of ammonia.

Ammonia precipitates the same green hydrate, but an excess redissolves it, forming a clear blue solution, from which *potassa* again precipitates the hydrate.

Sulphuretted hydrogen does not precipitate acid solutions of nickel. In neutral solutions, after a time, an inconsiderable black precipitate is formed; but in the presence of an alkaline acetate, aided by a gentle heat, sulphuretted hydrogen effects a complete precipitation.

Hydrosulphuret of ammonia produces a black precipitate, partially soluble in an excess of the precipitant; hence after the subsidence of the precipitate the fluid remains black.

Alkaline carbonates produce a pale green precipitate, soluble in carbonate of ammonia.

Phosphate of soda occasions a very pale yellow precipitate.

Ferrocyanide of potassium produces a pale yellowish green precipitate.

Cyanide of potassium throws down a greenish white precipitate ($NiCy$), which an excess redissolves into a brownish yellow liquid ($NiCy,KCy$); on the addition of a mineral acid, cyanide of nickel is again precipitated, and hydrocyanic acid set free.

Before the blowpipe, salts of nickel, heated in the outer flame with borax or microcosmic salt, give a reddish coloured bead. The addition of nitre changes the colour to dark purple or blue: heated in the inner flame on charcoal with carbonate of soda, reduction takes place, and renders the bead gray.

OXIDE OF COBALT (CoO).—*General Characters:* As obtained by the calcination of the carbonate, it is of an ash gray colour; as obtained by the combustion of the metal, it is blue or grayish blue; as precipitated from its solutions by caustic *potassa*, it has a fine blue colour. When this precipitate is boiled for some time, it assumes by degrees a violet, and finally a dirty red tinge, which, according to Proust, is the hydrate: the blue precipitate is considered by some chemists to be a basic salt. It dissolves by fusion with vitreous fluxes communicating to them a magnificent blue colour, or if in excess black.

Behaviour of Solutions of Oxide of Cobalt with Reagents.

Potassa produces a blue precipitate, insoluble in an excess of the precipitant, but soluble in carbonate of ammonia; the precipitate becomes green by exposure to the air, and dingy red when boiled.

Ammonia produces a blue precipitate, which an excess redissolves, forming a solution which is at first green, but which by exposure to the air becomes brown; if sal-ammoniac be present in sufficient quantity, neither *potassa* nor *ammonia* produce any precipitate, though, if air have access, the solution gradually becomes brown.

The alkaline carbonates produce a red precipitate, which upon being boiled becomes blue.

Phosphate of soda occasions a blue precipitate.

Ferrocyanide of potassium gives a green precipitate, which gradually turns gray.

Ferricyanide of potassium gives a dark reddish brown precipitate.

Sulphuretted hydrogen in acid solutions occasions no precipitate: in neutral solutions, after a time, a slight black precipitate, the solution acquiring a dark colour.

Cyanide of potassium precipitates cyanide of cobalt as a brownish white precipitate from acid solutions, soluble in, excess of the precipitant, and not again precipitated by acids.

Hydrosulphuret of ammonia produces a black precipitate, quite insoluble in excess.

Before the blowpipe, salts of cobalt are distinguished by the beautiful blue colour they communicate to borax and microcosmic salt, in both oxidating and reducing flames. Heated with carbonate of soda in the reducing flame, a gray powder, metallic cobalt, is produced.

OXIDE OF MANGANESE (MnO).—*General Characters:* It is of a grayish green colour. When prepared by igniting the carbonate or oxalate in an atmosphere of hydrogen, it absorbs oxygen from the air, gradually becoming brown. The oxide, prepared by fusing the chloride with anhydrous carbonate of soda, undergoes no alteration by exposure to the air. The hydrate when first precipitated is white, but on exposure to the air it gradually becomes brown. This oxide possesses, in common with magnesia and oxide of iron, the property of only being partially precipitated by ammonia, and of carrying with it a portion of silicic acid when precipitated from a liquid holding this acid in solution. The salts of oxide of manganese are sometimes colourless, and sometimes of a pale rose colour.

Behaviour of Solutions of Oxide of Manganese with Reagents.

Potassa and ammonia produce precipitates which at first are white, but soon become coloured; first yellow, then brown, and finally nearly black: if ammoniacal salts be present, *ammonia* occasions no precipitate, and *potassa* only a partial one, which slowly becomes brown by exposure to the air. A clear ammoniacal solution containing oxide of manganese gradually gets turbid by exposure to the air, brown hydrated sesquioxide of manganese being deposited.

The *carbonated alkalies* produce a white precipitate of carbonate of manganese, which is permanent in the air, and sparingly soluble in sal-ammoniac.

Phosphate of soda produces a white precipitate persistent in the air.

Ferrocyanide of potassium produces a pale red precipitate, soluble in free acids.

Ferricyanide of potassium gives a brown precipitate, insoluble in free acids.

Sulphuretted hydrogen does not precipitate either acid or neutral solutions.

Hydrosulphuret of ammonia produces a flesh-red precipitate insoluble in excess, but soluble in mineral acids and even in strong acetic acid; by exposure to the air it becomes oxidized, finally assuming a brownish black colour.

By fusing any salt of manganese on platinum foil with a mixture of nitre and carbonate of soda, *manganate of soda* of a fine green colour is produced; the smallest portion of manganese may in this manner be detected.

Before the blowpipe, fused in the oxidating flame with borax or microcosmic salt, salts of manganese give an amethyst coloured bead, the colour of which disappears in the reducing flame, but may again be produced in the oxidating flame.

PROTOXIDE OF IRON (FeO).—*General Characters:* This oxide, which is only obtained pure with extreme difficulty, is black, and has frequently a metallic lustre: it is brittle, fuses at a high temperature, and on cooling is converted into a brittle, brilliant, but not vitreous mass. It is dissolved in acids with great difficulty, after having been exposed to a red heat; but the salts formed are identical with those obtained by dissolving the metal itself in the respective acids. It is very feebly magnetic, by which it is distinguished from the ferrosoferric oxide, which is strongly magnetic. It combines with water, forming a hydrate which, when pure, is white; but by contact with the atmosphere it speedily becomes coloured; first gray, then green, then blueish black, and finally yellow. When boiled in an hermetically closed vessel, it parts with its water, and becomes black. It is the basis of all the protosalts of iron.

Behaviour of Solutions of Protoxide of Iron with Reagents.

Potassa and ammonia produce a flocculent precipitate of hydrated protoxide of iron, which at first is nearly white, but which readily becomes coloured by exposure to the air. The presence of ammoniacal salts prevents the precipitation of oxide of iron by *ammonia*, and in some degree by *potassa*.

Alkaline carbonates produce a white carbonate, gradually becoming coloured, though not so readily as the oxide. It is soluble in sal-ammoniac, but a coloured precipitate makes its appearance by exposure to the air.

Phosphate of soda produces a white precipitate, which after a time becomes green.

Ferrocyanide of potassium produces a precipitate, which, if air be entirely excluded, is white (K,Fe_3Cfy_2); but, if air or a small quantity of sesquioxide of iron be present, it has a blue tinge; by exposure to the air, or by contact with nitric acid or chlorine, it absorbs oxygen, and gives rise to the formation of Prussian blue. The transformation will be understood from the following equations:—

$$(a.)\ 3\,FeCl + 2\,K_2Cfy = 3\,KCl + KFe_3Cfy_2.$$

$$(b.)\ 3\,(K,Fe_3Cfy_2) + 4\,O = 2\,(Fe_4Cfy_3) + 3\,KO + FeO.$$

(*a.*) Three equivalents of protochloride of iron, and two equivalents of ferrocyanide of potassium react in such a manner as to form three equivalents of chloride of potassium and one of the white compound.

(*b.*) Three equivalents of the white compound, combine with four equivalents of oxygen, to form two equivalents of Prussian blue, three equivalents of potassa, and one of oxide of iron. Prussian blue is insoluble in hydrochloric acid; its colour is discharged by the fixed caustic alkalies.

Ferricyanide of potassium produces a beautiful blue precipitate, insoluble in acids, but easily decomposable by alkalies. The composition of this substance is Cfy_2F_3, and it is thus formed:—

$$3\,FeCl + K_3Cfy_2 = 3\,KCl + Cfy_2Fe_3.$$

Three equivalents of protochloride of iron, and one equivalent of ferricyanide of potassium, produce three equivalents of chloride of potassium, and one of Turnbull's blue.

Sulphuretted hydrogen does not precipitate acid solutions of oxide of iron; and neutral compounds very incompletely.

Hydrosulphuret of ammonia produces a black precipitate, speedily becoming brown by exposure to the air. It is insoluble in alkalies and alkaline sulphurets, but easily soluble in mineral acids.

Before the blowpipe, protosalts of iron heated on charcoal with borax or microcosmic salt in the oxidating flame give dark red beads, becoming lighter on cooling; in the inner flame the colour produced is green, which disappears on cooling, if the metal be not present in too large quantity. When fused with soda on charcoal in the reducing flame, a metallic magnetic powder is obtained.

SESQUIOXIDE OF IRON (Fe_2O_3).—*General Characters:* Its colour and physical appearance differ according to its mode of preparation. It is met with in nature of a gray colour, and crystalline; as prepared by the calcination of the subsulphate of the sesquioxide, it has a fine red colour; from the sulphate its colour is deeper, and when made from the nitrate it is brownish black; and it is sometimes met with quite black. By the action of a high heat it is converted into ferroso-ferric oxide (FeO, Fe_2O_3) with the disengagement of oxygen gas. It does not dissolve very readily save in concentrated acids, after having been strongly heated, though much more easily than the protoxide. It is not easily precipitated from its solutions by means of an alkali or an earth. If too little alkali be added, a subsalt is thrown down; if too much, a portion is precipitated with the oxide. When iron is oxidized by degrees in contact with a large quantity of water, a hydrate of the sesquioxide of a clear orange colour is formed.

Behaviour of Solutions of Sesquioxide of Iron with Reagents.

Potassa and ammonia produce a voluminous reddish brown hydrate, insoluble in excess. The precipitation is prevented by the presence of organic acids, sugar, &c.

The *carbonated alkalies* throw down precipitates of rather a lighter colour, carbonic acid being at the same time disengaged.

Phosphate of soda produces a white precipitate $(2\,Fe_2O_3, 3\,PO_5 + 13\ aq.)$ which becomes brown, and finally dissolves on the addition of ammonia.

Ferrocyanide of potassium produces a beautiful blue precipitate (Fe_4Cfy_3) by the following reaction:—

$$2\,FeCl + 3K_2Cfy = Fe_4Cfy_3 + 6KCl.$$

Two equivalents of sesquichloride of iron and three of ferrocyanide of potassium give rise to one equivalent of Prussian blue, and six equivalents of chloride of potassium.

Sulphuretted hydrogen produces in neutral solutions a white deposit of sulphur, the sesquioxide being reduced to protoxide thus:—

$$Fe_2O_3 + HS = 2FeO + HO + S.$$

Hydrosulphuret of ammonia produces in neutral solutions a black precipitate, insoluble in excess, and becoming brown by exposure to the air. This precipitation is preceded by the reduction of the sesquioxide into protoxide.

Before the blowpipe, salts of sesquioxide of iron behave in the same manner as those of the protoxide.

SESQUIOXIDE OF URANIUM (Ur_2O_3).—*General Characters:* The hydrate is a beautiful yellow powder, soluble in acids, forming fine yellow solutions; heated to about 300°, it loses its water and becomes anhydrous; it then has a bright brick red colour. Heated above that temperature, it loses oxygen and becomes converted into *uranoso-uranic oxide* (UrO, Ur_2O_3) of a deep gray colour. Sesquioxide of uranium reddens moistened turnsole paper, though it blues paper stained red with infusion of logwood. It produces, therefore, the reaction of acid and base. According to Berzelius, this substance should more properly be called *uranic acid*; its properties being rather those of an electro-negative than of an electro-positive oxide. It forms definite compounds with bases, all of which are insoluble in water; and, when precipitated from its solution in an acid by means of an alkali, the latter is divided into two portions, and the precipitate obtained is a *uranate.*

Behaviour of Solutions of Sesquioxide of Uranium with Reagents.

Caustic alkalies precipitate *uranates* of the bases of a pale yellow colour.

Alkaline carbonates produce pale yellow precipitates, soluble in excess of carbonate of ammonia, but again precitated by boiling.

Sulphite of ammonia produces at a boiling temperature a yellow precipitate.

Ferrocyanide of potassium gives a red brown precipitate.

Sulphuretted hydrogen reduces salts of sesquioxide with the deposition of sulphur; but sesquioxide is again produced by exposure to the atmosphere, or by the action of oxidizing agents.

Hydrosulphuret of ammonia produces a black precipitate.

Before the blowpipe, heated alone on charcoal, sesquioxide of uranium is converted into protoxide; heated with microcosmic salt on platinum wire in the oxidating flame, it dissolves, producing a clear yellow glass, which on cooling becomes green.

General Remarks on the Oxides of the Fourth Group.—Of the seven oxides constituting this group, *oxide of zinc* alone is soluble in *caustic potassa.* It is thus readily separated from the other six, and it is distinguished from *alumina, oxide, of chromium*, &c., members of the third group, by its being again precipitated from its alkaline solution by sulphuretted hydrogen. *Oxides of zinc, cobalt, iron,* and *manganese,* form with *ammonia* soluble double salts not precipitable by alkalies. *Oxide of iron* is easily eliminated from the other three oxides, by converting it into *sesquioxide,* by boiling with nitric acid. It is then completely precipitated by *ammonia,* provided no non-volatile organic matter be present. The same is the case with *sesquioxide of uranium. Hydrate of oxide of nickel* is dissolved by *ammonia,* but again precipitated by *potassa. Hydrated oxide of nickel,* and *hydrated oxide of cobalt* are both soluble in *carbonate of ammonia,* which is not the case with *hydrated protoxide of manganese,* which may thus, therefore, be separated from them. The perfect separation of *oxide of nickel* from *oxide of cobalt,* is attended with great difficulties. The presence of *nickel* may be recognised by the behaviour of the solution of its cyanide in cyanide of potassium with hydrochloric acid, which precipitates it, the same not being the case with cyanide of cobalt. In the former case a double cyanide of nickel and potassium ($NiCy, KCy$) is formed; but in the latter, with the presence of free hydrocyanic acid, a *cobalto cyanide of potassium* is formed. Thus:—

$$2\,CoCy + 3\,KCy + HCy = \\ K_3CO_2Cy_6 + H.$$

Two equivalents of cyanide of cobalt, three equivalents of cyanide of potassium, and one equivalent of hydrocyanic acid, give rise to one equivalent of *cobaltocyanide of potassium,* and one of hydrogen. Now, though the solution of cyanide of cobalt in cyanide of potassium is not precipitated by an acid, it may be so in the presence of nickel, and if that metal be present in the proportion of three equivalents to two equivalents of cobalt, the whole of the latter will be precipitated—the three equivalents of nickel replacing the three equivalents of potassium in the cobaltocyanide of potassium, and giving rise to cobaltocyanide of nickel ($N_3Co_2Cy_6$). Thus:

$$3\,(NiCy + KCy) + Co_2K_3Cy_6 = \\ 6\,KCy + Co_2Ni_3Cy_6.$$

Three equivalents of the double cyanide of nickel and potassium, and one equivalent of cobaltocyanide of potassium, giving rise to one equivalent of cobaltocyanide of nickel, and six equivalents of cyanide of potassium.

The blowpipe is, moreover, an infallible test of the presence of *oxide of cobalt.*

GROUP 5.

Metallic Oxides completely precipitated from their solutions, whether acid or alkaline, or neutral, by sulphuretted hydrogen, their sulphurets being insoluble in alkaline sulphurets—*Oxides of Lead, Silver, Mercury, Bismuth, Cadmium, Copper, Palladium, Rhodium, and Osmium.*

OXIDE OF LEAD (PbO).—*General Characters:* When pure, this oxide is yellow, but its powder has a reddish tint. When certain lead salts, as the sub-nitrate and oxalate, are decomposed by heat without fusion, they furnish an oxide of a pure sulphur yellow colour, which by trituration becomes red: in this state it is sometimes called *massicot.* By allowing a solution of oxide of lead, in caustic soda, to remain for some months exposed to the air, white, semi-transparent, dodecahedron crystals of anhydrous oxide may be obtained. The same crystals, according to Payen, are formed on mixing a dilute solution of acetate of lead, with great excess of caustic ammonia, and exposing to the rays of the sun. Oxide of lead becomes of a deep red colour when heated, regaining its primitive colour on cooling: at a red heat it fuses and cools in semi-transparent, deep brick-red, crystalline scales; at a still higher temperature it undergoes partial decomposition, the metal being reduced. It absorbs carbonic acid slowly from the air; hence an effervescence generally attends its solution in an acid. Pure water is capable of retaining in solution from $\frac{1}{7000}$ to $\frac{1}{12000}$ of oxide of lead; but water containing the smallest traces of saline matter does not dissolve it. The hydrate is white, and absorbs carbonic acid rapidly from the air. It loses its water at about 300°. Oxide of lead combines with alkalies and earths; its combinations with potassa and soda are crystallisable. It enters into fusion with, and dissolves, the earths with great facility. Its best solvent is nitric or acetic acids.

Behaviour of Solution of Oxide of Lead with Reagents.

Potassa and ammonia produce white precipitates, which are basic salts, soluble in a great excess of *potassa,* but insoluble in ammonia.

The *carbonated alkalies* produce white precipitates, soluble in *potassa.*

Phosphate of soda occasions a white precipitate, soluble in *potassa.*

Oxalic acid produces, in neutral solutions, a white precipitate.

Ferrocyanide of potassium produces a white precipitate, soluble in potassa.

Iodide of potassium produces a yellow precipitate, soluble in great excess by heat, and separating on cooling, in magnificent yellow spangles.

Chromate of potassa produces a fine yellow precipitate soluble in potassa, but insoluble in dilute nitric acid.

Hydrochloric acid and soluble chlorides produce a heavy white precipitate, soluble in boiling water, out of which it separates on cooling, in brilliant crystals. This precipitate is soluble in *potassa.*

Sulphuretted hydrogen produces a black precipitate, both in acid and neutral solutions.

Hydrosulphuret of ammonia produces a black precipitate, insoluble in excess.

Sulphuric acid and *soluble sulphates* produce a white precipitate (PbO,SO_3) sparingly soluble in dilute acids, but soluble in solution of potassa, and assuming a black colour when moistened with hydrosulphuret of ammonia.

Before the blowpipe, on charcoal, mixed with carbonate of soda, salts of lead are immediately reduced, furnishing a metallic globule, which gradually sublimes, leaving a yellow residue. The metallic globule can easily be flattened under the hammer.

OXIDE OF SILVER (AgO).—*General Characters:* As obtained by dropping solution of nitrate of silver into *caustic potassa*, it is a grayish brown powder; but, if the solutions are concentrated and boiling, the oxide precipitates as a heavy black powder. Exposed to the rays of the sun, it disengages a certain quantity of oxygen, and turns black. It is entirely reduced by ignition. It is slightly soluble in pure water, and in water of barytes. It reacts alkaline to test paper, and displaces from their combinations with the alkalies a portion of the acids, with which it forms insoluble compounds. It combines with caustic ammonia, giving rise to a dangerous substance (fulminating silver). It readily dissolves in nitric and other acids.

Behaviour of Solutions of Oxide of Silver with Reagents.

Potassa and ammonia produce a light brown precipitate, readily soluble in ammonia.

The *carbonated alkalies* produce a white precipitate, soluble in carbonate of ammonia.

Phosphate of soda produces, in neutral solutions, a yellow precipitate, soluble in ammonia. Solution of ignited phosphate of soda ($2\,NaO,PO_5 + 10\,HO$) gives a white precipitate.

Ferrocyanide of potassium gives a white precipitate.

Ferricyanide of potassium produces a reddish brown precipitate.

Chromate of potassa produces a rich brown precipitate.

Protosulphate of iron produces a white precipitate, consisting of metallic silver.

Hydrochloric acid and the *soluble chlorides* produce a white curdy precipitate even in exceedingly dilute solutions. This precipitate becomes violet, and finally black, without, however, suffering decomposition by exposure to light. It is insoluble in diluted acids, but readily soluble in ammonia. When heated it fuses, without decomposition, into a horny mass. If the solution of silver be exceedingly dilute, hydrochloric acid produces an opalescent appearance.

A bar of metallic zinc precipitates silver from its solution in the metallic state.

Sulphuretted hydrogen produces a black precipitate, both in acid and in neutral solutions.

Hydrosulphuret of ammonia gives a black precipitate, insoluble in excess.

Before the blowpipe, mixed with carbonate of soda, and heated on charcoal, salts of silver are readily reduced while no incrustation takes place.

SUBOXIDE OF MERCURY (Hg_2O).—*General Characters:* It is a black powder, which a very gentle heat converts into metallic mercury and oxide of mercury, and a stronger heat into mercury and oxygen gas. The black powder obtained by the long-continued agitation of the metal, and which was supposed to consist of this oxide, is probably only the metal in a state of very fine division. The soluble salts of this oxide redden litmus paper, and are decomposed, when mixed with much water, into soluble acid and insoluble basic salts.

Behaviour of Salts of Suboxide of Mercury with Reagents.

Potassa and ammonia produce a black precipitate insoluble in excess.

Alkaline carbonates produce a dirty yellow precipitate which turns black by boiling.

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium produces a white, gelatinous precipitate.

Ferricyanide of potassium gives a reddish brown precipitate, which gradually becomes white.

Iodide of potassium produces a greenish yellow precipitate, soluble in excess.

Chromate of potassa produces a red precipitate.

Sulphuretted hydrogen produces a black precipitate, both in acid and neutral solutions.

Hydrosulphuret of ammonia produces a black precipitate, insoluble in excess, but decomposed by *potassa* into *sulphuret of mercury* and *metallic mercury*. It is not decomposed or dissolved by boiling nitric acid, but easily by aqua regia.

A bar of metallic zinc throws down an amalgam of zinc and mercury.

Hydrochloric acid and soluble chlorides produce a white precipitate, insoluble in acids, but rendered black by potassa and ammonia, the suboxide being formed.

Protochloride of tin produces a gray precipitate, which, boiling, resolves into globules of metallic mercury. A drop of solution of a salt of suboxide of mercury, rubbed with a rag on a piece of bright copper, leaves a silvery stain, which disappears when it is heated to redness.

Before the blowpipe, mixed with carbonate of soda, and heated in a glass tube, metallic mercury sublimes in the form of a gray powder, which, on being rubbed with a glass rod, is resolved into globules.

OXIDE OF MERCURY (HgO).—*General Characters:* It is a brick-red crystalline powder; but when finely pulverized has a yellow tinge. At a slightly elevated temperature it turns black, but it regains its red colour on cooling. At a red heat it is resolved into oxygen gas and metallic mercury, and is entirely volatilized. In this manner the presence of impurities, red lead, or brick dust, may be detected. It dissolves readily in acids, but is not acted on by ammonia.

Behaviour of Solutions of Oxide of Mercury with Reagents.

Potassa produces a yellow precipitate (HgO,HO) insoluble in excess. If an insufficient quantity of the alkali be added, the precipitate is reddish brown. The presence of ammoniacal salts causes the formation of a white precipitate, which is a compound of *amidide of mercury* with undecomposed mercury salts. Thus,

$$2\,HgCl + NH_3 = (HgNH_2HgCl) + HCl.$$

Fixed carbonated alkalies produce a reddish brown precipitate, insoluble in excess, but converted, in the presence of ammoniacal salts, into the above white product.

Carbonate of ammonia produces a white precipitate.

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium produces a white precipitate, which eventually becomes blue.

Ferricyanide of potassium produces, in solutions of the nitrate and sulphate, a yellow precipitate; in solutions of the chloride, *none.*

Sulphuretted hydrogen and hydrosulphuret of ammonia give rise to different coloured precipitates according to the quantity of the reagent added. If it be added in small quantity, and the solution agitated, the precipitate is white, being a compound of sulphuret of mercury and undecomposed salt; the addition of larger quantities causes the precipitate to assume, successively, a yellow, orange, brown, red, and black colour. The sulphuret of mercury is soluble in solution of potassa, but not in boiling nitric acid, though it dissolves readily in aqua regia.

Iodide of potassium produces a cinnabar red precipitate, soluble in excess. It crystallizes out of a hot solution in magnificent crimson spangles.

Protochloride of tin, when added in excess, separates the metal in the form of a gray powder, which may be united into globules by boiling with hydrochloric acid. All the salts of mercury are decomposed when heated in a glass tube with a slightly moistened alkaline carbonate, the metal subliming in small globules: the metal is likewise reduced when the solution is brought into contact with clean metallic copper, and rubbed.

OXIDE OF BISMUTH, (Bi_2O_3).—When pure it is of a straw yellow colour, and melts at a strong red heat to an opaque glass, which, while hot, is dark brown or black, but on cooling becomes yellow; when melted with silica, alumina, or metallic oxides, it dissolves them readily. The oxide precipitated by water retains nitric acid, from which it may be freed by caustic potassa or soda, which convert it into a hydrate. It is easily reduced by ignition with organic substances or charcoal powder. It dissolves readily in water, forming colourless salts.

Behaviour of Solutions of Oxide of Bismuth with Reagents.

Potassa and ammonia produce a white precipitate, insoluble in excess.

Alkaline carbonates, and phosphate of soda produce white precipitates.

Ferrocyanide of potassium occasions a white precipitate insoluble in hydrochloric acid.

Ferricyanide of potassium produces a light yellow precipitate, soluble in hydrochloric acid.

Iodide of potassium produces a brown precipitate, readily soluble in excess.

Chromate of potassa produces a yellow precipitate, soluble in dilute nitric acid.

Sulphuretted hydrogen and hydrosulphuret of ammonia produce a black precipitate both in acid and neutral solutions, insoluble in excess, and in dilute nitric acid, but soluble in boiling nitric acid.

The neutral salts of bismuth are distinguished by their property of being decomposed by water into a soluble acid, and an insoluble basic salt. The chloride of bismuth exhibits this property in the most marked manner. The insoluble basic bismuth salt is distinguished from the basic salt of antimony formed under similar circumstances by its being insoluble in *tartaric acid.*

Before the blowpipe, heated on charcoal in the reducing flame, salts of bismuth are easily reduced to brittle globules, which spring to pieces under the hammer; the charcoal at the same time becomes covered with a yellow incrustation.

OXIDE OF CADMIUM (CdO).—*General Characters:* The colour of this oxide varies according to its state of aggregation. It is sometimes of a deep red brown, sometimes clear brown, and occasionally black. It is infusible, and does not volatilize at exceedingly high temperatures; but, when mixed with powdered charcoal, it is reduced by heat, and the metal burns and volatilizes. By long-continued gentle ebullition of the metal, the oxide may be obtained, according to *Herapath,* in long purple needles, opaque, and grouped in rays. Its hydrate is white; it loses its water by heat, and absorbs carbonic acid from the air. It is not soluble in the fixed alkalies, but it dissolves in caustic ammonia. It dissolves easily in acids, forming colourless solutions.

Behaviour of Solutions of Oxide of Cadmium with Reagents.

Potassa and ammonia produce a white precipitate (HO,CdO), insoluble in potassa, but easily soluble in ammonia.

The *carbonated alkalies* produce a white precipitate (CdO,CO_2), insoluble in excess: ammoniacal salts do not prevent the formation of this precipitate.

Phosphate of soda produces a white precipitate.

Oxalic acid produces a precipitate soluble in ammonia.

Ferrocyanide of potassium produces a slightly yellow precipitate, soluble in hydrochloric acid.

Ferricyanide of potassium produces a yellow precipitate, also soluble in hydrochloric acid.

Sulphuretted hydrogen and hydrosulphuret of ammonia produce a rich yellow precipitate, insoluble in excess, and in dilute acids and alkalies, but decomposed by boiling and concentrated nitric acid.

A bar of metallic zinc precipitates the metal from its solutions in the form of small glancing, gray-coloured spangles.

Before the blowpipe, heated with carbonate of soda on charcoal, the metal is reduced and volatilizes, leaving a dark yellow red incrustation.

OXIDE OF COPPER (CuO).—*General Characters:* It is pulverulent, and of a black colour: at a high temperature it fuses; and on cooling exhibits a crystalline fracture. By particular management Becquerel obtained it in the form of fine tetrahedral crystals, having a high metallic lustre. Heated with charcoal, or in contact with organic matter, it is reduced either to metallic copper, or to the suboxide. It dissolves easily in acids with the disengagement of heat, and its solutions have mostly a blue or a green colour. Its hydrate is blue; but at the temperature of boiling water it becomes black, a property which interferes with its employment as a pigment. It does not unite in the humid way with the caustic alkalies; but at a red heat it combines with both alkalies and earths, forming blue or green compounds. Caustic alkalies containing organic matters dissolve it, forming blue or purple compounds.

Behaviour of Solutions of Oxide of Copper with Reagents.

Potassa produces a voluminous blue precipitate (HO, CuO), which by boiling loses water and becomes black.

Ammonia added in small quantities produces a green basic salt, which dissolves in excess, forming a fine blue solution. In this solution potassa produces in the cold a blue precipitate, which by boiling becomes black.

Carbonate of potassa produces a greenish blue precipitate of basic carbonate of copper, which by boiling is converted into black oxide.

Carbonate of ammonia behaves precisely as ammonia.

Phosphate of soda produces a greenish white precipitate, soluble in ammonia, forming a blue solution.

Ferrocyanide of potassium produces a chocolate brown precipitate, insoluble in dilute acids, but decomposed by potassa.

Ferricyanide of potassium produces a yellowish green precipitate, insoluble in dilute acids.

Cyanide of potassium produces a yellowish green cyanide, soluble in excess of cyanide of potassium.

Chromate of potassa produces a reddish brown precipitate, soluble in ammonia, forming an emerald green solution, soluble also in dilute nitric acid.

Sulphuretted hydrogen and hydrosulphuret of ammonia produce a black precipitate, slightly soluble in excess of hydrosulphuret of ammonia, but insoluble in caustic alkalies, and in sulphuret of potassium, and in dilute acids. It is readily decomposed by boiling nitric acid, and is completely soluble in cyanide of potassium.

Metallic iron, when introduced into solutions of oxide of copper, becomes covered with a deposit of reduced copper.

Before the blowpipe, salts of copper heated with borax or microcosmic salt in the oxidating flame, gives a grass green bead, becoming blue on cooling; in the reducing flame the glass is red and opaque, mixed with carbonate of soda; and heated on charcoal in the inner flame the metal is reduced, and gives a bead of metallic copper.

Oxide of Palladium (PdO).—*General Characters:* It is a black powder, acted on with great difficulty by acids. The hydrate is of a deep brown colour, and parts with its water only at a high temperature. Its solution in nitric and nitro-hydrochloric acid has a red brown colour.

Behaviour of Solutions of Oxide of Palladium with Reagents.

Potassa precipitates a yellowish brown basic salt, soluble in excess.

Ammonia precipitates from solution of chloride of palladium a compound of chloride of palladium and ammonia $(PdCl, NH_3)$, soluble in excess of ammonia.

Carbonated alkalies precipitate a yellowish brown basic salt, soluble in excess of the precipitants.

Cyanide of potassium and cyanide of mercury produce a yellowish white precipitate of cyanide of palladium, soluble in great excess of hydrochloric acid.

Sulphuretted hydrogen and hydrosulphuret of ammonia produce a black precipitate, soluble in hydrosulphuret of ammonia.

Palladium salts are reduced by *sulphurous acid*, and by being heated with a salt of *oxide of iron*, or with a *formiate*.

Sesquioxide of Rhodium (R_2O_3).—*General Characters:* The metal, as well as the anhydrous sesquioxide, is insoluble even in boiling *aqua regia*. Both, however, are dissolved on fusion with *bisulphate of potassa*, or on heating a mixture of both with chloride of sodium to redness, and passing over it a stream of chlorine. The colour of the hydrated oxide is greenish gray. The haloid salts of this metal are red: the oxysalts yellow, red, or brown.

Behaviour of Salts of Sesquioxide of Rhodium with Reagents.

Potassa does not occasion any immediate precipitate; but after protracted digestion a precipitate of a greenish yellow colour makes its appearance.

Ammonia and carbonate of ammonia produce, after a time, a yellow precipitate, composed of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

Hydrosulphuret of ammonia and sulphuretted hydrogen produce, after a time, a dark brown precipitate. All the salts of rhodium are decomposed, and the metal is reduced by exposure to a gentle heat, in contact with dry hydrogen gas.

Oxides of Osmium $(OsO; Os_2O_3; OsO_2; OsO_4)$.—The presence of osmium is discovered in the salts by mixing them with a little carbonate of soda, and heating on platina foil, the metal is converted into osmic acid, which possesses an extremely acrid and penetrating odour like chloride of sulphur, attacking powerfully the olfactory and respiratory organs, and producing, even in minute quantities, a burning sensation in the eyes. It communicates also a considerable brilliancy to flame. The metal itself is whitish, like platinum, but less brilliant. It is easily pulverized. It dissolves in nitric acid and in aqua regia, osmic acid, passing over with the water of the acid. Osmic acid is easily reduced by many metals and organic compounds. Solutions of salts of oxide of osmium are precipitated by *hydrosulphuret of ammonia* and *sulphuretted hydrogen*, as a brownish black sulphuret insoluble in *hydrosulphuret of ammonia.*

General Remarks on the Oxides of the Fifth Group.

The metallic oxides constituting this group admit of a division into two sections by their comportment with hydrochloric acid. Three of them, viz., *oxide of lead*, *oxide of silver*, and *oxide of mercury* are precipitated by that reagent; the others are not. Of the chlorides thus formed, *chloride of silver* is easily separated from the other two by ammonia, in which it is perfectly soluble, and from which it is again precipitated by nitric acid. The same alkali decomposes *subchloride of mercury*, converting the metal into black protoxide, from which *chloride of lead* may be removed by boiling water, and the metal tested for in the clear solution by any of the reagents mentioned under its head. The insolubility of sulphuret of mercury in nitric acid serves to separate this metal from all the others in the group. The precipitates caused by *potassa* and *ammonia* in solutions of *oxide of cadmium* and *oxide of copper*, are soluble in *ammonia;* those of the others are not; but the *hydrated oxide of copper* is soluble also in *carbonate of ammonia. Hydrated oxide of cadmium* has no such property; moreover, the blue colour of the ammoniacal solution of *oxide of copper* is perfectly characteristic of that metal. *Cadmium*, again, is distinguished by the colour of its sulphuret, which, being insoluble in *hydrosulphuret of ammonia*, distinguishes it from the yellow sulphurets of some of the metals in the next group, all of which *are* soluble in hydrosulphuret of ammonia. *Oxide of bismuth* is readily detected by the decomposition of its salt by water. *Salts of palladium* are recognised by their behaviour with *cyanide of mercury* and *cyanide of potassium.* The insolubility of *oxide of rhodium* in acids, and the colour of its salts, serve to distinguish this metal; and the presence of *osmium compounds* is recognised by the penetrating odour of *osmic acid.*

GROUP 6.

Metallic oxides completely precipitated from their acid solutions by sulphuretted hydrogen; but not from their alkaline solutions, their sulphurets being soluble in alkaline sulphurets —Oxides of *Antimony, Arsenic, Tin, Platinum, Iridium, Gold, Selenium, Tellurium, Tungsten, Vanadium,* and *Molybdenum.*

SESQUIOXIDE OF ANTIMONY (Sb_2O_3).—*General Characters:* It is a white powder, having a great tendency to assume the crystalline form: by sublimation it is obtained in brilliant, white, prismatic crystals, in which state it is sometimes met with naturally; heated in the air, it burns emitting a white smoke, and becomes partly converted into *antimonious acid* (Sb_2O_4). Heated in a close vessel, it melts into a yellow liquid, which on cooling becomes nearly white and crystalline: at a higher temperature it sublimes, leaving no residue. It is dissolved in small quantities by boiling water. This oxide is insoluble in nitric acid; but it dissolves in hydrochloric acid, and the solution is decomposed by water, a basic salt being separated, which is readily dissolved by *tartaric acid* and *acetic acids;* and a certain quantity of the oxide is held in solution by the liberated acid.

Behaviour of Solutions of Sesquioxide of Antimony with Reagents.

Potassa and ammonia produce a white precipitate, soluble in *potassa.*

Alkaline carbonates and *phosphate of soda* behave in a similar manner.

Metallic zinc throws down metallic antimony as a black powder; if nitric acid be present, the sesquioxide is precipitated at the same time.

Sulphuretted hydrogen throws down from acid solutions an orange yellow precipitate, readily soluble in excess and in *potassa;* but very sparingly soluble in *ammonia*, and entirely insoluble in *carbonate of ammonia.* It is insoluble in dilute acids, but is decomposed by concentrated and boiling hydrochloric acid; the precipitate is very incompletely formed in neutral solutions.

Hydrosulphuret of ammonia produces an orange yellow precipitate, completely soluble in excess.

The solution of double tartrate of antimony and potassa (tartar emetic) is only precipitated after a time by alkalies and their carbonates.

Antimony possesses the property of forming a gaseous combination with hydrogen; the union of these two bodies may be brought about by adding zinc and sulphuric acid to a solution containing the oxide, which becomes deoxidized by the zinc; a portion of the metal unites with the hydrogen of the water, which is at the same time decomposed. *Antimoniuretted hydrogen* is inflammable, burning with a blueish green flame, and emitting copious fumes of sesquioxide; if the flame be allowed to impinge on a cold surface, such as a porcelain plate, a dark spot of reduced antimony will be produced. If the gas, as it proceeds from an evolution flask, be allowed to pass along a horizontal tube of hard German glass, and the tube be heated to redness at a certain point, decomposition of the gas will take place at that spot; on both sides of which a brilliant mirror of metallic antimony will be deposited: if now a stream of *dry* sulphuretted hydrogen be allowed to pass through the tube, the bright mirror will vanish, and a deposit of a more or less intense yellow colour will take its place, the antimony being converted into sulphuret. If now the flask in which sulphuretted hydrogen is generating be removed, and its place supplied by one containing the materials for generating hydrochloric acid gas, and if a gentle stream of this gas be sent through the tube, the yellow deposit will vanish, the sulphuret being converted into chloride, which being volatile may be conveyed with the gas into a vessel of water, in which the presence of antimony may then be proved by acidulating it with hydrochloric acid, and transmitting through it a stream of sulphuretted hydrogen gas.

Before the blowpipe, mixed with carbonate of soda on charcoal, oxide of antimony is easily reduced, and brilliant metallic globules obtained: the metal fumes and volatilizes, covering the charcoal with a white incrustation, amongst which needle-shaped crystals frequently appear.

ARSENIOUS ACID, (AsO_3).—*General Characters:* As met with in commerce, this acid is almost completely pure; it is without smell and almost without taste; if kept for some time in contact with the tongue, it induces a slightly bitter taste, which, however, leaves one of sweetness. It sublimes before entering into fusion; but with certain precautions it may be fused in close vessels, and obtained on cooling in the form of a colourless transparent glass. When sublimed in a current of air, it forms fine octahedral crystals. Its vapour is without colour or taste; the odour which accompanies it is due either to the reduction of the metal or to the formation of a lower oxide. This acid has two isomeric modifications, one of which is represented by the *vitreous* and the other by the *milky* variety. The latter was supposed to be merely the result ot an admixture of water; but it has been ascertained that the two varieties differ both in their specific gravity and in their chemical properties. The milky variety is much more soluble in water than the other, 100 parts of water at the ordinary temperature dissolving 1.25 of the former and 0.96 of the latter, and at the boiling temperature 11.47 of the former and 9.63 of the latter; while at 32° water retains in solution 2.9 parts of the milky and 1.78 of the vitreous acid. The aqueous solution of the vitreous variety reddens paper tinged with infusion of turnsole; that of the milky appears, on the other hand, to have rather an alkaline reaction. Rose has observed that a saturated solution of the vitreous acid in hydrochloric acid deposits on cooling octahedral crystals, during the formation of which flashes of light may be observed in the dark: neither of these phenomena occur with the milky variety. The great diversity of statements made with regard to the solubility of arsenious acid in water, have arisen not only from the difference of the two varieties in this respect, but also probably from the different manner in which the experiments have been made. Arsenious acid dissolves much more readily in acids than in water, and is deposited unaltered on cooling from hot solutions. It forms a class of salts called *arsenites*, all of which are poisonous, though not so eminently so as the acid itself. The best antidote to this poison is *hydrated sesquioxide of iron*, perfectly free from alkali, and which has not been dried, but preserved in a gelatinous state saturated with water: arsenious acid forms with this oxide a basic insoluble salt. Perhaps the best method of administering this antidote is in the form of a completely saturated solution of the hydrated sesquioxide in *acetic acid.*

Behaviour of Solutions of Arsenious Acid with Reagents.

Sulphuretted hydrogen produces in aqueous solutions of arsenious acid a very slow and incomplete precipitation; but in the presence of free hydrochloric acid an immediate precipitate of *sulpharsenious acid* ($As\,S_3$) of a bright yellow colour is produced. This precipitate is easily soluble in *alkalies*, alkaline carbonates, and alkaline sulphurets; it is also decomposed by boiling nitric acid, though it is nearly insoluble in hydrochloric acid. When fused with a carbonated alkali and nitre, it is decomposed, the products being arseniated and sulphated alkali. When an alkaline solution of sulpharsenious acid is boiled with oxide of copper, sulphuret of copper and arseniated alkali are formed. When a mixture of sulpharsenious acid and carbonate of soda is heated in a current of dry hydrogen gas, as shown in *fig.* 54, a reduction of a portion of the arsenic compound takes place, and a metallic mirror is formed within the tube, thus :—

$$2\,AsS_3 + 4\,NaO,CO_2 = NaO,AsO_3 + 3\,NaS,AsS_3 + 4\,CO_2.$$

Two equivalents of sulpharsenious acid, and four equivalents of carbonate of soda, producing one equivalent of arsenite of soda, and three equivalents of *sulpharsenico-sulphuret of sodium* + four of carb. soda.

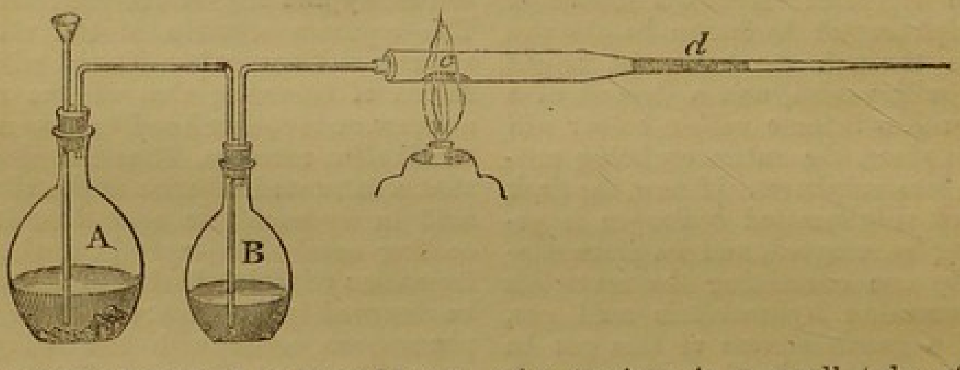
When the vapours of sulpharsenious acid are passed over ignited lime, sulphuret of arsenic and calcium and arseniate of lime are formed, with the separation of arsenic.

When sulpharsenious acid is fused with cyanide of potassium, *sulphocyanide* of potassium is formed, and arsenic set free, thus :—

$$2\,AsS_3 + 3\,KCy = 3\,KCyS_2 + As.$$

This experiment is best made by introducing a mixture of one part of sulpharsenious acid with ten or twelve parts of a mixture of two parts of dry carbonate of soda and one part of cyanide of potassium, into a glass tube drawn out as shown in *fig.* 53, and heated to redness; while a current of dry carbonic acid gas is passed over it, the arsenic is deposited on the cold surface of the narrow part of the tube in the form of a black mirror.

Fig. 53.



A is the flask containing lumps of solid marble, provided with a funnel tube, through which hydrochloric acid is poured for the generation of carbonic acid. B is a smaller flask containing oil of vitriol, in passing through which the carbonic acid becomes dried. C, the mixture of sulpharsenious acid with carbonate of soda and cyanide of potassium heated by a spirit lamp; *d*, the metallic mirror.

Sulpharsenious acid is also reduced by heating it with a mixture of equal parts of carbonate of soda and cyanide of potassium in a small tube of hard German glass closed at one end, and drawn out into a long and open point at the other.

Hydrosulphuret of ammonia produces in acid solutions of arsenious acid a yellow precipitate of sulpharsenious acid; in neutral or alkaline solutions no precipitate occurs.

Nitrate of silver produces in neutral solutions a yellow precipitate of *arsenite of silver* ($2\,AgO,AsO_3$), soluble in dilute nitric acid and ammonia.

Ammonio-nitrate of silver produces the same precipitate in acid solutions.

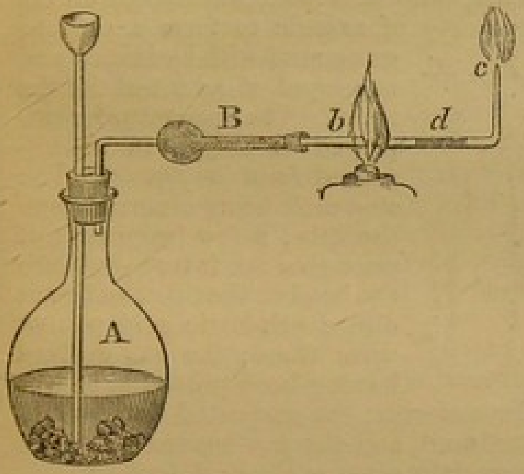
Sulphate of copper produces a yellowish green precipitate of arsenite of copper

Ammonio-sulphate of copper produces the same precipitate in acid solutions.

Lime water and *soluble lime salts* produce a white precipitate of arsenite of lime $(2\,CaO, AsO, AsO_3)$.

Arsenic, like *antimony*, forms a gaseous compound with hydrogen; the combination of the two elements may be effected by bringing together *arsenious acid* or an *arsenite* with *zinc*, *water*, and *sulphuric* or *hydrochloric acid;* this property is taken advantage of as a test for the metal, and forms a valuable means of isolating it. The materials for generating the hydrogen are introduced into the evolution flask, A, *fig.* 54, and the gas being filtered by passing through a tube filled with dry cotton wool, B, is inflamed at the point of the bent tube, C, (sufficient time being allowed to expel the atmospheric air from the apparatus,) and a porcelain plate depressed on the flame. If, after burning for some time, no incrustation or blackening appears on the plate, it is a sign that the materials in the evolution flask are free from arsenic; additional assurance is, however, obtained by heating a portion of the horizontal tube to redness at *b*, by means of a spirit lamp; no incrustation must be observed in the tubes. The liquid to be tested for arsenic is now introduced into the evolution flask through the funnel tube; and if it contain any traces of the poison, the flame of the hydrogen will acquire a blueish white colour, owing to the reduction and separation of the arsenic, and fumes of arsenious acid will make their appearance. On now depressing the porcelain plate upon the flame, brown arsenic spots will be obtained: these incrustations have a shining metallic appearance, those of antimony being black and possessing scarcely any metallic lustre. On applying the flame of the spirit lamp to the horizontal part of the tube, a beautiful incrustation of metallic arsenic will be formed on the cold part of the tube, which is darker and less silvery than that formed by antimony under similar circumstances; and on cutting off the tube near the deposit, and applying heat, the arsenic is converted into arsenious acid, which is recognised by its garlic odour, and which may be dissolved in hot water, and tested by nitrate of silver and sulphate of copper.

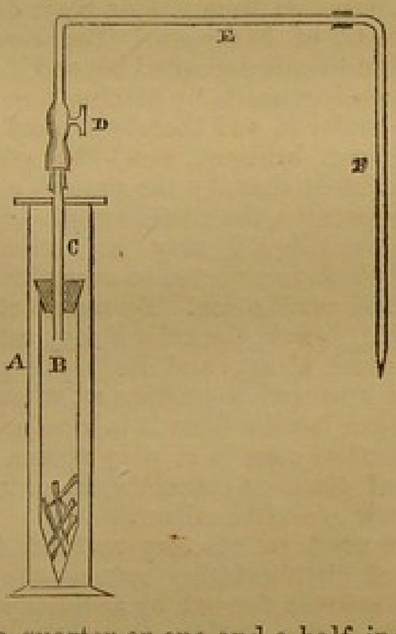
Fig. 54.



The following modification of Marsh's apparatus by the Academy of Sciences of Berlin, is described by Dr. Ure in his Supplement to his Dictionary of Arts, Manufactures, and Mines :—

A is a narrow glass cylinder open at top, about ten inches high, and one and a quarter or one and a half inch in diameter inside. B is a glass tube about one inch in diameter outside, drawn to a point at bottom, and shut with a cork at top. Through the centre of this cork the small tube C passes down air-tight, and is furnished at top with a stop cock, into which the small bent glass tube (without lead) E is cemented. The bent tube E is joined to the end of F by a perforated cork.

Fig. 55.



This apparatus is used as follows:—Introduce a few oblong slips of zinc free from arsenic into B, and then insert its air-tight cork with the attached tubes. Having opened the stop cock, pour into the tube A as much of the suspected liquid, acidulated with dilute pure sulphuric acid, as will rise to the top of the cork after B is full, and immediately shut the stop cock. The generated hydrogen will force down the liquid out of the lower orifice of B into A, and raise the level of it above the cork. The extremity of the tube F being dipped beneath the surface of a weak solution of nitrate of silver, and a spirit flame being placed a little to the left of the letter E, the stop cock is then to be slightly opened, so that the gas which now fills the tube B may escape so slowly as to pass off in separate small bubbles through the silver solution. By this means the whole of the arsenic contained in the arseniuretted hydrogen will be deposited either in the metallic state upon the inside of the tube E, or with the silver into the characteristic black powder. The first charge of gas in B being expended, the stop cock is to be shut, till the liquid be again expelled from it by a fresh disengagement of hydrogen. The ring of metallic arsenic deposited beyond E may be chased onwards by placing a second flame under it, and thereby formed into an oblong, brilliant, steel-like mirror. It is evident that, by the patient use of this apparatus, the whole arsenic in any poisonous liquid may be collected, weighed, and subjected to every kind of chemical verification. By means of the perforated cork, the tube F may readily be turned about, and its taper point raised into such a position as, when the hydrogen issuing from it is kindled, the flame may be made to play upon a surface of glass or porcelain, in order to form the arsenical mirror.

The most satisfactory method, however, of distinguishing between the metallic mirrors formed by antimony and arsenic under similar circumstances, is founded on the decomposition of sulphuret of antimony by hydrochloric acid gas, and the volatility of the chloride of antimony thus formed. We can thus not only distinguish an arsenical from an antimoniacal deposit, but when both metals are present we can separate them perfectly. We proceed thus:—The mirror having been obtained, a feeble stream of dry sulphuretted hydrogen is sent through the tube, a gentle heat being at the same time applied: if the metal be arsenic alone, sulphuret of that metal of a light yellow colour will be formed; if it be antimony alone, the sulphuret is either orange red or nearly black; if both metals be together, then both are converted into sulphurets; but the sulphuret of arsenic being more volatile than the sulphuret of antimony, it will be deposited in a more advanced part of the tube. A current of dry hydrochloric acid gas is now passed through the tube; *chloride of antimony* is formed *without the application of heat*, and is entirely removed in the current of gas. The sulphuret of arsenic remains unaltered, and may be distinguished from sulphur by its solubility in ammonia.

It was the late Mr. Marsh, of Woolwich, who first took advantage of the property of arsenic to form a gaseous compound with hydrogen, and employed it as a test for the metal. The apparatus he employed is shown in an improved form in *fig.* 56. The stop cock being removed from the tube, a few fragments of pure zinc are introduced into the bend of the tube, and pure dilute sulphuric acid poured upon them; the gas evolved having been proved to be free from arsenic, the suspected liquid is introduced, and the gas burned against a porcelain plate as above described.

Fig. 56.

Oxygen compounds of arsenious acid may be reduced by heating them in one of the small tubes figured above, over a spirit lamp, with a mixture of carbonate of soda and charcoal; the metal volatilizes and condenses in the cool part of the tube, forming a mirror of great lustre. Arsenious acid is reduced by merely heating it to redness in contact with a splinter of charcoal.

Metallic copper, when boiled with an acidified mixture containing arsenious acid, becomes covered with a steel-gray crust of metallic arsenic. This is an exceedingly delicate test, and will, according to its discoverer, *Reinsch*, detect arsenic when present in no more than a *millionth part* of the liquid; but as various other metals, *silver*, *gold*, *platinum*, *bismuth*, and *antimony*, are likewise precipitated under similar circumstances, it is necessary to submit the crust to a careful examination. When arsenious acid is heated with a dry *acetate* and *hydrate of potassa*, *oxide of kakodyl* is produced, the insupportable odour of which serves to detect very minute traces of arsenic. The following is the reaction which gives rise to the formation of this poisonous compound:

$$2(KO,C_4H_3O_3) + 2KO + AsO_3 = C_4H_6AsO + 4(KO,CO_2).$$

Two equivalents of acetate of potassa, two of potassa, and one of arsenious acid, producing one equivalent of oxide of kakodyl, and four of carbonate of potassa.

To prepare an organic mixture suspected to contain arsenic for the reception of sulphuretted hydrogen, Fresenius digests it in a water-bath, with an equal weight of concentrated hydrochloric acid, and as much water as will give the whole a thin consistence. *Chlorate of potassa* is then added, in portions of about half a drachm, at intervals of about five minutes, and until the contents of the basin have assumed a bright yellow, perfectly homogeneous, and a thin liquid appearance. When this point is attained, about two drachms more of chlorate of potassa are added to the mixture, and the basin is removed from the water-bath. When cool, it is filtered, and the residue washed, until all acid reaction ceases. The filtrate is concentrated to about a pint, and excess of *sulphurous acid* added, to reduce the *arsenic acid* to *arsenious acid*, the former being far less readily precipitated by sulphuretted hydrogen than the latter. The excess of sulphurous acid is then expelled by heat, and the fluid exposed to a slow stream of sulphuretted hydrogen gas for about twelve hours. The sulphuret of arsenic thus obtained is washed and treated with fuming nitric acid, evaporated to dryness, moistened with pure sulphuric acid, and gently heated, first on the water-bath, and afterwards at a higher temperature (not, however, above 300°), until the mass begins to crumble. The residue is treated with boiling-water, filtered; and the limpid fluid, after being acidified with hydrochloric acid, is again precipitated by sulphuretted hydrogen. The pure sulphuret of arsenic thus obtained is mixed with carbonate of soda and cyanide of potassium, and reduced in an atmosphere of carbonic acid, as above described.

MM. Duflos and *Hirsh* proceed as follows.—The suspected mass (the stomach, for instance, with its contents) is digested in a tubulated retort, with an equal weight of pure hydrochloric acid; the retort is connected with a receiver in which a little water is placed, the object of which is to collect any chloride of arsenic that might volatilize during the process. The retort is heated by a bath of chloride of calcium until the mass acquires the consistence of paste, when it is allowed to cool. It is then mixed with twice its weight of strong alcohol, and after some time the undissolved portion is collected on a filter, and washed with alcohol. The alcoholic liquid and the washings are lastly introduced into a retort, and the alcohol distilled off. The residue in the retort is mixed with the acid liquor which passed into the receiver during the first distillation, and the mixture is exposed to sulphuretted hydrogen.

Danger and *Flandin* heat the organic substance with one-sixth of its weight of concentrated sulphuric acid; the substance is carbonized without foaming; it is continually stirred till the charcoal is dry; a small quantity of nitric acid, or aqua regia, is then added, and the whole extracted with water. They observe, however, that the carbonizing process must only be had recourse to, when all attempts to obtain evidence of the poison without it have failed.

Dr. Letheby proposes the following method of treating organic substances, by which he states that it is not difficult to discover $\frac{1}{200}$ of a grain of arsenic in many ounces of organic matter. The substance of solid, such as the liver, intestine, or muscle, is cut into small pieces, and heated to dryness with aqua regia; the charred mass is boiled with two or three successive portions of water, slightly acidulated with nitric acid, and then boiled for about half an hour with pure granulated zinc; which is best prepared by exposing to a red heat, in a Hessian crucible, alternate layers of granulated zinc, and one-fourth of its weight of nitre, taking care to begin by a layer of saltpetre, and to finish by one of zinc; deflagration takes place, and when it is over, the scoriæ are removed, and the pure metal runs into an ingot; the arsenic will be deposited on the zinc, giving it a grayish black appearance. The arseniated zinc is introduced into a Marsh's apparatus of peculiar construction, and the evolved gas conveyed into a jar containing solution of *nitrate of silver*. According to *Lassaigne's* method, a black precipitate is produced; and by taking the precaution of not allowing the gas to come over too quickly, the whole of it is certain to be decomposed. To this black, turbid solution, hydrochloric acid is added, till all the silver is precipitated, and a little acid remains in excess. It is then boiled for a few minutes, filtered, and evaporated to dryness; the residue, if there is any, is boiled with distilled water, and carefully precipitated by *ammonia-nitrate of silver*. If any arsenic had been present, it would by this process have been converted into arsenic acid, which would give a red precipitate, with ammonia-nitrate of silver.

ARSENIC ACID, (AsO_5).—This acid, which is even more poisonous than arsenious acid, is remarkable for its analogy with common or tribasic phosphoric acid. Like the latter, it only partially dissolves in water, leaving a powder, which is only dissolved with great difficulty. At a red heat it is partially decomposed, and at a high temperature it is resolved into *arsenious acid* and *oxygen*. It is deliquescent, and strongly acid. The salts which it forms are called *arseniates;* they are mostly insoluble in water, but dissolve in hydrochloric acid; the alkaline arseniates are soluble in water. *Sulphurous acid*, aided by heat, reduces it into arsenious acid.

Behaviour of Solutions of Arsenic Acid, and the Arseniates, with Reagents.

Sulphuretted hydrogen produces no precipitate in neutral or alkaline solutions; but, in acid solutions, a yellow precipitate (AsS_5) is very slowly formed. Hence, previous to precipitating arsenic, when in the form of arsenic acid, by means of this reagent, it is reduced to arsenious acid by treatment with sulphurous acid.

Nitrate of silver produces a red brown precipitate of arseniate of silver ($3AgO,AsO_5$), soluble in dilute nitric acid, and in ammonia.

Ammonio-nitrate of silver behaves in a similar manner.

Sulphate and *ammonio-sulphate of copper* produce a greenish blue precipitate ($2CuO,AsO_5$).

Before the blowpipe, heated on charcoal in the inner flame arseniates are reduced, disengaging the peculiar garlic odour of suboxide of arsenic, by which minute traces may be recognised.

OXIDE OF TIN (SnO).—*General Characters:* When pure, it is black, but by trituration it acquires a gray, green, or brown tinge. It is not altered in dry air, but when brought into contact with bodies in a state of ignition it takes fire, burning with considerable intensity, emitting a white smoke, and is converted into white peroxide. The hydrated oxide, which is obtained by precipitating a solution of the metal in hydrochloric acid by carbonate of potassa, is a white powder, which also takes fire on being brought into contact with a burning body, and glows like tinder. It is more easily soluble in water than the anhydrous oxide. When boiled in water, it is decomposed, and a black powder is formed, which slowly absorbs oxygen, and acquires a lighter colour. Oxide of tin is dissolved by the fixed caustic alkalies, but the solution gradually decomposes, depositing metallic tin, the solution then containing a combination of *peroxide* and alkali. *Chloride* of tin is decomposed when brought into contact with water, an insoluble compound of oxide and chloride being formed. This decomposition is prevented by the addition of free hydrochloric acid.

Behaviour of Solutions of Oxide of Tin, with Reagents.

Potassa, ammonia, and their *carbonates* produce a white precipitate (SnO,HO), soluble in potassa; by repose, and more rapidly when boiled, the solution is decomposed, *metallic tin, peroxide of tin,* and *potassa* being formed thus:—

$$2SnO + 2KO = Sn + 2KO + SnO_2.$$

Phosphate of soda produces a white precipitate.

Ferrocyanide of potassium gives a white gelatinous precipitate.

Ferricyanide of potassium occasions a white precipitate, soluble in hydrochloric acid.

Sulphuretted hydrogen, and *hydrosulphuret of ammonia* produce a dark brown precipitate, soluble in potassa, and in alkaline sulphurets, particularly such as contain excess of sulphur, soluble also in hydrochloric acid; but nitric acid converts it by boiling into peroxide of tin; the solution of *sulphuret of tin* in *sulphuret of lime* is precipitated as a yellow *bisulphuret of tin* by hydrochloric acid.

A *bar of metallic zinc* precipitates tin in small grayish white metallic spangles.

Chloride of gold produces a purple precipitate, a mixture probably of peroxide of tin and metallic gold (purple of Cassium), insoluble in hydrochloric acid.

Chloride of mercury produces a white precipitate of *subchloride of mercury* (Hy_2Cl).

The salts of this oxide, from their tendency to absorb oxygen, are powerful reducing agents; they are all decomposed by exposure to the air passing into salts of the *peroxide.*

Before the blowpipe, heated in the inner flame on charcoal with a mixture of *carbonate of soda* and *cyanide of potassium,* protosalts of tin yield ductile grains of metallic tin without any incrustation taking place.

PEROXIDE OF TIN ($Sn\ O_2$).—*General Characters:* This oxide differs according to its mode of formation, not only in its physical but also in its chemical properties: it is found native and crystallized; the crystals are sometimes yellowish brown, and transparent, and sometimes nearly black: when prepared by the action of nitric acid on the metal, it is a white powder, and quite insoluble in acids, but by fusion with carbonate of potassa it is rendered soluble; the oxide produced by precipitating the perchloride by ammonia is easily soluble in acids; but after it has been ignited it is insoluble, but it is again rendered soluble by fusion with carbonate of potassa.

Behaviour of Solutions of Peroxide of Tin with Reagents.

Potassa and *ammonia* produce a white precipitate, soluble in *potassa,* and, in great excess, of *ammonia.*

Carbonate of potassa and *ammonia* produce a white precipitate, soluble in *carbonate of potassa,* but insoluble in *carbonate of ammonia.*

Phosphate of soda produces a white precipitate.

Sulphuretted hydrogen and *hydrosulphuret of ammonia* throw down from acid and neutral, but not from alkaline solutions, a yellow precipitate of bisulphuret of tin soluble in alkalies, alkaline carbonates, and sulphurets, and in concentrated boiling hydrochloric acid; *nitric acid* converts it into peroxide, and by fusion with nitre it gives rise to the formation of *sulphate* and *stannate of potassa.*

A *bar of metallic zinc* throws down a white gelatinous precipitate, hydrogen gas being disengaged.

Before the blowpipe, heated with carbonate of soda on charcoal in the inner flame, persalts of tin are reduced to the metallic state.

PEROXIDE OF PLATINUM ($Pt\ O_2$).—*General Characters:* The hydrate is obtained as a reddish brown voluminous precipitate, closely resembling *hydrated sesquioxide of iron,* by precipitating a solution of the nitrate by caustic soda; it contracts considerably on drying; heated in a retort, it loses its water and becomes black; at a higher temperature it parts with oxygen, leaving the metal. Platinum is insoluble in nitric and hydrochloric acids, but it dissolves in *aqua regia,* forming a red brown solution containing perchloride of platinum ($Pt\ Cl_2$).

Behaviour of Solutions of Platinum with Reagents.

Potassa produces a yellow crystalline precipitate, consisting of the double chloride of platinum and potassium; the addition of hydrochloric acid favours its formation; it is insoluble in acids, but dissolves with the aid of heat in *potassa;* it is very slightly soluble in water, and insoluble in strong alcohol.

Ammonia produces a similar yellow crystalline precipitate, the *double chloride of platinum* and *ammonium* having the same characters as the former, and soluble in excess of ammonia aided by heat; when exposed to a red heat it is completely decomposed, leaving the metal in a spongy form.

Subnitrate of mercury produces a yellowish red precipitate.

Chloride of tin communicates to solutions of *bichloride of platinum* a deep red brown colour without producing any precipitate.

Sulphuretted hydrogen and *hydrosulphuret of ammonia* produce in acid and neutral solutions a brownish black precipitate (PtS_2), soluble in excess of alkalies and alkaline sulphurets, insoluble in nitric and hydrochloric acids, but soluble in aqua regia.

PEROXIDE OF IRIDIUM ($Ir\ O_2$).—*General Characters:* This oxide has not yet been isolated; the metal itself is very slowly acted on by aqua regia, in which it forms a dark red brown solution containing $Ir\ Cl_2$, which is not precipitated by alkalies: *sulphuretted hydrogen* produces a brown precipitate, $Ir\ S_2$, which is soluble in *hydrosulphuret of ammonia, iodide of potassium, cyanide of potassium, protosulphate of iron,* and *oxalic acid,* all discolour solutions of iridium, without, however, producing any precipitate.

PEROXIDE OF GOLD ($Au\ O_3$).—*General*

characters: The hydrate of this oxide, which from its tendency to combine with bases, and from the little disposition which it has to combine with acids, ought perhaps more correctly to be called *auric acid*, is of a yellowish red colour; the anhydrous oxide is black or deep brown. The hydrate, dried without the aid of heat, is of a chestnut brown colour, and has a vitreous fracture. At 212° it loses its water, and becomes partially reduced; even in the dark it undergoes partial decomposition, and at a red heat it is resolved into metallic gold and oxygen. The metal is insoluble in nitric or hydrochloric acid, but it dissolves in aqua regia, forming a fine yellow solution, containing terchloride of gold ($Au Cl_3$).

Behaviour of Solution of Terchloride of Gold with Reagents.

Potassa after a time produces an inconsiderable reddish brown precipitate, consisting of *teroxide of gold* mixed with *terchloride of gold* and *potassa*.

Ammonia produces a yellow precipitate (aurate of ammonia, or fulminating gold).

Ferrocyanide of potassium communicates to solution of gold an emerald green colour.

Protosulphate of iron produces in concentrated solutions an immediate dark brown precipitate of metallic gold. In dilute solutions a blue colouring is first perceived, followed by a brown coloured precipitate.

Protonitrate of mercury occasions a black precipitate.

Oxalic acid produces a precipitate of metallic gold, thus:—

$$Au Cl_3 + 3(H O C_2 O_3) = Au + 3 H Cl + 6 C O_2.$$

Protochloride of tin, to which a drop of nitric acid has been added, communicates a reddish purple colour to very dilute solutions; in concentrated solutions a red purple precipitate (purple of Cassius) is formed.

A bar of metallic zinc precipitates metallic gold in the form of a brown coating.

Sulphuretted hydrogen, and *hydrosulphuret of ammonia*, precipitate from neutral and acid solutions of gold, the tersulphuret ($Au S_3$), soluble in great excess of hydrosulphuret of ammonia, and in aqua regia, but insoluble in all other acids and alkalies.

SELENIOUS ACID ($Se O_2$).—*General Characters:* On evaporating a solution of selenium in aqua regia, this acid remains in the form of a white saline mass, which at the temperature of about 600° assumes the form of a deep yellow gas, much resembling chlorine: on cooling, the acid condenses in long needles, and by allowing it to cool slowly it is deposited in the form of a semitransparent crust. When first prepared it has a brilliant appearance, but by exposure to the air it becomes dull, from the absorption of moisture. Its taste is distinctly acid, but it leaves a burning taste in the mouth; it is very soluble in boiling water: the solution deposits the hydrated acid on cooling in the form of striated prisms. The hydrated acid is also deposited from a hot solution in nitric acid in long prisms resembling nitre. It is easily reduced. On introducing a slip of *zinc* or *polished iron* into a solution of selenious acid mixed with hydrochloric acid, it immediately becomes covered with a copper-coloured deposit, and *selenium* precipitates by degrees in the form of red, brown, or grayish black flocks, according to the temperature. A mixture of *sulphuric* and *selenious* acids is slowly acted on, and the precipitate contains a little sulphur. Selenious acid is also decomposed by *silver*. *Selenium* is best precipitated from *selenious acid*, and the *selenites* by *sulphite of ammonia*. The liquor, which is at first clear, becomes yellow, then turbid, then cinnabar red, and after a few hours it deposits red flocks of *selenium*. If nitric acid be present, a perfect reduction cannot be effected.

Sulphuretted hydrogen produces in an acid solution a yellow precipitate of *sulphuret of selenium*, which is soluble in *hydrosulphuret of ammonia*.

Solid selenites, heated in a tube with *chloride of ammonium*, afford a sublimate of selenium, which is recognised by its peculiar odour.

Before the blowpipe, the minutest trace of selenium may be recognised by ignition on charcoal in the oxidating flame; a strong disagreeable smell similar to *decaying horseradish* is given off. If much selenium be present, a reddish vapour is evolved, and a steel-gray sublimate is deposited on the charcoal, which on the exterior edges sometimes passes into violet, and in their layers blue.

TELLUROUS ACID ($Te O_2$).—This acid is obtained in crystalline grains, by acting on *ellurium* with *nitric acid*, and, as a white flocculent hydrate, by precipitating the solution in nitric acid with water. The yellow colour which the acid frequently exhibits arises from impurities. When first laid on the tongue, it produces little taste; but after a time a very disagreeable metallic taste, similar to that of salts of silver, is experienced. It reddens litmus paper, though not immediately; it is very sparingly soluble in water. On being heated, it acquires a fine citron yellow colour; but on cooling it again becomes colourless; at a red heat it melts into a transparent deep yellow liquid, solidifying on cooling into a colourless crystalline mass; heated in the open air it fumes, and slowly sublimes; heated in open vessels with carbon, it is reduced with detonation, the greater part of the tellurium volatilizing; in close vessels the reduction takes place easily, but the metal is obtained with difficulty in a compact mass. It is also reduced, though not very readily, by hydrogen gas. It is very sparingly soluble in *acids*, in *ammonia*, and in the *carbonated alkalies*. The *caustic fixed alkalies*, on the other hand, dissolve it immediately. When *tellurous acid* is fused with an equal weight of *carbonate of potassa*, and the *tellurite of potassa* thus obtained dissolved in water, and mixed with a slight excess of nitric acid, a white voluminous hydrate is produced, which has an acrid metallic taste, instantly reddens litmus paper, and is soluble in water, and very soluble in nitric and other acids, and also in caustic ammonia and the carbonated alkalies.

Behaviour of Solution of Tellurous Acid with Reagents.

The *caustic alkalies* and their *carbonates* produce a white precipitate, soluble readily in *potassa*, and soluble also in alkaline carbonates.

Sulphuretted hydrogen produces a dark brown precipitate, very soluble in *hydrosulphuret of ammonia.*

Sulphurous acid, *alkaline sulphites*, and *metallic zinc* produce a black precipitate of metallic *tellurium.*

Protochloride of tin and *protosulphate of iron* produce a black powder, which on being rubbed assumes a metallic lustre.

Before the blowpipe, heated on charcoal, or in a glass tube open at both ends, a white sublimate with a reddish border is obtained in either flame, and which disappears with a beautiful blueish green tinge; when the reducing flame is directed on it in large quantities, the flame also becomes blue; if the peculiar smell of horseradish is perceptible, *selenium* is present; if the substance under examination contains other metals, as lead or bismuth, it should be mixed with boracic acid, which will dissolve those metals and prevent them from volatilizing.

Oxide of Tungsten ($W O_2$).—*General characters:* This oxide, when prepared by reducing *tungstic acid* by hydrogen gas, is brown; it may be obtained crystalline and of a metallic lustre by employing crystallized tungstic acid, such as is obtained by decomposing *tungstate of ammonia* in close vessels. The oxide in this state has, when pressed together, a deep copper colour. By pouring dilute hydrochloric acid on tungstic acid, and placing in the liquor a strip of *zinc*, it is gradually decomposed, and oxide of tungsten is obtained in the form of brilliant copper-coloured spangles, but it cannot be preserved or even dried in this state. It may also be obtained in the form of a beautiful violet brown precipitate by mixing *chloride of tungsten* with water, but it is very unstable: the oxide obtained in the dry way may be preserved without alteration. When heated below redness, it burns like tinder, and is converted into tungstic acid. It does not appear to form salts with acids, but it dissolves in concentrated *caustic potassa* with the disengagement of heat and the formation ot *tungstate of potassa.* This oxide is remarkable for a beautiful compound which it forms with *soda;* it is prepared by saturating fused *tungstate of soda* with tungstic acid, and reducing the mass by heat in a current of hydrogen gas: after having dissolved out the neutral undecomposed tungstate, the new compound remains in the form of regular cubes and scales of a golden yellow colour, possessing metallic lustre, and having all the appearance of *gold.* It is not acted upon by any acid but the *hydrofluoric; aqua regia* has no action on it, but it is decomposed by *oxygen gas*, *sulphur*, and *chlorine*, at a high temperature. No such compound can be formed with *potassa* or with the alkaline earths.

Tungstic acid, WO_3.—*General Characters:* This acid is generally prepared by fusing a mixture of finely powdered *wolfram* with an equal weight of carbonate of potassa, and half its weight of nitre. The alkaline tungstate thus formed is dissolved in water exactly neutralized by nitric acid, precipitated by nitrate of mercury, and the precipitate calcined in a platina crucible. It is of a fine yellow colour, becoming dark green when strongly heated; it also assumes a green tint by mere exposure to the rays of the sun; it is insoluble in water, but readily soluble in caustic alkalies. Hydrated tungstic acid is formed slowly as a gelatinous mass, by heating a diluted solution of an alkaline tungstate with dilute nitric acid; when washed and dried, it is a powder of a brilliant opaque yellow gray colour. *Tungstic acid*, like *molybdic acid*, unites with other acids, acting the part of a base.

Zinc produces, in acid, solutions of tungstic acid of a beautiful blue colour, owing to the formation of *oxide of tungsten.*

Sulphuret of tungsten is precipitated when a tungstate is decomposed by acids in the presence of *hydrosulphuret of ammonia.*

Before the blowpipe, tungstic acid is thus detected:—Mix a small portion of the mineral with five times its volume of *soda*, and heat strongly in a platinum spoon; dissolve in water, and precipitate the filtered solution with hydrochloric acid; the precipitate assumes, when heated, a beautiful yellow colour. The oxides of tungsten, when perfectly pure, liquefy with microscomic salt in the oxidating flame: in the reducing flame they become green, and when cold beautiful blue. The glass, when treated with tin on charcoal in the reducing flame, assumes a darker colour, which on cooling is *green.*

OXIDES OF VANADIUM ($V O$, $V O_2$, $V O_3$).—*General Characters: Suboxide of vanadium*, obtained by reducing *vanadic acid* at a red heat by a current of hydrogen gas, is a black crystalline powder: it is remarkable as being an excellent conductor of electricity, and as excelling, as a negative electromotive element, copper, and even gold or platina. It has not hitherto been made to combine with either acids or bases. It oxidizes gradually in the air, and under water it acquires a fine green colour. Heated in the air, it takes fire and burns, leaving a black mass: by chlorine it is converted into *chloride* and *vanadic acid.*

OXIDE OF VANADIUM, OR VANADIOUS ACID ($V O_2$). The anhydrous oxide is a black powder which has no action on test paper. It is insoluble in water, but when left for some time in contact with that fluid it oxidizes, becoming by degrees green. The hydrate, which when first formed is grayish white, oxidizes rapidly in the air, becoming first brown, then green, and finally black. The calcined oxide is slowly but completely dissolved in acids; the solution is blue; though acting the part of a base, it nevertheless combines with bases, giving rise to a class of salts called *vanadites.* It is dissolved by alkaline carbonates; the solution, which is of a deep brown colour, contains a *vanadite* and a *bicarbonate.* The bicarbonates also dissolve it, forming blue solutions, probably neutral double carbonates of the oxide and alkali.

VANADIC ACID ($V O_3$).—Prepared by decomposing *vanadate of ammonia* by heat. It is a rusty red brown powder, without taste or smell. It supports a high temperature without losing oxygen; but at a red heat it enters into fusion. In contact with organic matter at a red heat, it loses oxygen. It strongly reddens litmus paper. The fused acid crystallizes, on cooling, in the form of interlaced needles of a yellowish red colour; but if a small quantity of oxide be present it has a violet tint. It does not conduct electricity. It dissolves sparingly in water, forming a clear yellow solution. It cannot be obtained crystalline in the humid way, nor can it be obtained pure out of solution, as it combines with acids as well as with bases. It is easily reduced to the state of oxide under the influence of an acid, such as *coloured nitric acid, sulphurous, oxalic*, or *tartaric acids; alcohol* and *sugar* likewise effect its reduction, blue oxide of vanadium being formed. Hydrochloric acid dissolves it, forming an orange-coloured solution; but after a while *chlorine* is disengaged, and the liquid acquires the property of dissolving gold and platinum.

Behaviour of Solution of Oxide of Vanadium with Reagents.

Potassa produces a grayish white hydrate, soluble in excess of *potassa*, but insoluble in *ammonia.*

Sulphuretted hydrogen occasions no precipitate; but *hydrosulphuret of ammonia* produces a brownish black precipitate, soluble in excess, the solution having a purple colour.

Behaviour of Solution of Vanadic Acid with Reagents.

Nitrate of silver produces a yellow precipitate, becoming white by exposure to the air, and soluble in *nitric acid* and in *ammonia.*

Chloride of barium produces a bulky orange yellow precipitate, slightly soluble in water.

Hydrosulphuret of ammonia gives a brown precipitate (VaS_3), soluble in excess, forming a brown liquid.

Ferrocyanide of potassium produces a fine green precipitate.

Chloride of ammonium produces a white flocculent precipitate of *vanadate of ammonia*, quite insoluble in hydrochloric acid.

Before the blowpipe, oxides of vanadium, heated in the outer flame with borax or microcosmic salt, give a yellow bead; in the inner flame a fine green one, which again becomes yellow in the outer flame. *Vanadic acid*, heated on charcoal, leaves a compact mass the colour of plumbago (suboxide of vanadium); with borax and microcosmic salt it gives a beautiful green glass, which while hot is brown. It is not coloured blue by the addition of tin. *Chromic acid* gives with borax and microcosmic salt a green bead; but *vanadic acid* is distinguished from *chromic acid* from the circumstance that the green bead in the former can be changed in the oxidating flame to yellow, which is not the case with the latter.

OXIDES OF MOLYBDENUM (MoO, MoO_2 MoO_3).—*General Characters:* When to a solution of a *molybdate* in water hydrochloric acid is added, and the mixture digested with *distilled zinc*, the latter becomes oxidized at the expense of the molybdic acid; and the liquid becomes first blue, then red, brown, and finally black. From this solution *potassa* precipitates *hydrated oxide of molybdenum* in the form of a black flocculent mass. This hydrate is dissolved with difficulty in acids; the solutions are opaque and almost black, unless greatly diluted; the taste astringent, but not metallic. When heated to redness in vacuo, it takes fire, burning with vivid scintillations, and a hydrous oxide remains of a pitchy blackness, and insoluble in acids. Heated in the air, it burns and is converted into *molybdic oxide* (MoO_2). *Oxide of molybdenum* is not soluble either in *caustic potassa* or in solutions of the *fixed alkaline carbonates.* It dissolves, however, in *carbonate of ammonia.*

MOLYBDIC OXIDE (MO_2).—When pure, it is a powder of a deep brown colour; by the light of the sun it is *brilliant purple.* It is insoluble in alkalies and in acids, but it dissolves in small quantities in a mixture of *concentrated sulphuric acid* and *tartrate of potassa.* Nitric acid converts it into *molybdic acid.* Hydrated molybdic oxide is similar in appearance to *hydrated sesquioxide of iron.* It is, to a certain extent, soluble in water, the solution having a deep red colour, and it appears to form with some acids subsalts, which are soluble. If dried by exposure to the air it acquires a blue colour on the surface from the absorption of oxygen; the solution in water reddens litmus paper; it has an astringent and somewhat metallic taste. It is completely precipitated by sal-ammoniac, and when once dried cannot again be dissolved in water. Heated in vacuo, it loses its water, and brown anhydrous oxide remains. Though it reddens litmus paper, it has none of the other properties of an acid. Caustic alkalies do not dissolve it, though it is soluble in alkaline carbonates. The solution in *carbonate of ammonia* is entirely precipitated by boiling, and that in *carbonate of potassa* is by degrees converted into *molybdate of potassa.*

MOLYBDIC ACID (MO_3).—When pure, it is a light, porous, white mass; and when diffused through water it assumes the appearance of extremely small, silky, brilliant, crystalline scales. Heated to redness, it melts into a deep yellow liquid, which, on cooling, becomes pale straw yellow and crystalline, and on breaking divides into crystalline spangles. In close vessels it supports a strong red heat without volatilizing; but in open vessels it sublimes at its fusing point, its surface becoming covered with crystalline spangles. Water dissolves it in small quantities (about $\frac{1}{570}$th of its weight). The solution has a feeble metallic taste, and reddens litmus paper. Before calcination it is soluble in acids, forming compounds in which it acts the part of a base. It dissolves also in a saturated solution of *tartrate of potassa*, and in solutions of *caustic* and *carbonated alkalies.*

Behaviour of Solutions of Oxide of Molybdenum, with Reagents.

Potassa and *ammonia* produce a brownish black precipitate, insoluble in excess of the precipitants.

Carbonate of potassa and *carbonate of ammonia* produce a similar precipitate, slightly soluble in *carbonate of potassa*, more soluble in *carbonate of ammonia.*

Hydrosulphuret of ammonia gives a yellowish brown precipitate, soluble in excess of the precipitant.

Molybdic oxide is distinguished from *oxide of molybdenum* by its greater solubility in *carbonate of potassa.*

Behaviour of Molybdic Acid with Reagents.

Nitrate of silver produces a white precipitate, soluble in much water and in *nitric acid* and in *ammonia.*

Chloride of barium produces a similar precipitate, soluble in *nitric acid.*

Sulphuretted hydrogen, added in excess to an acid solution, produces, after a time, a brown precipitate, subsiding slowly; the supernatant fluid being blue or green.

Metallic zinc or *tin* produces in solutions containing free hydrochloric acid a blue colour, which becomes green and finally black.

Before the blowpipe, the oxides of molybdenum give to microcosmic salt in the inner flame a fine green colour, becoming more perceptible on cooling; with borax they produce in the inner flame a brownish red bead.

General Remarks on the Oxides of the Sixth Group.

Of the metallic oxides comprehended in this group, it will be only necessary to make a few remarks on the method of detecting *tin*, *antimony*, and *arsenic*, when these metals exist together in a compound. The three metals are obtained together in the form of *sulphurets* (SnS_2, SbS_5, AsS_5), by precipitating their solution in hydrosulphuret of ammonia by an acid. The dry sulphurets are fused with a mixture of *nitre* and *carbonate of soda,* by which operation the sulphur becomes converted into sulphuric acid, which combines with the potassa of the nitre; and the nitric acid furnishes oxygen, whereby the sulphurets are converted into oxides (SnO_2, SbO_5, AsO_5). These oxides act the part of acids, and combine with the *potassa*, giving rise to *stannate*, *antimoniate* and *arseniate*, of the alkali. The dry mass is treated with water, which dissolves out the *arseniate of potassa,* and also a small quantity of *stannate* and *antimoniate* of potassa. The two latter are removed from the filtered solution by the addition of a few drops of nitric acid, the solution is again filtered and exactly neutralized by ammonia, and arsenic acid detected by *nitrate of silver.* The white mass insoluble in water is fused in a porcelain crucible with *cyanide of potassium;* the globule of reduced metal is heated with nitric acid, and the oxides thus produced, after being well washed, are boiled with *tartaric acid,* in which *oxide of antimony* is soluble, and may be detected by *sulphuretted hydrogen.* A portion of the mixed oxides may likewise be tested before the blowpipe by fusing in the reducing flame on charcoal with a mixture of carbonate of soda and cyanide of potassium; the antimony is dispersed, leaving a characteristic white oxidation crust, and a ductile globule of metallic tin remains.

II. ACIDS.

Although acids cannot be classified with the same degree of perspicuity with which we are enabled to arrange the bases, there are certain reagents by which we can divide them into groups; the subdivision of which is afterwards effected by other reagents, which are called *special.*

The reagents for grouping the *inorganic* acids are *chloride of barium* and *nitrate of silver;* those for grouping the *organic acids* are *chloride of calcium,* and *sesquichloride of iron.*

Inorganic Acids.

I. Acids precipitated from their neutral solutions by *chloride of barium.*

Carbonic acid.
Sulphurous acid.
Hyposulphurous acid.
Hyposulphuric acid.
Sulphuric acid.
Selenic acid.
Phosphoric acid.
Phosphorous acid.
Hypophosphorous acid.
Boracic acid.
Silicic acid.
Hydrofluoric acid.
Chromic acid.
Arsenic acid.
Arsenious acid.
Other metallic acids.

II. Acids precipitated from their neutral solutions by *nitrate of silver.*

Hydrochloric acid.
Hydrobromic acid.
Bromic acid.
Hydriodic acid.
Iodic acid.
Periodic acid.
Hydrocyanic acid.
Hydrosulphuric acid.

III. Acids precipitated by neither *chloride of barium* nor *nitrate of silver.*

Nitric acid.
Nitrous acid.
Perchloric acid.
Chloric acid.
Chlorous acid.

Organic Acids.

I. Acids precipitated by *chloride of calcium.*

Oxalic acid.
Tartaric acid.
Pyrotartaric acid.
Citric acid.
Malic acid.

II. Acids precipitated by *sesquichloride of iron.*

Succinic acid.
Benzoic acid.
Tannic acid.
Gallic acid.

III. Acids precipitated by neither *chloride of calcium* nor *sesquichloride of iron.*

Acetic acid.
Formic acid.
Uric acid.
Meconic acid.

INORGANIC ACIDS.—1. Those precipitated from their neutral solutions by *chloride of barium.*

CARBONIC ACID, (CO_2).—*General Characters:* At common temperatures and pressures, this acid is a colourless transparent, irrespirable, and incombustible gas. It is heavier than atmospheric air in the proportion of 1.5 to 1, and totally unfit for supporting combustion. It has a sour and somewhat astringent taste. It reddens litmus paper, but as the gas volatilizes the blue colour returns. It may be poured from one vessel to another, and a small animal exposed to its influence instantly dies in strong convulsions. It is decomposed at a red heat in contact with carbon and other combustibles, carbonic oxide, an inflammable gas, being produced. A succession of electric sparks likewise decomposes it into carbonic oxide and oxygen. Water at ordinary temperatures and pressures absorbs rather more than its own volume of carbonic acid gas, and considerably more at a low temperature and under pressure. The solution has an agreeable, piquant, and feebly acid taste. At a temperature of 0°, and under a pressure of 36 atmospheres, it is condensed into a colourless liquid, and by peculiar management it may even be obtained in the solid state, having the appearance of a mass of snow. All the neutral carbonates, with the exception of those of the alkalies, are *insoluble* in water; they are, however, decomposed by nearly all acids that are soluble in water, the carbonic acid gas escaping with effervesence; but, to expel the whole, excess of acid must be added, in consequence of the formation of *bicarbonates.* Most of the carbonates lose their acid by ignition.

Behaviour of the Soluble Carbonates with Reagents.

Lime water and *water of barytes* produce white precipitates, insoluble in water, but soluble with effervescence in hydrochloric acid.

Chloride of barium and *chloride of calcium* produce white precipitates in solutions of neutral alkaline carbonates; but in solutions of *bicarbonates* no precipitate is formed until the second atom of carbonic acid is expelled by boiling, because both *bicarbonate of baryta* and *bicarbonate of lime* are soluble in water.

SULPHUROUS ACID (SO_2).—*General Characters:* At common temperatures and pressures it is a permanent gas, of a suffocating odour and a very disagreeable taste, not inflammable nor possessing the power of supporting combustion. It is very fatal to animal life. It is absorbed in large quantities by water, and still more copiously by alcohol. It destroys the colour of vegetable substances. Its acid properties are very weak. All acids but *carbonic* and *hydrocyanic acids* displace it from its combinations. The class of salts which it forms are called *sulphites;* they are all insoluble in water but those of the alkalies. All the acid salts of sulphurous acid are soluble. At a low temperature and under pressure it is reduced to a liquid.

Behaviour of Solutions of Sulphites with Reagents.

Chloride of barium and *chloride of calcium* produce a white precipitate, soluble in hydrochloric acid; if, however, the solution of the sulphite has been for some time exposed to the air, this precipitate is no longer completely soluble in hydrochloric acid.

Protonitrate of lead produces a white precipitate, soluble in cold nitric acid, but decomposing when boiled, *sulphate of lead* being precipitated, and nitrous fumes evolved.

Nitrate of silver produces a white precipitate (AgO, SO_2), becoming black by the application of heat, the metal being reduced, and sulphuric acid formed. Thus:—

$$AgO\ SO_2. = Ag + SO_3.$$

Protochloride of tin, acidified with hydrochloric acid, produces a yellowish brown precipitate (SnS_2).

Chloride of barium, when *boiled* with a solution of a sulphite, together with nitric acid, produces a white precipitate ($BalSO_3$).

Chlorine, *nitric acid* and *fused nitre* convert *sulphites* into *sulphates*.

Solid sulphites, when moistened with an acid, evolve sulphurous acid, which may be recognised by its odour; when ignited in a glass tube, they are decomposed into *sulphurets* and *sulphates*, and on treating the fused mass with a diluted acid, *sulphuretted hydrogen* gas is disengaged, provided the metallic sulphuret belongs to that class which decomposes water with the assistance of an acid.

Liquid sulphuretted hydrogen produces in solutions containing sulphurous acid a white precipitate of *sulphur*.

HYPOSULPHUROUS ACID (S_2O_2). The aqueous solution of this acid decomposes spontaneously into *sulphurous* acid and sulphur; the compounds which it forms with alkalies and alkaline earths are, with the exception of hyposulphite of baryta, soluble in water.

Behaviour of Solutions of Hyposulphites with Reagents.

Chloride of barium in concentrated solutions occasions a white precipitate.

Nitrate of silver produces a precipitate which at first is white, but it rapidly becomes yellow, and finally black; *sulphuret of silver* being formed and nitric acid set free, thus:—

$$AgO, NO_5 + NaO, S_2O_2 = AgS + NaO, SO_3 + NO_5.$$

Hydrochloric acid produces a yellow precipitate of sulphur, sulphurous acid being set free, thus:—

$$NaO, S_2O_2 + HCl = NaCl + SO_2 + HO + S.$$

Solutions of soluble hyposulphites possess the property of dissolving recently precipitated *chloride of silver;* the solution has an intensely sweet taste, leaving one of that nauseous bitterness peculiar to salts of silver.

HYPOSULPHURIC ACID (S_2O_5).—The aqueous solution of this acid, when heated, is resolved into *sulphuric* and *sulphurous acids;* its salts undergo the same decomposition by hydrochloric acid, aided by heat, thus:—

$$NaO, S_2O_5 = NaO, SO_3 + SO_2.$$

The hyposulphates are generally soluble in water.

SULPHURIC ACID (SO_3).—*General Characters:* In its pure anhydrous state it forms a tenacious crystalline mass resembling *asbestos;* exposed to the air it gives off thick opaque fumes; its affinity for water is so powerful, that it hisses like a red hot iron when brought into contact with it; *monohydrate* of sulphuric acid (HO, SO_3) is sometimes fuming, but as manufactured in England it does not fume, but has an oily consistence; hence its commercial name *oil of vitriol*. When pure it is colourless, the dark tinge that the acid sometimes has arising from the separation of carbon from organic substances, which it rapidly decomposes. It has a powerful affinity for water, abstracting it from the atmosphere with great rapidity; during its combination with water great heat is evolved; the monohydrated acid freezes at 31°, and boils at 617°; it distils without alteration; its acid properties are exceedingly powerful; it displaces all other acids from bases at temperatures below its boiling point; but at a higher temperature it is itself displaced by certain weaker acids which are not volatile; the greater number of its compounds with bases are soluble in water; the sulphates of *baryta*, *strontia*, and *lead* are, however, nearly insoluble, the first entirely so.

Behaviour of Solutions of Sulphates with Reagents.

Chloride of barium produces an immediate white precipitate (BaO, SO_3), even in highly dilute solutions, insoluble in water and in acids. The solution to be precipitated should not contain too much *nitric* or hydrochloric acid, as baryta salts which are very *soluble* in water are very sparingly so in acids; and a white precipitate might be formed which could be mistaken for *sulphate of baryta*. Such a precipitate would, however, be readily soluble in water.

Acetate of lead produces a white precipitate, soluble to a slight extent in dilute nitric acid, but completely insoluble in *boiling and concentrated* hydrochloric acid.

The sulphates of the alkaline earths and alkalies are not decomposed by heat alone; when heated in contact with charcoal they are reduced to sulphurets; the reduction is facilitated by mixture with carbonate of soda. On treating the reduced mass with an acid *sulphuretted hydrogen* is evolved, which may be detected by the odour, by lead paper, or by making the experiment on a bright silver surface. All the other sulphates, with the exception of that of *oxide of lead*, are decomposed at a high temperature, *sulphuric acid*, or a mixture of *sulphurous acid* and *oxygen*, being set free, and pure oxides, or the metals themselves, left. Insoluble sulphates are converted into carbonates by fusion with carbonate of soda, alkaline sulphates being formed.

Before the blowpipe, colourless sulphates may be detected by fusing them with *silicate of soda* in the reducing flame; a sulphuret is thereby formed, and the glass assumes a red or dark yellow colour, according to the quantity of acid present. *Coloured* sulphates are detected by fusing them with two parts of soda and one of borax, in the reducing flame, on charcoal, and placing the fused mass on a plate of silver, and moistening it with water. A tarnishing of the metal indicates *sulphur*.

SELENIC ACID (HO, SeO_3) produces a precipitate with *chloride of barium*, which is insoluble in nitric acid. *Seleniate of baryta* is, however, decomposed by boiling hydrochloric acid, chlorine being evolved. This is not the case with *sulphate of baryta*.

TRIBASIC PHOSPHORIC ACID ($3\,HO, PO_5$)—*General Characters:* When anhydrous, it has the form of white flakes, which rapidly absorb moisture from the atmosphere. The hydrate is a vitreous mass, and is known as *glacial phosphoric acid*. It deliquesces in the air to a syrupy liquid; it has a free acid, but not caustic, taste; if pure, it volatilizes without residue when strongly heated in an open platinum vessel; it attacks vessels of glass or porcelain when fused therein. The alkaline phosphates are soluble in water, but the neutral compounds of phosphoric acid with the earths and metallic oxides are insoluble in water, though they dissolve in excess of phosphoric acid and in nitric acid. By ignition they are not completely decomposed, but may thereby be converted into *pyrophosphates* or *metaphosphates*.

Behaviour of Solution of Phosphates with Reagents.

Chloride of barium and *chloride of calcium* produce, in solutions of neutral or basic phosphates, a white precipitate, soluble in *nitric, hydrochloric*, and *acetic* acids. *Phosphate of lime* ($2\,CaO, PO_5$) is slightly soluble in solution of sal-ammoniac.

Nitrate of silver produces, in solutions of neutral and basic phosphates, a lemon yellow precipitate ($3\,AgO, PO_5$), soluble in nitric acid and in ammonia, and sparingly soluble in acetic acid. Common phosphate of soda, after having been ignited, produces, with nitrate of silver, a curdy white precipitate, ($2\,AgO, PO_5$). The fluid in which the yellow precipitate is suspended has an acid reaction in consequence of the presence of free nitric acid, thus:—

$$3\,(AgO, NO_5) + (HO, 2\,NaO, PO_5) = (3\,AgO, PO_5) + 2\,(NaO, NO_5) + HO, NO_5.$$

The fluid in which the white precipitate is suspended is neutral, there being no excess of nitric acid, thus:—

$$2\,(AgO, NO_5) + 2\,NaO, PO_5 = 2\,AgO, PO_5 + 2\,(NaO, NO_5).$$

Acetate of lead produces a white precipitate, very sparingly soluble in acetic acid, but readily so in nitric acid. This precipitate, when fused on charcoal in the outer blowpipe flame, forms a bead, which crystallizes on cooling.

Sesquichloride of iron produces, in solutions of alkaline phosphates, a yellowish white gelatinous precipitate, insoluble in acetic acid. If to the solution of a phosphate of an alkaline earth in hydrochloric acid sesquichloride of iron be added in excess, and then ammonia in slight excess, a brown precipitate is produced, consisting of a mixture of *phosphate of sesquioxide* and *hydrated sesquioxide of iron*. The latter may be dissolved in acetic acid; and the former, after being well washed, is decomposed by digestion with hydrosulphuret of ammonia into *sulphuret of iron* and *phosphate of ammonia*. The whole of the phosphoric acid is thus brought into the form of a soluble salt.

Sulphate of magnesia and *soluble magnesian salts* produce a crystalline precipitate, which makes its appearance only gradually; but in the presence of ammonia a crystalline precipitate of basic phosphate of magnesia and ammonia ($2\,MgO, NH_4O, PO_5$) immediately subsides, and is favoured by agitation. This precipitate is insoluble in ammonia and in ammoniacal salts, but is soluble in free acids.

Before the blowpipe, phosphoric acid is detected by the following method of Berzelius:—Dissolve the subject of examination in boracic acid, upon charcoal, in the oxidating flame; introduce into the melted bead a piece of fine iron wire, and expose the whole to a strong reducing flame. The iron oxidizes at the expense of the phosphoric acid, and *borate* and *phosphate of iron* are produced.

The latter fuses in a strong red heat. When cold, the glass is removed from the charcoal, and broken into pieces on an anvil, between folds of paper. A globular metallic button of *magnetic phosphuret of iron* is thus produced. This operation requires address on the part of the operator. To detect phosphoric acid in an aluminous compound, Berzelius gives the following method: The substance, pulverized in an agate mortar, is rubbed with a mixture of six parts of soda and one and a half of silica, and the mass fused on charcoal in the oxidating flame. The fused residuum is boiled with water, in which phosphate and the excess of carbonate of soda dissolves, leaving the alumina in combination with silicic acid. The phosphoric acid is detected in aqueous solution as above directed.

PHOSPHOROUS ACID (PO_3).—*General Characters:* In its anhydrous state it is a white, but not crystalline powder. Its hydrate may be obtained in the form of deliquescent crystals, by evaporating the aqueous solution obtained by acting on *sesquichloride of phosphorus* by water. It slowly absorbs oxygen from the air, becoming converted into phosphoric acid. At an elevated temperature it is decomposed, phosphuretted hydrogen being formed, which inflames on the approach of a burning body, fumes of phosphoric acid making their appearance. The alkaline *phosphates* are soluble in water, and are powerful deoxidizing agents. They reduce solutions of *gold* and *silver*, and salts of *copper* and *mercury*, passing into *phosphates.* Heat also converts them into *phosphates*, hydrogen gas being evolved, which burns with a blue flame without producing any fumes of phosphoric acid. *Hypophosphites* are distinguished from *phosphites* from their giving rise to a spontaneously inflammable phosphuretted hydrogen when strongly heated, fumes of phosphoric acid being formed. All the *hypophosphites* are soluble in water.

BORACIC ACID (BO_3).—*General Characters:* This acid crystallizes, out of its aqueous solution, in brilliant scales, which are greasy to the touch. It has no smell, and a very faint acid taste. It is sparingly soluble in water. In the presence of aqueous vapours it sublimes easily, but alone it is perfectly fixed at a red heat, at which, however, it fuses into a colourless, transparent, brittle glass. It dissolves in alcohol, to the flame of which it communicates a green tinge, a property which is characteristic of this acid. It volatilizes with the vapour of alcohol as with that of water. The alkaline borates are soluble in water, but the borates of the earths and metallic oxides are almost insoluble, though they dissolve readily in acids and ammoniacal salts. They are all very fusible, and promote the fusion of other bodies when mixed with them; hence their uses as fluxes. Free boracic acid reddens turmeric paper like an alkali.

Behaviour of Solutions of Borates with Reagents.

Chloride of barium produces a white precipitate (BaO, BO_3), soluble in acids and in ammoniacal salts, and in a large quantity of water.

Nitrate of silver, in concentrated solutions, produces a white precipitate, soluble in ammonia, and in dilute nitric acid.

Chloride of calcium produces a white precipitate, soluble in acids and in ammonia, and in a large quantity of water.

Acetate of lead produces a white precipitate, soluble in acids.

Nitrate of suboxide of mercury produces an olive-brown precipitate, soluble in nitric acid and in ammonia.

Hydrochloric and *sulphuric acids* separate *boracic* acid from solutions of borates, at a boiling temperature, in the form of crystalline scales.

If a pulverized borate be moistened in a porcelain capsule with a few drops of sulphuric acid, and covered with alcohol, warmed and inflamed, the flame will have a green tinge, most perceptible at its borders. The presence of *chlorides* interferes with this test, in some measure, in consequence of the formation of hydrochloric ether; the flame, however, in this case, has a decided *blue* tinge.

Borate of soda ($2NaO, BO_3$) precipitates solution of sesquichloride of iron. The precipitate dissolves on heating to a dark red liquid, which might be mistaken for the reaction produced between *acetic acid* and the same reagent if the solutions are not very concentrated, only a darker colour is observable, and no precipitate.

Before the blowpipe, the following method of detecting boracic acid in salts and minerals has been recommended by *Turner:* Knead into a paste, with a few drops of water, a mixture of the finely divided substance, with 4½ parts of *bisulphate of potassa*, and 1 of powdered *fluor spar*, and fuse the mass on the ring of the platinum wire. At the apex of the blue flame *fluoboric acid* gas is liberated, which communicates to the outer flame a pure green colour.

Silicic Acid (SiO_3).—*General Characters:* Of this acid there are two isomeric modifications; one is insoluble in water, and resists the action of all acids but *hydrofluoric*. It is a white, tasteless powder, gritty between the teeth, and infusible at the strongest heat of a furnace, but fusing before a blowpipe flame urged with oxygen, into a limpid, colourless liquid. This form of silicic acid exists nearly in a state of purity in *rock crystal* and in *white quartz*. By fusion with a mixture of carbonate of potassa, or a mixture of carbonate of potassa and carbonate of soda, all silicious minerals are decomposed, basic alkaline silicates being formed, which are soluble in water, and from which acids separate silicic acid in its soluble modification; but, by drying, it again returns to the insoluble state. The soluble variety of silicic acid is obtained in the form of a gelatinous mass, by passing the gas obtained by heating together a mixture of powdered fluor spar and quartz, with sulphuric acid, into water. In this state water dissolves a small quantity, without, however, acquiring any taste, or the property of reddening litmus paper. By evaporation, the acid is obtained as a white, earthy, but not crystalline mass, which may again be dissolved in water; but, if a strong mineral acid be added to the water during its evaporation, the dry silicic acid is no longer soluble in water. Gelatinous silicic acid is soluble, to a considerable extent, in acids. No precipitation is therefore observed on adding hydrochloric acid to a dilute solution of an alkaline silicate, until the liquid has been concentrated by evaporation. In most silicious minerals, silicic acid exists in its insoluble form. There are, however, a number of native, hydrated silicates, denominated *zeolites*, which contain silicic acid in its soluble form, and which are, therefore, decomposed by concentrated hydrochloric acid even in the cold, forming a gelatinous mass soluble in water. There are other minerals which are only dissolved in hydrochloric acid by prolonged digestion, the silicic acid separating as a flaky powder, and not as a jelly. At ordinary temperatures, silicic acid is the weakest of the acids, dissolving in a boiling solution of the fixed alkaline carbonates, without expelling their carbonic acid, but at high temperatures it is capable of expelling all the volatile acids, not even excepting the sulphuric acid, from their combinations.

Diluted solutions of alkaline silicates, when nearly neutralized by nitric acid, are precipitated by most heavy oxides, and by the salts of the alkaline earths and by ammonia. The first step, therefore, in analyzing a mineral containing silicic acid, is to convert the silicic acid from its soluble to its insoluble condition, which is done by evaporating the hydrochloric solution to perfect dryness, and then dissolving out with acid the basic metallic oxides.

Before the Blowpipe, silicic acid is recognised by means of microcosmic salt and soda; the examination is generally performed on a platinum wire. The microcosmic salt is first fused into a bead, the silicate added, and the whole treated in the oxidating flame; the glass bead, while hot, is clear, and the separated silicic acid floats through it in a collected state; the bases combine with the free acid in the flux. Silicic acid with soda, on charcoal, gives a clear bead, carbonic acid escaping with effervescence; even when a small quantity of an earth is present, it still fuses to a clear glass. This is the case with *felspar;* but, if the silicate contain a large proportion of a non-alkaline base, the compound becomes infusible.

Hydrofluoric Acid (HF).—This acid is very volatile and corrosive, giving off dense fumes in the air; it is distinguished from all other acids by its property of dissolving the insoluble form of silicic acid; it cannot therefore be preserved in glass vessels. It combines with water with the same energy as sulphuric acid. It decomposes metallic oxides, giving rise to water and *metallic fluorides*. Towards metals it behaves in general in the same manner as the oxyacids, and it dissolves copper and silver gradually with the disengagement of hydrogen; in its concentrated state it acts on many substances with great energy, dissolving some bodies which are not acted on even by boiling aqua regia, such as *silicic, titanic, molybdic*, and *tungstic acids*. The concentrated acid acts with extreme violence on the skin, causing painful ulcers very difficult to heal. The alkaline fluorides are soluble in water, as are also the fluorides of *aluminum*, *tin*, *iron*, and *mercury*. The fluorides of the metals of the alkaline earths are almost insoluble, as are also the fluorides of *copper*, *lead*, and *zinc*, though they dissolve more or less readily in hydrofluoric acid. The greater number of the fluorides bear ignition without being decomposed; the insoluble fluorides are decomposed by fusion with alkaline carbonates.

Behaviour of Solutions of Fluorides with Reagents.

Chloride of barium produces a white precipitate soluble in hydrochloric acid.

Chloride of calcium produces a gelatinous and very transparent precipitate, almost insoluble in free acids, even in hydrofluoric acid: and in alkalies in the cold the addition of ammonia causes the complete subsidence of the precipitate $(\mathrm{Ca\,Fl})$.

Acetate of lead occasions a white precipitate soluble in hydrochloric acid.

Sulphuric acid at the boiling temperature decomposes all fluorides with the disengagement of hydrofluoric acid. The experiment is made by tracing lines on a plate of glass, covered with bees' wax, with a wooden point, so as to expose the glass; and laying the plate on a platinum crucible containing the pulverized fluoride and concentrated sulphuric acid, a moderate heat, insufficient to melt the wax, is applied to the crucible for about a quarter of an hour. The exposed lines are found etched, on the removal of the wax, which is effected by spirits of turpentine.

When a fluoride is mixed with a substance containing silicic acid, such as pounded glass, and heated together with concentrated sulphuric acid, fluosilicic acid is formed thus:

$$\mathrm{SiO_3 + 3\,CaF + 3SO_3 = SiF_3, + 3CaO,SO_3.}$$

This acid is disengaged as a gas which fumes strongly in a moist atmosphere, and when brought into contact with water is decomposed, with the separation of silicic acid in its gelatinous form, and the formation of *hydrofluosilicic acid* thus:—

$$\mathrm{3(SiF_3) + 3HO = SiO_3 + (3HF + 2SiF_3).}$$

One equivalent of every three equivalents of fluosilicic acid (or fluoride of silicon) combines with three equivalents of water, giving rise to one equivalent of silicic acid, which is precipitated, and three equivalents of hydrofluoric acid, which combines with the two remaining equivalents of fluosilicic acid to form hydrofluosilicic acid. This interesting reaction is observed by heating the materials in a test tube, and conveying the gas, by a bent tube, into another test tube containing water.

By cautiously fusing in a test tube equal parts of a finely pulverized fluoride, and bisulphate of potassa, hydrofluoric acid is rendered evident by the roughening and loss of transparency of the upper part of the tube.

CHROMIC ACID $(\mathrm{CrO_3})$.—This acid is obtained by the decomposition of bichromate of potassa by sulphuric acid, in the form of brilliant crimson needles, which absorb moisture from the air and pass into a deep brown viscous fluid; evaporated to dryness it is, while hot, black, but on cooling it becomes deep red; it has no smell; its taste is strongly acid, but not metallic; it tinges the skin yellow. It is soluble in alcohol; but the solution decomposes by the action of heat and light, an ether being formed, and hydrated oxide of chromium precipitated. When alcohol is dropped on the concentrated acid, it takes fire, and the acid becomes incandescent; an aqueous solution of chromic acid is gradually decomposed by the light of the sun, oxygen gas being liberated. All its salts are coloured yellow or red; the alkaline chromates and bichromates are soluble in water; most of the other salts of chromic acid are insoluble in water, though they are all soluble in nitric acid.

Behaviour of Solutions of Chromates with Reagents.

Chloride of barium produces a pale yellow precipitate soluble in nitric and hydrochloric acids.

Acetate of lead produces a yellow precipitate soluble in potassa, and sparingly soluble in nitric acid.

Nitrate of silver produces a dark purple precipitate, soluble in nitric acid, and in ammonia.

Subnitrate of mercury produces a brick red precipitate.

Sulphuretted hydrogen in neutral solutions reduces the chromic acid with the precipitation of sulphur, and oxide of chromium; *sulphuric* acid, and *water*, are at the same time formed, and the fluid becomes green: in the presence of a free acid the oxide of chromium is dissolved, at least in part, and sulphur precipitated.

Sulphurous acid likewise reduces chromic acid, *sulphuric* and *hyposulphuric* acids being formed.

Oxalic, tartaric, and *citric acids* reduce the acid to sesquioxide of chromium, carbonic acid being evolved.

Hydrochloric acid and *alcohol*, or *zinc*, on being boiled with solution of a chromate, reduce the acid, the fluid becoming green.

Insoluble chromates are decomposed by fusion with alkaline carbonates, alkaline chromates being formed.

II.—*Acids precipitated from their Neutral Solutions by Nitrate of Silver.*

HYDROCHLORIC ACID (HCl).—This acid is a transparent colourless gas, fuming strongly in a moist atmosphere: it has a pungent suffocating smell, and a strongly acid taste. At a low temperature, and under a pressure of about eighteen atmospheres, it becomes liquid: it is decomposed by those metals which decompose water, and by substances which combine with chlorine: it is also decomposed by metallic oxides. It is absorbed with the greatest avidity by water, the saturated solution forming what is called concentrated hydrochloric acid. This solution is colourless and strongly acid; the yellow tinge which the acid frequently has arises from impurities. The greater number of the chlorides are soluble in water; the principal exceptions are those of *lead* and *silver*, and *protochloride of mercury:* some chlorides volatilize without decomposition, as the chlorides of *tin, antimony*, and *arsenic:* some are fixed, and others undergo decomposition by heat.

Behaviour of Solutions of Chlorides with Reagents.

Nitrate of silver produces a white curdy precipitate even in highly dilute solutions, becoming violet-coloured, and finally black, when exposed to the light: it is quite insoluble in nitric acid, but readily soluble in ammonia: it fuses without decomposition, forming, when cold, a tough horny mass, and is reduced by hydrogen, and by fusion with carbonate of soda, or with resin.

Nitrate of suboxide of mercury produces a white precipitate (calomel, Hg_2Cl), becoming black when brought into contact with caustic alkalies.

Acetate of lead produces a white precipitate soluble in boiling water, less so in *nitric* and *hydrochloric* acids, and not altered by ammonia.

By heating a soluble chloride with peroxide of manganese and sulphuric acid, chlorine gas is evolved thus:—

$$NaCl + MnO_2 + 2SO_3 = NaO,SO_3 + MnO,SO_3 + Cl.$$

On heating a chloride with *chromate of potassa* and sulphuric acid, a brownish red gas is disengaged, which condenses into a blood red liquid, *chromate of chloride of chromium* ($CrCl_3$, $2\,CrO_3$), thus:—

$$3KO,CrO_3 + 3\,NaCl + 6HO,SO_3 = CrCl_3,2CrO_3 + 3KO,SO_3 + 3NaO,SO_3 + 6HO.$$

On the addition of ammonia a yellow liquid (chromate of ammonia) is formed, which becomes red on the addition of an acid, bichromate of ammonia being formed.

Before the blowpipe chlorides are thus detected: Dissolve oxide of copper in microcosmic salt on platinum wire, until a diaphanous bead is obtained in the oxidizing flame; the substance under examination is now added and heated: if chlorine be present, the assay will be surrounded by a beautiful blue-coloured flame inclining to purple, which after some time disappears, but can be reproduced by adding a fresh supply of the sample.

For the detection of chlorine in a compound soluble in water, the following method is also given by *Berzelius:*—A small quantity of sulphate of copper or iron is dissolved; a few drops of the solution placed upon a bright piece of silver, and the chlorine compound added, the silver will be blackened.

HYDROBROMIC ACID (HBr). — *General Characters:* It very much resembles hydrochloric acid gas; like it, it fumes strongly when allowed to escape into a moist atmosphere, and it acts in a similar manner with metals and metallic oxides: it dissolves freely in water, and the concentrated solution, which is denser than that of hydrochloric acid gas, is fuming: chlorine expels from it bromine, hydrochloric acid being formed. The aqueous solution dissolves a large quantity of bromine, and acquires a deep red colour: there is also a strong analogy between the bromides and chlorides.

Behaviour of Solutions of Bromides with Reagents.

Nitrate of silver produces a yellowish white precipitate, insoluble in nitric acid and soluble with difficulty in ammonia.

Nitrate of suboxide of mercury produces a yellowish white precipitate.

Acetate of lead produces a white precipitate insoluble in water, by which it is distinguished from *chloride of lead.*

Nitric acid, when heated with solution of a bromide, decomposes it, evolving bromine, which colours the solution yellowish red; when heated with a solid bromide, yellowish red vapours are produced, having an odour resembling that of chlorine; these vapours condense into red drops in the upper part of the test tube.

Concentrated sulphuric acid also decomposes bromides, with the separation of *bromine* and *sulphurous acid*, thus :—

$$KBr + 2\ SO_3 = KO,\ SO_3 + SO_2 + Br.$$

Dilute sulphuric acid decomposes bromides with the disengagement of hydrobromic acid, thus :—

$$KBr + HO,\ SO_3 = KO,\ SO_3 + HBr.$$

If a stream of chlorine be passed through a solution of a bromide, and the solution agitated with *ether*, the latter will dissolve all the evolved bromine, and assume a yellow colour: if the ethereal solution be removed with a pipette, and agitated with solution of potassa, the yellow tint will vanish, the bromine having passed into *bromide of potassium and bromate of potassa*, thus :—

$$6\ Br + 6\ KO = 5\ KBr + KO,\ BrO_5.$$

If this solution be evaporated to dryness, and ignited, the bromate is decomposed with evolution of oxygen, and bromide of potassium remains: in order to detect bromine in this residue, it is heated in a small retort, with peroxide of manganese and sulphuric acid, and the vapours received in a small receiver containing *starch paste*, which becomes tinged orange-yellow, the colour vanishing by exposure to the air.

On heating a bromide with *chromate of potassa and sulphuric acid*, a brownish red gas is produced, as in the case of a chloride: this gas, however, is *bromine*, and the colour vanishes on the addition of ammonia; this reaction serves, therefore, to distinguish between bromides and chlorides, and for detecting the presence of the latter in the former.

HYDRIODIC ACID (IH).—This acid gas, likewise, resembles in its properties hydrochloric acid: it is absorbed rapidly, and in large quantities, by water, the solution being colourless and fuming: there is also a strong analogy between the compounds of *iodine* and those of *bromine* and *chlorine.*

Behaviour of Solution of Iodides with Reagents.

Nitrate of silver produces a yellowish white precipitate, which blackens by exposure to the light, is insoluble in dilute nitric acid, and very sparingly soluble in ammonia.

Nitrate of suboxide of mercury produces a yellowish green precipitate.

Chloride of mercury produces a beautiful scarlet precipitate.

Acetate of lead produces an orange yellow precipitate, soluble in hot water, and in nitric acid, and crystallizing out of its solution in brilliant golden-coloured scales.

Protochloride of palladium produces a black precipitate in solutions of alkaline iodides: no precipitate is afforded by this reagent in solutions of bromides.

An aqueous solution of one part of crystallized sulphate of copper, and two and a half of protosulphate of iron, produce a dingy white precipitate ($Cu_2\ I$): this mixture has no effect in solutions of *chlorides* and *bromides.*

Chlorine, nitric acid, concentrated sulphuric acid and *peroxide of manganese* eliminate iodine from solutions of iodides, the solutions becoming coloured; and, if the solution is concentrated, *iodine* separates as a black precipitate: on applying heat, the characteristic violet vapours of iodine make their appearance: with excess of chlorine, a colourless *chloride* of iodine is formed.

With *starch paste* free iodine forms a blue compound, and this reagent serves to detect minute traces of iodine in insoluble as well as in soluble compounds of that element. The substance under examination is mixed in a retort with concentrated *nitric acid*, and a strip of *white cotton cloth*, moistened with solution of starch, suspended from the stopper; in a few hours the cloth will become coloured blue if the most minute trace of iodine be present: nitric acid is better as an oxidizing agent than chlorine, because of the formation of the colourless *chloride of iodine* above referred to. The blue colour of the iodide of starch disappears by heat, and by the action of certain deoxidizing agents.

If a solid iodide be heated with concentrated sulphuric acid and peroxide of manganese, violet vapours of iodine will make their appearance.

Before the blowpipe, metallic iodides, when treated with cupriferous microcosmic salt, impart a beautiful and deep green colour to the flame.

Bromic acid (HO, BO_5).—When concentrated, it is very sour but not caustic: it has very little odour: it first reddens, and then discolours blue litmus paper; *sulphurous, phosphorous* acids, and all the hydracids decompose it, liberating bromine: most of the bromates are soluble in water, and are converted by ignition into bromides, with evolution of oxygen: they are decomposed with violent deflagration when heated with combustible substances, such as *carbon, sulphur*, and *phosphorus*. These mixtures likewise detonate violently when moistened with a drop of concentrated sulphuric acid. Bromates, when treated with concentrated sulphuric and other oxygen acids in the cold, evolve oxygen and red vapours of bromine; they are likewise reduced by sulphuretted hydrogen with separation of sulphur.

Behaviour of Solutions of Bromates with Reagents.

Nitrate of suboxide of mercury produces a light yellow precipitate, soluble in nitric acid.

Acetate of lead produces a white precipitate, soluble in much water.

Nitrate of silver produces a white precipitate, soluble in ammonia, but soluble with difficulty in dilute nitric acid.

Sulphuretted hydrogen reduces bromates to bromides; *sulphuric acid* being formed and sulphur separated.

Sulphurous acid reduces bromates to bromides, sulphuric acid being formed.

Iodic acid (HO, IO_5).—The aqueous solution of this acid is, when concentrated, very sour: it first reddens, and then destroys the colour of litmus paper: it oxidizes all metals but *gold* and *platina*, and detonates violently when heated with combustible substances: with sulphuric, nitric, and phosphoric acid, it forms crystalline compounds, and when mixed with vegetable acids a decomposition of both takes place; *carbonic acid* being liberated, and *iodine* precipitated. The iodates are mostly insoluble in water, the neutral alkaline iodates are soluble.

Behaviour of Solutions of Iodates with Reagents.

Nitrate of silver produces a white precipitate, soluble in nitric acid and in ammonia.

Chloride of barium, chloride of calcium, and *acetate of lead*, give white precipitates, soluble in nitric acid. Iodates, when heated alone, are decomposed into iodides and oxygen; they deflagrate when heated with combustibles: they are decomposed by *protochloride of tin; binoxide of tin, sulphuric acid*, and *iodine* being separated; the latter may be made evident by adding starch paste.

Sulphuretted hydrogen reduces iodates to iodides, *sulphuric* acid and *water* being formed, and *iodine* separated.

Hydrocyanic acid (HCy).—In its pure, anhydrous state, this acid possesses the following properties: it is colourless, inflammable, very volatile, and possessing a strong odour analogous to that of bitter almonds: its taste is at first cool, then burning and disagreeable. Its specific gravity is 0.6957 at 66°, it boils at 80°, it volatilizes rapidly in the air, producing a degree of cold sufficient (if it be not perfectly anhydrous) to cause it to assume a solid form: it is feebly acid to test paper: it is the most energetic poison known, one drop being sufficient to destroy an animal of considerable size. It is rapidly decomposed, even in close vessels, becoming darker and darker in colour, and eventually quite black: a trace of sulphuric acid prevents this decomposition from taking place: strong acids cause its elements so to arrange themselves with the elements of water as to produce *formic* acid and *ammonia;* thus

$$\underbrace{H, C_2N}_{\text{Hydrocyanic acid.}} + 4HO = \underbrace{NH_4, O, C_2H\,O_3}_{\text{Formiate of ammonia.}}$$

by distillation the formic acid may be separated, the ammonia remaining in combination with the acid which occasioned the decomposition.

The alkalies are reduced by hydrocyanic acid, their metallic radicals combining with cyanogen, and water being formed, thus:—

$$KO + HCy = KCy + HO.$$

the metallic cyanides thus formed have an alkaline reaction; they are decomposed gradually when dissolved in water, rapidly when boiled, and instantly in contact with an acid, the result of the decomposition being *formiate* of the oxide of the metallic base and ammonia. *Cyanide of potassium* and *cyanide of sodium* may, however, be heated to redness out of contact of air, without suffering decomposition; but in contact with oxides of *tin*, *lead*, *copper*, and many other metals, they are converted into cyanates, the metals being reduced thus:—

$$KCy + 2\,PbO = KO,CyO + 2\,Pb.$$

The greater number of the metallic cyanides are insoluble in water: they comport themselves differently under the influence of heat, some being resolved into the metal and cyanogen, as is the case with *cyanide of mercury*, and others into carburets and nitrogen: the compounds of cyanogen with gold, silver, and other heavy metals, are not decomposed by dilute, and with difficulty with concentrated nitric acid; hydrochloric acid and sulphuretted hydrogen, however, decompose them easily and completely. The cyanides of *iron*, *cobalt*, *manganese*, and *chromium*, when brought into contact with alkaline cyanides, unite with their cyanogen, forming peculiar salt radicals, in which the presence of the heavy metal cannot be detected by the usual tests.

Behaviour of Solutions of Cyanides with Reagents.

Nitrate of silver produces a white curdy precipitate (Ag Cy) insoluble in dilute nitric acid, and sparingly soluble in ammonia, easily soluble in cyanide of potassium, and leaving pure silver when ignited; when moistened with hydrochloric acid, hydrocyanic acid is disengaged.

Acetate of lead produces a white precipitate (PbCy).

Subnitrate of mercury produces, in hydrocyanic acid, a gray precipitate of metallic mercury, cyanide of mercury remaining in solution, thus:—

$$Hg_2O + HCy = HgCy + Hg + HO.$$

Oxide of mercury dissolves freely in hydrocyanic acid, and alkalies occasion no precipitate in the solution; in no other alkaline fluid can oxide of mercury be held in solution; this reaction serves therefore as a test of the presence of hydrocyanic acid. In the presence of hydrochloric acid, *ammonia* produces a precipitate.

A solution of *protosulphate of iron*, which has been partially oxidized by exposure to the air (magnetic oxide of iron), occasions the formation of *Prussian blue* in solution of an alkaline hydrocyanate containing free hydrochloric acid; this reaction forms an excellent test for hydrocyanic acid, but it is essential that an alkali should be present, as also hydrochloric acid, to dissolve any oxide and sesquioxide of iron that may have been precipitated by the alkali together with the blue compound.

Protosulphate of iron produces, in solutions of alkaline *ferrocyanides*, a pale blue precipitate.

Sulphate of copper produces a chocolate brown precipitate.

Sesquichloride of iron produces, in solutions of alkaline *ferricyanides*, a deep blue precipitate.

Insoluble *ferro-* and *ferri-cyanides* are decomposed by fusion with alkaline carbonates, soluble alkaline *ferro-* and *ferri-cyanides* being formed. By distilling a ferrocyanide with dilute sulphuric acid, hydrocyanic acid is produced, and by heating it with a great excess of concentrated sulphuric acid, *carbonic* oxide is formed by the following reaction:—

$$K_2FeC_6N_3 + 9\,HO = \\ 6\,CO + 2\,KO + FeO + 3NH_3.$$

One equivalent of ferrocyanide of potassium and nine equivalents of water from the oil of vitriol and the water of crystallization of the ferrocyanide, give rise to six equivalents of carbonic oxide, two equivalents of potassa, one of protoxide of iron, and three of ammonia; the sulphuric acid, iron, potassa, and ammonia arrange themselves into a crystalline anhydrous iron alum, having the following composition (Fownes):—

$$2\,(Fe_2O_3 + 3SO_3) + \begin{matrix}KO,SO_3\\ NH_4O,SO_3.\end{matrix}$$

The most delicate and valuable test of the presence of hydrocyanic acid that has hitherto been proposed, is that of *Professor Liebig*, and is dependent on the fact that the higher sulphurets of ammonium are instantly deprived, by cyanide of ammonium, of the excess of sulphur they contain above the *monosulphuret, sulphocyanide of ammonium* (NH_4, CyS_2) being formed, which produces, with persalts of iron, a very deep blood-red colour. Mr. Alfred Taylor recommends the following method of applying this test :—Place the diluted hydrocyanic acid in a watch-glass, and invert over it another watch-glass, holding in its centre one drop of hydrosulphuret of ammonia containing sulphur in excess ; there is no apparent change in the hydrosulphuret, but if the watch-glass be removed after the lapse of from half a minute to ten minutes, according to the quantity of hydrocyanic acid present, sulphocyanide of ammonium will be obtained on gently heating the drop of hydrosulphuret and evaporating it to dryness. The addition of a drop of a solution of a persalt of iron to the dried residue brings out the blood-red colour instantly, which is intense in proportion to the quantity of sulphocyanide present ; the warmth of the hand may be employed to expedite the evolution of the vapour. This test is even more delicate and expeditious than the nitrate of silver test, in which the vapours are received in a solution of that salt, and will, according to Taylor, detect in five minutes hydrocyanic acid not exceeding $\frac{1}{713}$ of a grain in ten drops of a liquid.

Hydrosulphuric acid or sulphuretted hydrogen (HS).—This acid is a colourless gas, which under strong pressure becomes liquid ; it has a highly offensive odour resembling that of putrid eggs ; its taste is acid, astringent, and bitter ; it is inflammable, burning with a blue flame, and disengaging sulphurous acid ; it explodes violently when mixed with oxygen or atmospheric air and ignited ; when mixed with chlorine, sulphur is deposited and hydrochloric acid formed ; it is highly deleterious when inspired, even when mixed with a large quantity of air ; it is absorbed by water, which acquires its peculiar smell and a nauseous sweet taste ; the solution reddens litmus paper, and decomposes by exposure to the air, sulphur being deposited ; most metallic oxides are decomposed by sulphuretted hydrogen, *sulphuret of the metals* and *water* being formed. The *alkalies* and *alkaline earths*, and the oxides of *chromium*, *tantalum*, and *titanium*, do not exchange their oxygen for sulphur in the moist way. The sulphurets of the metals of the alkalies, and the alkaline earths, are soluble in water; they are decomposed by dilute mineral acids with the evolution of sulphuretted hydrogen, which is readily recognised by its odour and by its action on paper moistened with solution of lead. The sulphurets of the metals of the fourth group are insoluble in water, but are likewise decomposed by dilute mineral acids; all the other metallic sulphurets but *sulphuret of mercury* are decomposed by strong nitric acid, sulphuric acid being formed and sulphur generally separated ; aqua regia effects their decomposition more easily, it also dissolves sulphuret of mercury. As some metallic oxides, when dissolved in acids, are precipitated by sulphuretted hydrogen, while others are not, and as the precipitated sulphurets differ in colour and in other properties, sulphuretted hydrogen becomes a valuable reagent for detecting and separating metallic compounds. Most metallic sulphurets are decomposed by heat with access of air, evolving sulphurous acid ; the alkaline sulphurets thus treated are converted into sulphates.

When sulphuretted hydrogen, or a solution of an alkaline or earthy sulphuret, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates are formed ; either of these salts are therefore certain tests of the presence of this acid in the gaseous state ; a strip of paper moistened with solution of subacetate of lead is generally employed.

III.—Acids not precipitated by either *Chloride of Barium* or *Nitrate of Silver*.

Nitric acid (NO_5).—*General Characters:* This acid, which has never been obtained in an anhydrous state, forms with water, when pure, a colourless solution, which when concentrated fumes in the air ; it is very easily decomposed, mere exposure to the light of the sun causing it to become yellow and disengage oxygen gas; it is one of the strongest of the acids, and constitutes a reagent of the greatest value, from the facility with which it parts with a portion of its oxygen. The yellow fuming acid, containing nitrous acid, possesses generally the greatest oxidating power; the most highly concentrated acid is in many cases without action on bodies on which a diluted acid acts with violence ; thus the concentrated nitric acid does not attack *lead* or *tin*, while the addition of a small quantity of water causes an energetic action to take place. Organic substances are for the most part resolved by the concentrated acid into carbonic acid and water, the action in many cases being sufficiently energetic to cause them to take fire; the diluted acid generally converts them into oxalic, malic, and carbonic acids. Nearly all metallic oxides are dissolved by nitric acid, the exceptions are oxides of *tin* and *antimony, tellurous* and *tungstic acids.* All the neutral salts of nitric acid are soluble in water, and all are decomposed at a strong red heat, the nature of the products depending on the nature of the base; thus the alkaline nitrates yield oxygen and nitrogen, while other metallic nitrates give oxygen and an inferior oxide of nitrogen. When nitrates are ignited in the presence of other substances susceptible of oxidation, they take the liberated oxygen, and in some cases the combination is attended by deflagration; thus a nitrate thrown on red-hot charcoal causes the latter to throw off brilliant scintillations, a mixture of a nitrate with cyanide of potassium deflagrates vividly when heated on a platinum plate, and phosphorus and sulphur brought into contact with a heated nitrate occasion a violent detonation.

Methods of Detecting Nitric Acid in Solutions of the Nitrates.

Hydrochloric acid, added in excess to solution of a nitrate, gives it the property of dissolving gold leaf, in consequence of the following reaction:—

$$KO,NO_5 + 2\,HCl = NO_4 + KCl + 2\,HO + Cl.$$

One equivalent of nitrate of potassa, and two of hydrochloric acid, give rise to one equivalent of hyponitric acid, one of chloride of potassium, two of water, and free chlorine: the solubility of gold leaf in a liquid which has been heated with hydrochloric acid, is a certain proof therefore of the presence of nitric acid.

When a solution containing a nitrate is mixed with half its volume of concentrated sulphuric acid, allowed to cool, and a crystal of *protosulphate of iron* added, the liquid round the crystal assumes a reddish brown colour in consequence of the following reaction:—

$$10(FeO,SO_3) + 4\,SO_3 + KO,NO_5 = 3\,(Fe_2O_3,3SO_3) + KO,SO_3 + 4(FeO,SO_3)\,NO_2.$$

Ten equivalents of protosulphate of iron, four equivalents of sulphuric acid, and one of nitre, give rise to three equivalents of persulphate of iron, one of sulphate of potassa, and four of protosulphate of iron in a peculiar state of combination with nitric oxide: as the latter is very unstable, and is decomposed by heat, nitric oxide being set free, it is necessary that the liquid should be allowed to cool before making the experiment.

When a nitrate is heated in a test tube, with copper filings and concentrated sulphuric acid, nitric oxide gas is set free, which, combining with the oxygen of the air in the tube, forms ruddy fumes of nitrous acid.

When a solution of a nitrate is mixed with sulphuric acid, and a sufficient quantity of a solution of indigo in sulphuric acid added, to give it a blue colour, and the mixture heated, the colour is either discharged or turned yellow in consequence of the oxidation of the indigo at the expense of the nitric acid set free from the nitrate. This test is not, however, decisive, as other substances, especially free chlorine, cause the same discoloration.

The following test was proposed by *Runge*. Metallic zinc is dissolved in mercury in such a proportion that the fluidity of the mercury is only slightly diminished. A portion of this amalgam is placed in a little porcelain capsule, and barely covered with a neutral solution of protochloride of iron: a small piece of the nitrate is then laid upon the mercury in the solution, and after some time a black stain is produced upon the mercury, just at the spot where the nitrate had been placed.

NITROUS ACID (NO_3).—The properties of this acid in a state of purity are not well known. It is a very volatile liquid, which, at a low temperature, is colourless, but at ordinary temperatures it is a gas of a dark yellowish red colour; when brought into contact with water, it is decomposed, being resolved into nitric acid and nitric oxide, thus:—

$$3\,NO_3 = NO_5 + 2\,NO_2.$$

Almost all its salts are soluble in water: they very much resemble the nitrates in their properties, from which they may thus be distinguished:—

When submitted to gentle distillation, *nitrites* expel nitric oxide gas, the salt in solution being converted into a nitrate, and by boiling they are rapidly converted into solutions of nitrates.

When heated with concentrated sulphuric acid, they evolve nitric oxide gas, nitric acid remaining in solution; nitrites reduce *chloride of gold* and *nitrate of mercury* to the metallic state.

When treated with hydrochloric acid, solutions of *nitrites* do not acquire the property of dissolving gold leaf.

CHLORIC ACID (HO, ClO_5).—When concentrated, it is a yellowish oily-looking liquid, very sour, reddening, and finally bleaching, litmus paper; it is very unstable, being resolved by heat into *perchloric acid*, *oxygen*, and *chlorine:* it converts sulphurous into sulphuric acid, and is at the same time itself reduced to chlorine: it also converts sulphuretted hydrogen into sulphuric acid, sulphur, and water: all its compounds, with bases, are soluble in water: they do not possess bleaching properties, but when mixed with sulphuric acid they are decomposed; perchloric acid, chlorine, hypochloric acid and oxygen being formed, the solution becomes yellow, and it then possesses the power of destroying the colour of blue vegetable infusions, and by the application of heat decolourizes solution of indigo. The alkaline *chlorates*, when ignited, disengage oxygen, and become converted into *chlorides:* most other chlorates are resolved by heat into metallic oxides, and a mixture of oxygen and chlorine. When triturated with sulphur or phosphorus, chlorates detonate with dangerous violence: a mixture of a chlorate with sugar bursts into a flame on being touched with a drop of concentrated sulphuric acid.

The compounds of *perchloric acid* (HO, ClO_7), with bases, are distinguished from chlorates by their greater stability, not being decomposed by acids or reducing agents; their solutions do not therefore become yellow on being mixed with sulphuric acid. The *perchlorate of potassa* is remarkable for its difficult solubility in water.

The compounds of *hypochloric acid* (ClO) with bases have bleaching properties, and are decomposed on the addition of an acid with the evolution of chlorine only; they are powerful oxidizing agents, and are decomposed by heat or even by exposure to light: they decompose *manganese* and *lead salts*, precipitating from the former hydrated peroxide of manganese, and from the latter, first chloride, and then brown peroxide of lead.

ORGANIC ACIDS.

I.—Acids precipitated by *Chloride of Calcium;—Oxalic, Tartaric, Paratartaric, Citric, and Malic Acids.*

OXALIC ACID (HO, C_2O_3, or $\overline{O}$).—*General Characters:* It crystallizes in four-sided prisms, which are colourless, very soluble in water, very acid, and eminently poisonous. These crystals contain three equivalents of water of crystallization, which when sharply heated they lose, the dry acid subliming: at a high temperature oxalic acid is decomposed into *water, carbonic,* and *formic acids,* without blackening, by which it is distinguished from most other organic acids. The alkaline oxalates are soluble in water, as are also some other oxalates with a metallic base: they are all decomposed at a red heat; alkaline and earthy oxalates being thereby converted into carbonates.

Behaviour of Solutions of Oxalic Acid and Oxalates with Reagents.

Chloride of calcium, and all soluble lime salts, produce a white precipitate even in highly dilute solutions ($CaO, \overline{O} + 2\,aq.$), insoluble in water as well as in oxalic and acetic acids, but readily soluble in hydrochloric and in nitric acids; the presence of ammonia promotes the precipitation of oxalic acid by salts of lime.

Chloride of barium produces a white precipitate ($BaO, \overline{O} + aq$) almost insoluble in water, but soluble in nitric and in hydrochloric acids.

Nitrate of silver gives a white precipitate, soluble in nitric acid and in ammonia.

Acetate of lead produces a white precipitate.

When heated with concentrated sulphuric acid, oxalic acid and dry oxalates are decomposed, and the oxalic acid resolved into carbonic acid and carbonic oxide gases, which escape with effervescence. The latter gas may, if present in sufficient quantity, be kindled; it burns with a full flame: if the mixture becomes black, it is a proof that it contains some other organic substance.

TARTARIC ACID ($C_8H_4O_{10} + 2HO$; or $\overline{T}$).—This acid crystallizes in large rhombic prisms, which are soluble in water and have a pleasant acid taste; the solution decomposes by keeping, becoming covered with a mouldiness; when heated, the crystallized acid loses water, and gives rise to the formation of a series of new compounds; and when treated at a high temperature with a strong solution of *hydrate of potassa*, it is converted into *acetate* and *oxalate* of potassa, thus:—

$$\underbrace{2HO, C_8H_4O_{10}}_{\text{Crystallized tartaric acid.}} = \underbrace{HO, C_4H_3O_3}_{\text{Acetic acid.}} + \underbrace{2HO, C_2O_3.}_{\text{Crystallized oxalic acid.}}$$

The alkaline tartrates are soluble in water; all the salts of tartaric acid that are insoluble in water are easily soluble in hydrochloric acid.

Behaviour of Tartaric Acid and Solutions of Tartrates with Reagents.

Chloride of calcium produces a white precipitate almost insoluble in water, but soluble in ammoniacal salts, the presence of which, therefore, prevents its formation; it is soluble also in cold potassa, but excess must be avoided, or hydrate of lime will be precipitated; if the potassa solution be boiled, *tartrate of lime* separates as a gelatinous mass, which redissolves as the solution cools.

Lime water produces in solutions of neutral tartrates a white precipitate dissolving in tartaric acid, and also in ammoniacal salts.

Chloride of barium produces a white precipitate soluble in dilute acids.

Acetate of lead occasions a white precipitate of tartrate of lead, which when ignited out of access of air is decomposed, metallic lead in a fine state of division being formed, which burns when projected into the air.

Nitrate of silver produces a white precipitate of tartrate of silver, which by boiling is reduced to a shining mirror, adhering to the glass by agitation; the reduced metal separates in thin laminæ.

Where a salt of *potassa* (the acetate answers best) is added to free tartaric acid, and the mixture agitated, a sparingly soluble crystalline *bitartrate of potassa* separates; the addition of alcohol further diminishes the solubility of this salt, which is freely dissolved in alkalies and in mineral acids.

Tartaric acid possesses the property of preventing the precipitation of several metallic oxides by alkalies, in consequence of the formation of soluble tartrates not decomposed by alkalies; among the metallic oxides which it thus affects are *alumina*, *peroxide of iron*, and *protoxide of manganese*.

Tartrates, when heated, carbonize, emitting a very peculiar odour; the tartrates of the alkalies and alkaline earths are thus converted into carbonates.

PARATARTARIC ACID, OR RACEMIC ACID, $C_4H_2O_5, HO$ or $\overline{R}, HO$.—This acid is isomeric with tartaric acid, from which it is distinguished by the insolubility of its *lime salt* in excess of acid and in ammoniacal salts, and by the formation after a time of a precipitate with solution of *gypsum*.

CITRIC ACID ($C_{12}H_5O_{11}$, 3 HO or $\overline{Ci}$, 3 HO).—This acid forms large transparent crystals, very soluble in water, and of a strong but pleasant acid taste; its solution, like that of tartaric acid, decomposes by keeping. The acid itself carbonizes when heated to redness, emitting a pungent acid vapour; when heated with sulphuric acid in excess, it is decomposed into *carbonic acid*, *carbonic oxide*, *acetic acid*, and water, thus:—

$$C_{12}H_5O_{11} + 3HO = \\ 2CO_2, + 2CO, + 2C_4H_3O_3, + 2HO.$$

The alkaline citrates are soluble in water, the insoluble salts of citric, and in fact of all organic acids are decomposed by boiling with carbonate of soda soluble alkaline salts being thus obtained.

Behaviour of Citric Acid and Solutions of Soluble Citrates with Reagents.

Chloride of calcium produces in solutions of citrates, but not in citric acid, a white precipitate of neutral citrate of lime, insoluble in potassa, but readily soluble in sal-ammoniac, from which, however, a basic citrate of lime ($\overline{Ci}$, 3 CaO + CaO + aq.) is precipitated by boiling.

Lime water produces no precipitate in the cold; but, by boiling, basic citrate of lime is deposited, which is redissolved as the solution cools: this reaction serves to distinguish *citric acid* from most other organic acids.

Acetate of lead produces a white precipitate, sparingly soluble in ammoniacal salts and in ammonia, but readily soluble in citrate of ammonia.

Citric acid, like *tartaric acid*, prevents the precipitation of certain metallic oxides by alkalies.

MALIC ACID ($C_2H_4O_8, 2HO$, or $\overline{M}, 2HO$). This acid, which occurs in several acid fruits, crystallizes with some difficulty, and deliquesces rapidly when exposed to the air; at the temperature of 230° it gradually decomposes into *fumaric acid* (C_4H, O_3, HO), crystallizing in micaceous scales; at a higher temperature it is in a great measure converted into *maleic* acid ($C_8 H_2 O_6, 2 HO$), which rises as a crystalline sublimate, *fumaric acid* remaining in the retort. The salts which this acid forms with bases are mostly soluble in water.

Behaviour of Malic Acid and Solutions of Malates with Reagents.

Chloride of calcium does not produce any precipitate till alcohol is added, when white *malate of lime* is deposited.

Lime water produces no precipitate either in hot or cold solutions of malates, by which this acid is distinguished from *tartaric*, *racemic*, *citric*, and *oxalic* acids.

Acetate of lead produces a white precipitate, which, by repose, crystallizes in needles, and which fuses under the boiling point of water. The best test of malic acid is probably its comportment under heat.

II.—Acids precipitated by *Sesquichloride of Iron;—Succinic*, *Benzoic*, *Tannic*, and *Gallic* Acids.

SUCCINIC ACID ($C_4 H_2 O_3$, HO or $\overline{S}$, HO.) This acid is crystalline and volatile; its vapour is exceedingly acrid and penetrating; by distillation with sulphuric acid, it yields a new acid, the nature of which has not yet been exactly determined. The salts which it forms with bases are mostly soluble in water.

Behaviour of Succinic Acid and Solutions of Succinates with Reagents.

Sesquichloride of iron produces a brownish red voluminous precipitate, soluble in acids and decomposed by ammonia, hydrated sesquioxide of iron being formed.

Acetate of lead produces a white precipitate of succinate of lead, soluble in excess and in *tartaric* and *acetic acids*.

As the alkaline and earthy succinates are insoluble in alcohol, the acid after the addition of alcohol and ammonia is precipitated by *chloride of barium*.

BENZOIC ACID ($C_{14} H_5 O_3 HO$; or $\overline{Bz}$, HO). This acid is obtained by sublimation, in the form of light flexible pearly scales, or by precipitation as a crystalline powder. When pure, it has no smell. It is fusible and volatile, its vapour being like that of succinic acid, very irritating. It is not very soluble in cold water, more so in hot, and readily soluble in alcohol. Most of its salts are soluble in water.

Behaviour of Benzoic Acid and Solutions of Benzoates with Reagents.

On the addition of hydrochloric acid to the solution of a benzoate in water, benzoic acid separates as a white crystalline powder.

Sesquichloride of iron produces a pale yellow precipitate, decomposed by ammonia, and by strong acids, which combine with sesquioxide of iron, benzoic acid being precipitated.

Acetate of lead does not immediately precipitate free benzoic acid; but it produces a white flaky precipitate in solutions of fixed alkaline benzoates.

TANNIC ACID ($C_{18} H_5 O_9, 3 HO$; or $\overline{Qt}, 3 HO$).—When pure, this acid is nearly white, but not all crystalline. It is very soluble in water; the solution absorbs oxygen from the air, and is converted into *gallic* and *ellagic* acids. It has a most astringent but not bitter taste. It is almost insoluble in ether. On the addition of a mineral acid, a precipitate composed of tannic acid and the acid employed is determined. Solution of *gelatine* produces an insoluble curdy precipitate. The whole of the tannic acid in a solution may be removed by a piece of animal membrane.

Solution of starch, and most of the vegetable bases also produce precipitates.

Sesquichloride of iron gives a dark blue black precipitate.

GALLIC ACID ($C_7 HO_3, 2 HO$ or $\overline{G}, 2 HO$). This acid forms beautiful prisms of a silky lustre, and a slightly yellow colour. It is not very soluble in cold, but dissolves in three parts of boiling water. Its alkaline solution, when exposed to the air, becomes first yellow, then green, red, brown, and finally nearly black, by the absorption of oxygen. It is *not* precipitated by gelatine; its solution in hot sulphuric acid is precipitated by water as a reddish brown, crystalline powder, possessing colouring properties, and which, when heated, yields fine red prisms. By the action of heat it is converted into pyrogallic and metagallic acids.

Solutions of *gallic acid* give with salts of *sesquioxide of iron* a dark blue precipitate; with salts of *oxide of iron* the precipitate is black.

III.—Acids not precipitated by *Chloride of Calcium*, or by *Sesquichloride of Iron: Acetic, Formic, Uric, and Meconic Acids.*

Acetic acid ($C_4H_3O_3, HO$; or AcO_3, HO; or $\bar{A}, HO$).—The hydrated acid at temperatures below 60° is a crystalline solid. It melts at 62° or 63°, forming a liquid of a pungent, peculiar and agreeable smell, and a burning acid taste. It has a powerful action on the skin, on which it raises a blister, producing a painful sore. It boils at 248°, and its vapour is inflammable. It is decomposed by an hydrous sulphuric acid, and also by chlorine, two new acids, *sulphacetic* and *chloroactic acids*, being formed. It is also decomposed when passed in a state of vapour through a red hot tube, the products being *carbonic acid* and *acetone*. Thus:—

$$C_4H_3O_3 = CO_2 + \underbrace{C_3H_3O}_{\text{Acetone.}}$$

Acetates, when heated, are decomposed with the same transformation. The greater number of the acetates are soluble in water. *Acetate of silver*, and acetate of *protoxide of mercury* are crystalline, and only sparingly soluble. When heated with dilute sulphuric acid, acetates are decomposed with the liberation of acetic acid; when heated with concentrated sulphuric acid and alcohol, *acetic ether* is disengaged, which may be known by its peculiar odour; when an acetate is heated with *potassa* and *arsenious* acid, *oxide of kakodyl* is disengaged. With excess of oxide of lead, acetic acid forms a solution which has an alkaline reaction. Sesquichloride of iron exhibits no reaction with acetic acid; but in solutions of neutral acetates peracetate of iron is formed, which imparts to the solution a blood red colour.

Formic acid (C_2HO_3, HO; or FoO_3, HO). This acid in its most concentrated state fumes in the air and has a very pungent acid smell. At a low temperature it crystallizes in brilliant scales. It is highly corrosive, acting powerfully on the skin, and producing painful sores. It boils at 212° and its vapour is inflammable; all its salts are soluble in water. They have a general resemblance to the acetates, but are, nevertheless, quite distinct. When heated to redness, they give off carbonic acid and carbonic oxide, leaving the metal reduced, or carbonic oxide, leaving a metallic oxide. By the property which this acid and its salts possess of reducing the oxides of the precious metals, it is distinguished from acetic acid. When *nitrate of silver* or *protonitrate of mercury* are added to concentrated solutions of alkaline formiates, sparingly soluble precipitates are formed, and on the application of heat a reduction instantly takes place, carbonic acid and water being formed, thus:—

$$HO,C_2HO_3 + 2\,HgO = 2\,Hg + 2\,CO_2 + 2\,HO.$$

By gently heating chloride of mercury with an alkaline formiate, it is reduced first to subchloride, and then to metallic mercury.

When formic acid is heated with concentrated sulphuric acid, it is decomposed into water and carbonic oxide, thus:—

$$HO,C_2HO_3 + HO,SO_3 = 2\,CO + HO,SO_3 + 2\,HO.$$

The sulphuric acid withdraws from the formic acid the elements of water, and a transposition of its atoms takes place. The same decomposition occurs on heating a formiate with sulphuric acid.

Uric acid ($C_{10}H_4N_4O_5, HO$; or $\bar{U}, HO$).—This acid is separated from its compounds by mineral acids as a white crystalline powder. It is very sparingly soluble in water, the solution reddens litmus; all its salts are likewise very sparingly soluble. When uric acid is dissolved in *nitric* acid, the solution evaporated to dryness and *ammonia* added, a beautiful *purple* red colour is obtained. By fusion with alkalies uric acid disengages ammonia.

Meconic acid ($C_{14}HO_{11}, 3\,HO$; or $Me, 3\,HO$).—This acid, which is found only in opium, crystallizes, when pure, in the form of beautiful white silvery scales. It is soluble in water and in alcohol. The solution is decomposed by boiling; it is also decomposed by hydrochloric acid, and entirely so when heated with excess of *potassa; oxalic acid*, *carbonic acid*, and a *colouring matter* being the products. Its distinguishing character is that of causing a deep *blood red colour* in solutions of *persalts of iron*, without, however, any precipitation taking place.

CHAPTER IV.

On Systematic Qualitative Analysis.

In the last chapter the chemical comportment of a great number of substances with reagents has been described. Amongst the bases there have been omitted only a few metallic oxides of very rare occurrence, the history of which, and their relation to different reagents, have not been as yet made out; and amongst the acids, nearly all in the inorganic, and a great number of those in the organic kingdom that are of any thing like frequent occurrence, have been included. Now, when the student has made himself *experimentally* acquainted with the relations of these substances to reagents, and when he has become familiar with all the reactions that have been described, he is in a position certainly to pronounce a correct opinion as to the nature of almost any *simple compound*, by which is meant any arrangement of a *single base* with a *single acid*, that may be presented to his notice; but if he be called upon to decide the nature of a compound, consisting perhaps of a mixture of several substances, it is clear that a mere knowledge of the action of reagents *alone* will not serve him, but that he must possess the knowledge of a method of separating the various substances from each other, and of determining the *absence*, as well as the *presence*, of certain bases and acids: in short, he must know how to proceed on a *systematic method* of examination, without which chemical analysis would be little better than mere guess-work, and its *correctness* or incorrectness quite a matter of chance. Even in the examination of a compound which is known to be simple, the greatest advantage is derived from the systematic method, a great saving of time and labour is effected, and the result is arrived at in a far more satisfactory manner than it could be by the indiscriminate application of test after test, following no rule or order, but merely throwing out baits, as it were, with the hope of eventually meeting with appearances, and observing phenomena, that may enable us to recognise the presence of some particular substance. In this chapter our object will be to point out the manner in which this systematic method of qualitative analysis is to be conducted, illustrating the course of proceeding by examples; and our attention will be confined to those substances and combinations only which are of general occurrence. The subject will be thus rendered far more inviting, and less embarrassing, to the beginner; and, after the student has made himself thoroughly acquainted with the principles on which general examinations are conducted, and has acquired a dexterity in conducting the manipulatory processes, he will afterwards find no difficulty in encountering the analysis of compounds in which the rarer substances occur, to the existence of which a careful preliminary examination will, generally speaking, arouse his attention.

Preliminary examination. — Before submitting a compound to analysis, there are certain operations to be performed upon it, which should never be neglected, as they frequently furnish valuable hints for the subsequent examination, and always give some insight into the nature of the substance. In the first place, if the body be a solid, its physical characters, such as its *form*, *density*, *colour*, *hardness*, &c., should be noted; it should next be reduced to powder, and subjected to the action of heat, both alone, and also together with certain fluxes. The experiments are conducted in the following manner:—

1st. A small quantity of the substance is heated on a strip of platinum foil, and it is observed whether it undergoes any alteration. If it be wholly or partly volatile, its odour will frequently enable us at once to decide on the presence of some particular substances, such as *ammonia*, *sulphur*, *arsenic*, *benzoic acid*, &c. If fumes are evolved, a portion of the substance may be heated in a test tube, and notice taken of the appearance of a sublimate in the cool parts of the tube. It should be examined carefully with a pocket lens, and its physical characters minutely ascertained; sulphur, certain sulphurets, as those of mercury and arsenic, mercury, arsenic, cadmium, tellurium, selenium, and certain metallic seleniurets, oxide of antimony, arsenious acid, ammoniacal salts, and salts of mercury, may thus be detected. *Chlorine, nitrous acid, sulphurous acid, hydrocyanic acid,* &c., are thus also frequently discovered. If the substance under examination contains water, it will be condensed in drops on the upper part of the tube. These drops should be examined by test papers, and it should be noted whether they have an acid, alkaline, or neutral, reaction. If the substance changes colour without entering into fusion, certain metallic oxides, such as those of *tin, lead, bismuth,* or *zinc,* may be looked for; and, if it blackens, the presence of organic matter is nearly certain. It is advisable also to heat a little of the substance in a tube, with bisulphate of potassa; *nitrates* are thus decomposed, deep red fumes of nitrous acid being produced. Compounds of *iodine, bromine,* and *fluorine* are likewise decomposed, the former yielding violet fumes of iodine, the second, bromine in a gaseous state, and the last hydrofluoric acid, the presence of which is recognised by its action on the glass. The presence of a *sulphate* is proved by heating a portion of the thoroughly dried substance in a glass tube, with powdered charcoal: the sulphuric acid becomes thereby deoxidized, and fumes of sulphurous acid are evolved. *Metallic sulphurets* likewise disengage sulphurous acid when heated in a tube open at both ends, being thus exposed to a current of air. Under similar treatment *metallic arseniurets* furnish a crystalline sublimate of arsenious acid, sometimes mixed with the reduced metal; the sulphurets of arsenic yield arsenious acid and realgar; and compounds of antimony give a white sublimate of oxide of antimony, which is recognised by the readiness with which it is volatilized by a gentle heat. A similar sublimate is formed on heating *metallic tellurets* in an open glass tube; but it is distinguished from oxide of antimony by fusing into colourless drops when heated, a character which belongs also to volatilized chloride of lead. It is not easy, by means of the blowpipe, to distinguish *lead* from *bismuth,* as the oxides of both metals fuse into a dark yellow mass, which becomes lighter on cooling. The colour of oxide of lead is certainly lighter than that of oxide of bismuth, but the distinction is by no means definite.

2nd. The substance is heated on charcoal *alone,* before the blowpipe. If it fuses, and is absorbed, wholly or partly, by the charcoal, *alkaline salts* are probably present; if it deflagrates, *nitrates, chlorates, bromates,* and *iodates* must be particularly looked for. If, when strongly heated, it leaves a white residue, the *alkaline earths* may be expected to be met with.

3rd. The substance is mixed with carbonate of soda, and heated on charcoal in the reducing flame. By this treatment most metallic oxides are reduced, some with the production of metallic beads without any incrustation taking place on the charcoal, as *gold, silver, tin,* and *copper;* others are reduced with an incrustation, and with or without the production of metallic beads, as *bismuth, lead, cadmium, antimony,* and *zinc;* and others are reduced without giving either beads or incrustations, as *iron, cobalt, platinum, nickel. Manganese,* if present, is converted, in the outer flame, to *manganic acid,* which forms, with soda, manganate of soda of a green colour. *Chromium,* under similar circumstances, gives rise to chromate of soda of a yellow colour. When, however, the substances under examination contain several metallic bases, the student must not expect to meet with well-defined reactions; he will have to draw his conclusions from a comparison of the phenomena he will observe by submitting the subject of experiment to a variety of treatments. The formation of a glass is characteristic of the presence of silicic acid; the bead is, however, transparent only when there is a great excess of silicic acid. Quartz, felspar, with some other minerals and refractory clays, give limpid beads; but the glasses produced by most minerals containing silicic acid are coloured by the metallic oxides present. Silicic acid is remarkable as being almost the only substance insoluble by fusion in microcosmic salt.

4th. The substance is heated in a test tube with concentrated sulphuric acid; if any volatile acid be present, it will almost certainly be detected by this operation; thus, hydrosulphuric acid gas (sulphuretted hydrogen) is evolved from sulphurets, and is immediately recognised by its odour; sulphurous acid gas is liberated from the lower oxides of sulphur; a yellow gas (a mixture of chlorine and hydrochloric acid) is set free from chlorates; a mixture of bromine and oxygen from bromates; hydrochloric acid gas from chlorides; hydrofluoric acid gas from fluorides; bromine and iodine from bromides and iodides: by heating with sulphuric acid also, nearly all organic substances are decomposed; sulphurous and carbonic acid gases, and sometimes carbonic oxide, being evolved. If a cyanide be heated with dilute sulphuric acid, hydrocyanic acid is set free.

If the substance to be analyzed be a liquid, the first step is to evaporate a portion of it to dryness on platinum foil, in order to see whether it really contains any thing in solution, and then to ascertain, by means of test papers, whether it has an acid, or alkaline, or neutral reaction: if the first, it does not necessarily follow that the solution contains free acid, for it must be borne in mind that saline solutions of most of the heavy metallic oxides redden litmus paper: it is not difficult, however, to decide whether the acid reaction is occasioned by a metallic salt or by a free acid; the addition of a drop or two of solution of carbonate of potassa generally, in the first case, renders the liquid turbid, while, in the latter case, it remains clear. If the solution be alkaline, it can contain no metallic oxides that are soluble in alkaline liquids; and if it be perfectly neutral it probably consists only of salt of the alkalies, or alkaline earths.

These preliminary experiments having been made, and some insight into the general nature of the substance under examination having thereby been obtained, its relation to solvents is next to be examined. It is reduced to a fine state of division by trituration in an agate mortar, and a portion digested for some time in a test tube with distilled water; if it be entirely dissolved, the quantitative analysis of the aqueous solution may at once be proceeded with, taking about twenty-five or thirty grains of the substance. If a complete solution do not take place, a drop or two of the clear liquid is to be evaporated to dryness on platinum foil, in order to see whether water has dissolved any thing. If the evaporated liquid leave a residue, then the substance must a second and a third time be digested with fresh portions of distilled water, filtered, and the filtrate set aside for subsequent examination. The undissolved residue is next gradually heated to the boiling point, with dilute hydrochloric acid, and if complete solutions be not effected, the fluid is decanted and the residue digested with concentrated hydrochloric acid, particular attention being paid to the nature of the gases evolved. If an effervescence take place, carbonic acid, sulphuretted hydrogen, and hydrogen gases, may be looked for; the first betrays the presence of carbonates, the second that of sulphurets, the third that of certain metals: the evolution of chlorine indicates peroxides or chromates, and hydrocyanic acid points out the existence of certain cyanides. If complete solution of the substance be not effected by concentrated hydrochloric acid, a fresh portion is to be digested with nitric acid; a few of the metals only escape solution by this acid (*gold*, *platinum*, *palladium*, &c.), *tin* and *antimony* are oxidized by it, but the oxides are not dissolved: it moreover decomposes all sulphurets, with the single exception of sulphuret of mercury, setting free sulphur, which is easily recognised by its colour and levity, and its being completely evaporated when heated on a strip of platinum foil: if nitric acid fail to dissolve the substance completely, aqua regia may be tried, and, if this leave a residue, recourse must be had to fusion with an alkali or an alkaline carbonate, the following preliminary experiments being first performed upon it:—

1st. A small portion is heated on a slip of platinum foil, the odour of sulphurous acid is conclusive as to the presence of sulphur, and, if no other substance be present, the whole will be dissipated by a very moderate heat; in this case, a prolonged digestion of the residue in aqua regia will, generally speaking, give a clear solution, the whole of the sulphur becoming oxidized into sulphuric acid.

2nd. A small quantity is moistened with hydrosulphuret of ammonia; if it immediately become black, an insoluble *silver*, *mercury*, or *lead*, salt is present.

3rd. A small portion is mixed with carbonate of soda, and heated in the inner blowpipe flame; a metallic reduction, accompanied by a yellow incrustation, indicates *lead*.

4th. A small quantity is digested with carbonate of potassa; if it become black, *protochloride of mercury* is present, which is further confirmed by mixing a portion of the residue with slightly moistened carbonate of soda, and heating it in a glass tube, small globules of mercury are easily recognised with the aid of a lens.

5th. Another small quantity may be digested with ammonia, and the clear ammoniacal liquid supersaturated with nitric acid; the formation of a white precipitate, insoluble in the nitric acid, indicates *silver*.

Besides insoluble compounds of *silver*, *lead*, and *mercury*, the residue, insoluble in aqua regia, may contain *sulphates of the alkaline earths, silicates, fluorides, certain phosphates and arseniates, and the insoluble modifications of oxides of tin, antimony*, and *chromium*. *Sesquioxide of iron* also is dissolved only with great difficulty, after having been strongly ignited. All these compounds may, however, be brought into a soluble state by fusion with carbonate of soda, or with a mixture of carbonate of soda and cyanide of potassium; or they may have their constituents transposed in such a manner as to admit of their easy detection by a proper subsequent treatment. For example, if the original substance undissolved by nitric acid or by aqua regia contain sulphates of the alkaline earths, the result of a fusion with carbonate of soda is to bring them to the state of carbonates, which, though insoluble in water, are readily dissolved by dilute hydrochloric acid, and the bases are then easily detected in the hydrochloric solution: the sulphuric acid with which these bases were previously combined is found in the *aqueous* solution of the fused mass, in the form of *sulphate of soda*. Again, if the insoluble residue contain *chloride, iodide*, or *bromide of silver* or *lead*, the result of the fusion with an alkaline carbonate, which in this case must be performed in a porcelain and not in a platinum crucible, is to transfer the *chlorine, bromine*, or *iodine* to the metal of the alkaline base, forming compounds easily soluble in water, and therefore easy of detection in the aqueous solution of the fused mass; while the *metal* or *metals* with which the chlorine, iodine, or bromine was originally combined, being of course insoluble in water, may be dissolved in nitric acid, and detected by the appropriate tests. If *baryta, strontia*, and *lime* be present, besides the oxides of *silver* and *lead*, the two latter metals are precipitated from the nitric solution by sulphuretted hydrogen: the liquor filtered from the precipitate is mixed with hydrofluosilicic acid, by which the *baryta*, after a time, is precipitated. To the liquor filtered from this precipitate, solution of sulphate of potassa is added, which precipitates the *strontia* in company, perhaps, with a little of the lime, and on filtering off the precipitated sulphate of strontia, adding to the filtrate ammonia, and then oxalate of ammonia, a white precipitate, indicating the presence of *lime*, is determined. *Silicic acid*, if present, passes into the state of silicate of soda, and is discovered by adding excess of hydrochloric acid to the aqueous solution of the fused mass, evaporating to perfect dryness, and treating the residue with water; by this treatment the silicic acid is brought to its insoluble condition, and remains undissolved.

It thus appears that when we have before us a complex substance, which is partly soluble in water, and not wholly dissolved by either hydrochloric acid, nitric acid, or aqua regia, three distinct analytical operations may be performed on it, viz:—1, Examination of the aqueous solution. 2, Examination of the acid solution. 3, Examination of the insoluble residue. If the operator be desirous of obtaining a precise knowledge of the mode of arrangement of the different acids and bases in such a complex mixture, he must make these three distinct analyses; but, if his object be only to ascertain what acids and bases are present, he may generally omit a distinct analysis of the aqueous solution, and after a careful preliminary examination he may confine his attention to the acid solution (the substance not having been previously exhausted by water), and to the mass obtained by fusion of the residue with an alkali.

I.—*Examination for Bases: Principles on which the Method depends.*

In the last chapter it was shown that by means of certain *general* reagents metals may be arranged into groups; some of which by other reagents may again be subdivided into minor groups, each of the individuals composing which may be recognised by their comportment with certain other reagents, which may be called *special*. The general reagents are *sulphuretted hydrogen, hydrosulphuret of ammonia, carbonate of ammonia, caustic ammonia*, and *potassa*, and they are of the greatest use and importance to the analytical chemist in conducting a systematic qualitative analysis. Thus, if on the addition of sulphuretted hydrogen to an acid liquid no precipitate should occur, the operator is assured that none of the metals composing the fifth or sixth groups can be present; and if, after having neutralized the liquid with ammonia, no precipitate or decided change of colour should occur on the addition of hydrosulphuret of ammonia even on the application of heat, a proof is obtained that the solution can contain no bases, but some one or more of those included in the first or second groups; and, lastly, the addition of carbonate of ammonia will show at once whether any of the alkaline earths are present. If this reagent should give no precipitate, then the solution in question can contain no metallic oxides but magnesia and those contained in the first group; and if phosphate of soda and ammonia should occasion no precipitate, it must be a solution of some salt or salts of some one or more of the alkalies proper. Supposing, however, that sulphuretted hydrogen *has* occasioned a precipitate in the acid liquid, this precipitate must be a sulphuret of some one or more of the metals of the fifth or sixth groups; and it may contain the whole of the metals of both groups. By digesting it with hydrosulphuret of ammonia, we easily separate these two groups; the metals of the sixth being soluble in that reagent, while those of the fifth are insoluble. The two groups being thus separated, the individual metals are sought for by the application of special tests.

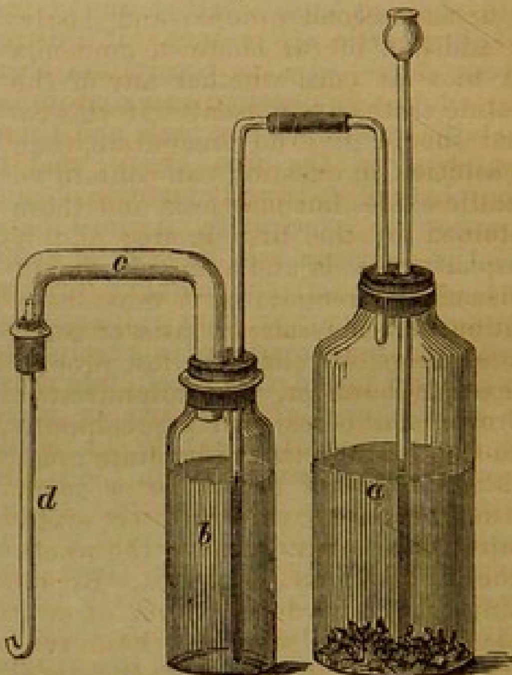
Again, suppose that the filtrate from the precipitate occasioned by sulphuretted hydrogen should furnish a precipitate with hydrosulphuret of ammonia, this precipitate may contain any or all of the metals of the *third* and *fourth* groups, and it may also contain *phosphates, oxalates, borates,* and *hydrofluates* of the *alkaline earths;* but it can contain no metal belonging to the fifth or sixth groups; neither can it contain either of the alkalies proper. The colour of this precipitate furnishes some guide to the substances present: if it be white, it can contain neither *iron, cobalt,* or *nickel;* it may, however, contain small quantities of *manganese* and *chromium:* if it be black, then *iron, cobalt,* and *nickel,* either or all must be present. *Potassa* and *ammonia* are the general reagents employed for the further examination of the precipitate, which is treated in the following manner:—It is washed and digested with dilute hydrochloric acid; if complete solution take place, neither *cobalt* nor *nickel* is present, as the sulphurets of these metals are decomposed only by a protracted digestion with concentrated hydrochloric acid; if complete solution do not take place, then regard must be had to these metals in the subsequent examination by special tests: *nitric acid* is added to the hydrochloric solution, and the mixture is boiled: complete solution of every thing takes place, with the exception, perhaps, of the separated sulphur, which is removed by filtration. To a portion of the clear solution salammoniac is added, and then *ammonia* in excess. If a precipitate be produced, the whole of the solution is treated in the same manner. The precipitate produced by ammonia may contain the oxides of the second group in the form of certain salts (phosphates, oxalates, borates, hydrofluates); the oxides of the third group, *as oxides,* and of the metals of the fourth group, *iron,* in the state of sesquioxide. The filtrate from the precipitate produced by ammonia may contain all the other metals of the fourth group (*nickel, cobalt, zinc,* and *manganese*). *Potassa* now becomes an important reagent in the further analysis both of the precipitate and the filtrate, as will be seen presently, when we minutely describe and illustrate the whole analytical process.

But, again, suppose after having acidified with hydrochloric acid the filtrate from the precipitate occasioned by hydrosulphuret of ammonia, and well boiled it till it has lost all odour of sulphuretted hydrogen, it should give a white precipitate when digested with *carbonate of ammonia,* the presence of some one or more of the members of the *second group* (the alkaline earths) may with certainty be inferred: as this precipitate can contain no metallic oxide of either of the other groups, special testing is at once had recourse to for the detection of *baryta, strontia,* and *lime.* The filtrate from the precipitate occasioned by carbonate of ammonia can contain only *magnesia* and the *alkalies proper.* It is first examined as to its perfect freedom from *baryta, strontia,* and *lime,* by testing a small portion with sulphate of potassa for the two former earths, and a small portion with oxalate of ammonia for the latter. The absence of these earths being proved, another portion is specially tested for *magnesia* by phosphate of soda, and, its presence having been proved, the whole of the remainder of the filtrate is evaporated to dryness, and the ammoniacal salts expelled by ignition; the residue is dissolved in water, and *baryta water* added as long as any precipitate of magnesia is formed; the solution is then boiled and filtered, and dilute sulphuric acid added to the filtrate till it becomes acid; the fluid is then filtered off from the precipitated sulphate of baryta, and the filtrate specially tested for the alkalies.

By the above course of treatment, no base can escape detection but *ammonia*, which is specially tested for in the original solution by heating it with an excess of a concentrated solution of potassa; the ammonia if present is thus discharged in its gaseous form, and its presence is indicated by its odour, or by the white fumes produced on bringing near the mouth of the test tube a feather moistened with strong acetic acid. In following out the foregoing operations, there are certain precautions to be observed, in order to ensure accuracy and to lead to just conclusions. In the first place, it must be borne in mind that, if we employ hydrochloric acid to acidify our solution previous to subjecting it to sulphuretted hydrogen, certain metals (silver, mercury, lead) are precipitated, as chlorides. The two former may be completely removed from the solution by adding a sufficient quantity of hydrochloric acid, and of course, therefore, need not be sought for in the subsequent analysis. *Lead*, however, will not be completely separated in this manner, and must, therefore, be had regard to. The operator must take especial care that the precipitates of the several groups be most completely removed, by washing, from the solution containing the members of the following groups. The greatest confusion and perplexity will arise from neglecting this precaution. He must also be careful that the precipitation by the general reagents be complete, which object is attained by adding the reagent by degrees as long as any precipitation takes place; and in the case of the sulphuretted hydrogen, by continuing to pass the gas through the solution till it smells strongly of it after agitation, and which sometimes requires two or three hours; the deposition of the newly formed sulphuret is much facilitated by gently heating. Should the preliminary examination have indicated *arsenic* in the form of *arsenic acid*, the metal must be brought into the state of *arsenious acid* by boiling the solution with *sulphurous acid*, before subjecting it to the action of sulphuretted hydrogen.

Fig. 57 represents the arrangement of the apparatus for passing a current of sulphuretted hydrogen through a solution; *a* is a wide-mouthed bottle containing water and fragments of protosulphuret of iron. It is closed with a good sound cork, through which are inserted, perfectly air tight, two tubes, one surmounted by a funnel, the other bent at right angles and joined, by a connector of caoutchouc, with a third tube also bent at right angles, and which passes to the bottom of the bottle *b* containing water. Into the cork with which this second bottle is closed is cemented the stout wide tube *c*, bent twice at right angles; the delivering tube *d*, slightly curved at one end, is connected with the tube *c* by means of a good sound cork. When this apparatus is about to be used for transmitting a stream of sulphuretted hydrogen gas through a liquid, the solution to be operated on is placed in a beaker, or in a Phillips' precipitating jar, and the tube *d* being immersed in it is united by its cork with the tube *c*. Sulphuric acid is now poured into *a* through

Fig. 57.



the funnel, the gas is immediately evolved, and in passing through the water in *b*, which should be quite cold, it becomes washed, and thus passes in a state of purity into the solution. Sometimes, when the evolution of gas is too rapid, portions of protosulphuret of iron and of sulphuric acid are carried forward with it; both are, however, retained in the wash bottle *b*. When the solution has become thoroughly saturated with the gas, the delivering tube *d* is removed, and after being rinsed out, or, if required, cleaned with a small feather, it is fit for another operation.

II.—Examination for *Acids*.

The following is the systematic course for the detection of acids, inorganic and organic, pursued in the Royal College of Chemistry. The author is indebted for it to Mr. Bloxam, one of the assistants in the laboratory of that institution.

General Rules.

1st. All the bases, except alkalies and alkaline earths, should be removed before testing for acids.

2nd. *Chromic acid*, if present, should be reduced by sulphuretted hydrogen, and the oxide separated by ammonia.

3rd. *Silicic acid* should be separated by evaporating to dryness, with excess of hydrochloric acid, redissolving the residue in dilute hydrochloric acid, and neutralizing by ammonia.

Note.—In this case the volatile acids —viz. *hydrocyanic*, *hydrobromic*, *hydriodic*, *acetic*, *formic*, *succinic*, and *benzoic* acids—cannot be found in the solution. *Acetic* acid may be tested for specially with sulphuric acid and alcohol. The presence of silicic acid does not interfere with the testing for *succinic* and *benzoic acids* by *sesquichloride of iron*, nor with that of *hydrocyanic acid*, *hydrobromic acid* and *hydriodic acid* by *nitrate of silver*.

4th. If the substance be insoluble in water, but soluble in acids, and has been found by the preliminary examination to contain an organic acid, or *hydrocyanic*, *hydrobromic*, or *hydriodic acid*, it should be boiled with *carbonate of soda;* the base remains in the residue either free or combined with carbonic acid, and the acid is dissolved in combination with soda. The solution should be exactly neutralized by nitric acid previous to testing for acids.

5th. If the solution to be tested for acids contain ammoniacal salts, *boracic*, *tartaric*, and *citric acids* cannot be recognised by the usual reagents. In such a case the *boracic acid* may be tested for specially; or the ammoniacal salts may be removed by long-continued boiling with potassa, and the solution afterwards neutralized by nitric acid.

6th. If the substance be insoluble in water, but soluble in acids, and *not* a compound of an organic acid, or of *hydrocyanic*, *hydrobromic*, or *hydriodic* acids, a part may be dissolved in hydrochloric acid, and tested for all acids but hydrochloric, and another part in nitric acid, and tested for hydrochloric acid by nitrate of silver.

7th. *Carbonic*, *hydrosulphuric* and *sulphurous* acids should be separated, if present, by a strong acid, and the solution neutralized, one part with *potassa*, in order to test for *boracic*, *tartaric*, and *citric* acids, the other part with ammonia, to test for the other acids. *Carbonic acid* may be recognised by the precipitate caused by transmitting the gas through baryta water. *Hydrosulphuric* acid is recognised by its odour and by its reaction with a salt of lead, and sulphurous acid is also recognised by its odour and by the white precipitate occasioned by passing the gas through a solution of sulphuretted hydrogen.

I.—*Absence of Organic Acids.*

1. To the neutral solution *chloride of barium* is added; if a precipitate be produced, it may be, *sulphate*, *borate*, *oxalate*, *phosphate of baryta*, and *fluoride of barium*, all or any. It is digested with hydrochloric acid, which dissolves every thing but *sulphate of baryta;* a white residue indicates therefore *sulphuric acid*.

2. The solution filtered from the sulphate of baryta is exactly neutralized with ammonia, and *chloride of calcium* added. If a precipitate be produced, it may consist of *borate*, *oxalate*, and *phosphate of baryta*, and *fluoride of barium*, all or any. It is digested with *acetic acid*. If complete solution be not effected, the residue may be *oxalate of lime* and *fluoride of calcium*, both or either, and the solution may contain *phosphate and borate of lime*.

a. Examination of the precipitate.—It is digested with hydrochloric acid. If complete solution do not take place, the residue is *fluoride of calcium;* and the presence of *fluoride* is confirmed by heating the original substance in a tube with concentrated sulphuric acid. The hydrochloric solution is heated with excess of ammonia; if a white precipitate be produced, it is *oxalate of lime.* The presence of *oxalic acid* is confirmed by heating the original solution with concentrated sulphuric acid in a test tube; *carbonic oxide* is evolved, which burns with a blue flame.

b. Examination of the filtrate.—*Ammonia* is added; if this fail to produce a precipitate, *no phosphoric acid* can be present; but, in the presence of ammoniacal salts, *borate of lime* may be held in solution. The original solution is therefore specially tested for *boracic acid* by sulphuric acid and alcohol. If a precipitate be produced by ammonia, *phosphoric acid* is specially tested for in the original solution by ammonia, chloride of ammonium, and sulphate of magnesia.

3. To another portion of the original solution, *nitrate of silver* is added. If a precipitate occur, it may be *phosphate, borate, oxalate, chloride, bromide, iodide,* and *cyanide of silver,* any or all. It is digested with nitric acid. *Phosphate, oxalate,* and *borate of silver,* if present, are dissolved; but, as these acids have already been detected in the precipitate by chloride of calcium, no further attention need be bestowed on the solution.

Examination of the residue insoluble in nitric acid.—It may consist of *chloride, iodide, bromide, cyanide,* and *sulphocyanide of silver,* either or all.

It is gently heated with excess of ammonia, by which *chloride, bromide,* and *cyanide of silver* are dissolved, *iodide* and *sulphocyanide of silver* remaining.

a. Examination of the solution.—*Nitric acid* is added. *Chloride, bromide,* and *cyanide of silver,* if present, are precipitated. If *bromine* has *not* been found in the preliminary examination, the precipitate is washed, dried, and ignited; it is then boiled with nitric acid. By the ignition the cyanide of silver is decomposed, the metal being reduced, which is dissolved by the nitric acid; and, if any residue remain insoluble in the nitric acid, it is chloride of silver, and indicates *hydrochloric acid* in the substances under examination. To the nitric acid solution hydrochloric acid is added. If a precipitate be produced, it indicates that silver had been dissolved, and consequently that *hydrocyanic acid* existed in the original solution. The confirmatory tests for hydrocyanic acid are—1st, the prussian blue test; 2nd, a few drops of the original solution are heated for some time with hydrosulphuret of ammonia, a film of sulphur appears on the watch glass, and the addition of a drop of *sesquichloride of iron* produces a deep red colour, owing to the formation of *sulphocyanide of iron.*

If *bromine* has been found in the preliminary examination, a portion of the original solution is first tested for hydrocyanic acid; from another portion the *iodine,* if it contain any, is separated by a mixture of *sulphate of copper* and *protosulphate of iron;* and the excess of the oxides of copper and iron having been removed by potassa, the filtered solution is concentrated by evaporation, and a stream of chlorine passed through; it is then agitated with ether, the brown colour communicated to which indicates *bromine.* The ethereal solution is agitated with *potassa,* evaporated to dryness, and the residue treated with sulphuric acid and peroxide of manganese; red brown vapours of bromine are evolved.

b. Examination of the residue.—It consists of iodide and *sulphocyanide of silver,* either or both. The original solution is tested for *iodine* by *chloride of mercury* and by *starch paste,* after the addition of chlorine. Another portion of the original solution is specially tested for *sulphocyanic acid* by *sesquichloride of iron.*

4. A portion of the original solution is mixed with *sulphuric acid,* and a crystal of *protosulphate of iron* added. The formation of a brown halo indicates *nitric acid,* which is confirmed by boiling with sulphuric acid and *metallic copper.*

5 A portion of the original substance, in a solid form, is heated with dilute hydrochloric acid. The production of a deep, pungent, yellow gas, which explodes on the contact of flame, disengaging chlorine, indicates *chloric acid.*

6. A portion of the original solid is treated with acetic acid in the cold. The evolution of chlorine indicates *hypochlorous acid.*

7. If the original substance evolve oxygen when ignited, and if it give off red fumes when gently heated with sulphuric acid, and if the solution cause a precipitate of metallic mercury in a solution of the nitrate, the presence of *nitrous acid* may be inferred.

II.—*Presence of Organic Acids.*

1. To a neutral solution of the sub-

stance chloride of barium is added. If a precipitate be produced, it may be *sulphate*, *phosphate*, *borate*, *oxalate*, *tartrate*, and *citrate of baryta*, and *fluoride of barium*, either or all. The precipitate is digested with hydrochloric acid, which dissolves every thing but *sulphate of baryta*. A white residue indicates therefore *sulphuric acid*.

2. To the hydrochloric solution, neutralized exactly by ammonia, *chloride of calcium* is added. The precipitate may contain *phosphate*, *oxalate*, *borate*, and *tartrate of lime*, and *fluoride of calcium*, either or all. The solution may contain *citrate of lime*.

a. Examination of the precipitate.—It is divided into two parts. To one part *acetic acid* is added, which dissolves *borate* and *phosphate of lime* if they be present. The further treatment of this solution has been described above. *Oxalate of lime* and *fluoride of calcium* remain undissolved; hydrochloric acid is added, which dissolves the *oxalate of lime*, while the *fluoride of calcium* remains. On the addition of ammonia to the hydrochloric solution, *oxalate of lime* is again precipitated. The other portion of the precipitate is digested with *potassa*. *Tartrate of lime*, if present, is dissolved, but by boiling is again precipitated. *Borate*, *phosphate*, and *oxalate of lime*, and *fluoride of calcium* remain undissolved by the *potassa*. The object of this operation is the detection of *tartaric acid*.

b. Examination of the solution.—It is boiled for some time. If any precipitate take place, it is *citrate of lime*, indicating *citric acid*.

3. To another portion of the original neutral solution *nitrate of silver* is added. The object here being the detection of *bromine*, *iodine*, *hydrocyanic*, and *sulphocyanic acids*, without reference to any of the organic acids, the method of treatment is precisely as has been already described.

4. To another portion of the original neutral solution, *sesquichloride of iron* is added. If a light brown precipitate be produced, *benzoate* and *succinate* acids, either or both, are present. If the precipitate be black, it contains *tannic* or *gallic* acids, or both. If no precipitate be determined, or if, after the subsidence of the precipitate, the solution have a deep red colour, *sulphocyanic* or *acetic* acids, or both, are present.

a. Treatment of the precipitate.—It is digested with *ammonia*, by which it is decomposed, all the acids present combining with the alkali and sesquioxide of iron, being separated from which, the solution must be filtered off.

The solution is divided into three parts:—

To one portion, *alcohol* and *chloride of barium* are added; the formation of a white precipitate indicates *succinic acid*.

Another portion is concentrated by evaporation, and hydrochloric acid added; a white crystalline precipitate indicates *benzoic acid*.

The third portion is exposed to the air; if it assume a red colour, *gallic acid* is present, and if on the addition of sulphuric acid a thick precipitate take place, the presence of *tannic acid* is to be inferred, which is confirmed by the curdy precipitate produced on the addition of solution of gelatine.

Acetic acid is specially tested for by heating the original solution with sulphuric acid and alcohol, acetic ether, of a peculiar and unmistakeable odour, being evolved.

Nitric, *nitrous*, *chloric*, and *hypochlorous acids* are tested for as above described.

Uric acid is specially tested for by mixing a portion of the original solution with nitric acid, evaporating nearly to dryness, and then adding ammonia; a fine purple colour indicates *uric acid*.

Sulphocyanic acid is specially tested for in the original solution, by boiling with sulphuric acid; the liquor becomes of a red brown colour, and by continued boiling deposits a lemon yellow powder.

EXAMPLES FOR ILLUSTRATION.

Example 1.

Examination of an Aqueous Solution containing one Acid and one Base, regard being had to the latter only.

It is neutral to test paper: evaporated to dryness on a slip of platinum foil, it leaves a white residue; boiled with caustic potassa, it emits no smell of ammonia.

I. To a portion in a test tube, a few drops of hydrochloric acid are added: no precipitate; absence of *silver*, *protoxide of mercury*, and probably also of *lead*.

II. To another portion, acidified with hydrochloric acid, solution of sulphuretted hydrogen is added: no precipitate or discolouration; absence of all the metals of the fifth and sixth groups.

III. To another portion, ammonia and hydrosulphuret of ammonia are added: no precipitate, even after boiling; absence of all the metals of the third and fourth groups.

IV. To another portion, carbonate of ammonia, containing a little caustic ammonia, is added: no precipitate, even after long boiling; absence of *baryta*, *strontia*, and *lime:* phosphate of soda is then added; no precipitate after agitation and subsequent repose; absence of *magnesia;* absence of all the metals of the second group.

V. The remainder of the solution is divided into three parts: to one portion *tartaric acid* is added, in slight excess and well shaken; a crystalline precipitate subsides: to another portion, concentrated by evaporation, *chloride of platinum* is added, which occasions a yellow crystalline precipitate: the remaining portion of the solution is evaporated nearly to dryness, alcohol added and ignited; the flame is tinged *violet.* These three tests concur in proving that the base sought after is *potassa.*

Example 2.

A fluid slightly acid to test paper, evaporated to dryness on platinum foil, it leaves a black residue, which does not *disappear* on ignition.

I. Hydrochloric acid occasions no precipitate; absence of *silver* and *protoxide of mercury*, probably also of *lead.*

II. Sulphuretted hydrogen gives a black precipitate: present some metal of the fifth or sixth group. The solution is heated, to facilitate the subsidence of the precipitate, which is then digested with hydrosulphuret of ammonia, by which it is dissolved; present therefore some metal of the sixth group: from the colour of the precipitate, it must be either *platinum* or *gold.*

III. To a portion of the original solution, concentrated by evaporation, a few drops of protosulphate of iron are added: no brown precipitate or discolouration; absence of *gold.*

IV. To another portion, concentrated by evaporation, *chloride of potassium* is added; this immediately occasions a fine yellow crystalline precipitate, indicating *platinum.*

Example 3.

Examination of a solid Substance, consisting of one Acid and one Base: detection of both Acid and Base.

Preliminary.—It is a yellow powder: heated alone on a platinum foil, its colour becomes deeper, but it regains its original colour on cooling. It suffers no further change by heat, either on platinum foil or on charcoal. Heated with microcosmic salt; it gives in both flames of the blowpipe a yellowish green glass, becoming emerald green on cooling. Heated in a test tube with concentrated sulphuric acid, it becomes white, and, on the addition of water, a yellowish green solution is obtained. It is insoluble in water. Digested with hydrochloric acid, a green solution is obtained, and chlorine is evolved, but complete solution does not take place. Digested with nitric acid, a red solution is obtained, but the substance is not completely dissolved, even by aqua regia. These experiments render it certain that the subject of the analysis is *chromic acid* in combination with some metallic oxide.

Examination for Base.

I. It is fused with about three times its weight of a mixture of carbonate of potassa and carbonate of soda, in a platinum crucible; the fused mass is digested with distilled water, and the residue, after being well washed, is dissolved in hydrochloric acid and filtered.

II. Sulphuretted hydrogen occasions no precipitate; absence of all the metals of the fifth and sixth groups.

III. Hydrosulphuret of ammonia produces no precipitate; absence of all the metals of the third and fourth groups.

IV. Carbonate of ammonia gives an immediate precipitate; present, *baryta*, *strontia*, or *lime.*

V. To a portion of the hydrochloric solution, solution of gypsum is added: an immediate precipitate is formed, indicating *baryta*, which is confirmed by adding to another portion *hydrofluosilicic acid;* a colourless crystalline precipitate is formed.

Examination for acid.—Although the preliminary experiments indicated *chromic acid* with sufficient distinctness, it is advisable to perform some confirmative experiments on the filtrate from the fused mass.

I. To a portion of the clear fluid *nitrate of silver* is added; a dark purple precipitate, soluble in nitric acid and in ammonia, is produced.

II. To another portion *acetate of lead* is added; a yellow precipitate is formed, which changes to red on the addition of ammonia.

III. To another portion *sulphurous acid* is added; the colour of the solution changes from yellow to green.

The substance examined is, therefore, *chromate of baryta.*

Example 4.

A Solid Crystalline Compound, consisting of one Acid and one Base.

Preliminary examination.—It is a white crystalline heavy substance, having a nauseous metallic taste. Heated on platinum foil, it fuses, leaving a residue which, while hot, is deep red, but on cooling becomes yellow: on increasing the heat, it gradually disappears, leaving no residue. Heated, alone, in a test tube, it fuses, and gives off red nitrous vapours; and, on continuing to apply heat to the red residue, it is decomposed, the upper part of the tube becoming lined with a metallic film. Heated in a test tube with concentrated sulphuric acid, nitrous fumes are evolved, and a white crystalline mass remains. Heated with carbonate of soda in a glass tube, a gray metallic crust is formed, from which metallic globules are obtained by rubbing with a glass rod.

These experiments are quite conclusive as to the nature of the compound; *nitrate of protoxide of mercury.*

The following are the confirmatory experiments.

I. A portion is boiled with distilled water, a yellow insoluble residue remains (basic nitrate).

II. To a portion of the solution, a drop of hydrochloric acid is added, a copious white precipitate is formed (protochloride of mercury).

III. To another portion, *potassa* is added, a black precipitate is formed (protoxide of mercury).

IV. A drop of the solution is rubbed on a plate of polished copper; a bright silvery white colour appears, which varnishes on the application of heat (metallic mercury).

V. To another portion of the solution, *protochloride of tin* is added, a gray precipitate is determined, which by boiling with hydrochloric acid unites into globules metallic mercury.

Example 5.

A Powder containing one Acid and one Base.

Preliminary examination.—It is a white amorphous tasteless powder; heated on a strip of platinum foil, it first blackens, and then ignites, and on removing the source of heat continues to glow, and metallic globules make their appearance. Heated on charcoal in the reducing flame, a white metal speedily appears, and the charcoal becomes covered with a yellow incrustation. Heated in a glass tube, with concentrated sulphuric acid, it blackens, carbonic and sulphurous acids being disengaged. The substance must, therefore, be some organic acid in combination with the oxide of one of the heavy metals.

Examination for base.—A portion is dissolved in dilute nitric acid, a clear solution is obtained.

I. To a portion of the solution, a drop of hydrochloric acid is added; a white precipitate is formed, which, on the addition of water and the application of heat, is redissolved, but which is undissolved and unaltered by ammonia (chloride of lead).

II. To another portion of the solution, a drop of sulphuric acid is added; a white precipitate is formed, insoluble in dilute acids (sulphate of lead.)

III. To another portion of the solution, chromate of potassa is added; a yellow precipitate is produced, soluble in potassa, but insoluble in dilute acids (chromate of lead).

In this case, the preliminary examination having pointed to *oxide of lead* as the probable base, special testing for that oxide was at once had recourse to.

Examination for acid.—The preliminary examination shows that the metallic base is combined with some organic acid. A portion of the substance is therefore digested with hydrochloric acid, and then boiled with carbonate of soda, in excess, filtered, and the filtrate exactly neutralized with hydrochloric acid; a sufficient quantity of ammonia is now added to give the fluid a feebly alkaline reaction, then muriate of ammonia and a drop or two of *chloride of calcium:* no precipitate, but on boiling it becomes turbid, and deposits a white precipitate; this is characteristic of *citric acid.*

The substance examined is, therefore, *citrate of lead.*

Example 6.

Examination of a Fluid consisting of several Bases and Acids, regard being had to the former only.

Preliminary.—It is strongly acid, and of an olive green colour: a few drops evaporated on platinum foil leave a brown residue; this residue, when strongly heated, fuses, but does not volatilize

Heated with carbonate of soda in the reducing flame, it fuses into a black globule, but there are no visible metallic particles. Heated with sulphuric acid, it gives off fumes of hydrochloric acid gas. Heated in a tube open at both ends, hydrochloric acid and chlorine gases are evolved; and, boiled with caustic potassa, it liberates ammoniacal gas.

A.

The addition of hydrochloric acid causes no precipitate or turbidity; absence of *silver* and *protoxide of mercury*, probably also of *lead*.

NOTE.—Had hydrochloric acid caused a precipitate, it may have consisted of *chloride of silver*, *chloride of lead*, or *protochloride of mercury*, either or all. It may also have been occasioned by *benzoic acid*, *uric acid*, *arsenious acid*, *antimonic acid*, and *basic salts of antimony and bismuth*. In either of these latter cases, however, the precipitate vanishes on the addition of a large excess of hydrochloric acid and boiling: this is not the case if the precipitate contains *silver* or *mercury;* which metals, if present, must be completely precipitated by adding excess of hydrochloric acid to the solution; and the precipitate, after having been washed and dried, must be tested for *mercury*, *silver*, and *lead*, as described at page 79. The *benzoic acid*, *uric acid*, &c., remain in solution, provided a sufficient quantity of hydrochloric acid has been added, and are detected in subsequent stages of the analysis.

B.

A small portion of the solution, when agitated with solution of sulphuretted hydrogen, becomes black. A stream of the gas is therefore passed through about three-fourths of the whole solution until it smells strongly of it: a copious black precipitate is formed: present, some metal or metals of the fifth or sixth groups, or of both.

NOTE.—Had the precipitate occasioned by sulphuretted hydrogen been of a milky white colour, it would have been sulphur, and would have indicated *peroxide of iron*.

Examination of the Precipitate.—It is separated by filtration from the solution, and well washed; it is then digested with sulphuret of potassium, the original fluid having indicated copper by testing with a clean knife blade; it is *not* completely dissolved.

NOTE.—Sulphuret of potassium is employed instead of hydrosulphuret of ammonia, because bisulphuret of copper is not altogether insoluble in the latter reagent.

B. 1. *Examination of the portion soluble in Sulphuret of Potassium.*—It is separated by filtration from the insoluble portion, diluted with distilled water, and boiled with acetic acid in excess, a precipitate is formed, which has a brownish black colour; it certainly, therefore, contains *gold* or *platinum*, or both; and it may also contain all the other members of the sixth group.

B. 1. a. *Special testing for Gold.*—To a portion of the original solution, a few drops of protochloride of tin, containing a little bichloride, are added; the solution acquires a reddish brown colour: to another portion, concentrated by evaporation, solution of protosulphate of iron is added; no brown precipitate or colouration; absence of *gold*.

B. 1. b. *Special testing for Platinum.*—The reddish brown colour produced in the last experiment on the addition of protochloride of tin is characteristic of *platinum:* a portion of the original solution is concentrated by evaporation, and, mixed with muriate of ammonia, a yellow crystalline precipitate is formed; presence of *platinum*.

B. 1. c. *Special testing for Arsenic.*—The black precipitate produced by acetic acid is well washed, and a portion mixed with equal parts of nitre and carbonate of soda, dried at a gentle heat, and then carefully fused in a small porcelain crucible. The fused mass is digested with hot distilled water, filtered, nitric acid added in slight excess, and heat applied; the liquid remains perfectly clear, from which absence of *tin* may be inferred. Nitrate of silver is then added, and the fluid after it is cool is filtered; dilute ammonia is now carefully dropped on the surface of the solution contained in a test tube, and it is allowed to remain at rest for some time; no precipitate or brown colouring between the layers of liquid is perceptible; absence of *arsenic*, which is further confirmed by precipitating the remainder of the solutions by neutral acetate of lead, and examining the precipitate before the blowpipe on charcoal.

NOTE.—The fusion of the precipitate with nitre and carbonate of soda must be performed with great care, a violent explosion may otherwise take place. The best method of proceeding, is to mix the precipitate with twice or thrice its bulk of nitre and carbonate of soda, and to project it, in small portions at a time, into a small Berlin capsule, in which a mixture of carbonate of soda and nitre is kept in a state of fusion over a Mitscherlich lamp. (*fig.* 19).

B. 1. d. *Special testing for Antimony.*—The remainder of the precipitate is boiled with hydrochloric acid, filtered, and concentrated by evaporation; a portion is mixed with water, there is not the slightest turbidity. Another portion, when mixed with solution of sulphuretted hydrogen, gives no orange-coloured precipitate, indicating absence of *antimony.*

Note.—When *antimony* and *tin* are both present, they are most safely detected thus. Into the hydrochloric solution of the precipitate, diluted with water, a rod of metallic zinc is placed; the *antimony* and *tin* become thereby reduced, and are deposited in a pulverulent form on the zinc, from which they are easily removed. The finely divided metals are digested with nitric acid, and the oxides thus formed are heated with a hot saturated solution of bitartrate of potassa, or with a solution of tartaric acid. If complete solution take place, *antimony* alone is present, and may be confirmed by sulphuretted hydrogen; if a residue remain after a protracted digestion, it consists of *peroxide* of tin, the presence of which is confirmed by reduction before the blowpipe, with a mixture of cyanide of potassium and carbonate of soda on charcoal.

B. 1. e. *Special testing for Tin.*—The remainder of the hydrochloric solution is evaporated to dryness, and the residue fused on charcoal, with a mixture of cyanide of potassium and carbonate of soda, before the reducing flame of the blowpipe: no metallic globules make their appearance; absence of *tin.*

The only metal present, therefore, of the sixth group, is *platinum.*

B. 2. *Examination of the portion insoluble in Sulphuret of Potassium.*—It is boiled with nitric acid; it dissolves completely with the exception of a light flocculent residue of sulphur: absence of *mercury;* there may, however, be present, all the metals of the fifth group, with the exception of *silver.*

Note.—Had a black residue remained insoluble, or but very sparingly soluble in nitric acid, it would have consisted of sulphuret of mercury; a small quantity of *sulphate of lead* may also have been present. To ascertain whether the mercury existed in the compound in the state of *suboxide* or as *oxide*, the black residue should be heated in a glass tube; if it sublime without change or decomposition, the metal was in the state of oxide; if the sublimed sulphuret be mingled with globules of metallic mercury, it was in the state of suboxide.

B. 2. a. *Special testing for Copper.*—To a portion of the solution, ammonia in excess is added, a blue liquid is obtained. To another portion ferrocyanide of potassium is added, a chocolate brown precipitate is produced; presence of *copper.*

B. 2. b. *Special testing for Cadmium.*—To another portion of the solution, ammonia is added, then hydrochloric acid in slight excess; the solution is then boiled with *carbonate of ammonia:* no white precipitate; absence of *cadmium.* Ammonia not having occasioned any precipitate in the nitric solution renders it unnecessary to test for *lead* and *bismuth*, neither of which can be present.

Note.—Had ammonia caused a precipitate, the nitric solution would have been tested for lead by dilute sulphuric acid; and for bismuth, by evaporating a portion to a small bulk, adding a few drops of hydrochloric acid and mixing with a large quantity of water.

When *lead*, *bismuth*, *copper*, and *cadmium* are present in a solution, the two latter metals are very conveniently separated from the two former by cyanide of potassium, with which they form soluble double salts. The nitric solution of the sulphurets is precipitated by carbonate of potassa, and the moist and washed precipitate is digested with cyanide of potassium; the double salts which copper and cadmium form with cyanide of potassium are removed by filtration. The insoluble carbonates of lead and bismuth are boiled with diluted hydrochloric acid: the solution is divided into two parts; to one, sulphuric acid is added, sulphate of lead immediately precipitates; the other portion is concentrated by evaporation, filtered, and the filtrate dropped into water; a turbidity or milkiness indicates bismuth. Into the filtrate containing the double salts of copper and cadmium with cyanide of potassium, sulphuretted hydrogen is passed; which, provided there be present excess of cyanide of potassium, precipitates only sulphuret of cadmium, which is recognised by its behaviour before the blowpipe. The sulphuret of copper remains dissolved, and may be precipitated by the addition of hydrochloric acid.

C.

Examination of the Filtrate from B.—A few drops are evaporated upon a strip of platinum foil; a residue remains. A portion is rendered slightly alkaline by ammonia, and, disregarding a bulky precipitate that is thereby produced, *hydrosulphuret of ammonia* is added; this occasions a copious black precipitate: the whole of the filtrate is therefore treated in the same manner, the reagent being slowly added till it ceases to occasion a further precipitation. This precipitate may contain any or all of the metals of the third and fourth groups: it may, moreover, contain *phosphates, borates, oxalates*, and *hydrofluates* of the alkaline earths; the precipitate being black renders it certain that *iron, cobalt*, or *nickel*, either or all, must be present.

Examination of the Precipitate by Hydrosulphuret of Ammonia.—It is washed with water, to which a few drops of hydrosulphuret of ammonia have been added; it is then digested with dilute hydrochloric acid, it does not completely dissolve (presence of *cobalt* or *nickel*, or both). Nitric acid is then added, and the solution boiled and filtered: a small portion of the filtrate is mixed with sal-ammoniac, ammonia added, and heat applied, a dark-coloured precipitate is formed; presence of *peroxide of iron, alumina, oxide of chromium, phosphate of magnesia, and phosphates, oxalates, hydrofluates*, and *borates* of the other *alkaline earths*, any or all, *iron certainly*, from the dark colour of the precipitate. The whole of the filtrate is then treated in the same manner, and the precipitate filtered and washed.

C. 1. *Examination of the Precipitate by Ammonia.*—It is digested with caustic potassa, by which entire solution is not effected, a brown bulky mass remaining, which is separated by filtration.

C. 1. a. *Special testing of the Alkaline Solution for Oxide of Chromium.*—It is boiled for some time: no precipitate. A portion is then slightly acidified with hydrochloric acid, ammonia added, boiled, and the precipitate thereby occasioned, after being washed and dried, is heated with microcosmic salt in the blowpipe flame; the glass on cooling has no tinge of green; indicating absence of *chromium* in the alkaline solution.

C. 1. b. *Special testing of the Alkaline Solution for Alumina.*—It is supersaturated with hydrochloric acid, and then boiled with excess of ammonia, the precipitate, after having been well washed, is heated on charcoal before the blowpipe; moistened with solution of protonitrate of cobalt, and again strongly heated, a deep sky blue colour is obtained on cooling; presence of *alumina.*

C. 1. c. *Special testing of the portion insoluble in Caustic Potassa for Sesquioxide of Iron.* — A portion is washed, and digested with hydrochloric acid; the solution, which must be as nearly neutral as possible, is filtered, and to the clear solution a drop of ferrocyanide of potassium is added; a deep blue precipitate is formed; indicating *iron.*

Note.—To ascertain whether the iron existed in the original solution as protoxide or as peroxide, solution of perchloride of gold is added to a portion: if a brown powder of metallic gold be produced, it is a proof that the iron was in the state of *protoxide;* if, however, the original solution contained a protosalt of tin, this test is not altogether conclusive.

C. 1. d. *Special testing of the portion insoluble in Caustic Potassa for Sesquioxide of Chromium.*—Although no traces of chromium could be detected in the alkaline solution, it is nevertheless necessary to search for that metal in the insoluble residue, because, when sesquioxide of iron and sesquioxide of chromium are together submitted to the action of caustic potassa, they are acted on by that reagent in a manner regulated by their respective quantities. If, for instance, the quantity of oxide of iron be large, and that of oxide of chromium small, very little, if any, of the latter will be dissolved. But if the quantity of oxide of chromium be large, and that of oxide of iron small, the latter will accompany the former in its solution in the alkali: in the case before us the quantity of sesquioxide of iron being evidently very considerable, it is very possible that it may be found to contain traces of sesquioxide of chromium; a small portion is therefore fused in a thin Berlin capsule with a mixture of nitre and carbonate of soda; when cold, it is digested with water: a colourless solution is however obtained, giving no coloured precipitates with either nitrate of silver or acetate of lead; absence of *chromium.*

C. 1. e. *Special testing of the portion* *insoluble in Caustic Potassa for Phosphates, Oxalates, Hydrofluates and Borates of Alkaline Earths.*—The remainder of the insoluble portion is dissolved in hydrochloric acid, filtered, and tartaric acid having been added to prevent the precipitation of the sesquioxide of iron, excess of ammonia is added, a white precipitate is formed indicating the *presence* of some one or more of the above salts.

C. 1. f. *Special testing for Oxalic Acid.*—A portion of the white precipitate, after being well washed, is heated to redness on platinum foil, by which any oxalate present will be converted into carbonate; the residue does *not*, however, effervesce on the addition of a drop of hydrochloric acid; absence, therefore, of *oxalic acid.*

C. 1. g. *Special testing for Phosphoric Acid.*—Another portion of the white precipitate is dissolved in hydrochloric acid, sesquichloride of iron added, and then ammonia to alkaline reaction, a bulky reddish brown precipitate is produced, in which all the phosphoric acid (if any be present) is contained; the alkaline earth with which it was combined previously remaining in solution as chloride: the precipitate is thrown on a filter, and after being well washed is digested with hydrosulphuret of ammonia and again filtered; all the phosphoric acid (if any be present) is in the filtrate, as phosphate of ammonia: the clear liquid is accordingly treated with sal-ammoniac and sulphate of magnesia, by which a crystalline precipitate is produced, increasing on agitation; *phosphoric acid* is, therefore, present.

C. 1. h. *Special testing of the original Solution for Hydrofluoric Acid.*—A portion is evaporated to dryness, and the residue heated in a watch glass with concentrated sulphuric acid, a second watch glass being placed over the first; no roughening of the surface of the upper glass is observed after a considerable time; absence, therefore, of *hydrofluoric acid.*

C. 1. i. *Special testing of the original Solution for Boracic Acid.*—A portion is highly concentrated by evaporation, and digested with sulphuric acid and alcohol; on inflaming the mixture, the characteristic flame of boracic acid is not produced; absence, therefore, of *boracic acid.*

Phosphoric acid is, therefore, the only acid present in the white precipitate, and, by the treatment described in C. 1. g. this acid is removed from the earth or earths with which it was in combination, the metallic base or bases being retained in solution in the form of chlorides. This solution is, therefore, to be examined.

C. 1. k. *Special testing of the Solution* (C. 1. g.) *for the Alkaline Earths and for Magnesia.*—It is digested with carbonate of ammonia mixed with a little caustic ammonia, the precipitate is filtered off, and the filtrate tested for magnesia by phosphate of soda; a crystalline precipitate makes its appearance on agitation; *magnesia* is, therefore, present. The precipitate, after being washed, is redissolved in hydrochloric acid, and divided into two parts; to one part solution of gypsum is added: no precipitate after standing for some time; absence of *baryta* and *strontia:* to the other part oxalate of ammonia is added; an immediate precipitate ensues; presence of *lime.*

The white precipitate is, therefore, a mixture of *phosphate of lime* with *phosphate of magnesia.*

Note.—Had oxalic acid been found, the alkaline earth with which it was combined would have been detected thus:—the ignited white precipitate (C. 1. f.) is dissolved in hydrochloric acid, and to the clear solution caustic ammonia, free from carbonate of ammonia, added, the phosphate of the alkaline earth is precipitated, the chloride remains in solution, and is tested for in the usual manner.

C. 2. *Examination of the Filtrate from the Precipitate by Ammonia.*—It has a blueish tinge, from which the presence of nickel is inferred. It is digested with hydrosulphuret of ammonia, a precipitate is formed, which is filtered, washed, and dissolved in aqua regia.

C. 2. a. *Special testing for Oxide of Zinc.*—To the solution in aqua regia pure caustic potassa is added in excess, the clear alkaline liquor is then treated with sulphuretted hydrogen: no precipitate; absence of *zinc;* had a precipitate been formed, the presence of zinc must have been confirmed by the blowpipe.

C. 2. b. *Special testing for Oxide of Manganese.* — The precipitate thrown down by caustic potassa, which has an apple green colour, having been well washed, is agitated for some time with a solution of carbonate of ammonia, containing a little caustic ammonia, complete solution takes place; absence, therefore, of *manganese.*

NOTE.—Had an insoluble residue remained, it must have been tested for manganese with carbonate of soda before the blowpipe.

C. 2. c. *Special testing for Cobalt.*—The ammoniacal solution (C. 2.b.) is evaporated to dryness: redissolved in a few drops of hydrochloric acid, and again evaporated to a moist mass, a portion of which is heated with borax in the blowpipe flame, a yellow glass without a tinge of blue is formed; indicating absence of *cobalt.*

C. 2. d. *Special testing for Nickel.*—The remainder of the moist residue is dissolved in water and treated with cyanide of potassium: a precipitate is formed, soluble in excess of the cyanide, but, on the addition of dilute sulphuric acid, a greenish precipitate again makes its appearance; indicating presence of *nickel.*

D.

Examination of the Filtrate from the Precipitate of Hydrosulphuret of Ammonia (C.).—A few drops are evaporated on platinum foil, a residue remains. To a small portion, phosphate of soda and ammonia are added and strongly agitated; a precipitate occurs, indicating the presence of some one or more of the alkaline earths. Hydrochloric acid is then added to the whole filtrate, and it is boiled till it has lost all odour of sulphuretted hydrogen. It is filtered and boiled with excess of carbonate of ammonia mixed with a little caustic ammonia, the precipitate formed is examined for *baryta, strontia* and *lime,* and a portion of the filtrate for magnesia precisely as described above (C. 1. k.); *lime* and *magnesia* are found.

NOTE.—Had an immediate precipitate occurred on the addition of solution of gypsum, both *baryta* and *strontia* may have been present; both earths must, therefore, have been specially tested for as follows:—

Special test for Baryta.—A portion of the hydrochloric solution is heated with fluosilicic acid, the formation of a colourless crystalline precipitate either immediately or after a time indicates *baryta.*

Special test for Strontia. — Another portion of the hydrochloric solution is evaporated to dryness and redissolved in alcohol, the alcoholic solution is inflamed: if it burn with a carmine red flame, it indicates *strontia.*

Examination for the fixed Alkalies.—The remainder of the filtrate from the precipitate, occasioned by carbonate of ammonia, and which had not been tested for magnesia by phosphate of soda, is evaporated to dryness and ignited, and, magnesia having previously been proved to be present, the residue is dissolved in water, and baryta water added as long as any precipitation occurs: the solution is then boiled and filtered. Sulphuric acid is added to the filtrate in slight excess, in order to remove the excess of baryta, and the solution is again filtered and evaporated to dryness.

E. 1. *Special Testing of the residue for Potassa.*—It is dissolved in alcohol, and a portion of the solution is ignited; the flame has a distinct violet tinge, indicating the *absence* of soda and the presence of *potassa.* The remainder of the alcoholic solution is mixed with chloride of platinum, a yellow precipitate immediately takes place, confirming the presence of potassa.

NOTE.—If the alcoholic flame had not been tinged violet, but rather yellow, *soda* must have been specially tested for by antimoniate of potassa; and, if magnesia had not been found, the treatment of the filtrate with baryta water might have been omitted, and the filtrate itself at once evaporated to dryness, and tested for alkalies.

Ammonia had been found in the preliminary examination.

The following were therefore the bases present in the mixture analysed: oxides of *platinum, copper, iron, nickel,* and *aluminum, lime* and *magnesia,* in combination with *phosphoric acid;* also *lime* and *magnesia* in combination with some other acid; *potassa* and *ammonia.*

A systematic search for acids is next instituted, but as we have so fully described the principles on which this examination is conducted, both by general and by special testing, we deem it unnecessary to illustrate the process by any examples. The only acid with which there is any difficulty in a mixed compound insoluble in water, but soluble in acids, is *phosphoric acid,* the detection of which is sometimes troublesome, especially when *alumina, magnesia, lime, strontia* or *baryta* are present, together with metallic oxides, which cannot be precipitated except by hydrosulphuret of ammonia. In this case, and where there are also present metallic oxides that are precipitated by sulphuretted hydrogen, *Rose* gives the following method for the detection of phosphoric acid:—

The substance under examination is dissolved in nitric acid, and the metallic oxides capable of being precipitated by sulphuretted hydrogen are removed by that reagent. The filtered liquor is heated until all odour of sulphuretted hydrogen is removed; after which dilute sulphuric acid is added, which precipitates the *baryta* and *strontia*, and the *lime* also, if a sufficient quantity of alcohol be added. The liquor filtered from these earths is evaporated until all the alcohol has disappeared, and excess of caustic potassa is added, by which oxides of *iron, cobalt, nickel*, and *manganese* are precipitated: *magnesia* also, if present, is thrown down, carrying with it perhaps a small quantity of the phosphoric acid; but the greater portion remains in the filtered liquor in combination with the *alumina* and *oxide of zinc*, if the latter base be present. If *alumina* alone be present, it may be precipitated in the form of *double silicate of alumina* and *potassa*, by adding to the alkaline liquor solution of *bisilicate of potassa;* (prepared by fusing together one part of silica and two and a half of carbonate of potassa;) the liquor filtered from this gelatinous precipitate contains the *phosphoric acid*, which may be detected by adding slight excess of hydrochloric acid, neutralizing by ammonia, and adding *chloride of calcium;* or by substituting nitric for hydrochloric acid, and precipitating by *acetate of lead*. Phosphate of lead is easily recognised by the blowpipe: the phosphoric acid, in phosphate of alumina, is also recognised by dissolving in nitric acid, adding to the solution nitrate of silver, and then just sufficient ammonia to neutralize the nitric acid, when a yellow precipitate of phosphate of silver will make its appearance. If *oxide of zinc* be present, it must be precipitated from the alkaline solution by hydrosulphuret of ammonia, taking care that there is sufficient potassa present to keep the phosphate of alumina in solution; the sulphuret of zinc having been removed, the hydrosulphuret of ammonia in the filtrate must be decomposed, and the method described above adopted for the detection of phosphoric acid.

If the substance under examination contain no alumina or magnesia, the metallic oxides capable of being precipitated by hydrosulphuret of ammonia are precipitated by that reagent, the liquor having been previously saturated with ammonia; the phosphoric acid is then detected in the filtered liquor in the usual manner. Rose observes that the analysis of the oxidized combinations which are insoluble in water may be rendered much more easy by fusing the compound with carbonate of soda. The acids are thus procured separate from the bases, and are found in the aqueous solution of the fused mass.

The analysis of insoluble *cyanides* and *ferrocyanides* is sometimes attended with difficulty when conducted in the usual manner: the detection of cyanogen in *simple cyanides* is sufficiently easy, as they are all decomposed by boiling with concentrated hydrochloric acid, cyanogen being evolved, which is recognised by its odour, and chlorides of the metallic bases being formed; but the decomposition of the class of *double cyanides* by means of an acid is not so simple. Fresenius, therefore, recommends that a different treatment should be adopted in their analysis. For this purpose he directs them to be boiled with solution of carbonate of potassa, having previously removed by water every thing soluble in that fluid; the solution is filtered, and the residue washed: this residue contains the bases, and is treated in the usual manner. The filtrate contains the cyanogen, and perhaps other acids; it may also contain iron, cobalt, manganese, and chromium, in the form of *ferrocyanide, cobalticyanide* &c. *of potassium*. The cyanogen is recognised by mixing a portion of the filtrate with hydrochloric acid till it is strongly acid, and then adding solution of the double proto and perchloride of iron. If cyanogen be present, prussian blue precipitates. The metals are detected by evaporating another portion of the filtrate to dryness, with great excess of nitric acid, and fusing the residue (cautiously for fear of explosion); the *iron, manganese*, and *cobalt* become hereby oxidized, and are separated in the usual manner: the *chromium*, if present, is converted into chromic acid, and is obtained as soluble chromate of potassa.

Should the compound be insoluble in carbonate of potassa, it is boiled with caustic potassa, and the alkaline solution is treated with sulphuretted hydrogen. If any precipitate should be formed, it is removed, and the filtered liquor, having been acidified with hydrochloric acid, is again subjected to sulphuretted hydrogen, by which all sulphurets soluble in alkalies (sulphuret of tin, sulphuret of antimony, &c.) are removed: the filtrate is tested for *cyanogen, cobalt, iron, manganese, chromium,* and acids as above. If the object be merely to detect the bases in these insoluble cyanogen compounds, simple fusion with carbonates of soda and potassa will, in most cases, be sufficient, the metals are thus obtained either in their metallic state or combined with carbon. If the fusion be performed with nitre, the operator must guard carefully against the consequences of an explosion, which is very likely to occur.

QUALITATIVE ANALYSIS OF NATURAL SILICATES.

The usual constituents of this extensive class of native substances are *silica, lime, magnesia, alumina, oxide of iron, oxide of manganese, alkali,* and *water.* Rare oxides, such as *yttria* and *glucina* (in gadolenite), *zirconia* (in eudialite), *lithia* (in lepidolite), are sometimes met with in silicious minerals, and for these a special method of analysis must be pursued: but, in the absence of such oxides, a very simple course of examination is adopted.

The first constituent to be sought for is *water,* the presence or absence of which is ascertained by heating a portion of the mineral, finely pulverized, in a test tube, first gently, and then strongly in a flame urged by the blowpipe; water if present will rise, and be condensed in the upper portion of the tube.

From 50 to 100 grains of the mineral are next reduced to a coarse powder in the steel mortar, (*fig.* 41,) and then ground to the finest possible powder in the agate mortar (*fig.* 42). It is easy for the beginner to be deceived as to the degree of pulverization required; it does not in most cases suffice that the mineral shall be reduced to what may seem mere dust, but it must be ground down with water if necessary, till it has almost, or entirely, lost all grittiness between the teeth. With many minerals this can only be effected by elutriation, that is by grinding it with water into a paste in the agate mortar or on an agate slab, and then diffusing it through water in a tall jar, allowing it to stand for a short time, and then decanting the cloudy liquid, and collecting the fine powder, which after some time settles at the bottom of the vessel. It is always, however, better to avoid elutriation when the mineral can be brought to an impalpable powder in the dry way; but a very fine state of division is generally an indispensable condition for its decomposition, whether by hydrochloric acid or by fusion with an alkali.

If the silicate to be analyzed belong to that class which is decomposed by hydrochloric acid, the powder is drenched with this acid: a bulky gelatinous mass is with many (the zeolites, &c.) immediately formed without the application of heat, and on adding water, the silicic acid separates in flakes, leaving the bases with which it was combined dissolved in the form of chlorides. Other silicates, such as *stilbite* (silicate of alumina, lime and water), *pyrosmalite* (lime, tersilicate of oxide of iron and manganese), and *pitchblende* (uranium ore), &c., are only decomposed by prolonged digestion with hot acid, and then not completely, unless they are in an extremely fine state of division; the silicic acid in these cases separates in the form of a fine powder. If the silicate belong to that class which resists the action of acids, amongst which may be mentioned *felspar, mica,* and *talc,* it is fused in a platinum crucible with a mixture of five parts of carbonate of potassa and four of carbonate of soda, the fused mass is treated with water, and subsequently evaporated to dryness in a porcelain basin with excess of hydrochloric acid: the dry mass, when cold, is moistened with concentrated hydrochloric acid, and after standing for about an hour water is added; the bases present dissolve as chlorides, and the silicic acid remains in the form of an insoluble powder.

Some minerals, as *zircon* and *cyanite,* are only decomposed by fusion with caustic potassa.

When the mineral contains an alkali, it must be analyzed, by igniting it in a silver crucible with four or five times its weight of pulverized and dry nitrate of baryta; the fused mass, after supersaturation with hydrochloric acid and evaporation to dryness, is redissolved in water, filtered, and sulphuric acid added to precipitate the greater part of the *baryta:* carbonate of ammonia in excess is then added to separate the remainder of the baryta, together with the *alumina* and *peroxide of iron*, and, these precipitates having been filtered off, magnesia and the alkalies are sought for in the filtrate, as has been already recommended.

Silicious minerals containing alkali may also be analyzed, by mixing them with powdered fluor spar, and, heating to incipient redness in a platinum dish with concentrated sulphuric acid, the silica passes off as *fluoride of silicum:* the dry mass is digested with water, precipitated with carbonate of ammonia, and proceeded with as above.

The bases are found in the hydrochloric solution after the separation of the silica in a very simple manner. If the blowpipe has shown that the mineral contains *iron*, that metal is brought to the state of sesquioxide by adding a few drops of nitric acid to the hydrochloric solution and heating; *ammonia* is then added in excess, *alumina* and *sesquioxide of iron* are thereby precipitated; the former is separated from the latter by digestion with caustic potassa, and its presence in the alkaline solution proved by the addition of *sal-ammoniac*, which produces a white flocculent precipitate.

To the filtrate from the precipitate by ammonia, *oxalate of ammonia* is added; a white precipitate indicates *lime.*

To the filtrate from the precipitate by oxalate of ammonia, *phosphate of soda* is added; the formation of a crystalline precipitate indicates *magnesia.* The operator must, however, be certain that the *whole* of the lime had previously been precipitated by oxalate of ammonia.

The alkalies are detected in the manner described (page 92), the method of proceeding depending on the presence or absence of *magnesia.*

Manganese is best recognized by the blowpipe.

For the detection of *glucina*, *yttria*, and other rare substances found in a few minerals, such as the *emerald*, *gadolenite*, *pyrothite*, &c., the student is referred to Rose's Manual of Chemical Analysis*.

QUALITATIVE ANALYSIS OF MINERAL WATERS.

The principal constituents are detected *qualitatively* in a brief and simple manner, the rarer substances are most conveniently found in the *quantitative* analysis, the method of conducting which will be subsequently described.

Detection of free Carbonic Acid.—Add to a portion of the water which has been recently collected and kept in a well-stopped bottle, a small quantity of *lime water*, if a precipitate be formed, which redissolves on the addition of a further quantity of the water, *carbonic acid* in a free state is present.

Detection of sulphuretted Hydrogen.—The odour of the water is, in most cases, a sufficient evidence of the presence of this gas, which is confirmed by adding to a small flask, nearly filled with the water, a few drops of solution of acetate of lead and well agitating, a black precipitate, or a more or less brown coloration of the fluid indicates sulphuretted hydrogen, or an alkaline sulphuret.

Detection of Sulphuric Acid.—A portion of the water is slightly acidified with hydrochloric acid and gently warmed, chloride of barium is then added, the formation of a white precipitate indicates sulphuric acid.

Detection of Hydrochloric Acid.—A portion of the water is acidified with nitric acid, warmed, and nitrate of silver added; a curdy precipitate, or a turbidity, indicates hydrochloric acid.

Detection of Nitric Acid.—A considerable quantity of the water is evaporated to dryness, the residue is dissolved in a small quantity of water, and tested with protosulphate of iron and sulphuric acid. (See page 72).

Detection of Iodine.—A large quantity (four or five gallons) of the water is reduced to a small bulk by evaporation, and a portion of residual fluid is tested with starch paste and nitric acid. (See page 68).

Detection of Bromine.—Another portion of the residual fluid is treated with chlorine water and ether, as described page 68.

DETECTION OF BASES.

Detection of Lime.—Add to a portion of the water oxalate of ammonia, and allow it to stand for a considerable time in a warm place; a white precipitate indicates *lime.*

Detection of Magnesia.—Concentrate the filtrate from the oxalate of lime, if necessary, by evaporation, and add to the clear residue ammonia and phosphate of soda; a crystalline precipitate indicates magnesia.

Detection of Iron.—Introduce into

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* A new translation from the French, and the Fourth German Edition, by A. Normandy.—William Tegg and Co.

a flask of white glass, containing no lead, a quantity of the water, to which a few drops of hydrosulphuret of ammonia have been added, the formation of a black precipitate indicates iron. Or, should this test fail from the smallness of the quantity of that metal present, it may be detected by *tincture of nut galls*, a few drops of lime water being also added. As the iron generally exists in mineral waters in the form of carbonate of the protoxide, these tests should be applied as soon as possible after the water has been collected from the spring: if the presence of iron be indicated after the water has been boiled, the metal does not exist as carbonate, but as some other salt.

Detection of Lime in the form of Bicarbonate.—To a portion of the water muriate of ammonia is added, and then *ammonia*, the formation of a white precipitate indicates bicarbonate of lime: should a notable quantity of iron be present, the precipitate has a more or less yellow tinge; and this is also the case if the water contain organic matter.

Detection of the Alkalies.—Should the water contain iron, that metal must be brought to the state of sesquioxide by means of chlorine: it is then precipitated together with all the other bases, but magnesia, by carbonate of ammonia: the further process for the detection of the alkalies is conducted precisely as described page 92.

Detection of Ammonia.—A few drops of hydrochloric acid are added to a considerable quantity of the water, which is then evaporated nearly to dryness, at a very gentle heat: the residue is tested for ammonia by caustic potassa or hydrate of lime, as directed page 33. Besides the above acids and bases, there are found occasionally in mineral waters the following substances:—*lithia*, *alumina*, *strontia*, *oxides of manganese*, *zinc* and *copper* amongst bases: and *sulphurous*, *boracic*, *phosphoric*, *hydrofluoric*, and *silicic acids* among electro-negative bodies. These bodies are never, however, found all together in the same water; and as they always exist in very small quantities only, they are, as before observed, best detected in the quantitative examination.

The student, after having carefully gone through the reactions described in the third chapter, "on the comportment of substances with reagents," is recommended to practise himself thoroughly in systematic qualitative examinations, commencing with simple arrangements of one acid and one base, and proceeding gradually to more complicated mixtures, following the course we have attempted to sketch out perspicuously in the preceding pages. The mixtures analyzed should be prepared by another person, and the operator must carefully guard himself against drawing hasty conclusions, as well as against arriving at results by any but the legitimate road. The preliminary examination will, in many cases, point out to him with certainty the composition of the substance he is examining: he should not on that account, however, neglect to perform the confirmative experiments, remembering that his object is to acquire a practical knowledge of the general system of analysis, and not merely to ascertain the composition of the substance. If he carefully and conscientiously follow the system here given, in all its details, and the advice we here offer him, we venture to assure him that in a short time he will find himself in a condition to undertake the qualitative examination of almost any substance that may be brought under his notice.

QUALITATIVE DETECTION OF POISONS.

Poisons have been divided by toxicologists into three classes:—1, *Irritants.* 2, *Narcotics.* 3, *Narcotico-Irritants.* In the first class are included the mineral and certain vegetable acids; the alkalies; certain metals and salts; certain vegetable acrids, as *croton oil*, *gamboge*, &c.; and certain animal poisons, such as *cantharides*, *poisonous fish*, and decayed and diseased animal matters. In the second class are comprized, *opium*, *hyocyamus*, *narcotine*, *hydrocyanic acid*, *oil of bitter almonds*, *laurel water*, *cyanide of potassium*, *morphia*, &c.; and amongst those comprehended in the third class may be mentioned *nightshade*, *tobacco*, *hemlock*, *strychnia*, *nux vomica*, certain poisonous *fungi* and *mosses*, *poisonous grain*, *alcohol* and *ether*. Now, although the chemical evidence in charges of poisoning is generally considered as the most decisive of all branches of proof, it happens, unfortunately, that with few exceptions the present state of chemistry enables us to identify with certainty mineral poisons only; and the detection of these, disguised and obstructed as the action of reagents may be by the organic mixtures in which the poison has generally to be sought for, is, in many cases, by no means so simple, or so easy of execution, as may at first be imagined. The poisons to which we propose to confine ourselves in this section are the following:—The *mineral acids; oxalic acid; hydrocyanic acid; arsenic; mercury; lead; copper; antimony;* and *zinc;* and we shall endeavour to describe minutely the methods of detecting these substances both in simple fluids, and in complicated organic mixtures, as at present pursued by toxicologists.

THE POISONOUS ACIDS.

1. *Sulphuric Acid.*

For the properties of this acid in its concentrated state, see p. 62. The most striking character by which it may be recognized is that of its yielding sulphurous acid gas, of a peculiar pungent odour, when heated in contact with charcoal, copper, or mercury. In its diluted state it is detected with the greatest facility by the precipitate which is formed on the addition of nitrate of baryta, or chloride of barium. This precipitate, when dried and ignited with charcoal, is converted into sulphuret of barium, which disengages sulphuretted hydrogen on the addition of diluted hydrochloric acid. It is hereby distinguished from seleniate and fluosilicate of baryta. The detection of sulphuric acid in organic mixtures is often attended with great difficulties; so much so, indeed, that, according to Dr. Christison, a satisfactory process still remains to be discovered. The difficulty arises, 1st, from the probable presence of neutral sulphates, together with some free acid, which would obviously give the same reaction with barytic salts as dilute sulphuric acid itself; 2nd, from the possible presence of a bisulphate; and 3rd, from the possible neutralization of the acid (in cases of poisoning) by the substances administered as antidotes. If the substance to be examined be a liquid, a small portion should be evaporated to dryness to ascertain whether it leaves any residue; if it does, the following experiment may be made, in order to learn whether the acidity of the liquid is wholly or in part occasioned by a bisulphate, or whether there is reason for supposing that the reaction with the barytic salt may have been occasioned by some neutral sulphate, the acidity being produced by some other acid. Weigh out two equal quantities of the liquid, precipitate one with nitrate of baryta, and determine the amount of sulphate of baryta formed; evaporate the other to dryness, calcine, redissolve in water, and, having added nitric acid, precipitate also with nitrate of baryta, and determine the amount of sulphate formed. Compare the weights of sulphate of baryta obtained in the two experiments; if they are the same, it is then tolerably clear that no sulphuric acid in a free state was present in the liquid under examination; but, if the quantity of sulphate obtained in the first experiment be greater than that in the second, the excess may fairly be set down to free sulphuric acid in the mixture. When the contents of the stomach and other complex mixtures have to be examined for sulphuric acid, the mixture should be boiled with distilled water; and having proved the existence of sulphuric acid, or a soluble sulphate, by nitrate of baryta, the whole should be distilled from an oil bath at 240°, and about four-fifths drawn over. The distillate should be tested for hydrochloric and acetic acids, and the residue should be divided into three parts, one of which is to be tested for nitric acid, another for oxalic acid, and the remainder for sulphuric acid.

Sulphuric acid is sometimes maliciously thrown on articles of clothing; and in such cases the chemist is occasionally called upon to pronounce on the nature of the corrosive substance. Owing to its strong affinity for water, sulphuric acid remains on cloth and linen for a long time, keeping the stain in a moist state; and, according to Mr. Taylor, it may be easily detected after many years' exposure. The process of analysis is very simple: the injured part is cut out, digested in distilled water, filtered, and the solution treated with nitrate of barytes. Mr. Taylor recommends the following method as delicate and easy of application: a minute quantity of the injured fabric is gently heated in a small glass tube, and a piece of paper, saturated with starch and moistened with a drop of *iodic acid*, is brought near the mouth of the tube; sulphurous acid is generated by the decomposition of the sulphuric acid, which, reacting on the iodic acid, liberates iodine, and the test paper becomes blue.

Detection of free Sulphuric Acid in Wines.—This cannot be effected by barytic salts, because all wines contain a greater or less quantity of the sulphates of potassa and lime. M. Lassaigne gives the following simple process, by which he states that he is able to detect one-thousandth part of sulphuric acid in red wine. When a piece of common glazed paper, which has been touched with pure wine, is dried at a gentle heat, the spotted portion is unaltered; whereas, if sulphuric acid be present, it reddens and becomes brittle and friable between the fingers when slightly rubbed, before the white paper becomes at all coloured. Pure wine, to which nothing has been added, leaves, by spontaneous evaporation, a violet blue spot, whereas wine, to which sulphuric acid has been added, gives, by drying, a rose red spot.

2. *Nitric Acid.*

For the properties of this acid in its concentrated state, see p. 71. The most simple test for it is the action of copper turnings, by which it is rapidly decomposed, deep red fumes of nitrous acid being evolved, and a green solution formed. The dilute acid is also decomposed by boiling with copper turnings unless a large proportion of water is present, the colour of the solution being blue. Other tests for nitric acid are—1st, *morphia*, which is turned in a few seconds to a beautiful red by it, and, after a longer contact, bright yellow; 2nd, *narcotin*, the solution of which organic base in sulphuric acid is changed from yellow to blood red; 3rd, *brucine*, an alkaloid which occurs along with *strychnine* in nux vomica, and which is applied as a test for nitric acid in the following manner:—About a drachm of concentrated sulphuric acid, free from nitric acid, is to be placed in a small beaker; to this is added a few drops of the liquor supposed to contain nitric acid; the whole is mixed together with a glass rod, a small piece of brucine introduced, and the liquid well stirred. If nitric acid be present, a red colour will immediately be developed, which will afterwards pass to yellow. If there be no nitric acid, the brucine will not dissolve. According to Berzelius, by this means the presence of $\frac{1}{10000}$th part of nitric acid may be detected in a liquid. 4th, *protosulphate of iron.* This test is best applied in the following manner:—Add to a small quantity of sulphuric acid the solution to be examined, in such a proportion that the quantity added should equal three-fourths of the bulk of the acid. When the mixture has become cool, drop in a concentrated solution of protosulphate of iron; if any nitric acid be present, it is immediately decomposed; nitric oxide is evolved, which produces a rose red, purple, or, if the quantity of nitric acid present be exceedingly small, a pink tint. One part of nitric acid in 24,000 parts of water may thus be detected. In testing for nitric acid, the liquid should be neutralized with potassa and evaporated to dryness. It should be observed whether crystals of nitre are formed on allowing the concentrated solution to cool. The dry residue should be mixed with an equal bulk of copper filings, introduced into a small glass tube, and heated with a few drops of sulphuric acid. The evolution of red fumes is quite conclusive as to the existence of nitric acid in the residue left on evaporation. Mr. Taylor wraps a minute portion of the suspected nitrate in a piece of the finest copper gauze, and drops the pellet thus formed to the bottom of a small tube; he then adds a drop of water and a drop of sulphuric acid. By this means, and using a tube only one-eighth of an inch in bore, he obtains satisfactory results with one-tenth of a grain of nitre. When nitric acid has to be tested for in thick and viscid organic liquids, the mixture is digested with distilled water, and filtered, the clear liquid is evaporated to dryness with potassa, and treated with copper filings, or gauze and sulphuric acid, as above described. Nitric acid produces on the skin a yellow stain, which may be distinguished from any other spot of a similar colour by the action of ammonia, which renders it for a time brighter. It acts powerfully on woollen cloth, staining it yellowish, or orange red, or brown, and entirely destroying its texture. To discover the presence of the acid, the injured parts are removed and digested in two or three successive portions of distilled water, the liquid is filtered, and, its acidity having been proved by litmus paper, it is evaporated to dryness with potassa, and the residue treated as above. It must be borne in mind that, in consequence of its volatility, and the facility with which it undergoes decomposition in contact with organic matter, we cannot hope, as in the case of sulphuric acid, to obtain chemical evidence of its presence after the lapse of a few weeks.

3. *Hydrochloric Acid.*

For the properties of this acid, see p. 67. In searching for it in organic mixtures, Orfila boils, if necessary, with distilled water, filters, and distils at a gentle heat, till the residue acquires the consistence of a thin syrup; he then adds to the extract in the retort a slight excess of a strong solution of *tannin*, the object of which is to precipitate the organic principles, to which hydrochloric acid adheres with great obstinacy; he then continues the distillation nearly to dryness, at a temperature not above 240°, and examines the distillate for hydrochloric acid by nitrate of silver. In this operation, it is necessary to guard against a fallacy which may arise from the presence of a neutral chloride, such as common salt and sulphuric acid, and which can, of course, be only obviated by proving the absence of sulphuric acid. The precipitate occasioned in a solution supposed to contain hydrochloric acid by nitrate of silver, may be *cyanide*, or *oxalate* of silver: these two salts are, however, easily distinguished from the *chloride* of the same metal. *Cyanide of silver* is soluble in hot nitric acid; it evolves hydrocyanic acid when digested in hydrochloric acid, and when heated in a small tube, it evolves a gas (cyanogen) which burns with a blue flame. *Oxalate of silver* is completely dissolved in cold nitric acid, and when thoroughly dried and heated on thin platinum foil, it is dissipated in a white vapour with a slight detonation. *Chloride of silver* is quite insoluble in nitric acid and in caustic potassa, though it is very soluble in ammonia, and when heated on a strip of platinum foil, it fuses into a horny looking substance. *Iodic acid* also gives, with nitrate of silver, a precipitate, soluble in ammonia, but insoluble in nitric acid; it is, however, decomposed by caustic potassa, oxide of silver being separated. It is in the highest degree improbable that this acid should occur in any compounds which are the subject of toxicological investigation. Iodate of silver is immediately known from chloride of silver, by adding to the liquid starch and sulphurous acid, when the blue *iodide of farina* is produced.

4. *Oxalic Acid.*

For the properties of this acid, see page 73. It is soluble in from twelve to fourteen times its weight of water (Taylor). In its crystalline form it differs entirely from citric, and tartaric, and other common vegetable acids; but it greatly resembles sulphate of magnesia, for which it has been often and fatally mistaken. Its taste is intensely acid, by which it is at once known from Epsom salts, which are well known to be strongly bitter: moreover, oxalic acid, when heated on platinum foil, is entirely volatilized, if pure; Epsom salts, on the other hand, loses only its water of crystallization. In testing for this acid, a portion of the fluid, having been proved to be acid by litmus paper, should be concentrated by evaporation, and ammonia added; a radiated crystallization of oxalate of ammonia should be produced, a property which, according to Dr. O'Shaughnessy, distinguishes it from every other acid. The best tests for oxalic acid are—1st, *nitrate of silver*, which produces a precipitate in a solution containing only the $\frac{1}{4000}$th part by weight of oxalic acid (Taylor). The oxalate of silver is distinguished from the *citrate* and *tartrate* of that metal by its property of fulmination, and by its leaving, on ignition, no carbonaceous residue. 2nd, *sulphate of lime*, or any soluble lime salt, which occasions a white precipitate, readily soluble in nitric acid, not very easily dissolved in dilute hydrochloric acid, and quite insoluble in acetic, tartaric, and all vegetable acids. 3rd, *sulphate of copper* which gives a greenish white precipitate, not readily soluble in hydrochloric acid. Neither of the mineral acids are precipitated by this test, nor is acetic, tartaric, or citric acid affected by it. When this poison has been received into the stomach, the well-known antidotes, magnesia and chalk, will probably have been administered. The following process for detecting it, under these circumstances, may be advantageously followed.

The suspected fluid is macerated with distilled water, and allowed to remain at rest for some time; the supernatant liquid, if not acid, may be thrown away; the residue is made into a thin paste with water, and boiled for two or three hours, with about a twentieth of its weight of carbonate of potassa, till the organic matter is all dissolved. By this operation the oxalate of lime or magnesia will have become decomposed, and the fluid will contain oxalate of potassa. It is filtered when cold, then rendered faintly acidulous with nitric acid, again filtered, and the filtrate rendered very faintly alkaline with carbonate of potassa. It is now a third time filtered, and the clear liquor treated in the following manner:—Acetate of lead is added as long as any precipitate is formed: the precipitate is collected on a filter, washed, and dried between bibulous paper. It consists of oxalate of lead, together with organic matter in union with oxide of lead. It is stirred up very carefully while moist with water, and sulphuretted hydrogen gas is transmitted briskly through it for an hour; the lead is thus removed as sulphuret, and the solution contains oxalic acid tolerably pure. The sulphuret of lead is removed by filtration; the filtrate is boiled, evaporated to dryness, redissolved in water, filtered, and the clear solution tested for oxalic acid, by nitrate of silver and sulphate of lime (Christison). Mr. Taylor modifies this proceeding, and shortens the process, by digesting the precipitated oxalate of lead in hydrosulphuret of ammonia, taking care not to use a great excess; he thus obtains the oxalic acid in the filtered liquid in the form of oxalate of ammonia. By this process, Dr. Christison states that he has detected a grain of oxalic acid in a decoction of an ounce of beef in six ounces of water; and two grains of oxalate of lime in a similar decoction, in which some fragments of beef were purposely left, to complicate the process. Mr. Taylor obtains equally satisfactory results, by digesting the precipitated oxalate of lead in water containing a small quantity of sulphuric acid. Sulphate of lead is formed, and oxalic acid set free; the latter is separated by filtration, together with the excess of sulphuric acid: it is cautiously neutralized by ammonia, and, when quite clear, tested with nitrate of silver and sulphate of lime. The presence of sulphate of ammonia does not in the least interfere with the action of these tests.

5. *Hydrocyanic Acid.*

For the properties of this acid, see page 69. Its chemical tests are, 1st, *nitrate of silver.* 2nd, *sulphate of copper.* 3rd, *protosulphate of iron.* 4th, *hydrosulphuret of ammonia*, with a *persalt of iron.* The properties of cyanide of silver have been mentioned above. It is identified in the most marked manner, by its yielding cyanogen gas, which burns with a blue flame, by simply heating it in a glass tube. One-tenth of a grain, corresponding with about one-fiftieth of a grain of anhydrous acid, will thus furnish good evidence. (Taylor.) Cyanide of silver is insoluble in cold nitric acid; but by boiling it is decomposed, nitrate of silver being formed, and hydrocyanic acid set free. *Sulphate of copper*, when added to a fluid containing hydrocyanic acid, rendered alkaline with potassa, gives a greenish precipitate, becoming nearly white on the addition of hydrochloric acid: this precipitate is cyanide of copper. According to Lassaigne, this test will discover hydrocyanic acid when dissolved in 20,000 parts of water; but, as the precipitate is white, it has not much toxicological value. When a solution of *protosulphate of iron* is added to a liquid containing hydrocyanic acid, rendered slightly alkaline by potassa, a grayish green precipitate is produced; and on adding diluted hydrochloric or sulphuric acid, and agitating, *prussian blue* is formed and precipitated. This test is free from all objections: it will act in cases where nitrate of silver gives no precipitate; and it possesses this great advantage over the last-named test, that it is applicable in circumstances under which nitrate of silver might give rise to embarrassment; as for instance, where the poison has to be sought for in fluids containing common salt. For the method of applying the hydrosulphuret of ammonia test, see page 71. When hydrocyanic acid is to be sought for in organic mixtures, Mr. Taylor urges the importance of obtaining evidence of its presence before resorting to the process of distillation, in order to avoid an objection which may be raised, to the effect that the acid might have been a product of distillation. He gives the following method, which he finds to succeed with the blood, muscles, and viscera, as well as with the liquid contents and solid substance of the stomach. The liquid is acidulated with sulphuric acid and placed in a wide-mouthed bottle, the aperture of which is capable of being covered with a watch-glass, or a saucer of white porcelain. The inside of the glass or saucer is moistened with nitrate of silver and placed over the mouth of the bottle: if hydrocyanic acid be present, the spots of nitrate will become white in the course of a few seconds, or in from ten minutes to a quarter of an hour, according to the quantity of poison present, and the closeness of the test to the liquid. No heat need be applied to the liquid—a temperature of 64° suffices for the result, but the warmth of the hand accelerates the action. Mr. Taylor mixed *two-thirds of a grain* of anhydrous hydrocyanic acid with *eight ounces* of porter, and obtained a well-defined deposit of cyanide of silver in the watch-glass in a quarter of an hour, and by substituting in the watch-glass weak caustic potassa for nitrate of silver, and after a few minutes adding sulphate of iron and hydrochloric acid, he obtained prussian blue from *two-thirds* of a grain of anhydrous hydrocyanic acid mixed with eight ounces of porter: the process was equally successful with the stomach of a dog, after it had been thoroughly washed with water, and had been removed from the body twenty-four hours. These experiments prove the great volatility of the poison, and the diffusibility of its vapour. The silver test serves the analyst as a guide, for Mr. Taylor finds that, unless the white film is formed on the nitrate of silver, the application of the prussian blue test will also fail. Prussian blue may even be procured from the cyanide of silver: for this purpose, caustic potassa is added to the film of cyanide in the watch-glass, and heat applied; the cyanide is dissolved, and brown oxide of silver precipitated; to the filtered liquid sulphate of iron is added, and after a time dilute sulphuric acid, prussian blue is immediately produced. When it is found necessary to distil the fluid, *Lassaigne* and *Christison* acidulate with sulphuric acid, and distil from a vapour bath till one-eighth part of the fluid has passed into the receiver. The tests are then applied to the distillate; if the quantity of poison is small, nitrate of silver or potassa may be placed in the receiver to fix the acid as it passes over.

Liebig makes the following remarks on this fearful poison:—"Its rapid action on the blood is very remarkable. Comparatively large quantities of the acid in aqueous solution may be taken into the digestive apparatus without producing any very perceptibly noxious effects; while the same quantity inhaled as vapour causes immediate death. Thus a cat can bear the administration of from two to three drops of anhydrous hydrocyanic acid diluted with from four to six ounces of water, without being in the least affected by it. If two drops of the anhydrous acid be inserted into the mouth of the same animal, taking care at the same time to prevent it from breathing by stopping its mouth and nostrils, no perceptible effect is produced; but the cat dies the very instant it is permitted to breathe, and consequently as soon as the vapour of the acid gets into the lungs."

With respect to the quantity of hydrocyanic acid requisite to destroy life, the matured opinion of Mr. Taylor is, that a quantity of Scheele's acid (at five per cent.), *above twenty drops* (i.e. *one grain of anhydrous acid*) or an equivalent portion of any other acid would commonly prove fatal. Even less than this—seven-tenths of a grain might, under favourable circumstances, destroy life. The largest dose from which an adult has been known to recover is *forty minims* at three and a quarter per cent., which is equivalent to about a grain and a third of anhydrous acid. It may be well to observe that the acid of commerce differs much in strength, according to the process by which it has been prepared, and independently of decomposition by keeping. The medicinal acid long used in this country is intended to be an imitation of that of *Vauquelin*, which contains 3·3 per cent.; but the London College of Physicians have improperly (as Dr. Christison observes) altered the strength to two per cent.: that of *Giese*, which keeps well, is of the same strength as the first; that of *Schrader* contains only one per cent.; that of *Göbel* 2·5 per cent.; that of *Ittner* 10 per cent.; that of *Robiquet* 50 per cent. Of the alcoholic solutions the best known are,—that of *Schrader*, which contains about 1·5 per cent. of pure acid; that of the *Bavarian Pharmacopœia*, which contains four per cent.; that of *Duflos* nine per cent.; that of *Pfaff* 10 per cent.; and that of *Keller* 25 per cent. The medicinal dose is from a minim to two minims of *Scheele's* acid, and from three to five minims of the London Pharmacopœial acid gradually increased.

Every grain of anhydrous acid yields five grains of cyanide of silver. Suppose 100 grains of a sample to have yielded 45 grains of cyanide, it follows that the acid contains nine grains of anhydrous acid to 91 grains of water. To procure an acid containing two per cent. of anhydrous acid, would require the addition of nine grains of anhydrous acid to 441 grains of water: now, as the acid in question contains already 91 grains of water in every 100 grains, it is evident that we need only add 350 grains of water to every 100 grains of the acid, in order to prepare an acid of two per cent. strength 441 — 91 = 350.

With strong acids, hydrocyanic acid undergoes the same decomposition as metallic cyanides do with caustic alkalies; with the elements of water, its elements are transposed into formic acid and ammonia, thus:—

$$C_2NH + 3HO = C_2HO_3 + NH_3;$$

one equivalent of hydrocyanic acid and three equivalents of water produce one equivalent of formic acid and one of ammonia.

The Poisonous Metals.

6. *Arsenic.*

Of all poisons this is by far the most important, being the one which, on account of its cheapness, and the facility with which it is procured, is the most commonly resorted to, both by the suicide and the murderer. From the parliamentary return of the cases of fatal poisoning brought before the coroners of England in two years ending with 1838, it appears that no less than a hundred and eighty-five cases of poisoning by white arsenic occurred, being more than all the others put together, with the exception of opium and its compounds. This fearful disclosure has induced toxicological chemists to pay especial attention to the methods of detecting the compounds of this metal in organic mixtures; their investigations have been attended with the happiest results, and the detection of $\frac{1}{11}$th part of a grain of arsenious acid even in such substances as gruel, milk, and porter, can now with certainty be effected. In page 49, *et seq.*, the chemical characters of arsenious acid, and its comportment with reagents, have been described; as also most of the important processes that have been proposed for detecting it in organic mixtures. A few additional particulars may be appropriately introduced here. First, with respect to the taste of arsenious acid, we have stated that it is "without smell and almost without taste, though if kept for some time in contact with the tongue it induces a slightly bitter taste, leaving one of sweetness;" this description certainly accords with our own experience, and is made, moreover, on the high authorities of Dr. Christison and Mr. Taylor; Professor Orfila, however, continues to describe the poison as having "a rough, not corrosive, slightly styptic taste, perceptible after a few seconds; very persistent, and attended with salivation." These sensations must, as Dr. Christison observes, be either imaginary, or else the indications of an organ peculiarly constituted, as it is certain that in general the poison makes no impression on the palate at all, and that most of the persons who have been criminally or accidentally poisoned by it, have not been aware of any taste in swallowing the poisoned food. It must, indeed, be regarded as an unfortunate circumstance that arsenious acid is so destitute of taste; had the contrary been the case, many lives would undoubtedly have been saved.

Second.—With respect to the solubility of arsenious acid, we have observed that a great diversity of opinion exists on the subject, and that the transparent and opaque varieties exhibit a marked difference in their degrees of solubility in water. Mr. Taylor's latest experiments on the subject gave the following results:—Hot water, cooling from 212° on the poison in powder, dissolves about the 400th part of its weight, being in the proportion of nearly a grain and a quarter of arsenious acid to a fluid ounce of water. Water boiled for an hour on the poison, and allowed to cool, holds dissolved the fortieth part of its weight, or about twelve grains to an ounce. Cold water allowed to stand for many hours on the poison, does not dissolve more than from the 1000th to the 500th part of its weight; that is, half a grain to one grain of arsenic to nearly one fluid ounce of water. The presence of organic matter in a liquid considerably impairs its solubility; thus Dr. Christison found that a cup of tea left beside the fire, at a temperature of 200°, for half an hour, upon two grains of arsenious acid, did not entirely dissolve even that small quantity. It may be well to mention that the appearance of arsenious acid, as it crystallizes out of an aqueous solution, greatly resembles that of *pounded sugar.*

Third.—The quantity of arsenic necessary to destroy life:—This has been variously stated. It has been alleged by some writers that *four* and even *two* grains of arsenious acid may prove fatal to a man. The smallest fatal dose on record, however, is *four and a half grains*, which destroyed a child four years old in six hours; and Dr. Christison quotes a case, on the authority of Valentini, in which *thirty* grains of the oxide in powder killed an adult in six days. There is no doubt, however, that death may be occasioned by a much smaller quantity than this; and that, though some constitutions will of course be more affected by the poison than others, so small a quantity as a grain, or even half a grain, may produce very alarming consequences. Mr. Taylor thinks that the cases on record warrant the conclusion that *three grains* are very likely to prove fatal to an adult; he refers to a case in which a gentleman took rather more than *two grains* in a glass of port wine; violent vomiting and other alarming symptoms occurred, though the effects were undoubtedly modified by the circumstance of the poison having been received on a full stomach. It is well worthy of remark, that, by certain mechanical admixtures, arsenic in moderate doses may be entirely deprived of its poisonous properties. It was shown by *Orfila* that if certain insoluble powders, such as clay, are introduced into the stomach immediately after arsenic has been swallowed, the violent effects may be greatly mitigated, if not altogether prevented; the cause of which appears to be referable to the envelopment of the arsenical powder by the inert substance, and the consequent prevention of its coming into contact with the membrane of the alimentary canal. Dr. Christison observes that the sparing solubility of arsenious acid occasions its influence to be greatly modified by the condition of the stomach as to food at the time it is swallowed. If the stomach be empty, it adheres to the villous coat, and acts with great energy; if the stomach be full at the time, the first portions that come in contact with the inner membrane may cause vomiting before it can be diffused, so that the whole or greater part is discharged. He quotes a case, on the authority of *Wibmer*, where a man swallowed *an ounce and a half* of arsenic after a hearty meal, had merely a severe attack of vomiting with subsequent colic, and got well in four days; and another case, on the authority of *Mr. Kerr*, in which nearly *three quarters of an ounce* were retained after a meal for two hours, without causing any serious mischief.

Fourth.—Antidotes to the Poison:—There is but one substance which can at all be considered as a chemical antidote to arsenic; viz., the hydrated sesquioxide of iron; its precise mode of action is by no means well understood; it has already been alluded to in page 49. Dr. Christison recommends that it should be kept in readiness in every druggist's establishment, as it cannot be prepared when wanted without great loss of time. The quickest way to make it is to dissolve the common anhydrous sesquioxide in dilute sulphuric acid, aided by a gentle heat; to decompose the hot solution with an excess of strong ammonia; to filter off the fluid by means of a cloth filter, and wash the precipitate well with warm water; and then to let it drain thoroughly, squeezing out as much of the water as possible by compression. This substance was announced by Drs. *Bunsen* and *Berthold* in 1834, as an effectual remedy, even when given some time after the arsenic has been swallowed; it must be administered in large quantities, it having been ascertained by Dr. Douglas Maclagan, that, in order to remove one part of arsenic from a state of solution, twelve parts of the oxide in a moist state are required, and sixty parts if it has been previously dried; the presence of ammonia also seems necessary, in order to effect an insoluble combination with the arsenic. Mr. Alfred Taylor does not appear to place much reliance on the antidotal effects of this substance; "numerous recoveries," he says, "are said to have occurred under the use of this alleged remedy; but, so far as I have been able to ascertain in severe cases, emetics and the stomach pump were also freely used; and in the lighter cases recovery would probably have equally taken place without it. It is to the use of emetics and the stomach pump that we must chiefly rely, in treating a case of arsenical poisoning; viscid and mucilaginous liquids may also be freely exhibited, as these will serve to suspend the powder mechanically, and sheathe the coats of the stomach from its action."

Fifth.—Tests for Arsenic:—The following observations may be useful in addition to what has already been said on this subject, pp. 50, *et seq.*:—When the poison is obtained in the state of arsenious acid, it may be reduced to the metallic condition by igniting it in a small glass tube with some reducing agent. Dr. Christison employs a soda flux, made by grinding crystals of carbonate of soda with one-eighth of their weight of charcoal, and then heating the mixture gradually to redness, so as to drive off all the water. Mr. Taylor recommends, as the most convenient, the residue of the tartrate or acetate of soda (incinerated in a covered platinum crucible) which consists of carbon and carbonate of soda. He prefers this to cyanide of potassium, inasmuch as it does not deliquesce, and may be kept for years without change. Two or three parts of the flux should be employed to one of arsenious acid; the tube should be of hard German glass, about three inches long, and one-eighth of an inch in diameter; the metal sublimes, and forms a ring, of an iron-gray colour, on the cool part of the tube; a peculiar odour, very similar to that of garlic, is at the same time perceptible. The physical properties of the metallic crust are very characteristic, sufficiently so to enable the operator to distinguish arsenic from any other substance capable of being sublimed by a low red heat. The surface next the glass has the appearance of polished steel; it is somewhat darker in colour, but of equal brilliancy; the inner surface, when examined with a lens, appears brilliantly crystalline, like the fracture of cast-iron. On applying the flame of a spirit lamp to the crust, it disappears, settling on the cooler portion of the tube, and it may be chased up and down the tube by the flame, until it is entirely reconverted into arsenious acid, which, when viewed through the lens, appears in the form of little octahedral crystals of adamantine lustre, on which triangular facets may be distinguished. Dr. Christison remarks that the characters of the arsenical crust are distinct when weighing only a 300th of a grain, and that a crust of this weight, a tenth of an inch broad and four times as long, may show characteristically all the physical peculiarities of an arsenical sublimate a hundred times larger. A few of the principal objections, if objections they can be called, that have been raised against this test must be alluded to. 1st. A deposit of charcoal may, it is said, be mistaken for arsenic; but not only is there no similarity whatever between the two deposits, that of charcoal being brown, and without the least lustre, but any doubt that might exist on the subject may at once be removed by submitting the deposit to the action of the spirit flame. 2nd. Preparations of *antimony* and *zinc*, it has been alleged, yield sublimates closely resembling the arsenical crust; but Dr. Christison and Dr. Turner have shown that no preparation of either of these metals can be reduced to a metallic state, either by charcoal or black flux, with the fullest red heat of the blowpipe. 3rd. *Cadmium* is a metal which is said to form a metallic sublimate like arsenic. It is hardly within the bounds of possibility that the toxicologist should encounter any preparation of this metal, it being a rare substance, and not used in medicine in any way. It is true, however, that oxide of cadmium may be reduced and sublimed, but the sublimate is altogether different from arsenic: its lustre resembles that of tin, and it is generally surrounded with a brown margin of reproduced oxide. It evolves no odour, and, when heated, it does not volatilize, but turns brown. 4th. It has been said by Mr. Donovan that the action of the flux on glass which contains lead causes a stain similar to an arsenical crust: this objection is overruled by employing German glass, which contains no lead; but the metallic lead stain, besides differing altogether from arsenic in appearance, is easily distinguished from the latter by its comportment under heat, it is fixed; whereas the arsenical crust is volatile. Lastly, it has been said that a crust may be produced from the arsenic contained in the tube. This, however, is absolutely impossible: arsenic is undoubtedly sometimes used in glass making, and it is just possible that a trace of it may be retained in some opaque glasses or enamels; but in an extended inquiry into the subject, which was undertaken by the Parisian Academy of Medicine at the request of the French government, the poison could not be detected by any process of analysis in any of the clear glass met with in commerce, the whole having been volatilized during the manufacture.

In cases where the quantity of arsenious acid is so minute as to be scarcely ponderable, Mr. Taylor suggests that it should be dropped into a dry and warm tube, not more than an eighth or a tenth of an inch in diameter, and well-dried charcoal in the proportion of about three or four times its bulk dropped upon it. The upper part of the charcoal should be brought to a high temperature before the arsenious acid is heated. In this way distinct arsenical sublimates may, he says, be procured, the weight of which is considerably less than the 1000th part of a grain.

With regard to the *liquid tests* for arsenic when the poison is in solution, it may be remarked that, though objections may be raised to each individually, their combined evidence cannot be otherwise than conclusive: for example, a solution of *phosphoric acid* is precipitated by ammonio nitrate of silver, exactly like a solution of arsenic; but ammonio sulphate of copper gives no precipitate, or one of a pale *blue* colour with phosphoric acid, while the precipitate which the same reagent occasions in solutions of arsenic is of a rich green colour: again, ammonio-sulphate of copper strikes a green precipitate in certain organic fluids like arsenite of copper, though no arsenic be present: but the same solutions would fail to give the characteristic rich yellow precipitate with ammonio nitrate of silver, and the lemon yellow precipitate with sulphuretted hydrogen; Dr. Christison is, therefore, of opinion that the use of these liquid tests in the present modes of analysis for arsenic has been unjustly neglected: the method is not only extremely convenient and delicate, but by using small tubes it is easy to operate with precision on minute portions of a suspected fluid. The sulphuretted hydrogen test is one of extreme delicacy: it begins to give a yellow tinge when the liquid contains only the 4000th part of a grain of arsenious acid in ten drops of water, the arsenic therefore forming about the 40,000th part of the solution (Taylor). Dr. Christison says that it acts on arsenious acid in a hundred thousand parts of water. The proper colour of the precipitate is lemon or sulphur yellow, which when vegetable or animal matter is present acquires a shade of white or brown. The evidence is not considered complete unless the sulpharsenious acid is reduced, and a metallic mirror of arsenic formed. This is best effected in the manner described, page 50. In applying Marsh's process, Dr. Christison arranges a bent tube containing a little distilled water over the flame, by which he obtains a solution of arsenious acid, which he subsequently examines by the liquid reagents. A solution containing a millionth part of arsenious acid will, he says, readily part with it in the form of arseniuretted hydrogen, and the slightest trace of that gas in the hydrogen is indicated by the method he pursues. M. Danger and Flandin, likewise, burn the gas in connection with a cooled receiver, in order to obtain a solution of arsenious acid. It has also been proposed to conduct the arseniuretted hydrogen over dried oxide of copper, instead of burning it: the gas is absorbed without the aid of heat, and is afterwards obtained by heating the oxide of copper in a tube. Mr. Taylor does not speak very favourably of Berzelius's modification of Marsh's apparatus, described page 51: its advantages are not, as he thinks, compensatory for the inconveniences attending its use. Of Reinsch's process (see p. 52), on the other hand, he speaks in the highest terms, considering it of all the methods of detecting arsenic the most simple, speedy, and easy of execution. Mr. Taylor employs the finest copper gauze or woven wire instead of copper foil. The surface thus presented to the arsenical liquid is very great, and after the deposit has taken place he dries it first by pressure between folds of blotting paper, and then above the flame of a lamp: he then rolls it into a small compass, and introduces it into a reduction tube, where it is slowly heated, and octahedral crystals of arsenious acid are thus obtained. In this way Mr. Taylor has detected the 144th part of a grain of arsenious acid in two fluid drachms of gruel, milk, porter, and other organic liquids in so many different experiments. It has also been thus easily separated from wine, brandy, and the liquid contents of a person poisoned by arsenic. He recommends it as a *trial* test when examining organic liquids supposed to contain the poison; for which purpose the liquid, after having been filtered through muslin, cotton, or paper, should be strongly acidulated with hydrochloric acid, and boiled with a slip of bright copper; should the brightness of the metal remain unimpaired at the expiration of half an hour, no arsenic, or only an extremely minute quantity, can be present; should, however, the copper be covered with a gray deposit, it must be dried and heated in a reduction tube, with the view of procuring from it crystals of arsenious acid. Dr. Christison, also, in speaking of Reinsch's process, says, "It is the best yet proposed for the detection of arsenic in solution." He directs the fluid to be mixed with one-tenth of its volume of hydrochloric acid, and to be heated to boiling before the copper is introduced, otherwise the metal may become tarnished, though no arsenic be present: in the feeblest solutions, ten or fifteen minutes elapse before arsenic is visibly deposited, and forty minutes should be allowed for complete deposition.

In all medico-legal inquiries it is necessary to perform a preliminary experiment with distilled water, and the hydrochloric acid used, in order to be sure that the latter is perfectly free from traces of the poison. According to Dr. Christison, this process will detect at least the 250,000th part of arsenic in solution; and it removes from the fluid every particle of the poison, as none can afterwards be discovered in it, even by Marsh's method. It is not subject to any fallacy; for, though solutions of bismuth, tin, zinc, and antimony, produce a coating more or less similar to the arsenical one, still the subsequent conversion of the metallic arsenic into arsenious acid, and the examinations of a solution of the latter by liquid tests, completely puts aside these sources of error. It must be observed that the non-formation of a crust on the copper is perhaps not absolute proof of the *absence* of arsenic, since, according to Fresenius and Von Babo, all nitrates and various salts of mercury and other metals render the separation of arsenic by copper difficult, or even impossible. It is a fact of especial importance in a medico-legal point of view, that a person may have died from the effects of arsenic, and yet not a trace of the poison be found in the stomach or its contents. In such cases the solid parts of the body, the liver, and the blood, will have to be examined; and the best method of preparing these substances for the reception of the sulphuretted hydrogen test is that proposed by Fresenius and Von Babo. (See p. 53.) When, however, Reinsch's process is to be followed, the plan recommended by Dr. Christison is this:—Cut the viscus into very small pieces, and boil them in a mixture of one part of pure hydrochloric acid and ten of water for two hours, or till the whole of organic matter becomes a soft magma. The liquid is then to be strained, and the residue pressed: if the quantity of liquid be large, it may be concentrated by evaporation: the copper gauze or foil should then be introduced; should a deposit be formed after half an hour or an hour, it is treated as above directed. The assertion of M. Couerbe, and afterwards of Orfila, that arsenic sometimes exists naturally in the human body, has been proved to have been founded on error.

7. *Mercury.*

Although this metal is not, in its metallic form, possessed of noxious properties, most of its preparations are poisonous in an eminent degree, scarcely less so, indeed, than the compounds of arsenic. The most important salt of mercury, in a toxicological point of view, is *corrosive sublimate*, which in its power is somewhat similar to arsenious acid. Like the latter, it has been known to have been received into a full stomach in large quantities, without producing fatal consequences; and, like arsenic also, it has been known to destroy life in so small a quantity as three grains. Mr. Taylor thinks that, under favourable circumstances, from three to five grains, or even less, would destroy an adult. The general characters of corrosive sublimate are as follows:—It is generally met with either in the form of a heavy white powder, or in heavy crystalline cakes. It is permanent in the air, but slowly decomposed by the light of the sun, a gray insoluble powder being formed. Its taste is strongly styptic, metallic, and acrid, so that it is impossible for the smallest quantity of it to be received into the mouth without the individual becoming aware of it; in which it differs strikingly from arsenious acid, which, as has been already observed, has scarcely any taste. It is very soluble in water, and speedily sinks in it, wherein again it differs remarkably from arsenic. According to *Thenard*, it is soluble in 20, and according to *Orfila*, in 11 parts of temperate water. From Mr. Taylor's experiments it results, that 100 parts of a cold saturated solution hold dissolved six grains of the salt. Its solution faintly reddens litmus paper. Boiling alcohol dissolves its own weight of corrosive sublimate, and retains, on cooling, a fourth part. It is very soluble in ether, which takes up a third of its weight, and is capable of abstracting it from its aqueous solution,—a property which is sometimes taken advantage of in toxicological investigations.

Chemical Tests for Corrosive Sublimate in a Solid State.

1. Heated on platinum foil it fuses, and is dissipated in white fumes leaving no residue. 2. Heated in a test tube, it sublimes and condenses in a white crystalline mass. 3. When dropped into a solution of caustic potassa or soda, it becomes yellow, oxide of mercury and chloride of potassium or sodium being formed. This reaction with potassa and soda distinguishes it at once from *calomel*, which becomes black on the addition of the fixed caustic alkalies, *suboxide of mercury* being formed. 4. Ammonia dropped on corrosive sublimate occasions no discolouration; with calomel, on the other hand, an immediate blackening takes place. 5. Dropped into a solution of hydrosulphuret of ammonia, it turns black. 6. When solution of iodide of potassium is dropped upon corrosive sublimate, a fine crimson colour is produced: the same reagent brought into contact with calomel gives rise to a dirty olive green colour. 7. Rubbed on a plate of polished copper with a mixture of one part of hydrochloric acid and two of water, a silvery stain is produced, which entirely vanishes on the application of heat. 8. Heated with three or four parts of calcined carbonate of soda in a small tube, similar to that employed for the reduction of arsenic, a ring of bright globules of mercury is sublimed; the tube must be quite dry. This test is conclusive, there being no other metal capable of being sublimed in globules. The residue in the tube is common salt, as may be proved by dissolving it in water, and adding to the solution nitrate of silver.

Chemical Tests for Corrosive Sublimate in Solution.

1. *Sulphuretted hydrogen gas* transmitted through the solution causes a dark brownish black precipitate of sulphuret of mercury, which is insoluble in nitric acid. If the solution be concentrated, the precipitate which is first formed by sulphuretted hydrogen has a white or yellowish tinge, by which it is, according to Pfaff, distinguished from all other metals that are thrown down black from their solutions, by this reagent. Hydrosulphuret of ammonia gives a similar precipitate, which, according to some chemists, passes slowly to a bright cinnabar red. The sulphuret of mercury, when dried and heated with carbonate of soda or metallic silver, readily furnishes a ring of pure metallic mercury. According to Dr. Christison, sulphuretted hydrogen detects corrosive sublimate where its proportion does not exceed a 35,000th of the solution. The test is not, however, to be considered conclusive without a reduction of the sulphuret; since several other metals give black precipitates with sulphuretted hydrogen. 2. *Solution of caustic potassa* occasions in solutions of corrosive sublimate a precipitate which is first reddish, but becomes yellow on the addition of an excess of the alkali; when dried, it is easily reduced by being heated *alone* in a test tube. 3. *Protochloride of tin.* This reagent occasions a precipitate which is at first white, and consists of *calomel;* a part of the chlorine of the corrosive sublimate having been abstracted by the protochloride of tin, which consequently becomes bichloride.

The white colour of this precipitate speedily changes to gray, and becomes finally nearly black. If the solution be very dilute, the precipitate is grayish black from the first. On warming the liquid it becomes clear, and a heavy precipitate, consisting for the greater part of metallic mercury, subsides. The presence of the metal may be demonstrated by throwing the precipitate on a filter and squeezing it gently between folds of bibulous paper, by which the minute globules generally cohere into one or two large ones. Dr. Christison says that protochloride of tin will affect solutions which contain only an 80,000th of the salt. It is not liable to any fallacy; being neither suspended in its action by the coexistence of any saline compounds, or by the presence of most animal or vegetable substances. 4. Iodide of potassium causes a beautiful pale scarlet precipitate, which rapidly deepens in tint: this precipitate is soluble both in iodide of potassium and also in corrosive sublimate itself; it is dissolved also by common salt, nitre, and probably also by other neutral salts; according to *Devergie*, when skilfully used, it acts where the salt forms only a 7000th of the solution. 5. On immersing a polished plate of copper in a solution of corrosive sublimate acidulated with hydrochloric acid, it soon becomes coated with the reduced metal, which may be readily obtained in globules by heating the copper (gauze) in a reduction tube. Dr. Frampton recommends *powdered sil-*

ver as a substitute for copper, by which more satisfactory results are obtained, and a larger quantity of mercury procured in the sublimate. 6. *The galvanic test.* On placing a drop of a strong solution of corrosive sublimate on a gold coin, and touching the latter through the solution with an iron point, the mercury will be deposited on the coin in the form of a bright silvery stain. This elegant test has been modified in a variety of ways. By the following process of *Deverge,* distinct indications are obtained where the poison does not form more than an 80,000th part of the water. A thin plate of gold, and another of tin, a few lines broad, and two or three inches long, being closely applied to one another by silk threads at the ends, and then twisted spirally, this small galvanic pile is left for twenty-four or thirty-six hours in the solution previously acidified with hydrochloric acid; upon which the gold is found whitened, and mercury may be obtained in globules by heating the gold in a tube. For facility of application, an important condition is, that the quantity of fluid should not exceed three or four ounces, because, in a larger quantity, the pile of the size stated cannot remove the whole of the mercury.

Detection of Corrosive Sublimate in Organic Mixtures.

From the researches of *M. Boullay* and *Professor Orfila,* it appears that various vegetable fluids, extracts, &c., possess the power of decomposing corrosive sublimate, a portion of the chlorine being gradually disengaged in the form of hydrochloric acid; the salt is consequently converted into calomel, which is deposited in a state of mixture, or combination with vegetable matter. It has been further shown by *Professor Taddei* of Florence, that *gluten* possesses the same property in a remarkable degree, and that that vegetable principle is capable of removing the poison completely from its solution, forming with it a ternary compound of *protochloride of mercury* and *gluten.* Among soluble vegetable principles *albumen, casein,* and *gelatin* possess similar properties; hence solution of albumen constitutes a convenient and effectual antidote against the effects of the poison. Various *insoluble* animal principles have been likewise shown to act on corrosive sublimate in the same manner as vegetable gluten, and this chemical action appears to be the source of the corrosive property of the poison. With these facts before us, it is evident that, in examining cases of poisoning by corrosive sublimate, we must not always expect to find it in a state of solution, even though it may have been received into the stomach in considerable quantities. The attention of the toxicologist must, therefore, be directed to both the liquid and the solid portions.

1. *Examination of the Liquid Portion.*—It is filtered from the solid matter, and a portion tested with protochloride of tin, or by the galvanic test. Should evidence of the poison be thus obtained, the remainder of the solution is mixed with half its volume of ether and well agitated: on allowing it to stand some time the greater part of the ether rises to the surface, and may be removed by a pipette. It should then be filtered, and evaporated to dryness, or distilled; and the residue, being redissolved in water, is submitted to the proper tests. Mr. Taylor does not find this process to answer unless the poison is present in a moderately large proportion. He therefore recommends to acidulate the suspected fluid with hydrochloric acid, and to immerse in it a narrow slip of finely laminated zinc, round which a spiral slip of fine gold foil has been twisted: if at the end of five or six hours the gold still retains its bright colour, no corrosive sublimate is present. Should it, on the other hand, be tarnished, it is washed, first in ether, and then in water, dried and heated in a small reduction tube to obtain a sublimate of the metal.

2. *Examination of the Insoluble Matters.*—They are boiled with distilled water, and the liquid having been filtered is tested as above described. Should no trace of the poison be thus obtained, Dr. Christison triturates the whole of the insoluble matters with protochloride of tin, and collects and washes the coagulum formed; he then boils it with a moderately strong solution of caustic potassa in a glazed porcelain vessel till all the lumps have disappeared. The animal and vegetable matters, and oxide of tin united with them are thus dissolved, and a powder of metallic mercury, generally easily discernible with a small magnifier, subsides. To separate it, the solution is allowed to remain at rest at a temperature little short of ebullition for fifteen or twenty minutes, the vessel is then

filled up with hot water, and the fatty matters which float on the surface skimmed off. After two or three effusions the black powder is transferred to a smaller vessel, and finally dried, and sublimed in a small tube. By this mode of operating, Dr. Christison has detected a quarter of a grain of corrosive sublimate mixed with two ounces of beef, or with five ounces of new milk, or porter, or tea, made with a liberal allowance of cream and sugar. He has also thus detected a tenth part of a grain in four ounces of the last mixture, that is in 19,200 times its weight. Mr. Taylor directs that the coagulum obtained by triturating the organic mixture with protochloride of tin should be well boiled in strong hydrochloric acid previous to digesting it with caustic potassa, in order to separate the mercury from the oxide of tin and organic matters, and to estimate it quantitatively. In cases where the quantity of poison is small, he has found this mode of treatment to be troublesome and not unattended with risk. In such cases, he prefers the galvanic test, by which he states that he has detected one-sixteenth part of a grain of corrosive sublimate dissolved in one ounce of organic liquid, and obtained metallic mercury from it in less than half an hour; and he does not think it possible to conceive a case where, in an analysis of this kind, the galvanic test would not be immediately applicable. In the *Comptes Rendus*, 31 *Mars*, 1845, MM. Danger and Flandin have described their method of extracting mercury from the *liver* of an animal poisoned by corrosive sublimate: the process is nothing more than a modification of the galvanic test, but the experiments are valuable as proving the absorption of the poison. Their process is as follows:—The animal substance finely cut up is heated to about 212°, with one-third or half its weight of strong sulphuric acid; in an hour or two the whole forms a dark carbonaceous-looking liquid. It is allowed to cool, and chloride of lime gradually added. The liquid becomes whiter and more viscid. The quantity of chloride used is about equal to the weight of the sulphuric acid: it is added until the whole appears like a white calcareous mass. The dried residue is then digested in absolute alcohol, which dissolves the mercurial compound. It is now diluted with water, and the earthy residue repeatedly washed, the liquids being afterwards mixed and concentrated. The concentrated liquid is placed in a funnel terminating at an angle of 90° in a capillary point—the galvanic plates of gold and tin being introduced into the contracted part of the funnel. In this way every drop of the liquid comes in contact with the metals, and the gold is slowly covered with mercury. They state that they have thus detected the metal in a solution containing the 100,000th part. According to Mr. Taylor, it is easy to detect corrosive sublimate in organic solids by simply boiling them with *copper gauze* and a few drops of hydrochloric acid.

It must be observed that *Orfila* takes an exception to the employment of tin and gold as the galvanic elements, and on these grounds:—"Some *tin*," he says, "may, after a time, be dissolved, and precipitated on the gold, and thus simulate the appearance of mercury; the whitened gold, when exposed to heat, may even recover its golden colour; the whitening of the gold does not, therefore, absolutely demonstrate the existence of a mercurial compound in the suspected substance; and, if the fluid metal cannot be afterwards obtained in distinct globules, the evidence must be regarded as inconclusive."

When corrosive sublimate is contained in organic substances (albumen, &c.) insoluble in water, *Rose* recommends to digest them in *ammonia* in preference to *potash*, the mercury being subsequently precipitated on copper much more readily from an ammonical than from a potash solution; and, in cases where ammonia fails to effect a solution, he prefers the following method of treatment to the ordinary one of digesting with nitric acid:—The dried substance mixed with about a quarter of its weight of carbonate of potassa is introduced into a capacious retort, and distilled at a heat gradually increasing to redness: the mercury rises and is condensed in the neck of the retort, where it can easily be distinguished from the brown viscid empyreumatic oil which passes over at the same time. If the organic matter contained only slight traces of mercury, the whole of the metal is found in the neck of the retort, none passing with the oil into the receiver.

8. *Copper.*

The chemical tests for salts of copper when in a state of solution are:—1. *Ammonia*, which produces a pale blue precipitate dissolving in excess, and forming a fine blue solution. 2. *Sulphuretted hydrogen, or hydrosulphuret of ammonia,* which occasion a dark brownish black precipitate. 3. *Ferrocyanide of potassium,* which gives a rich claret red precipitate. 4. A slip of *polished iron,* which, when immersed in the solution, speedily becomes covered with a coating of reduced copper. And, 5. *The galvanic test,* in applying which a drop of the suspected liquid is placed on a strip of platinum or silver, and touched with a zinc wire, when metallic copper is immediately deposited on the platinum or silver plate if any salt of that metal be present in solution.

All the salts of copper are possessed of poisonous properties; the two most commonly known are the sulphate (blue vitriol), and the subacetate (verdigris). It is not often that the medical jurist is called upon to examine cases of wilful poisoning with salts of copper, as their deep colour and strong metallic taste unfit them for the purposes of the murderer.

Detection of Copper in Organic Mixtures.—It was long ago shown by *Orfila* that albumen, milk, tea, coffee, &c., possess the property of decomposing solutions of the salts of copper, throwing down the oxide in union with various proximate principles. He also found that red wine, bile, vomited matters, and the tissues composing the stomach, although they do not decompose the soluble copper salts, alter materially the action of reagents on them. The following method, however, is applicable to all cases. If the suspected substance be a liquid it is filtered, and, as a trial test, a clean needle is suspended in it, and allowed to remain for some hours; if, at the expiration of that time, no red coating should be deposited on it, it is certain that no detectable quantity of the poison is present. That the presence of a large quantity of organic matter does not interfere with the action of this simple test, is proved by the following experiment of Mr. Taylor. He dissolved one-third of a grain of sulphate of copper in water, and mixed the solution with four ounces of thick gruel. Ammonia produced no effect on this liquid, and ferrocyanide of potassium gave only a faint reddish brown discoloration. Two drops of diluted sulphuric acid were added, and a bright needle suspended in the liquor by a thread: in twenty-four hours the needle was covered with a distinct film of copper. The quantity of copper salt here present was less than the six-thousandth part of the solution. If, then, the needle has indicated copper, a stream of sulphuretted hydrogen is passed through the liquor, and the precipitated sulphuret of copper washed, dried, and digested with strong nitric acid, by which it is converted into a mixture of nitrate and sulphate; it is filtered off from the separated sulphur, and the blue solution submitted to the above-mentioned tests for the detection of the metal. If the substance to be examined is too viscid for filtration, Dr. Christison passes it through a muslin sieve, adds two volumes of rectified spirit when cool, and then filters. Another process may be adopted. The filtered liquid is placed in a platinum crucible, dilute sulphuric acid added, and a strip of zinc introduced, wherever the platinum is touched by the zinc metallic copper is deposited, and after having in this way coated the platinum capsule, the surplus liquid is poured off, and the capsule well washed out; a few drops of nitric acid, with a small quantity of water, may be used to dissolve out the copper. In this way a pure solution of nitrate of copper may be obtained, and the metal, if in moderate quantity, may thus be separated from the most complex organic fluids.

But all these processes may fail to give any proofs of the existence of copper, and yet the poison may be present in a state of intimate union with some organic principles, or with the mucous membrane of the stomach, in which cases it would be insoluble. The following process must then be adopted. The solid substance is cut into small pieces, and added in successive portions to an equal weight of nitric acid; the mixture is then heated in a porcelain basin, with a fifteenth of chlorate of potassa. After the whole has been added, the product is heated till it becomes dark red and thick. The charring being complete, the carbonaceous mass is pulverised, then boiled with nitric acid diluted with its own volume of water, evaporated to dryness, redissolved, and the clear filtered solution tested with reagents. It must be mentioned, however, that objections have been raised against this mode of treatment, or rather against the conclusions that might be drawn from them, on the ground that copper exists *naturally* as a constituent part of many animal and vegetable substances, and more especially in the organs of the human body. *Meissner* and *Sarzeau* have examined a great many vegetable substances, and the latter chemist states that he has succeeded in separating metallic copper from *chinchona bark*, *madder*, *coffee*, *wheat*, and *flour*. *Devergie*, *M. O. Henry*, and *Orfila* assert that they have detected traces of copper by the process of incineration, in the bodies of animals not poisoned with the preparations of that metal. *Chevreul*, on the other hand, could detect no traces of copper in beef, veal, or mutton, and more recently *MM. Danger* and *Flandin* have positively denied that copper is ever found naturally in the human body. An extensive inquiry into this subject was undertaken by *M. Boutigny*, who thinks that he has traced the presence of copper in vegetable substances to its existence in the manures used for raising the different crops, and in animal substances either to their having been preserved or prepared in copper vessels, or to the animals having been fed on vegetables which had received a cupreous impregnation from the cause above mentioned. Another chemist traced the copper which made its appearance in his experiments to the filtering paper he was using. Mr. Taylor remarks, in reference to this subject, that in a practical view the objection amounts to nothing, since there would be very few cases in which all the chemical evidence rested on the incineration of the viscera, abundant proofs of the poison being generally afforded by an analysis of the contents of the stomach; the normal copper said to exist in food has not been found to form more than the 100,000th part of the food examined; and if the imputation of poisoning were well founded, and copper were discovered at all, the metal would be in infinitely larger proportion, so as to leave no doubt of its actual admixture.

A not unfrequent cause of accidental poisoning by salts of copper arises from the action of certain articles of food on the metal when used for culinary purposes. Pure water may be kept for any length of time in a clean copper vessel, without becoming in the least impregnated with the metal, provided the air be excluded; if, however, air has access, a hydrated carbonate, mixed with oxide of copper, is gradually formed. If the water contains common salt, or various other saline matters, it is found to exert a greater or less action on the metal, and to become impregnated with it. It appears, however, from the experiments of *Falconer* and *Eller*, that neither, milk, tea, coffee, beer, cabbage, potatoes, and sundry other vegetables, exert the least action on clean copper vessels, even by long boiling; but, if the vessel is not thoroughly clean, all acid substances dissolve the carbonate that encrusts it, especially if left in it for some time. Oily and fatty matters, also, if left for some time in copper vessels, become contaminated to such an extent as to acquire a nauseous coppery taste and a distinct green colour.

It was observed by *Dr. Falconer* that syrup of lemons might be boiled for fifteen minutes, in copper or brass pans, without acquiring any sensible impregnation; but if it was allowed to cool, and remain in the pans for twenty-four hours, the impregnation was discoverable by the test of metallic iron, and was perceptible to the taste. *Proust* made the same observations with regard to food prepared in copper vessels; and *Dr. Christison* quotes a fatal accident which occurred from a servant having left some sour krout for only a couple of hours in a copper vessel which had lost the tinning. As a general rule, no articles of food which contain saline, acid, or oily principles, should be prepared in copper vessels. Vinegar is occasionally found to contain traces of copper; and it is a well-known fact that sulphate of copper is sometimes employed for the purpose of giving a rich green colour to preserved fruits and vegetable pickles; the presence of the poisonous metal is easily detected by the iron test. In many old cookery books, halfpence are directed to be put amongst the pickles, to give them a fine green colour. In order to prevent accidental impregnations, copper vessels employed in cookery are coated with an alloy of tin and lead; there is no danger to be apprehended from the latter metal, for, although some of its salts are poisonous, it has been ascertained that the substances which possess the property of dissolving lead cannot attack that metal before the whole of the *tin* in the alloy is oxidated. Sulphate of copper was, some years ago, extensively employed in France by bakers, who used it to accelerate the panary fermentation; the proportion required being an ounce of the salt in two pints of water for every hundredweight of dough. Some chemists have denied that sulphate of copper possesses any such property as that imputed to it by the French bakers; but, from the experiments of *Meylink*, it appears that not only does the fermentation of the dough take place more quickly, but that the adulterated loaves, when taken out of the oven, are much whiter and much better raised than those not adulterated; he found that, if more than eight grains of the salt were added to half a Flemish pound of dough, it could be detected by a peculiar taste and a slight green colour. He found, moreover, that the employment of the salt of copper, even in the small proportion of one grain, had the singular effect of bringing about the complete fermentation of the dough with considerably less loss of weight than occurs in the common process of baking; the loss in the sound and in the adulterated loaves being in the proportion of 116 to 100. These remarkable results appear to require confirmation; but, if they are correct, the object of the French bakers in employing sulphate of copper is easily explained, the practice being a fraud on the public, by enabling them to make their loaves of a standard weight with a less allowance of nutritive material. It does not appear that this practice has extended to England. A case of poisoning by copper, from the use of German silver, which contains fifty per cent. of copper, is mentioned by Mr. Taylor. It appears that a spoon made of this material had been left in an earthenware vessel in which eels had been cooked with butter and vinegar; and chemical analysis showed that the cupreous poison had thereby been introduced.

9. *Lead.*

The preparations of this metal, which require the particular attention of the toxicologist, are the *protoxide*, the *carbonate*, the *acetate*, and the *subacetate*.

For the chemical properties of *litharge* (protoxide of lead), see page 43. It is extensively used in the arts, and is occasionally brought under the notice of the toxicological chemist in consequence of its intentional, as well as its accidental, introduction into articles of food and drink. The vegetable acids, and alkaline and fatty substances, dissolve the protoxide of lead, forming salts of a poisonous character; and as earthenware vessels employed for culinary purposes are well known to be glazed with litharge, the accidental adulterations of food and liquids which have been prepared or allowed to remain for some time in such vessels, are not of uncommon occurrence. Pies which have been baked in a newly glazed vessel have been known to become contaminated with oxide of lead, and to have occasioned the peculiar symptoms of lead poisoning in the persons partaking of them. The presence of the deleterious metal in the food, in cases of this kind, is proved by moistening the articles with hydrosulphuret of ammonia, by which they become of a more or less brown colour; and lead is detected in the glaze of the vessels by boiling in them acetic acid or caustic potash, by which the oxide becomes dissolved. Cases of poisoning by the accidental impregnation of articles of drink with oxide of lead would probably be more frequent, but for the property possessed by some vegetable substances, particularly those containing tannin or gallic acid, of forming insoluble compounds; but, as a general rule, no substances used for food should be kept in leaden vessels, neither should liquids containing free acid, or in which a vegetable acid is likely to be formed, be kept for any length of time in a newly glazed earthenware vessel. Dr. Christison relates a case in which lead colic, paralysis, and death were occasioned by eating the cream which formed on milk kept in a leaden cistern. Wines have been accidentally impregnated with oxide of lead, in consequence of the bottles having been cleaned with shot, and some of the pellets left behind; the impregnation is not very likely to occur to any injurious extent in good wine, such as port or sherry, but in acid wines, such as currant or gooseberry, a sufficient quantity of the oxide might be dissolved to produce serious consequences. Wines have been also designedly adulterated with oxide of lead, to remove their acidity, and to give them a sweet taste; this fraud was formerly practised to a considerable extent. It was detected and exposed in France by Fourcroy. In this country it does not appear to have been pursued to any material extent; though, before the poisonous nature of lead compounds was generally known, British wines must have been frequently adulterated, for, in an old cookery book, quoted by Sir G. Baker, the following recipe occurs:—

"*To hinder Wine from turning.*—Put a pound of melted lead in fair water into your cask, pretty warm, and stop it close."

Cider, also, is apt to become impregnated with salts of lead, in consequence of the metal being used for various purposes in the construction of the cider house; and although the source of the contamination was long ago pointed out by Sir George Baker, so recently as 1841, a set of cases which presented the incipient symptoms of lead colic were traced by *MM. Chevalier* and *Ollivier* to cider having been adulterated with lead to the amount of nearly two grains and a half per quart, in consequence of a publican having kept his cider for two days in a vessel lined with lead. The poisonous salt was found to be *malate*. *New rum* is often found to contain lead, which it derives from the worm of the still; this action might probably be prevented by alloying the lead with *tin*. *Old rum*, on the contrary, never contains the poison; a circumstance which affords a good illustration of the action of *tannin* in precipitating the metal in an insoluble form, for *Dr. Traill* states that the rum intended for immediate consumption is collected at once from the still into glass bottles, while that intended to be kept is received into oak casks.

When *oxide of lead* has to be looked for in liquids containing organic substances, a little nitric acid should be added previous to filtration, in order to redissolve any insoluble compound formed by the salts of lead with albumen and other organic principles, sulphuretted hydrogen is then transmitted through the clear liquor: if a dark-coloured precipitate is formed, the whole is boiled and the precipitate collected on a filter. It is washed and dried, and then boiled with strong nitric acid, by which the sulphuret of lead is wholly or in part converted into nitrate, which being soluble in water is filtered, neutralized by ammonia, and submitted to the general reagents as directed, page 43. Should it be necessary to examine the insoluble matters, they are to be cut in small pieces and incinerated in a crucible with four parts of black flux, any lead that may be present will be found fused into a small button at the bottom of the crucible, and may be removed from the carbonaceous matters by washing with water. If the metal is in the form of dry oxide, it is readily detected by the blowpipe on charcoal, or by mixing it with paste, spreading the mixture on a piece of card, drying and burning it, when metallic lead is immediately produced.

Poisoning by *carbonate of lead* is very common amongst white lead manufacturers and painters, the poison finds its way into the system continuously and insidiously in minute quantities, inducing the complaint known as *colica pictonum* and paralysis. Cases of this form of poisoning have not been so frequent in the manufactories of white lead since the practice has been adopted of grinding the carbonate in water. Dr. A. T. Thompson considers that the *carbonate* is the only compound of lead which possesses poisonous properties; and that, if any other salt in small doses becomes so, it is in consequence of its conversion into carbonate in the body. This opinion is not, however, adopted by Dr. Christison, or by Mr. Alfred Taylor. Carbonate of lead is known by the following properties:—1, it is blackened by sulphuretted hydrogen; 2, it is soluble with effervescence in nitric acid; if however, as is frequently the case, with the commercial carbonate, it contains sulphate of lead or sulphate of baryta, the two latter substances remain undissolved by the nitric acid. The presence of oxide of lead in the nitric acid solution is proved by the tests mentioned page 43. 3, it is decomposed when ignited on platinum foil, leaving oxide of lead of a yellow colour; 4, it is reduced on charcoal by the blowpipe, metallic lead being produced.

The *acetate of lead* (*sugar of lead*) is the salt most frequently employed for criminal purposes, though there are but few cases on record of its having been so used. It is not by any means an active poison, and has been administered medicinally in quantities of from thirty to forty grains daily without any serious effects. In appearance it greatly resembles loaf sugar; it has a sweet taste, succeeded by one of astringency: it is very soluble in water. An emetic of sulphate of zinc is recommended as the best antidote in cases of poisoning by it. Milk or albumen may likewise be administered in large quantities; these substances precipitating the oxide of lead in an insoluble form. The soluble alkaline sulphates, those of soda and magnesia may also be given, but carbonates should be avoided, the carbonate of lead being poisonous. *Goulard's extract* (*the diacetate*), which contains more oxide of lead than the neutral acetate, is a much more powerful poison than the latter. It cannot readily be procured in a solid or crystalline state, and its solution is distinguished from that of acetate of lead by its being precipitated by solution of *gum acacia*.

Among the most important forms of poisoning by lead is that occasioned by the action exerted by pure water on the metal. That water is liable to acquire noxious properties by travelling through lead pipes was known to the Roman architect, *Vitruvius*, who, it is believed, lived in the time of *Julius Cæsar* and *Augustus*. *Galen* also condemns the use of lead pipes on the grounds that the water transmitted through them acquires poisonous properties. The conditions under which lead becomes corroded by water were first made the subject of investigation by *Dr. Lambe*, and the inquiry was afterwards taken up by *Guyton-Morveau;* these two chemists, however, came to opposite conclusions from their researches; the former asserting that spring waters possess the greatest power of corrosion in consequence of their saline ingredients, and the latter stating that some natural waters hardly attack the metal at all, being prevented from doing so by the salts they hold in solution. Dr. Thomson, of Glasgow, who subsequently examined the subject, sided with Dr. Lambe with respect to the action of spring water on lead, but maintained that the metal was not dissolved, but merely held in suspension. In this conflicting state of the evidence on a matter of such great practical importance, Dr. Christison undertook an extended investigation of the whole subject of the action of different waters on lead, and some valuable observations have still more recently been made by Colonel Yorke and Mr. Taylor.

It appears that distilled water, from which all gases have been expelled by boiling, if excluded from contact with the air, has no action on lead; if, however, air, free from carbonic acid, be allowed to have access, a quantity of white matter is soon formed, which goes on increasing for some time and finally settles as a white powder at the bottom of the vessel, this white powder consists of the hydrated oxide; but, if the surface of the water be exposed to the open air, the substance formed consists of minute brilliant pearly scales and is a basic carbonate, composed, according to the analysis of Dr. Christison, of two equivalents of neutral carbonate and one of hydrated protoxide; a minute quantity of lead amounting, according to Colonel Yorke's experiments, to a 10,000th part, is dissolved by the water. It results from these observations that distilled water cannot with safety be kept in leaden vessels; and it is important further to state that the distilled waters of aromatic plants possess a power of acting on lead to an extent equal to that of water itself, hence these preparations should never be preserved in leaden vessels. All neutral salts possess in a greater or less degree the property of impairing the corrosive power of water; thus, according to the experiments of Dr. Christison, $\frac{1}{4000}$th part of sulphate of lime, $\frac{1}{2000}$th of muriate of soda, and $\frac{1}{30000}$th of phosphate of soda exert a preservative power. Mr. Taylor found that, when sulphate of lime formed not more than $\frac{1}{5000}$th part of the weight of the water, no carbonate of lead was formed. The preservative power depends upon the acid and not the base of the salt. In the case of sulphate of lime, sulphate of lead appears to be formed, which invests the metal, and thus protects it from the action of water; so that a water which affords a copious precipitate with a salt of baryta, which is not redissolved by free acid, is not very likely to become impregnated to any serious extent by passing through lead pipes or by standing in leaden vessels. Rain and snow water, as might be supposed, act upon lead almost as rapidly as distilled water, hence rain water collected from leaden roofs and gutters, particularly if recently erected, is unfit for cooking purposes. As most spring waters contain muriates and sulphates, their action on lead is generally inconsiderable; it is always, however, advisable to have a careful analysis of the water made before it is allowed to be conveyed through leaden pipes or preserved in leaden vessels. If the water does not contain the requisite amount of sulphates or muriates, it must not be considered safe for domestic purposes after it has been allowed to come into contact with lead. An effectual protection has, however, lately been introduced by a patent invention for covering lead pipes both externally and internally with a thin coating of *tin*. It may lastly be observed, that though it may be practically safe to keep some waters in leaden cisterns, it may be unsafe to use *covers* of this metal, because the water which condenses on the covers must be considered as pure water, and thus white lead may be formed and introduced into the water.

10. *Antimony.*

The only preparation of this metal that is likely to occasion accidents from its incautious use is *Tartar Emetic.* The characters by which it may be known are the following:—As commonly met with in commerce, it is a white or yellowish white powder; it is soluble in fourteen parts of cold, and two of boiling, water (Taylor); its taste is acrid and metallic; its solution in water decomposes by keeping; when heated in a porcelain crucible it chars, and the charred mass may be reduced by strong ignition in a hard glass tube, but no sublimate is formed; when boiled with strong hydrochloric acid and metallic copper, it is decomposed, and antimony is deposited on the copper; the aqueous solution of tartar emetic is precipitated in the form of *sub-nitrate* by dilute nitric acid, the precipitate is redissolved by excess of nitric acid and also by *tartaric acid;* it is *not* precipitated by ferrocyanide of potassium; *sulphuretted hydrogen* throws down a sulphuret of antimony of an orange yellow colour, if the solution be very dilute the colour may be yellow, but it is at once distinguished from sulphuret of arsenic by its solubility in strong hydrochloric acid, and subsequent precipitation by the addition of water. Tartar emetic is likewise precipitated by *hydrosulphuret of ammonia*, which is not the case with a solution of arsenic. When a solution of tartar emetic is introduced into a flask containing the materials for generating hydrogen gas, it is decomposed, a gaseous compound of antimony and hydrogen being formed; if this gas be allowed to pass along a horizontal tube of hard German glass, and the tube be heated to redness at a certain point, decomposition of the gas will take place at that spot; on both sides of which a brilliant mirror of antimony will be deposited. For the method of distinguishing this deposit from the mirror formed by arsenic under similar circumstances, see pp. 49 and 52.

When tartar emetic has to be sought for in organic mixtures, it may be necessary to examine the solid as well as the liquid portions, in consequence of the property possessed by certain organic principles, particularly such as contain *tannin*, of forming with oxide of antimony insoluble precipitates. The subject of analysis is acidulated with hydrochloric and tartaric acids and filtered. As a trial test, a piece of paper may be dipped in the clear liquid, and then immersed in hydrosulphuret of ammonia; the production of an orange-red stain indicates antimony. The whole of the filtrate is now treated with sulphuretted hydrogen, and the precipitate, after being well washed, is boiled with strong hydrochloric acid, and the solution mixed with a large quantity of water; the formation of a dense white precipitate is characteristic of antimony (the oxychloride). Should no indication of antimony be obtained from the liquid portion, the solid residuum on the filter must be boiled for some time with a strong solution of tartaric acid, filtered, and treated precisely as above. It may still be necessary to examine the tissues of the body. *Orfila* proceeds thus:—The thoroughly dried viscera, &c., are boiled with concentrated nitric acid until dissolved; the mass is then evaporated to dryness and carbonized; the carbonized residue is digested with nitro-muriatic acid, by which all the antimony is converted into chloride; a portion is then examined in Marsh's apparatus for an antimonial sublimate, and another portion, after being evaporated to dryness, is moistened with hydrosulphuret of ammonia. In this way *Orfila* succeeded in obtaining proof that antimony is absorbed; he thus detected it in the liver.

It must be remembered that, as preparations of antimony are used as medicine, it is not the discovery of small quantities of the metal that can be received as a proof of intentional poisoning, as in the case of arsenic. Mr. Taylor says that tartar emetic is by no means as poisonous as it is often described to be, and that, though in doses of from half an ounce to an ounce or less it must be regarded as an irritant poison, it has been administered in doses of forty grains in twenty-four hours to an adult without occasioning any serious mischief.

11. *Zinc.*

This metal is used in medicine in the form of sulphate. It acts as an emetic, and as such is frequently administered in cases of poisoning by other substances. When given in over-doses, it acts itself as an irritant poison, and has destroyed life; but that it may be received into the stomach in considerable quantities without producing any serious consequences, is evident from the circumstance of Dr. Babington having administered to a patient *thirty-six grains* three times a day, for several weeks, without even sickness being produced. Regarded as a poison, therefore, sulphate of zinc does not claim much notice; but it is necessary that the toxicologist should be familiar with its action with reagents, in consequence of its medicinal use, and the probability of his encountering it while searching in the contents of the stomach for more formidable poisons. For the behaviour of solutions of oxides of zinc with reagents, see p. 39. The most characteristic test is the action of sulphuretted hydrogen, by which it is precipitated *white.* In order to precipitate it effectually, the oxide should be precipitated and redissolved by ammonia, and the gas then passed into the alkaline solution. Mr. Taylor warns the analyst to beware of mistaking a *yellow* precipitate, which may be produced by sulphuretted hydrogen in solutions of oxide of zinc, for *arsenic,* an error which has been committed; zinc sometimes contains traces of *cadmium,* which metal is precipitated yellow by sulphuretted hydrogen. Sulphuret of cadmium is distinguished from sulphuret of arsenic by its insolubility in hydrosulphuret of ammonia.

CHEMICAL MANIPULATION

AND

ANALYSIS.

PART II —QUANTITATIVE.

CHAPTER I.

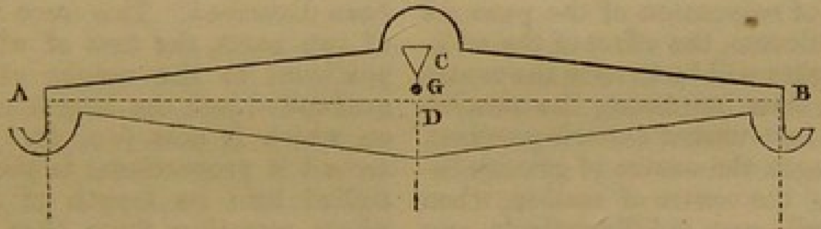
On Quantitative Operations.

Weighing.—*The Balance.*—Of the various implements required by the analytical chemist in the prosecution of his labours, the *balance* is the most important; for of what value would the most elaborate and exact experiment be without a means of ascertaining the quantitative result? The *balance* therefore demands our first attention.

The process of weighing may be performed in a variety of ways, and with various kinds of machines; but the instrument invariably employed by the chemist for determining the weights of the substances on which he is engaged, is what is generally known as the common balance, which is a lever of the first kind, with equal arms. A detailed investigation of the circumstances which regulate the sensibility of a balance, and a mathematical development of the principles on which it is constructed, would be out of place here*: it may not, however, be amiss to describe briefly some of the most important points connected with its construction and properties.

The philosophical balance may be described as an uniform inflexible lever or beam, *fig.* 1, made as light as is consistent with a proper degree of strength, and having three axes, one the fulcrum or centre of motion, C, on which it turns, and the other two, A and B, situated at equal distances from the fulcrum near to the extremities of the beam, and from which the scales or pans depend: the beam thus supports the scales, and is itself supported by means of fine edges of hard steel working on steel, agate, or garnet, in order that the motion may be free and the distances of the points precisely defined. The scales hanging from fixed points in the beam act on them always in the direction of gravity; and the effect is the same as if the whole weight were concentrated in those points.

Fig. 1.



The requisites for a good balance are:—

1st. That the centre of gravity, G, shall be immediately below the fulcrum or centre of motion, C.

2nd. That the fulcrum or centre of motion shall be in the same right line with the points of suspension of the scales; so that a straight line drawn from one extremity of the beam to the other, shall be exactly perpendicular to the straight line, C D, joining the centre of gravity with the centre of motion; and

3rd. That the arms shall be of equal length.

For if, in the first place, the centre of gravity and the centre of motion be coincident, the beam will rest in any indifferent position, the scales being equally loaded; but if the centre of

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* The student will find the subject fully and clearly discussed in the 2nd *Treatise on Mechanics, Elements of Machinery*, Part I.

K

gravity be above the centre of motion, then the slightest impulse will cause the beam to upset (*see* chap. iv. Treatise 1, on Mechanics): if, however, the centre of gravity be immediately under the fulcrum, then the line joining it with the latter will always settle itself so as to be in a vertical direction; this line has the properties of a pendulum, the shorter it is the greater the angle formed by its vibration from a given impulse, consequently the nearer the centre of gravity to the centre of motion, the greater the effect of a given weight added to the scale; or, in other words, the more delicate the balance. The nearer also the centre of gravity of a balance is to its fulcrum the slower will be the oscillations of the beam. The number of oscillations, therefore, made by the beam in a given time, affords the most accurate method of judging of the sensibility of the instrument, which will be the greater as the oscillations are fewer.

In the second place, if the points of suspension of the pans are situated below the centre of motion of the beam, the effect of each addition of weight to the scales will be to *lower* more and more the centre of gravity; and this we have just seen diminishes the sensibility of the balance. If, on the other hand, the points of suspension of the pans are *above* the fulcrum, the effect of the addition of weights will be to *raise* the centre of gravity, thus increasing the sensibility of the instrument (*cæteris paribus*), until at length the centre of gravity becomes itself the centre of motion, when the beam will rest indifferently in any position, and finally, by a further addition of weights, the centre of gravity becomes raised above the fulcrum, and the balance upsets from the smallest disturbance.

In the third place, with respect to the equality of the arms, this condition is of course essential to a good balance; it is nevertheless possible to weigh as accurately with a balance with unequal arms as with one of the same workmanship with equal arms; for this purpose the substance to be weighed is put into either scale and counterpoised by sand, shot, or any other material, with the greatest accuracy; the substance is then removed and the balance once more brought into a state of equilibrium by substituting weights, which, it is perfectly obvious, must, under these circumstances, absolutely represent the weight of the substance under examination. It is not unfrequent to meet with commercial balances constructed with unequal arms for fraudulent purposes, the substance to be sold being always put into the scale depending from the longer arm; the fraud is detected by simply transposing the substance and the weights after equilibrium has been established between them.

Sensibility and *stability* are two properties essential to a good balance.

The sensibility of a balance is estimated by observing the angle through which a very small weight inclines the beam; thus, supposing we wish to compare the sensibility of two balances, and that a grain weight put into a scale of each inclines the beam of the first 4°, and that of the second only 2°, then the first is twice as sensible as the second. Now, as the force which acts in turning the beam is proportional to the weight multiplied into the length of the lever at the extremity of which it acts, it is evident that, for a given weight, the sensibility of the balance—all other circumstances being equal—is proportional to the length of the beam.

The stability of a balance is the force with which the beam endeavours to recover its equilibrium, and oscillate about its position of rest after it has been disturbed. This force is made up of two parts, the first of which is proportional to the weight of the beam multiplied into the length of the lever on which it acts (C G, *fig.* 1); and the second is proportional to the load multiplied into its length of lever; the whole restoring force then, and that which the preponderating weight has to overcome in turning the scale, is proportional to the weight of the beam multiplied into the length of the lever on which it acts, added to the load multiplied into its length of lever. It is evident, then, that *sensibility* and *stability* are two properties in some degree opposed to each other, and that whatever tends to increase the one diminishes the other. The best construction is to make the lever through which the load acts equal to nothing, and this is done by placing the three points of action, A B C, *fig.* 1, in the same straight line as has already been explained, and by keeping the centre of gravity a little below that line: the sensibility of the balance is thus rendered independent of the load, and this important property is still further increased, by making the beam as light as possible.

The conditions of a perfect balance, as determined by theory, are the guide of the artist in the construction of a good instrument; and although an absolutely perfect balance is practically unattainable, nevertheless, by attending carefully to the principles above explained, the sensibility may be carried to a surprising extent. There is, in the possession of the Royal Society, a balance made by Ramsden, which weighs ten pounds, and is said to turn with the ten-millionth part of that load, or the thousandth part of a grain. The balances constructed by the late Mr. Robinson have long enjoyed a just celebrity. They are thus described by Captain Kater*, who has himself constructed an instrument for verifying the national standard bushel, which is probably the most sensible that has yet been made†. "The beam of Robinson's balance is only ten inches long. It is a frame of bell-metal, in the form of a *rhombus*. The fulcrum is an equilateral triangular prism of steel, one inch in length; but the edge on which the beam vibrates is formed to an angle of 120°, in order to prevent any injury from the weight with which it may be loaded. The chief peculiarity in this balance consists in the knife edge which forms the fulcrum bearing upon an agate plane throughout its whole length. The supports for the scales are knife edges, each six-tenths of an inch long. These are furnished each with two pressing screws, by means of which they may be made parallel to the central knife edge. Each end of the beam is sprung obliquely upwards and towards the middle, so as to form a spring, through which a pushing screw passes, and serves to vary the distance of the point of support from the fulcrum, and at the same time, by its oblique action, to raise or depress it, so as to furnish a means of bringing the points of support and the fulcrum into a right line. A piece of wire, four inches long, on which a screw is cut, proceeds from the middle of the beam downwards. This is pointed to serve as an index, and a small brass ball moves on the screw, by changing the situation of which the place of the centre of gravity may be varied at pleasure. The fulcrum, as before remarked, rests upon an agate plane throughout its whole length, and the scale-pans are attached to planes of agate which rest upon the knife edges, forming the points of support. This method of supporting the scale-pans is believed to be due to Mr. Cavendish. Upon the lower half of the pillar, to which the agate plane is fixed, a tube slides up and down by means of a lever which passes to the outside of the case. From the top of this tube arms proceed obliquely towards the ends of the balance, serving to support a horizontal piece, carrying at each extremity two sets of Ys, one a little above the other. The upper Ys are destined to receive agate planes, to which the scale-pans are attached, and thus to relieve the knife edges from their pressure; the lower to receive the knife edges which form the points of support: consequently these latter Ys, when in action, sustain the whole beam.

"When the lever is freed from a notch in which it is lodged, a spring is allowed to act upon the tube we have mentioned, and to elevate it. The upper Ys first meet the agate planes carrying the scale-pans and free them from the knife edge. The lower Ys then come into action and raise the whole beam, elevating the central knife edge above the agate plane. This is the usual state of the balance when not in use; when it is brought into action the reverse of what we have described takes place. On pressing down the lever, the central knife edge first meets the agate plane, and afterwards the two agate planes carrying the scale-pans are deposited upon their supporting knife edges."

A balance of this kind was employed by Captain Kater in adjusting the national standard pound. With a pound troy in each scale, the addition of $\frac{1}{100}$th of a grain caused the index to vary one division, equal to $\frac{1}{10}$th of an inch; and Mr. Robinson adjusted these balances so that, with one thousand grains in each scale, the index varies perceptibly on the addition of one-thousandth of a grain, or of one-millionth part of the weight to be determined.

Such is Robinson's balance; we shall now describe the chemical balance, as constructed by Mr. Oertling, of Store Street, Bedford Square, illustrating the description with engravings of two instruments recently made by that ingenious mechanic for the writer of this treatise. It must be mentioned, how-

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* Lardner's Cyclopædia. Treatise on Mechanics.
† Philosophical Transactions for 1826.

ever, that Mr. Oertling constructs balances much more sensible than the one we shall first describe, in which the scale-pans are attached to agate planes, as in the balance of Robinson, while the increased length of the beam and other mechanical arrangements give them a decided superiority over the latter.

Fig. 2 represents a balance intended to carry from 700 to 1000 grains, and which will, when loaded, indicate the $\frac{1}{100}$th of a grain. It is represented in the figure with a Liebig's potash apparatus attached to one of the pans, the object being to show the facility which a long beam gives to the operator, for weighing these awkward pieces of apparatus. The beam of this balance is 16 inches long. The balance, as seen in the figure, is at rest, so that a weight placed in one of the pans will not affect the equilibrium of the beam. By turning the knob in the front part of the case between the two drawers from right to left, the arm supporting the beam will descend, and the balance will be free; the oscillations of the beam will then be observed by the index moving over an ivory scale in front of the stand. The fulcrum, or centre knife edge of the beam, works upon agate, with which, however, it is only in contact when the balance is free. The pans are suspended by fine platina wire, and are provided with steel hooks, which hang in rings attached to the ends of the beam; these rings are ground out conically from each side, so as to form a perfect edge. The apparatus fixed at the right side, above the beam, serves to move a small weight along that arm, which, as well as the other, is accurately divided into ten equal parts. This movement is effected by means of a small knob outside the case. The weight used for this purpose is made of fine gilt wire, with a loop at the top. It weighs $\frac{1}{10}$th of a grain, consequently, when placed at the 1st, 2nd, 3rd, &c., division of the beam, it represents one, two, or three hundredths placed in the pan. By subdividing each division the weight may be ascertained with great accuracy, and all weights less than $\frac{1}{10}$th of a grain may be dispensed with. The knob seen above the centre of the beam can be raised or lowered, and serves to adjust the centre of gravity, which ought to be a little below the fulcrum, or centre of motion. The beam has also adjustments for bringing the ends and the centre knife edge into the same straight line, and also for equalizing the lengths of the arms; these contrivances could not, however, be well represented in the figure.

Fig. 2.

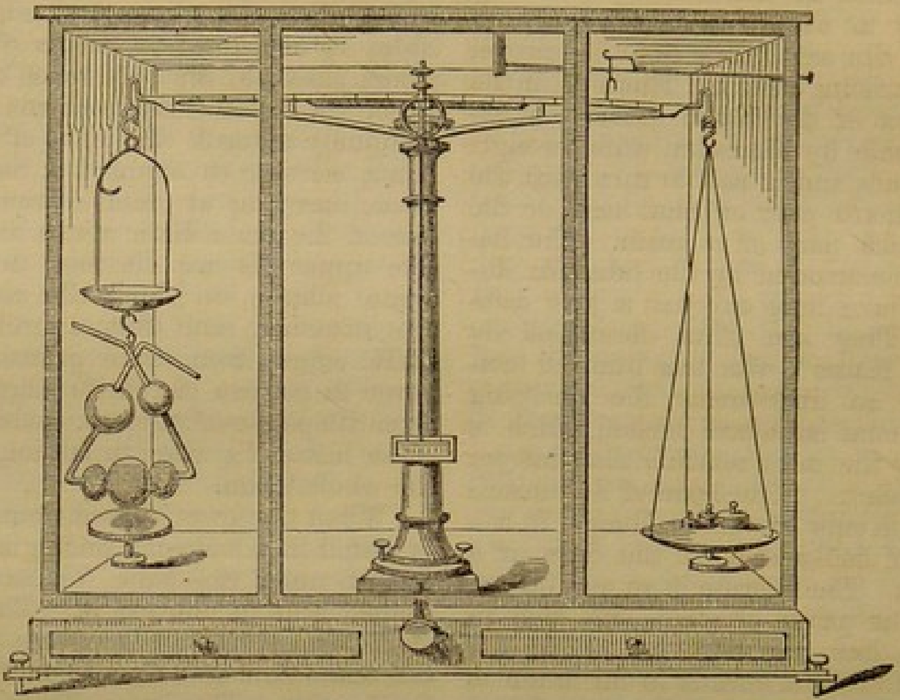
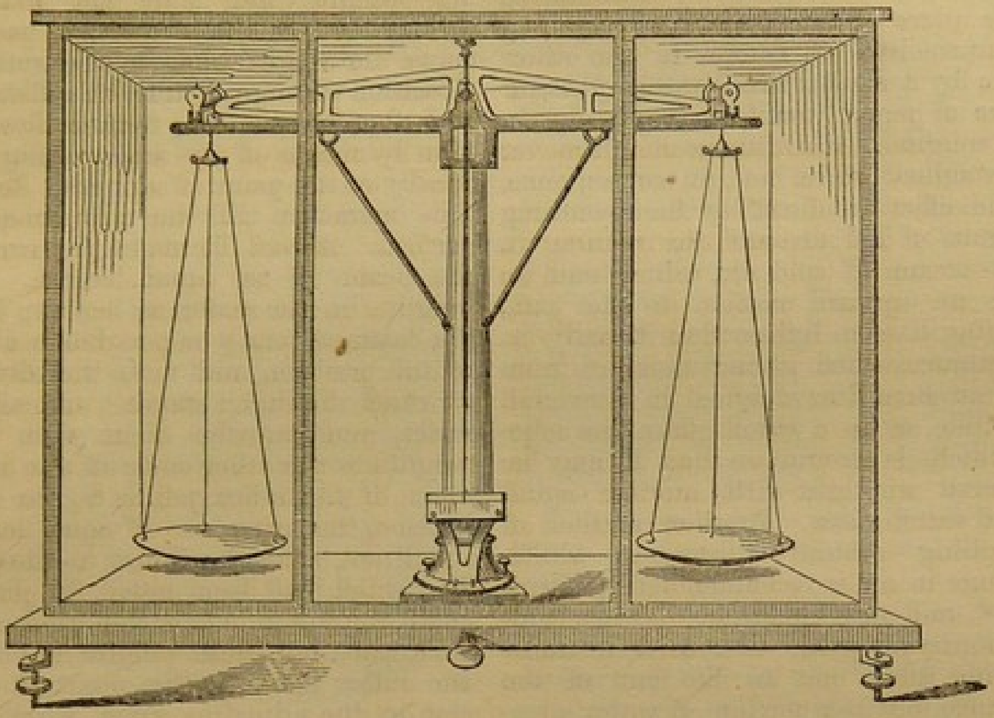


Fig. 3 exhibits a balance of a larger description. It is an admirable instrument. Its beam is 18 inches long, and it is intended to carry from two to three pounds in each pan; and when loaded with such a weight it indicates dis-

Fig. 3.



tinctly $\frac{1}{50}$th of a grain. In order to obtain such a degree of delicacy with so large a weight, it is necessary that the best construction should be adopted. The great distinction, therefore, between this balance and the one just described is, that here the beam is furnished with a straight knife edge at each end, upon which the pans are suspended by agate planes; by this construction, not only a greater delicacy and durability, but also a greater constancy is obtained than could be arrived at with any other kind of balance. The instrument is represented in the figure as set free for oscillation, and on turning the knob in front from left to right, the straight arms close under the beam are raised, and receive the end pieces to which the pans are suspended by the small cylinders indicated in the figure; therefore, when the balance is at rest, the centre knife edge of the beam is taken off the agate plane of the stand, and the agate planes with the pans are taken off the knife edges of the beam. The oscillations of this balance are also observed by an index moving over an ivory scale, in front of the stand.

Of these two balances, the latter is the most generally serviceable in the laboratory, on account of the large weight which it will carry. The pans are made of brass, and are six inches in diameter; they are supported by stout brass wire, and the distance from the centre of the pans to the small brass plate to which the supporting wires are attached is 10½ inches; evaporating dishes and flasks of considerable size may therefore be weighed, and mineral waters and filtrates contained in large beakers may be estimated by weight instead of by measure, a method always to be preferred. Both balances are inclosed in glass cases, having convenient doors at the front and sides, and the smaller one is provided with a contrivance for steadying the pans during the operation of weighing, as seen on the left hand side of the figure.

In performing the process of weighing, the student will do well to observe the following rules:—1. Always to use the same pan for the same purpose, for although in a good balance it is obviously a matter of indifference which pan receives the weights and which the substance, nevertheless, an attention to the practice of always placing the substance to be weighed in the same scale, serves in a great measure to obviate any error which may arise from inequality in the length of the arms; as, if the weights are always put into the same pan, the substance weighed in the other will be in the same proportion as the weights, though not exactly equal to them; and, in chemical experiments, proportional quantities are in general of far greater importance than *real* weights. 2nd. Never to place the substance to be weighed *directly* on the scale, but upon some interposed substance, as a watch glass, or, occasionally, on a piece of hot-pressed wove paper, counterpoised of course in the other scale by a similar sized watch glass, or piece of paper, previous to putting in the weights. A substance should never be weighed while hot, in consequence of the effect produced by the ascending current of hot air, and the rushing in of a stream of cold air, which tend to give an upward motion to the pan, making it seem lighter than it really is. Substances which attract moisture from the air should be weighed in a covered crucible, or in a watch glass, the edge of which is ground so that it may be covered air-tight with another equal sized watch glass. Another method of weighing certain substances which change in air is recommended by *Faraday**, and may sometimes be very conveniently adopted. It consists in transferring them not to the pan of the balance, but to a portion of water, alcohol, &c., as the case may be, of known weight, and ascertaining the increase of weight so occasioned, the analysis or experiment is then made with the solution instead of the solid body. A third important rule to be observed in weighing is never to make any adjustment of weights or substance in the scales while the beam of the balance is free, but always to take it off its support previous to interfering in any way with the contents of the pans. The neglect of this precaution will soon entail serious injury on a delicate balance.

The following method of examining a newly purchased balance, prescribed by Captain Kater, may be usefully inserted here, by way of conclusion to the few observations we have thought it advisable to make on the subject of this important instrument. *First.* To ascertain whether the points of suspension and the fulcrum are in a right line, make the vibrations of the balance very slow by moving the weight which influences the centre of gravity, and bring the beam into a horizontal position by means of small bits of paper thrown into the scales. Then load the scales with nearly the greatest weight the beam is fitted to carry. If the vibrations are performed in the same time as before, no further adjustment is necessary; but if the beam vibrates quicker, or if it oversets, cause it to vibrate the same time as at first, by moving the adjusting weight, and note the distance through which the weight has passed; move the weight then in the contrary direction through double this distance, and then produce the former slow motion by means of the screw acting vertically on the point of support. Repeat this operation till the adjustment is perfect. *Second.* To make the arms of the beam of an equal length. Put weights in the scales as before; bring the beam as nearly as possible to a horizontal position, and note the division at which the index stands; unhook the scales, and transfer them with their weights to the other ends of the beam, when, if the index points to the same division, the arms are of equal length, but if not, bring the index to the division which had been noted, by placing small weights in one or the other scale. Take away half these weights, and bring the index again to the observed division by the adjusting screw, which acts horizontally on the point of support. If the scale-pans are known to be of the same weight, it will not be necessary to change the scales, but merely to transfer the weights from one scale-pan to the other.

Weights.—The unit of weight adopted in this country is the *grain*, and in France and Germany the *gramme*.

It must be regarded as an unfortunate circumstance, that we have in England two different sets of weights expressed by the same names. The pound and the ounce troy and avoirdupoise have different values. The avoirdupoise pound is greater than the troy pound, the former weighing 7000 grains, and the latter 5760; but as there are in the avoirdupoise pound sixteen ounces, while in the troy pound there are only twelve, it follows, that the troy ounce is greater than the avoirdupoise ounce, the latter weighing 437½ grains, and the former 480. In order to avoid fractions, and as there are no other grains than troy grains, troy weight is always used for philosophical purposes.

The standard to which troy weight is referred, is the weight of one cubic inch of distilled water, which at 62° Fahr. and 30 inches barometer weighs 252.458 grains. The troy weight table is

gr.		dwt.		oz.		lb.
24	=	1				
480	=	20	=	1		
5760	=	240	=	12	=	1

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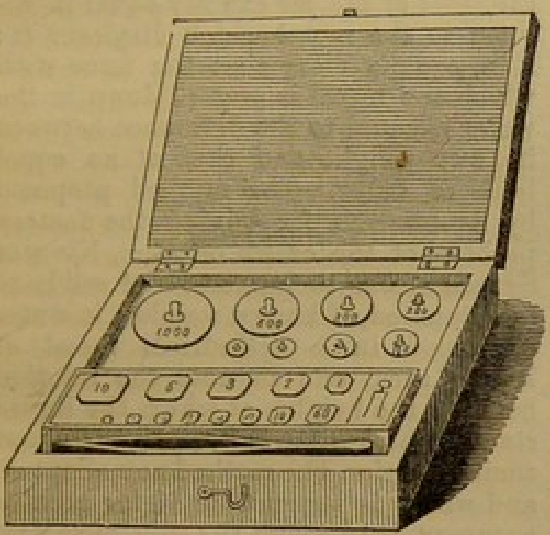
* *See* "Chemical Manipulation," p. 44.

Fig. 4.



These denominations are never, however, employed in chemistry, the weights of substances being always reckoned in grains, and in the decimal divisions of the grain, viz. .1, .2, .3, &c., .01, .02, .03, &c. *Fig.* 4 represents the most convenient arrangement of the grain weight system. The material of the weight is brass, from 1000 down to ten grains, and platina from the grain downwards; the former are cylindrical; the set consisting of 1000, 600, 300, 200, 100, 60, 30, 20, 10 grains. The latter are made of square pieces of the sheet metal, one corner being turned up for the convenience of taking them up by the forceps, from 10 grains to .1, and consist of the following series: 10, 6, 3, 2, 1, .6, .3, .2, .1 grain. Below .1 grain the weights are made of small slips of thin platina foil, the number of angles into which each slip is bent indicating its value. Thus, the piece with six angles represents .06, that with three angles, .03, that with two angles, .02, and the small straight slip, .01. The hundredths of a grain are not required in weighing with the balance *fig.* 2, all weights from .1 downwards being most quickly and conveniently determined by the small loop of gilt wire suspended from the different divisions of the arm of the balance, as already explained. These little loops are called "riders," and the weight box is supplied with half a dozen of them; the small platina weights are kept in their places by a strip of glass, and the brass weights are fitted into cylindrical cavities bored in the bottom of the box, which is about $4\frac{1}{2}$ inches long, 3 wide, and 1 deep. For the large balance *fig.* 3, a series of similar cylindrical brass weights, consisting of 10,000, 6000, 3000, 2000, and 1000 grains are provided, in an appropriate box.

The standard to which the French *gramme* is referred, is the weight of $\frac{1}{100}$th part of a cubic metre[*] of distilled water, at the temperature of melting ice. A gramme is equal to 15.434 grains troy, whence the following comparative table of French with troy weight.

		Gramme.		Troy grains.
Milligramme	=	.001	=	.01543
Centigramme	=	.01	=	.15434
Decigramme	=	.1	=	1.5434
Gramme	=	1	=	15.434
Decagramme	=	10	=	154.34
Hectogramme	=	100	=	1543.4
Kilogramme	=	1000	=	15434
Myriagramme	=	10,000	=	154340

The kilogramme is equal to 2 lbs. 3 oz. 4.428 drams avoirdupoise, and to 2.679 lbs. troy weight.

As the French gramme system is universally employed on the continent, the student should be provided with a box of these weights, which are fitted up by Oertling in precisely the same manner as the grain system just described. The weights from 50 grammes to 1 gramme, consisting of 50, 20, 10, 10, 5, 2, 1, 1, 1, gramme, are cylinders of brass; and those from 1 gramme down to .001 are cut out of platina foil, running in the same serial order, viz., 1, 0.5, 0.2, 0.1, 0.1, 0.05, 0.02, 0.01, 0.01. The weights below the centigramme are constructed as in the lower divisions of the grain, of slips of thin platina foil, the values being indicated by angles; "*riders*" are also provided for using with the balance *fig.* 2; the weights, each of which being exactly .01 gramme, enables the operator to weigh any small quantities from a centigramme to milligramme, without the trouble of putting any other small weights into the pan of the balance.

The student should assure himself once for all, on purchasing a set of weights, that they are correct among themselves, and if he has an opportunity of comparing them with standard weights, he should do so: for the purpose of adjustment, the small spherical knobs screwed into the centre of the cylindrical weights are provided with small cavities under the screws, to receive portions of fine wire; a very simple method of making the small weights

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[*] One metre = 39.37 inches.

expressing the decimal parts of a grain, is to determine with great care the weight of three or four feet of fine silver, or platina wire, and then to cut off such portions as are equal to the weights required. The weight box, as well as the balance, must be carefully kept out of the contact of acid or other vapours; the brass weights may be gilded (previous to adjusting them) to keep them bright and clean; it is not, however, to be concluded that they necessarily become incorrect by getting tarnished, for *Fresenius* states, that he has examined many weights of this description, and has found them as exactly corresponding with each other in their relative proportions as when they were first used. As a general rule, however, the weights should not be touched by the hand, to prevent the necessity for which the weight boxes are provided with convenient brass forceps for the small weights, and with forks or tongs for the large ones. It is desirable to keep a shallow dish, containing quicklime, inside the glass case of the balances, in order to preserve the atmosphere in a state of dryness, and thus to prevent the oxidation of the fine steel edges and other metallic parts of the apparatus.

Specific gravity.—It is very frequently an object of importance to compare the density of a substance, solid, liquid, or gaseous, with that of another substance assumed as a standard: this operation is called the determination of its specific gravity. The density of solids and liquids is compared with that of pure distilled water; gaseous fluids are usually compared with atmospheric air. It is only when very great accuracy is required, that the temperature of the water is of importance, and in such cases it is far more convenient to take the temperature of the maximum density of that fluid, (viz., about 39°.4 Fahr.,) at which temperature it can be more easily maintained without variations than at 62°, at which it is generally taken in this country, or at the temperature of melting ice, 32°, at which it is taken in France: generally speaking, in the determination of specific gravities, it is sufficient to note the temperature, and to apply a correction depending on the known density of water at different degrees of the thermometer.

Determination of the specific gravity of a solid.—This depends on the principle discovered by *Archimedes*, that a body, when immersed in a fluid, loses just as much of its weight as is equal to the weight of an equal volume of that fluid; thus supposing a piece of gold suspended from one of the pans of a balance by a fine thread or hair, to be accurately weighed in air, and then immersed in a jar quite full of water, it is evident that a quantity of water will be forced over the sides of the jar exactly equal in volume to the metal which displaces it: it is equally clear that the force with which the metal is pressed down in the water is equal to the difference between its own weight and that of an equal bulk of water. The method proposed by Archimedes for solving the famous problem of the crown of *Hero*, King of Syracuse, was to immerse the solids to be compared, of known weights, in water contained in a cylindrical vessel of known area, and to note the relation between the heights at which the liquid stands, which gives the relation between their densities. The method now adopted, and which is susceptible of far greater accuracy, is to weigh the substance first in air, and then in water, and to divide the weight in air by the loss it sustains when weighed in water, the quotient is the specific gravity of the substance; thus, suppose the piece of gold before alluded to, to weigh in air 77 grains, and in water 73 grains, the loss in this case is 4 grains, and we have the proportion—

$$4 : 77 :: 1 : 19.25;$$

19.25 is, therefore, the specific gravity or density of the gold.

If the solid, the density of which is to be determined, is lighter than water, there are two ways of proceeding.

By the first method the dimensions of that part of the solid immersed, while it is floating on the surface of water, is compared with its whole magnitude; the two results bear the same proportion to each other as the specific gravity of the solid bears to that of water; the experiment is performed thus:—A glass vessel, having perpendicular sides, and as narrow as the magnitude of the solid will admit, is filled to a certain mark with distilled water; the substance is then set to float in it, and the point to which the surface of the water rises in the vessel accurately marked: the body is then totally submerged, and the point to which the surface of the water rises again observed. The elevations of the surface produced by the partial and total submersion, indicate the portions of the solid in each case immersed, and are therefore in the ratio of the specific gravity of the solid to that of the liquid. This method is not, however, very often adopted. The following is more convenient:—The body, the density of which is to be ascertained, is attached to another which is heavier than water, and of such a size that the united weights of the two will be greater than the weight of the water which they displace, and the whole consequently sinks when immersed. The weight of the united substances is then determined, first in air, and then in water; the weight lost by immersion is equal to the weight of a quantity of water corresponding in bulk to the united bulks of the solids. The lighter solid is then detached, and the weight lost by the heavier by immersion in water ascertained; this is the weight of a quantity of water equal in bulk to the heavier solid. This loss of weight being subtracted from the loss sustained by the combined masses, the remainder is the weight of a quantity of water equal in bulk to the lighter solid; the proportion of the weight of the lighter solid to this will determine its specific gravity.

This process may be still further simplified thus:—Weigh the substance, the specific gravity of which it is desired to ascertain, first in *air*, then attach it loosely to a piece of heavy metal, the weight in *water* of which has been determined, and weigh the combined substances in water, the aggregate weight will be found less than that of the heavier body. Now subtract the weight of the lighter body from that of the heavier, and add the remainder to the weight of the former in air; we thus obtain the weight of a quantity of water equal in bulk to the lighter body, and by dividing the weight of the lighter body in air by this last mentioned sum, the quotient is the specific gravity required.

Example.—A piece of indigo covered with a thin coating of varnish (to prevent its absorbing water) weighed in air 105.1 grs.: a piece of sheet lead which was used for ballast weighed in water 124.9 grs. The indigo and the lead were now tied together, not closely, but in such a manner that the water could have free access to any part of each substance, and weighed in water, the aggregate weight was 108.5 grs.; that is, 16.4 grs. lighter than the weight of the lead alone in water. Now $16.4 + 105.1 = 121.5 =$ the weight of a quantity of water of equal bulk to the indigo, and $\frac{105.1}{121.5} = 0.865 =$ the specific gravity of the indigo*.

When the solid, the specific gravity of which is to be determined, is in the form of a powder, or in minute pieces, it may be placed in a cup which is counterpoised first in air, and then in water, in the usual manner. Or the same method may be pursued which is adopted in taking the specific gravity of a soil. A small bottle containing, when filled and its stopper adjusted, a certain known quantity of water, is about half filled with distilled or rain water, and a weighed quantity of the dry powder introduced. It is then well shaken, and after the solid matter has settled it is completely filled with water, the stopper put into its place, and then weighed. The weight obtained will be obviously less than that of the united weights of the bottle full of water and the substance added, and the difference is the weight of a quantity of water equal in bulk to the solid substance added, and by dividing the weight of the powder by this difference of weight we obtain the specific gravity required.

Example.—A bottle filled with distilled water and closed with its glass stopper weighed 750 grs. About half the water was poured out, and 500 grs. of a certain powder introduced. The water and the powder were well mixed by agitation, and then allowed to settle. After a while the bottle was completely filled up with water, closed with its stopper, and weighed.

Weight of bottle, powder, and water	1050 grs.
United weights of bottle full of water and powder added	1250 „
Difference, expressing the weight of a quantity of water equal in bulk to the powder	200 „

Therefore—

$\frac{500}{200} = 2.5 =$ specific gravity of the powder.

Determination of the specific gravity of a liquid.—The specific gravities of

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* For the methods of M. Say and of Mr. Leslie, for determining the specific gravity of powders and porous bodies, *see* Annales de Chimie, xxiii. p. 4; or Nicholson's Quart. Journ., vol. i. p. 325; and Faraday's Chem. Manipulation.

liquids may be determined in two ways: *first*, by weighing them in flasks or bottles of known magnitude; and, *second*, by weighing a certain solid in the liquid to be examined, and comparing the loss of weight with that which it sustains by immersion in pure water. Bottles are sold by the philosophical instrument makers which hold, when full and closed with their stoppers, a certain quantity, 1000, 500, or 200 grains of distilled water. The stoppers of these bottles are usually perforated, with the view of affording a free passage for the excess of fluid when the stopper is inserted in its place; there is, however, no occasion for this, and indeed it is very objectionable with corrosive fluids, such as sulphuric acid, and with volatile fluids such as ether. The bottles are accompanied with brass weights which exactly counterpoise them when filled with distilled water. The method of determining the specific gravity of a fluid by means of one of these bottles is very simple: we have only to fill the bottle with the liquid in question and weigh it; its weight gives at once its specific gravity without any calculation. Thus, supposing the bottle employed to hold 1000 grains of distilled water at 62°, and at the same temperature 1845 grains of oil of vitriol, and 918 grains of spirit; these numbers represent the densities of the liquids, water being 1000; or, if water be taken as unity, then the specific gravity of oil of vitriol is 1.845 and that of the spirit .918. In determining the specific gravity of liquids in this manner, due regard must be had to temperature, otherwise the results obtained will not admit of exact comparison. The bottle should be verified before it is used, and if it should be found incorrect, that is, not to hold exactly 1000, 500, &c., grains at 62°, its capacity at that temperature must be rigorously determined once for all, and the weight of water found must be used as the divisor of the weight of any other fluid. Thus, suppose the bottle is found to hold exactly 995 grains of distilled water and 1836 grains of oil of vitriol, then $\frac{1836}{995} = 1.845 =$ the specific gravity of the acid.

The determination of the specific gravity of a liquid by weighing in it a certain solid, depends on the proposition, that if a solid specifically heavier than water, and also specifically heavier than the liquid whose specific gravity is to be determined, be successively immersed in water and in that liquid, the losses of weight will be proportional to the specific gravities of water and the liquid: and if the number expressing the loss of weight in the liquid be divided by the number expressing the loss of weight in the water, the quotient will be the specific gravity of the liquid.

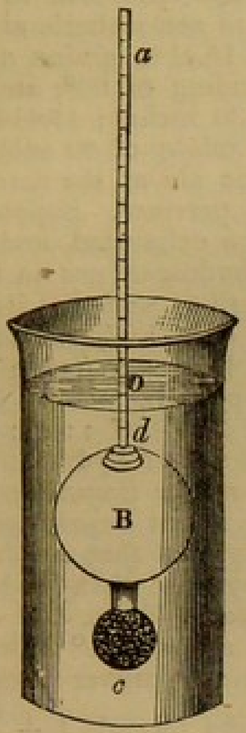
Example.—Suppose a ball of glass, when weighed in water, to lose 200 grains, and when weighed in oil of vitriol, 369 grains, then $\frac{369}{200} = 1.845$ = the specific gravity of the oil of vitriol; but suppose the same ball, when weighed in spirit, to lose 183.8 grains, then $\frac{183.8}{200} = .918 =$ specific gravity of the spirit.

A series of hollow bulbs of different specific gravities, called "specific gravity bulbs," are also sold by philosophical instrument makers. Their use is almost entirely confined to practical chemical operations on the large scale, though they are sometimes of great convenience in the laboratory for determining the degree of concentration of liquids. These bulbs are generally numbered. They indicate the density of the fluid by sinking or floating in it, as the case may be.

In cases where moderate accuracy only is required, the *hydrometer* is extensively employed for the determination of the specific gravities of liquids. Its use is principally confined to commercial purposes, where expedition is of greater consequence than great exactness. The indications of these instruments depend upon the fact, that a body when it floats in a liquid displaces a quantity of the liquid equal to its own weight; and their accuracy depends upon giving them such a shape that the part of them which meets the surface of the liquid in which they float is a narrow stem of which even a considerable length displaces but a very small weight of the liquid. Thus any error in observing the degree of immersion entails upon the result an effect which is inconsiderable.

The hydrometer shown in *fig.* 5 is an arrangement of considerable delicacy, and is peculiarly useful for measuring the specific gravity of mineral waters,

Fig. 5.



in the absence of the balance and specific gravity bottle. This is one of the many forms which have been given to the instrument[*]. It consists of a ball of glass three inches in diameter, with another joining it and opening into it of one inch in diameter, B and *c*, and a brass neck, *d*, into which is screwed a wire *a o*, about 10 inches long and 1-40th of an inch in diameter, divided into inches and tenths of an inch. The whole weight of this instrument is 4000 grains when loaded with shot in the lower ball. It is found that when plunged into water in the jar a grain laid upon the top *a* makes it sink one inch; therefore the tenth of a grain sinks it the tenth of an inch. Now it will stand in one kind of water a tenth of an inch lower than in another, which shows that the bulk of one kind of water equal to the bulk of the instrument weighs one tenth of a grain less than an equal bulk of the other kind of water; so that a difference in specific gravity of one part in 40,000 is thus detected. This weight of 4000 grains is convenient for comparing water; but the quantity of shot in the lower ball may be varied so as to make it lighter or heavier, and so adapt it to measure the specific gravities of lighter or heavier liquids. It will always be an accurate and very delicate measure for liquids of nearly the same weight. Indeed its delicacy is so great that an impurity too slight to be detected by any ordinary test, or by the taste, will be discovered by this instrument.

In using the hydrometer there are certain precautions to be observed, which have been pointed out by *Faraday*[*]. Thus if the surface of the stem does not moisten freely with the fluid in which it floats, the instrument may be made to stand two or three degrees or more higher or lower in the same liquid, and this tendency is increased by the presence of any unctuous or greasy matter, care must therefore be taken to keep the stem of the instrument perfectly clean, and to touch it as little as possible with the hands. It should be put gently into the liquid, and when it has settled at rest it should be depressed about an inch lower, so as to moisten a portion of the stem, and its indications should not be noted until, after repeated raisings and depressings and oscillations, an uniformity is observed when it has become stationary.

Determination of the specific gravity of a gas.—This is very simple in principle, though from the facility with which gases undergo alterations in volume by changes of temperature and pressure, it is, in practice, an operation of great delicacy and difficulty. It is conducted as follows:—A light glass globe of about 50 cubic inches' capacity is first accurately weighed when full of air; in order to avoid numerous corrections for variations in the density, temperature, and hygrometric state of the air, during the continuance of an experiment, the film of moisture which adheres to the glass, and the displacement of air by the solid materials of the balloon, Regnault, in his late refined experiments, always counterpoised his balloon by a similar globe of the same glass. The weight of the balloon when full of air being determined, it is exhausted by the air pump, and again weighed in an empty state, the difference in the weighings represents the weight of atmospheric air equal to the capacity of the globe which has previously been accurately determined by measuring the volume of water required to fill it.

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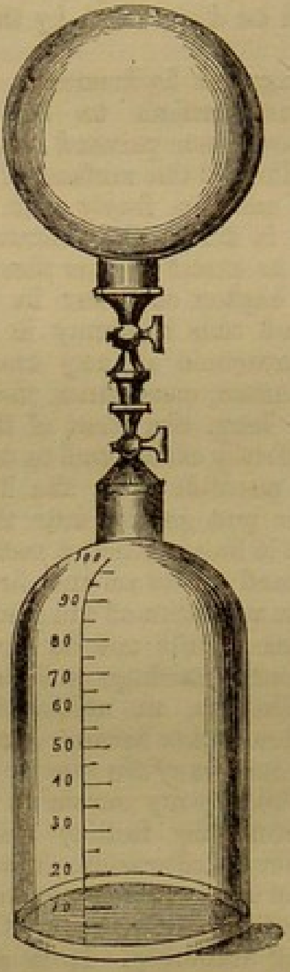
[*] For further details respecting hydrometers, and specific gravity generally, the reader may consult with advantage the Treatise on Hydrostatics, in the *Library of Useful Knowledge*, from which the description of the hydrometer in the text is taken, and in Lardner's Cabinet Cyclopædia.

[*] *See* Chemical Manipulation, p. 59, 1st Edition.

The globe in its empty state is now screwed on to the receiver containing the gas to be weighed, as shown in *fig.* 6, and which may either be standing

Fig. 6.



over mercury, the gas having been transferred to it in a state of dryness by passing through a drying tube containing chloride of calcium, or standing over water, the gas having been conveyed to it completely saturated with moisture; perfect dryness or perfect saturation with aqueous vapour being indispensable conditions; in the latter case a due correction may be made by the aid of a table, which will be given presently. The globe being attached perfectly air-tight to the receiver, the stop-cocks are opened and the globe becomes filled with the gas rushing from the jar, its place in the latter being supplied by the water or mercury of the trough. It is now removed from the jar and again weighed with its charge of gas at the atmospheric temperature and pressure, and the difference between its weight and that of the balloon in its exhausted state, is the weight of volume of gas from which its specific gravity is determined, air being 1.000.

Example.—Suppose the capacity of the globe to be exactly 50 cubic inches, and that the difference in its weight when full of atmospheric air and when empty, is 15.4145 grains, the thermometer standing at 60°, and the barometer at 30 inches; 15.4145 grains is then the weight of 50 cubic inches of atmospheric air at the normal temperature and pressure. Suppose now the globe to be exhausted, and then filled with dry hydrogen gas in the manner above described, and that its increase in weight is only 1.07, then the specific gravity of the latter gas is determined by the proportion,

As 15.4145 : 1.07 : : 1 : 0.0693 = specific gravity of hydrogen gas.

Corrections for temperature.—According to the recent experiments of Regnault, it appears that a volume of gas expands by heat $\frac{1}{459}$th of its bulk for each degree of Fahr., and calling the volume of a gas at 0° Fahr. unity, its volume at any higher temperature is found by the formula $1 + \frac{\text{temp. Fahr.}}{459}$

The determination of the volume of a gas at one temperature from its known volume at another temperature may be attained by the following formula:—

Let t be the temperature Fahr. at which the volume of gas is observed, t' the temperature to which it is to be reduced, x the observed volume at t, and x' the volume at t' required.

$$\text{Then } x' = \frac{(459 + t')\,x}{459 + t}.$$

Example.—Suppose the balloon to be filled with a gas at the temperature of 50°, and that it has been previously ascertained that its content is exactly 50 cubic inches. The above formula enables us to calculate the real volume of the gas at the normal temperature, thus:

$$\frac{(459 + 60) \times 50}{459 + 50} = 50.982;$$

so that we actually have in the globe 50.982 cubic inches of gas, and our calculation for specific gravity must be made accordingly.

Suppose, however, that the temperature of the gas is 70°, or 10° above the normal temperature, we have then less than 500 cubic inches present, for

$$\frac{(459 + 60) \times 50}{459 + 70} = 49.054;$$

and our calculation must be made accordingly.

Correction for pressure.—This is very simple: for although there is reason to doubt the absolute accuracy of the law known as "the law of Mariotte," viz., that gases are expansible to an indefinite extent, in the proportion that pressure upon them is diminished, and to be contractible under increased pressure, exactly in proportion to the compressing force, yet the correctness at such pressures as occur naturally, and are indicated by the barometer, is generally admitted. The following is the rule for calculating the volume which a gas should possess at one pressure from its known volume at another pressure. As the pressure to which the gas is to be reduced is to the observed pressure, or height of the barometer, so is the observed volume to the volume required. Thus, suppose a volume of gas has been observed at 120 cubic inches, when the barometer is standing at 28.8 inches, we find its real volume at the normal pressure, thus:

As 30 : 28.8 : : 120 : 115.2 = the volume which the gas would occupy at 30 inches barometer; or, if the barometer at the time of the experiment stands at 30.6, then

As 30 : 30.6 : : 120 : 122.4 = the volume which the gas would occupy at 30 inches barometer. When the correction of a gas is to be made both for temperature and pressure, the reduction is first made for temperature, and the corrected volume is afterwards reduced according to the pressure. In determining the specific gravity of a gas, it is always, if possible, weighed in a perfectly dry state; when, however, this is impracticable, it becomes necessary to make a correction for the aqueous vapour which it contains: this may be done with the aid of the following table, given by *Faraday*[*], and founded on the experiments of *Dalton* and *Ure*. It exhibits the proportion, by volume, of aqueous vapour existing in any gas standing over or in contact with water, at the corresponding temperature, and at the mean barometric pressure of 30 inches.

When the correction for aqueous vapour is about to be made, the observed temperature of the gas should be looked for in the table, and opposite to it will be found the proportion in bulk of aqueous vapour, at a pressure of 30 inches. The volume to which this amounts must then be corrected to mean temperature, and the result subtracted from the observed volume of gas, after it has been reduced to the mean temperature and pressure[†].

°		°	
40	.00933	61	.01923
41	.00973	62	.01980
42	.01013	63	.02050
43	.01053	64	.02120
44	.01093	65	.02190
45	.01133	66	.02260
46	.01173	67	.02330
47	.01213	68	.02406
48	.01253	69	.02483
49	.01293	70	.02566
50	.01333	71	.02653
51	.01380	72	.02740
52	.01426	73	.02830
53	.01480	74	.02923
54	.01533	75	.03020
55	.01586	76	.03120
56	.01640	77	.03220
57	.01693	78	.03323
58	.01753	79	.03423
59	.01810	80	.03533
60	.01866		

Method of determining the specific gravity of a vapour.—There are two ways of effecting this important object; the first, which is the simpler of the two, though not the most generally applicable, was contrived by the celebrated French chemist, *Gay Lussac*. The liquid to be experimented upon is introduced in quantities of three or four grains, into one or two little glass bulbs. The manner of filling these bulbs is as follows:—The bulb having been first accurately weighed, is warmed gently over the flame of a spirit lamp, and then allowed to cool, with its point immersed in the liquid with which it is to be filled; as the bulb cools a certain portion of the fluid enters, this is then boiled in the bulb till all the air is expelled, and the bulb is filled with the pure vapour of the substance; the point is then dipped under the surface of the liquid; as the vapour condenses, the fluid rushes up to supply its place, and the whole becomes full; the point of the bulb is then sealed by the blowpipe, and when cool it is weighed, the differ-

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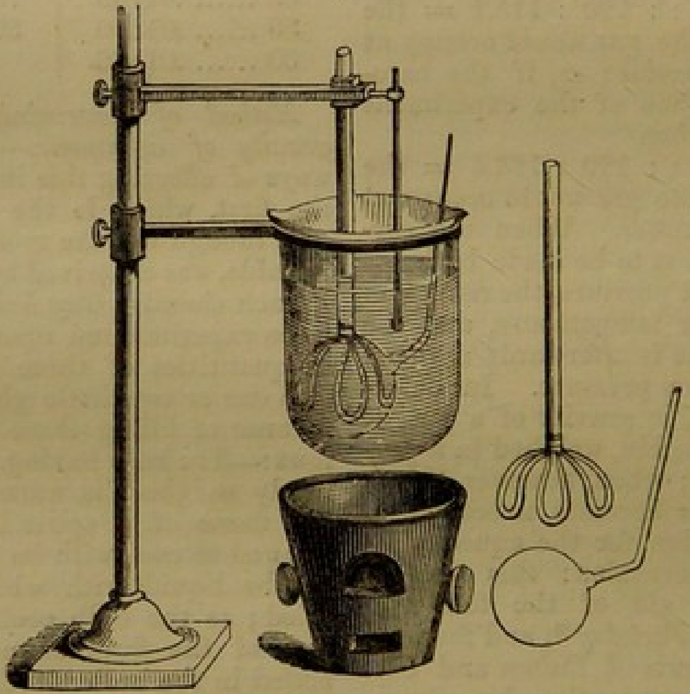
[*] *See* Chemical Manipulation, p. 376, 1st Edition.

[†] The subject of the correction of a gas for temperature, pressure, and tension of aqueous vapour, will be returned to further on, when the method of analyzing organic substances containing nitrogen is under consideration.

ence of weight gives, of course, the weight of the quantity of liquid which it contains. Two or three bulbs, being thus filled, are introduced under the edge of a narrow graduated jar, filled with, and standing over, a dish of mercury, placed upon a small furnace, or over a lamp. The jar is covered with a glass cylinder, open at both ends, and secured on the mercury dish. This cylinder is filled, above the top of the jar, with colourless oil. All things being thus arranged, the furnace or lamp is lighted; as the temperature of the mercury and oil rises, the liquor in the little bulbs forms steam, which at length bursts the bulbs, and the level of the quicksilver in the jar immediately falls, the vapour occupying the space above it. When the mercury ceases to descend, it is known that the whole of the liquid has been converted into vapour; the temperature of the oil, necessarily the same as that of the vapour, is ascertained, and by the graduation on the jar, the volume occupied by the vapour is easily read off. The weight of the vapour is known, it being that of the liquid in the bulbs; its volume at the temperature of the oil is thus found, from which its volume at the mean temperature may be calculated and compared with that of an equal weight of atmospheric air at the mean temperature and pressure.

The second method, which is that of Dumas, is applicable to all temperatures below the melting point of glass, and to the determination of the vapours of all substances vaporizable under that temperature, and which do not suffer decomposition by vaporization. Its discovery has, therefore, been of the greatest service to science, and has led to results of the most important scientific character. It is conducted as follows:—A globe of difficultly fusible glass, and capable of holding from 15 to 30 cubic inches, (*fig.* 7) is, after being thoroughly dried, drawn out to a long neck, having a capillary orifice; this neck is bent, as shown in the figure. It is then weighed while full of atmospheric air, the temperature and barometric pressure being noted. About 120 grains of the substance to be examined are poured into a glass, (if a solid, it must be liquefied by heat,) and the globe having been warmed, its point is immersed in the liquid, and 80 or 100 grains allowed to enter; this part of the operation may be hastened by cooling the globe by dropping ether upon it. The globe is then fitted in a sort of wire cage, by which it is securely fixed in the centre of the bath in which it is to be heated, as seen in the figure. The bath is charged either with oil or with a saturated solution of chloride of calcium. The capillary beak of the tube must be long enough to project over the surface of the bath, as shown in the figure. The temperature of the bath is then increased to the desired point; when the

Fig. 7.



globe becomes sufficiently heated, the liquid boils, and its vapour in passing away carries off the air which had previously filled the globe. The force of the steam increases, at first, with the temperature of the bath, by degrees it diminishes, and finally ceases altogether; the operator then knows that the excess of vapour has passed away, and that the globe is filled with the vapour of the substance, in a state of purity. Should any of the vapour have condensed in the neck of the globe, it must be chased away by a piece of red hot charcoal. The orifice of the capillary neck is now closed air-tight by means of the blowpipe, the temperature of the bath being at the same moment carefully noted; it is then removed, allowed to cool, cleaned, and weighed. The next point is to ascertain exactly the capacity of the globe, with which view the extremity of the neck is broken off under mercury; this is done by first making on it a slight scratch with a file, and then plunging it underneath the surface of the fluid metal, and breaking it off by a slight tap against the side of the trough; the mercury immediately rushes into the globe, filling up the vacuum caused by the condensation of the vapour. If the experiment has been well conducted, the whole of the globe becomes filled, but if there was a small quantity of air still remaining at the time of sealing the neck, a bubble will remain in it. The globe full of quicksilver is then emptied into a graduated jar, by which the quantity of the quicksilver being measured, the capacity of the globe is known, and all the elements for calculating the specific gravity of the vapour are thus ascertained. Thus, the volume of the globe being known, the weight of the atmospheric air it contained is ascertained by calculation, and the globe having been weighed full of air, by deducting the weight of that volume of air, the weight of the empty globe is ascertained, and deducting this weight from that of the globe when filled with the vapour of the substance, or rather when containing the liquid resulting from the condensation of that vapour, we obtain the weight of the vapour of the substance at the temperature of the bath. The weight of the atmospheric air filling the globe at the temperature of the bath is now ascertained by calculation, by the rules already given, and this being known, the determination of the density of the vapour is made by the simple rule of proportion. As the weight of the air filling the globe at the temperature of the bath is to the weight of the vapour filling the globe at the same temperature, so is 1 to the density required.

By way of illustrating this beautiful operation, we quote an experiment made by the author of the process (*Dumas*), the weights and measures being reduced to the English standard; we have omitted certain corrections applied by the French chemist, such as that for the expansion of the glass, and the reduction of the indications of the mercurial thermometer to those of the air thermometer according to the experiments of *Magnus;* the results of these corrections not having a very significant bearing on the general result.

The experiment is the determination of the specific weight of camphor vapour. The particulars are as follows:—

Temperature of the air at the time of the experiment .	56°.3 Fahr.
Height of the barometer	29.2 inches.
Temperature of the bath at the time of sealing the balloon	471°.2 Fahr.
Increase in the weight of the balloon	10.93 grains.
Capacity of the balloon as determined by the volume of mercury	17.96 cubic ins.

1. Reduction of the volume of atmospheric air which the balloon contained, at the temperature, and under the atmospheric pressure at the time of weighing it—to 32° Fahr. and 29·8 barometer.

(*a.*) Correction for pressure:—

As 29.8 : 29.2 : : 17.96 : 17.6 cubic inches = the volume of air at the standard pressure.

(*b.*) Correction for temperatures; according to the formula given, p. 128:—

$$\frac{459 + 32 \times 17.6}{459 + 56.3} = \frac{8641.6}{515.3} = 16.76$$

cubic inches = the volume of air at 32°.

2. Weight of the air.

According to the experiment of *Regnault* 100 cubic inches of atmospheric air at 32° Fahr. and 29.9 barometer weigh 32.58684 grains; therefore 16.76 cubic inches weigh 5.46 grains.

The content of the balloon filled with

dry atmospheric air, reduced to 32° Fahr. and 29.8 barometer, is 16.76 cubic inches = 5.46 grains :—

Now, the increase in the weight of the balloon with its charge of camphor vapour was 10.93 grains: if, therefore, we add this number to the calculated weight of the air, we shall obtain the actual weight of the vapour thus :— $10.93 + 5.46 = 16.39$ = the weight of the camphor vapour.

3. Calculation of the volume of camphor vapour, equal to 16.39 grains at 29.8 barometer and 32° Fahr.

(*a.*) Correction for pressure :—

As $29.8 : 29.2 :: 17.96 : 17.6$ = the volume at the observed temperature, viz., 471°.2 Fahr.

(*b.*) Correction for temperature :—

$\frac{459 + 32 \times 17.6}{459 + 471.2} = \frac{8641.6}{930.2} = 9.29$ cubic inches = the volume of the vapour at 32°, and which consequently weigh 16.39 grains.

One hundred cubic inches weigh, therefore, 176.42 grains. Now, as 100 cubic inches of atmospheric air weigh at 32° 32.58684 grains, the specific weight of camphor vapour is found by the proportion—

As $32.58684 : 176.42 :: 1 : 5.43$.

The specific gravity of camphor vapour is therefore 5.43. *Dumas*' calculation, with the corrections for the expansion of the glass globe, and the reduction of the mercurial on the air thermometer, and with a different formula for the correction for temperature, is 5.52.

Measuring.—In the quantitative examination of liquids, recourse is generally, when practicable, had to weighing, in preference to measuring. For this purpose the balance *fig.* 3 is well adapted. When, however, it is deemed expedient to resort to the latter, the imperial pint and its subdivisions is a convenient standard for large quantities, and the cubic inch and its subdivisions for small quantities of liquid. The measure of the imperial pint is 34.65925 cubic inches, and it contains 8750 grains of distilled water, at 62° Fahr., and at 30 barometer. It is divided into 20 parts, each part having a capacity of 1.7329625 cubic inches, and containing one ounce avoirdupois, or 437.5 grains of distilled water. The cubic inch consists of 252.458 grains of distilled water at the standard temperature and pressure, and of 3425.35 grains of mercury.

Lipped jars of the imperial pint, half-pint, and quarter-pint capacity, graduated into ounces and half-ounces, *figs.* 8 and 9, are articles of commerce, and are easily obtained. The chemist never, however, takes it for granted that these gradations are correct, but verifies each jar for himself by weighing into it successive quantities of water or mercury, and making a mark or scratch with a file or diamond at the correct division, should it not coincide with that previously made on the jar. Bottles, having an exact cubic inch capacity, and holding, therefore, 437.5 grains of distilled water, and 3425.35 grains of mercury, when the stopper is in its place (*fig.* 10), are also to be obtained at the philosophical instrument makers; and, when correct, they are exceedingly useful, and save a great deal of time.

Fig. 8.

Fig. 9.

Fig. 10.

For the measurement of gases various sized jars are required, (*figs.* 11, 12, 13, and 14); they are always in this country graduated into cubic inches, tenths, and hundredths; the laboratory should be furnished with a good supply of them; and some of them, as *fig.* 12, should be sufficiently stout to bear, without risk, their weight, when filled with mercury, during the manipulations at the mercurio-pneumatic trough. As a general rule, all jars, whether for gases or for liquids, should be carefully verified before they are used for quantitative experiments; tubes, in particular, that are intended to be employed in gaseous analysis, must be rigorously tested; and it is better that the chemist should graduate them himself than

Fig. 11.

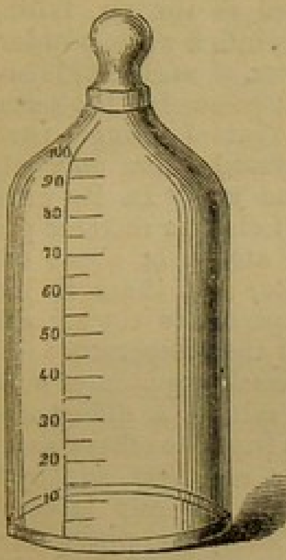


Fig. 12.

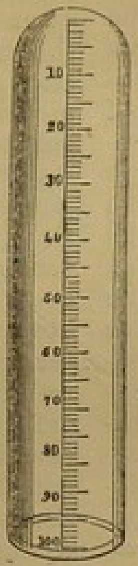


Fig. 13.

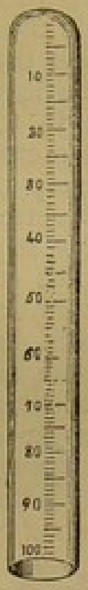
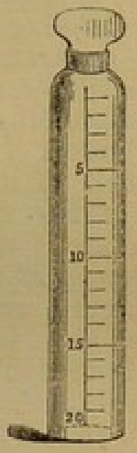


Fig. 14.



trust to the accuracy of those met with in commerce. For this purpose, having selected a tube of the desired size and thickness, and of clear faultless glass, it is placed in a perfectly vertical position, with its closed end on a flat surface. A small piece of glass tube, (*fig.* 15,) of known capacity, the edge of which is ground so that it may be closed air-tight with the piece of ground glass, serves as a measure or gauge; this is filled with mercury, and all bubbles of air having been expelled by passing a rod of glass down the internal sides of the tube, its contents are transferred to the jar or tube to be graduated; the surface of the fluid metal is marked on the outside of the glass with a pencil. In doing this the operator must be aware of the cohesive attraction existing between the mercury and the glass, the tendency of which is to depress that part of the surface of the metal which verges towards the sides of the tube; hence a mark made to correspond with that surface would include a space in the tube somewhat larger than that occupied by the metal. *Faraday** proposes to get rid of the difficulty by using mercury which is not quite clean, but which, from containing a little of some other metal, as tin, lead, &c., has a film formed on its surface which gives it a flat surface in the tube. A second, and a third, &c., measure of mercury is introduced and marked, till the tube is filled. It is then emptied of its contents, and covered with a thin coat of transparent engraver's varnish, by means of a camel's hair pencil. When dry, the pencil marks, which are distinctly seen through the varnish, are laid bare by a sharp steel dividing instrument, every fifth division being made somewhat longer than the others by way of distinction. The figures at each tenth division are cut through the varnish by the point of a steel pen, and the whole is then covered with hydrofluoric acid, which, attacking the glass where it is laid bare at the divisions and figures, effectually engraves them. If a relative division of the tube only is required, it is a matter of no consequence what the capacity of the little gauge A may be; but when the object is to graduate tubes with reference to a standard measure, as, for instance, the cubic inch, then it will be found most convenient to weigh into it successive portions of mercury: thus, to divide the tube into tenths of a cubic inch, successive additions of 342.535 grains of mercury must be made, to divide it into hundredths, the weight of the metal must be 34.25 grains. In making the adjustments of the mercury in the pan of the balance, the small graduated pipette, (*fig.* 16), provided with a stop-cock and air screw, will be found very useful.

Fig. 15.

Fig. 16.

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* Chemical Manipulation, p. 75.

In measuring the volume of a gas in a jar standing over the hydro-pneumatic trough, care must be taken to bring the water inside and outside the jar to the same exact level, in order that the gas may be influenced by the normal atmospheric pressure only: in the case of gases standing over the mercurio-pneumatic apparatus, this may not always be practicable, and a reduction must be made accordingly. Thus, supposing 20 cubic inches of a gas to be standing on the shelf of the mercury trough, the level of the fluid within being three inches above that without, and the barometer at 29.4, then the three inches of mercury within the jar counterbalancing three inches of barometric pressure, instead of 29.4, the latter is effectively only 26.4, and the corrections will be, as 30 : 26.4 : : 20 : 17.6 cubic inches = the actual measure of the gas *.

Exsiccation, or the operation of drying.—Before the quantitative analysis of any substance can be proceeded with, it is absolutely necessary that its relations to water should be accurately ascertained. In some cases, it is merely necessary to obtain the body free from moisture previous to weighing it for analysis: in other cases, the *amount* of water present has to be ascertained. Bodies differ very much in their relative powers of absorbing and retaining water, but it is necessary carefully to distinguish between the water which a substance may contain in accidental admixture, and that which belongs to it essentially, being a part of its constitution; in the preliminary operation of drying, this latter water must not be interfered with. There are some salts which cannot be exposed to a dry air at common temperatures without losing the whole of their water of crystallization; others lose a part only, and others again absorb water from a moist atmosphere, eventually running into a liquid. *Sulphate* and *carbonate of soda* are examples of salts possessing the first property—viz., that of *efflorescence*, in a remarkable degree. The former, which crystallizes in six-sided prisms, contains ten equivalents, or 56 per cent. of water; by exposure to the air it loses the whole of this water and falls into a white powder. *Carbonate of soda*, which crystallizes in flat, oblique, rhomboidal prisms, also contains ten atoms of water of crystallization, the whole of which it loses when exposed to the air, falling, like the sulphate, into a white powder. *Common phosphate of soda* affords an example of a salt possessing the second property—viz., that of losing a part of its water of crystallization only when exposed to the air. In its crystalline state, that of oblique rhombic prisms, it contains 25 atoms, or about 62.71 per cent. of water; of these it loses ten atoms by exposure to the air, and fourteen more at the temperature of boiling water; the remaining atom of water must exist in the salt in a different state of combination from the others, as it is only expelled by a red heat, and by its loss the nature of the salt is completely changed. Thus, on evaporating the aqueous solution of the salt, which has been dried at 212°, it is reproduced in its original state—viz., with 25 atoms of water of crystallization, but, on evaporating a solution of the salt after it has been ignited, we obtain a salt which contains only 10 atoms of water of crystallization, and which produces, with a neutral solution of nitrate of silver, a white precipitate, whereas the precipitate formed by the original salt is yellow. As an illustration of a salt which gains water by exposure to the atmosphere, *carbonate of potassa* may be quoted. This salt may be obtained in the form of oblique rhombic octohedrons, containing two atoms of water; but, by exposure to a moist atmosphere, it speedily loses its crystalline form and becomes liquid. *Chloride of calcium* is also a salt eminently remarkable for its power of absorbing water, a property which renders it very valuable for drying gases for experimental purposes, and for removing water from liquids, as in the rectification of alcohol.

The preparation of efflorescent and deliquescent crystals in a state fit for analysis is rather difficult, it is obviously inadmissible to expose them to the air, they must, therefore, be deprived of their water of admixture by pressing them in a finely pulverized state between folds of bibulous paper until there is no longer signs of moisture on the latter. There are many substances, particularly organic, which, though they do not lose their water of admixture in a dry atmosphere at common temperatures cannot nevertheless be exposed to the temperature of 212° with-

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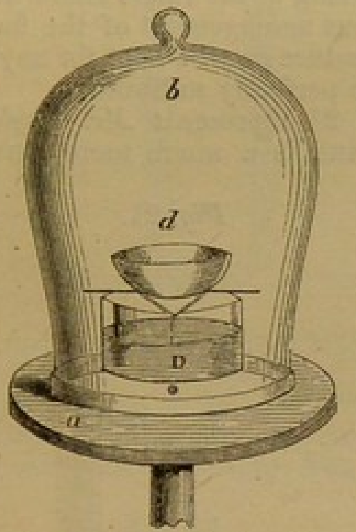
* For minute instructions relative to the management and manipulation of gases, the student is referred to *Faraday's "Chemical Manipulation,"* our limits preventing us from going into the subject more fully here.

out undergoing decomposition. The exsiccation of these substances is elegantly and effectually accomplished by placing them in convenient vessels underneath the receiver of an air pump, in close proximity to some substance having a powerful affinity for moisture, and exhausting the air. *Fig.* 17 shows the arrangement ; *b* is the receiver, the edge of which, ground and greased, stands on the brass plate *a* of the air pump, *d* is the vessel, a watch glass or a shallow evaporating dish containing the substance to be dried ; it is supported by a triangle of wire over the shallow basin containing concentrated sulphuric acid. This basin is sometimes made as in the adjoining figure, to avoid the necessity of using a triangle. On exhausting the air, a liberation of aqueous vapour takes place from the substance to be dried, which is rapidly condensed upon coming into contact with the sulphuric acid, and its place supplied by fresh moisture from the substance, which is in its turn condensed as before, and thus the process goes on, the aqueous vapour travelling from the substance to the acid till it is completely dried. The desiccation of these substances may likewise be effected without the employment of the air pump. Thus, one body may be suspended in a watch glass from a small support over the surface of sulphuric acid contained in a beaker, as shown in *fig.* 18 ; the edge of the beaker is ground so that it may be closed accurately by a ground glass plate *b*, in the centre of which there is a hole, through which the cork *c* is inserted, and from which the support hangs bearing the substance to be dried in the watch glass *d*, immediately over the surface of the sulphuric acid

Fig. 17.



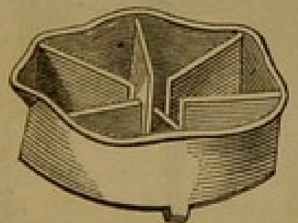
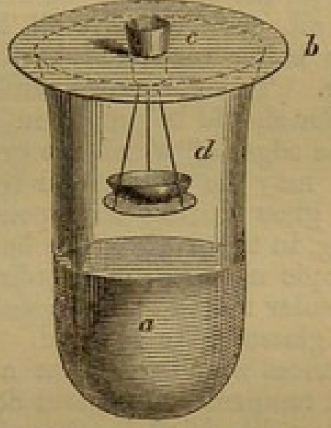


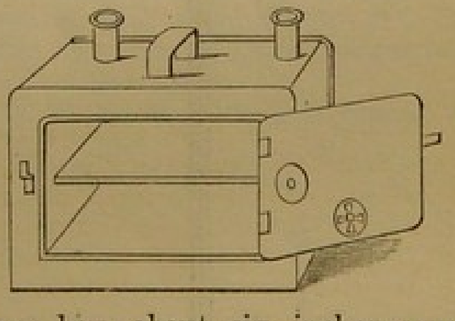
Fig. 18.



Another method which may be adopted, is to place the acid and the substance to be dried on a ground glass plate of sufficient size, and smeared with grease, the whole is covered with a well ground receiver, and then by raising the latter and introducing for a moment the flame of a spirit lamp and suddenly replacing the receiver an imperfect exhaustion is obtained, by which the process of exsiccation is considerably facilitated.

Substances which will bear the heat of boiling water may be dried in the water bath, *fig.* 19. It consists of a copper box, about six inches square provided with a water-tight jacket or coating, the edges being soldered with brass ; it is furnished with a door in which is cut a small ventilating aperture, which can be opened or closed at pleasure by means of a handle ; one of the chimneys on the top of the box communicates with the jacket ; through this the charge of water is given to the ap-

Fig. 19.



paratus, it serves also for the introduction of a thermometer to enable the operator to regulate the temperature of the bath ; the other chimney communicates with the interior chamber, in which the substance to be dried is placed on a watch glass ; by this arrangement a current of air is determined through the chamber, which greatly expedites the drying of the substance. If a higher temperature than boiling water is required, the bath may be filled with a fixed oil, such as olive oil, the temperature being regulated by the thermometer. The substance undergoing desiccation should be placed in a watch glass, the edges of which are ground so that it may be closed air-tight by another glass during the operation of weighing, in the event of its being of a hygroscopic nature. The student must be particular not to take the weight before the glasses have got cold.

Substances which will bear a tolerably high temperature without decomposition may be dried in the air bath. *Fig* 20 represents the arrangement known as *Rammelsberg's* air bath ; it consists of a small cylindrical box of stout copper provided with a stage about midway between the cover and the bottom for supporting the platinum crucible or dish containing the substance to be dried ; the cover is provided with two apertures, one is left open to serve as a chimney for the escape of the vapour, the other is closed with a cork, through which a thermometer passes to govern the temperature ; the bath is heated over a small spirit or gas lamp on the ring of the retort stand, and by a judicious management of the flame the temperature may be kept for any length of time perfectly uniform.

Fig. 20.

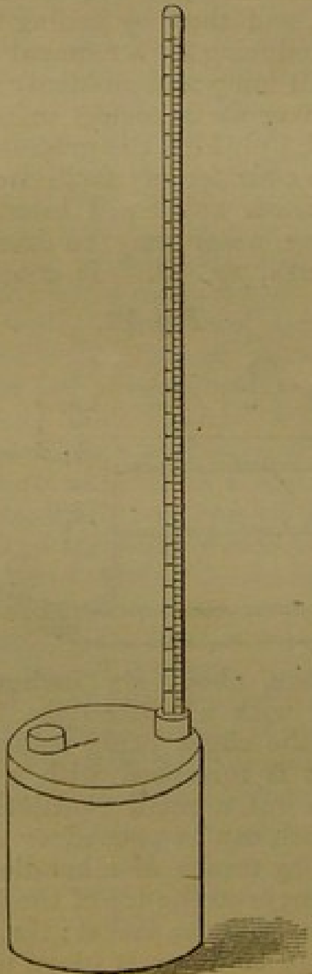
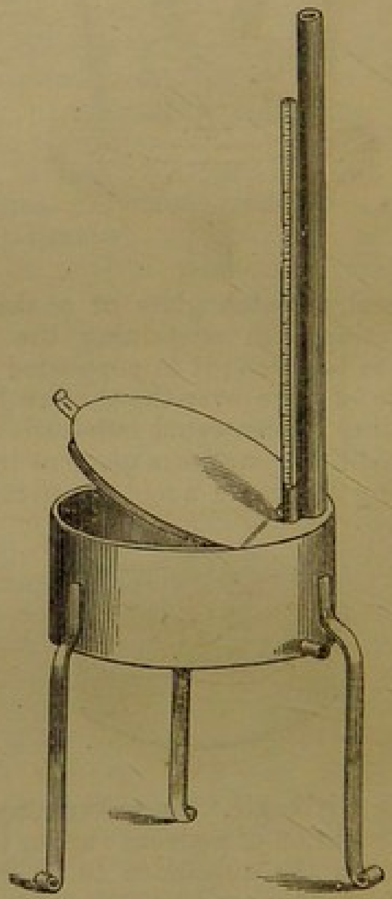


Fig. 21 represents *Mr. Taylor's* air bath, and is a much more convenient apparatus than the one just described. It consists of a cylindrical box of copper or japanned tinned iron, provided with a jacket or double casing, and a false bottom pierced with holes for the more equable diffusion of air through the interior. It is provided with a thermometer for regulating the temperature, and the great advantage which it possesses over Rammelsberg's bath, besides its size, consists in its being furnished with a tall chimney, the effect of which

Fig. 21.



is to determine a powerful current of air through the chamber, thereby greatly increasing the rapidity of the desiccation. If deemed necessary, the cover of the box being closed, a tube of chloride of calcium may be adapted to the aperture seen at the bottom of the back of the box, and thus a current of dry air swept through the apparatus. The substances to be dried are placed in dishes or watch glasses on a trellis work of iron or copper wire, supported about an inch above the false bottom.

Fig. 22.

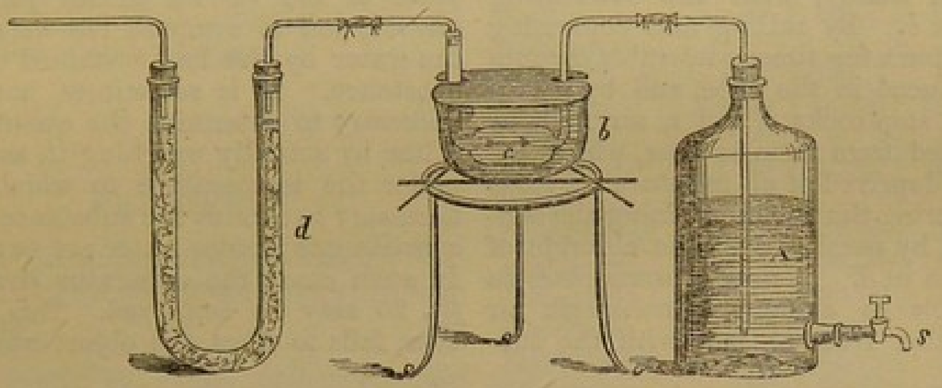
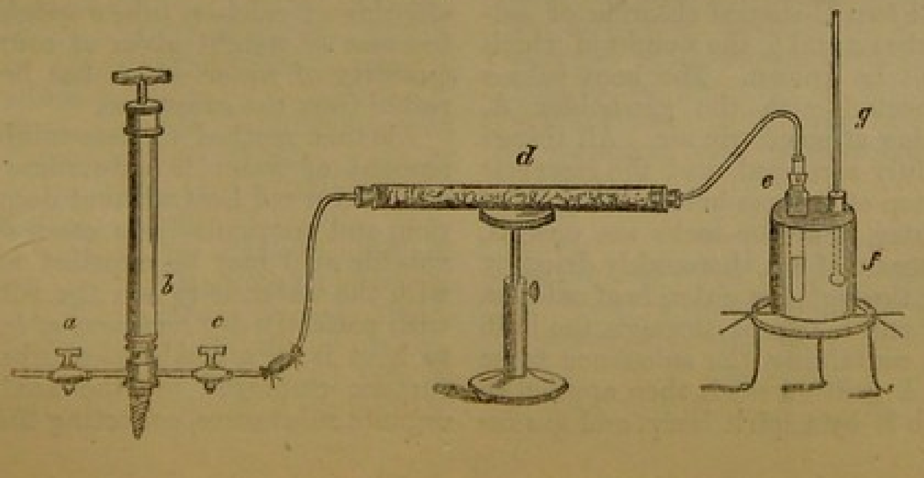


Fig. 23.

Fig. 22 represents an arrangement for drying substances in a current of dry air produced by the efflux of water. For this purpose a known weight of the substance is introduced into the small bent glass tube (*fig.* 23), which has also been weighed, the body of this tube is plunged into a copper water bath *b*, charged with a saturated solution of common salt; it is kept in its place by a cover furnished with two apertures for the arms of the drying tube; the wider arm is united by means of bent tubes and a caoutchouc connector with the U-shaped tube, and containing fragments of chloride of calcium and the narrow end is connected with a bent tube, which passes through the cork of the bottle A nearly down to its bottom. This cork must fit the bottle perfectly air-tight, and all the joints and connections of the whole apparatus must be perfect. The bottle A is filled with water, which on turning the stop-cock *s* flows out in a small stream, its place being supplied by the air drawn through *c*, and which becomes dried during its passage through the chloride of calcium, tube *b*. The bath is charged with water, a saturated solution of common salt, or of chloride of calcium, according to the degree of heat required, and it is kept boiling by means of a spirit or gas lamp placed underneath.

Fig. 24 shows the arrangement for

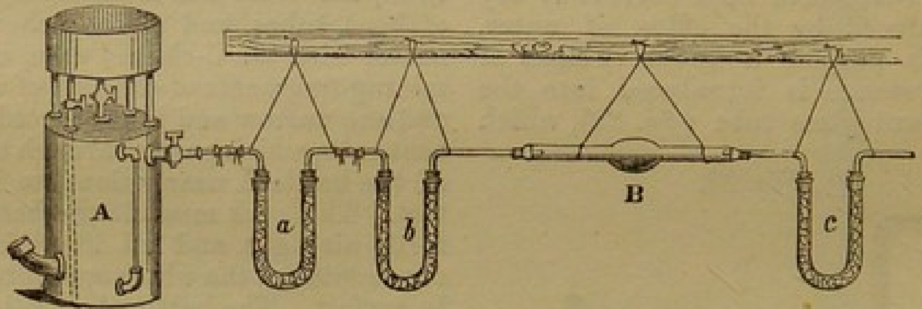
Fig. 24.



drying at any required temperature in vacuo. The substance under examination is introduced into the glass tube *e*, which passes through a copper collar into the Rammelsberg's air bath *f*, this tube is closed air-tight with a good sound cork, into which a bent glass tube is inserted, establishing a communication with the chloride of calcium tube *d*, and, finally, with the exhausting syringe *b*. By raising and depressing the piston a few times a tolerable vacuum is produced in the tube, and by means of the stop-cocks *a* and *c*, air may be admitted from time to time, which becomes deprived of all moisture previous to entering the tube containing the substance, by passing over the chloride of calcium in *d*. It may in some cases be desirable to exclude atmospheric air altogether from contact with the substance; in such cases carbonic acid or hydrogen gas may be introduced into the tube *e*, by connecting the stop-cock *d* with a proper gasometer filled with the gas required.

In the determination of the amount of water in organic substances, it suffices in general to submit a known quantity of the compound to heat, by one or other of the various modes just described, and to compute the weight of the water by the loss sustained by the substance. It is sometimes, however, necessary to determine the quantity of water by actually weighing it, as when under the temperature to which it is necessary to submit the substance other constituents besides water are expelled. In such cases the apparatus shown in *fig.* 25 may be employed. This, however, fails to effect the object when the volatile matters given off together with the water are absorbable by chloride of calcium; in such cases the direct determination of the water is very difficult, if not impossible.

Fig. 25.



The subject of the experiment is introduced into the bulb B, and carefully weighed, the weight of the empty tube must also be known. The tube is connected on the right hand by means of a sound cork and bent tube with the U-shaped chloride of calcium tube *c*, the weight of which has been noted, and on the left side it is connected air-tight with the two U-shaped chloride of calcium tubes *a* and *b*, the weight of which need not be known. The bent tube *a* is connected with the gas-holder A, containing atmospheric air. All things being duly arranged, and the reservoir on the top of the gas-holder being filled with water, the stop-cocks are opened, and a stream of air, thoroughly dried by passing through the chloride of calcium tubes *a* and *b*, sweeps through the bulb tube B, containing the substance to be dried. A gentle heat is then applied to the bulb B by a spirit lamp, and gradually increased beyond the boiling point of water, taking especial care that the straight end of the tube nearest the bent chloride of calcium tube *c*, shall be sufficiently hot to prevent any condensation of moisture from taking place there; towards the end of the operation the substance in the bulb must be heated nearly to redness (if it will bear it). After the whole of the water has been expelled the tube is allowed gradually to cool, still causing a stream of air to pass through; when quite cold, the apparatus is taken apart and the chloride of calcium tube *c* weighed; its increase of weight gives of course the quantity of water which has been expelled from the substance.

Another method of determining the amount of water in substances which will bear a red heat without decomposition, and particularly in cases where a volatile acid may be expelled together with the water, is to mix the substance with perfectly dry *carbonate of lead*, and to heat it in a combustion tube in the furnace employed for the analysis of organic substances, collecting the water evolved in a properly arranged chloride of calcium tube. The details of the operation will be better understood when the method of conducting organic analysis has been described.

For the method of conducting the various other operations of quantitative analysis, such as *solution*, *precipitation*, *collecting and washing the precipitate*, *evaporation*, *distillation*, &c., the student is referred to Chapter I., in the first part of this Treatise.

CHAPTER II.

On the Quantitative Estimation of Substances, and their separation from each other.

The following Table, exhibiting the *Names*, *Symbols*, and *Chemical Equivalents*, or combining Proportions, by Weight, of all those Substances at present considered as Elementary, according to the latest Authorities, is taken from the new edition of Graham's "Elements of Chemistry."

Names of Elements.	Symbol.	Equivalents.	
		Hydrogen = 1.	Oxygen = 100. Hydrogen = 12.5.
Aluminum . .	Al	13.69	171.17
Antimony . .	Sb	129.03	1612.90
Arsenic . . .	As	75.	937.5
Barium . . .	Ba	68.64	858.01
Bismuth . .	Bi	70.95	886.92
Boron . . .	B	10.9	136.2
Bromine . . .	Br	78.26	978.3
Cadmium . .	Cd	55.74	696.77
Calcium . . .	Ca	20.	250.
Carbon . . .	C	6.	75.
Cerium . . .	Ce	46.	575.
Chlorine . . .	Cl	35.5	443.75
Chromium . .	Cr	28.15	351.82
Cobalt . . .	Co	29.52	368.99
Copper . . .	Cu	31.66	395.70
Didymium . .		...	......
Fluorine . .	F	18.70	233.80
Glucinum . .	Gl	26.6	331.26
Gold	Au	98.33	1229.16
Hydrogen . .	H	1.	12.5
Iodine . . .	I	126.36	1579.50
Iridium . . .	Ir	98.68	1233.5
Iron	Fe	28.	350.0
Lanthanum .	Ln	48.	600.0
Lead	Pb	103.56	1294.50
Lithium . . .	Li	6.43	80.37
Magnesium .	Mg	12.67	158.35
Manganese . .	Mn	27.67	345.9
Mercury . .	Hg	100.07	1250.9
Molybdenum .	Mo	47.88	598.52
Nickel . . .	Ni	29.57	369.68
Niobium . .		...	......
Nitrogen . .	N	14.	175.00
Osmium . . .	Os	99.56	1244.49
Oxygen . . .	O	8.	100.00
Palladium . .	Pd	53.27	665.9
Pelopium . .	...	...	......
Phosphorus .	P	32.02	400.30
Platinum . .	Pt	98.68	1233.50
Potassium . .	K	39.00	487.5
Rhodium . .	R	52.11	651.39
Ruthenium .	Ru	52.11	651.39
Selenium . .	Se	39.57	494.58
Silicium . . .	Si	21.35	266.82
Silver . . .	Ag	108.00	1350.00
Sodium . . .	Na	22.97	287.17
Strontium . .	Sr	43.84	548.02
Sulphur . . .	S	16.0	200.00
Tantalum . .	Ta	92.30	1153.72
Tellurium . .	Te	66.14	801.76
Thorium . .	Th	59.59	744.90
Tin	Sn	58.82	735.29
Titanium . .	Ti	24.29	303.66
Tungsten . .	W	94.64	1183.00
Uranium . .	U	60.00	750.
Vanadium . .	V	68.55	856.89
Yttrium . . .	Y	32.2	402.51
Zinc	Zn	32.52	406.59
Zirconium . .	Zr	33.62	420.20

In describing the methods to be pursued for bringing the several substances mentioned in the above Table into a state fit for estimation, and separating them quantitatively from other sub stances, we shall follow, as nearly a possible, the same arrangements which we adopted in treating of the comportment of substances with reagents, viz., by arranging them into a series of Groups. With respect to the Bases there will be no difficulty in following out this method; in treating of the Acids, a variation may probably appear desirable.

I. BASES.

Group 1st.—*The Metals of the Alkalies proper, Potassium, Sodium, Ammonium, Lithium.*

Potassium.

This metal is quantitatively determined as *sulphate, chloride, nitrate,* and *as double chloride of platinum and potassium.*

Quantitative determination as Sulphate.—Potassium is in general estimated in the form of this salt when no other bases are present; the solution containing it must be carefully evaporated to dryness, and the residue dried for some time before it is transferred to a platinum crucible to be ignited; this precaution is necessary to guard against a loss from decrepitation. It fuses at a strong red heat with volatilization, or decomposition. Its composition is

One equivalent	of KO	... 47	... 54.02
One do.	of SO_3	... 40	... 45.98
One do.	of KO, SO_3	87	100

If the solution contain excess of sulphuric acid, the *hydrated bisulphate* is obtained by evaporation: this salt must be reduced to the neutral sulphate, which is done by igniting it in a platinum crucible containing a fragment of carbonate of ammonia, and loosely shut with its cover, the excess of sulphuric acid flies off in an atmosphere of carbonate of ammonia; a gentle ignition must be continued till the salt assumes the solid state, the neutral sulphate being far less fusible than the acid sulphate.

Quantitative estimation as Nitrate.—When the alkali exists in a solution in the form of nitrate it may be weighed as such; it should not be fused, as it is thereby capable of being partially decomposed. It is anhydrous. Its composition is

One equivalent	of KO	... 47	... 46.54
One do.	of NO_5	... 54	... 53.46
One do.	of KO, NO_5	101	100

Quantitative estimation as Chloride.—Potassium may likewise be weighed in the form of this salt, when it exists as such in a solution, it should not be heated above feeble redness, and the crucible should be loosely covered, or a loss may be sustained. Its composition is

One equivalent	of K	... 39	... 52.34
One do.	of Cl	... 35.5	... 47.66
One do.	of KCl	74.5	100

Quantitative estimation as double Chloride of Platinum and Potassium.—For this purpose the alkali must be in the state of chloride; the solution is evaporated to a small bulk, and excess of bichloride of platinum and free hydrochloric acid added; the mixture is then evaporated to dryness on the water bath, and the crystalline residue digested with spirits of wine, which removes the excess of bichloride; it is then transferred to a weighed filter, washed with spirits of wine and dried at 212°. Its composition is

One equivalent	of K	39	... 15.97
One do.	of Pt	98.68	... 40.41
Three do.	of Cl	106.5	... 43.62
One do.	of $KCl+PtCl_2$	244.18	100

If the operator be certain that no other base but potassa is present, and that it exists in the solution in the state of neutral sulphate or as chloride, it may then be determined in an indirect manner, by estimating the sulphuric acid as sulphate of baryta, or the chlorine as chloride of silver, and calculating the amount of alkali present from the quantity of sulphuric acid or of chlorine thus obtained.

Sodium.

This metal is quantitatively determined as *sulphate, carbonate* and *chloride:*

Quantitative estimation as Sulphate.—The same method is followed as with sulphate of potassa. It does not decrepitate. Its composition is

One equivalent	of Na O	...30.97...	43.63
One do.	of SO_3	....40.00...	56.37
One do.	of Na O, SO_3	...70.97...	100

Quantitative estimation as Chloride.—The salt must be well dried before it is ignited, to prevent decrepitation; the crucible should be loosely covered. Its composition is

One equivalent	of Na	.....22.97.....	39.28
One do.	of Cl	.......35.50.....	60.72
One do.	of NaCl	......58.47....	100

Quantitative estimation as Carbonate.—As carbonate of soda does not attract moisture from the air so rapidly as the corresponding potassa salt; sodium may be weighed as such. It may be fused without volatilization or decomposition. Its composition is

One equivalent of NaO	30.97	58.46
One do. of CO_2	22.00	41.54
One do. of NaO, CO_2	52.97	100

Separation of Soda from Potassa.—The only method that yields accurate results is to determine the potassa in the form of double chloride of platinum and potassium, and to estimate the soda either *directly* or *indirectly*. The following is the method of proceeding :—The mixed alkalies are converted into chlorides; in most cases this may be done by simply digesting and evaporating with hydrochloric acid ; if, however, the alkalies are combined with sulphuric acid, that acid must first be precipitated by chloride of barium, and the excess of baryta removed by carbonate of ammonia mixed with a little caustic ammonia ; the solution is filtered, and the filtrate is evaporated to dryness, and ignited : the residue is redissolved in hydrochloric acid, and the alkalies are thus brought to the state of chlorides.

If the alkalies are combined with *phosphoric acid*, the solution is evaporated to dryness, ignited, redissolved in water, and precipitated by neutral *nitrate of silver*, the fluid is filtered from the precipitated phosphate of silver, and the excess of nitrate of silver is removed by hydrochloric acid.

If the alkalies are in combination with *boracic acid*, the best method of separating them is by decomposing the boracic acid into gaseous fluoride of boron : for this purpose the dry compound is digested in a platinum crucible with three or four parts of pure powdered fluor spar and concentrated sulphuric acid, and the heat is continued as long as fumes continue to be evolved ; the alkalies are thus converted into sulphates, which are changed into chlorides as above directed.

The mixed alkaline chlorides, being carefully weighed, are dissolved in a small quantity of water and mixed with excess of an aqueous solution of bichloride of platinum, the solution is evaporated to dryness on the water-bath, and the dry mass is treated with a mixture of sulphuric ether and spirits of wine; the potassium is estimated as above described ; the spirits of wine poured on the evaporated residue must acquire a yellow colour, if it does not, it is a proof that sufficient bichloride of platinum has not been added, and the experiment must be repeated with a fresh portion. *Berzelius* recommends to mix the dry chlorides with 3¾ times their weight of the crystallized double chloride of platinum and sodium, a quantity just sufficient to convert the whole mass into double chloride of platinum and potassium, supposing it to consist *entirely* of chloride of potassium ; the process is conducted precisely as before. The soda is either calculated from the difference between the quantity of chloride of potassium found and the original weight of the mixture analyzed, or in a *direct* manner as follows :—The filtrate from the double potassium salt is mixed with solution of *sal ammoniac* in excess, and strong alcohol added, all the platinum salt is thus removed, and the colourless filtrate being evaporated to dryness, the residue is gently ignited and weighed as *chloride of sodium*.

Pagenstecher's method of estimating the amount of Soda in crude Potash.—This is founded on the property possessed by a saturated solution of sulphate of potassa of still dissolving a large amount of sulphate of soda. A certain weight of the sample to be examined is mixed with water, and sulphuric acid added to it until the liquid has an acid reaction ; it is then evaporated to dryness, and the residue ignited and weighed. The powdered saline mass is well agitated in a graduated cylinder with six times its weight of a concentrated solution of sulphate of potassa, the liquid drawn off the sediment with a syphon, and the same quantity of the solution of the sulphate of potassa again poured over the residue. After some time the residue is brought upon a weighed filter, the funnel covered during filtration, the filter, when the liquid has drained off, weighed moist, and then, after being dried at 212°, the difference is the evaporated water of the solution of sulphate of potassa, the degree of concentration of which is known. It is known, therefore, how much of the salt was dissolved in the evaporated water ; this quantity is subtracted from the weight of the saline residue. If the potassa was free from soda, the weight of the sulphate of potassa now remaining must be the same as that first obtained; but if it contained soda, this has been removed as sulphate of soda, and the weight of the first saline residue has been reduced. From the loss the amount of the soda present can be calculated ; if the loss $= V$, the amount of the soda is calculated thus :—

$$\text{As } 70.97\ (NaO, SO_3) : 52.97\ (NaO, CO_2) :: V : X$$

$X =$ the amount of carbonate of soda present in the specimen.

It should, however, be observed that when soda is used to adulterate potassa, a kind is employed that contains about 20 per cent. of sulphate of soda. Before making the weighings, it is well to take the specific gravity of the filtered solution of the sulphate of potassa; if it is the same as before it can have removed nothing, and if it has taken up sulphate of soda its density has naturally been raised.—*Chem. Gaz. Jan.* 1848.

Indirect separation of Potassa from Soda.—This method is founded on the difference which exists between the combining numbers of potassium and sodium, and is applicable to both sulphates and chlorides. It is deduced from the following considerations:—Suppose the alkalies to be in the state of sulphates, and 100 grains of the mixture to have yielded 152.8 grains of sulphate of barytes = 52.6 grs. of sulphuric acid. Let the quantity of *sulphate of potassa* present be called A, and that of *sulphate of soda* B: then

$A + B = 100$, or $100 - B = A$. That is the proportion of sulphate of potassa in the mixture is the weight of the mixture analyzed *minus* the proportion of sulphate of soda:—

Now one part of sulphate of potassa contains... .4598 sulphuric acid.
And one part of sulphate of soda contains......... .5637 do.

The 52.6 grs. of sulphuric acid found in the mixture must, therefore, be $(A \times .4598) + B \times .5637$: that is, the number of units present of *sulphate of potassa* multiplied by the quantity of sulphuric acid in *one* unit, added to the number of units present of *sulphate of soda* multiplied by the quantity of sulphuric acid in *one* unit:—

$$(A \times .4598) + (B \times .5637) = 52.6$$

$$\text{consequently } A = \frac{52.6 - (B \times .5637)}{.4598};$$

but A has been shown above to be $= 100 - B$; substituting this value, therefore, for A, we have

$$100 - B = \frac{52.6 - B \times .5637}{.4598}$$

$$\text{or, } 100 \times .4598 - (B \times .4598) = 52.6 - (B \times .5637)$$

$$\text{or, } 45.98 - (B \times .4598) = 52.6 - (B \times .5637)$$

and, putting the two B's on the same side of the equation, we have

$$(B \times .5637) - (B \times .4598) = 52.6 - 45.98$$

$$\text{or, } B = \frac{52.6 - 45.98}{.5637 - .4598} = \frac{6.62}{.1039} = 63.7$$

The mixture contains, therefore, 63.7 per cent. of sulphate of soda, and 36.3 per cent. of sulphate of potassa.

Suppose the alkalies to be in the state of chlorides, and 133 grains of the mixture to have given 287 grains of chloride of silver = 71 grains of chlorine;

Then let the quantity of chloride of potassium be . . A
And that of chloride of sodium B

then $A + B = 133$; and $A = 133 - B$.

Now one part of chloride of potassium contains . . . .4766 chlorine
And one part of chloride of sodium contains . . . .6072 do.

Therefore, as before,

$$71 = (A \times .4766) + (B \times .6072),$$

$$\text{consequently } A = \frac{71 - (B \times .6072)}{.4766};$$

$$\text{or, } 133 - B = \frac{71 - (B \times .6072)}{.4766};$$

$$\text{or, } 133 \times .4766 - (B \times .4766) = 71 - (B \times .6072);$$

$$\text{or, } 63.38 - (B \times .4766) = 71 - (B \times .6072);$$

$$\text{and } (B \times .6072) - (B \times .4766) = 71 - 63.38;$$

$$\text{therefore } B = \frac{71 - 63.38}{.6072 - .4766} = \frac{7.62}{.1306} = 58.34$$

The mixture is therefore composed of 58.34 grains of chloride of sodium, and 74.66 grains of chloride of potassium.

From the above calculations the following rule for the indirect determination of soda and potassa, when together present in a mixture, in the state of sulphates, is derived:—

From the *quantity of sulphuric acid subtract the product obtained, by multiply-*

ing the weight of the mixture into the quantity of sulphuric acid in a unit of sulphate of potassa, and divide the remainder by the difference between the quantity of sulphuric acid in a unit of sulphate of soda, and the quantity in a unit of sulphate of potassa; the quotient is the quantity of sulphate of soda in the mixture.

Example.—In 100 grains of a mixture of the two sulphates, 50 grains of sulphuric acid are found.

$$\frac{50 - (100 \times .4598)}{.5637 - .4598} = \frac{50 - 45.98}{.1039} = \frac{4.02}{.1039} = 38.69 = \text{the sulphate of soda;}$$

consequently, 100 — 38.99 = 61.31 = the sulphate of potassa.

The same rule applies to the determination of the alkaline chlorides, substituting chlorine for sulphuric acid; the results are tolerably accurate, but the determinations of sulphuric acid and chlorine require to be made with the greatest care.

Alkalimetry.—The commercial value of the several varieties of potash and soda depends entirely on the amount of carbonated or caustic alkali which they contain; it is important, therefore, to the purchaser of these articles to be in possession of a simple and expeditious method of determining, with tolerable accuracy, the amount of available alkali in the crude salt—a complete chemical analysis of such a heterogeneous mixture requiring great skill and time. Two methods are adopted for this purpose:—the first, that of *Gay Lussac*, depends on the constant saturating power of sulphuric acid of a certain determinate strength, being founded in common with every other process involving chemical combination or decomposition on the law of definite proportions: the second, that of *Fresenius and Will*, depends on the determination of the amount of carbonic acid evolved from a given weight of the salt, during its decomposition by sulphuric acid.

1. *Modification of the method of Gay Lussac.—Preparation of the standard acid:* 170.1 grains of pure carbonate of soda, obtained by igniting the best bicarbonate in a platinum crucible, are dissolved in four or five ounces of hot distilled water: common oil of vitriol is diluted with ten or twelve parts of water, and when cold, the burette, *fig.* 26, which is accurately divided into 100 equal parts, each division corresponding to ten grain measures of water, is filled to 0 with the diluted acid; the solution of carbonate of soda is transferred into a small beaker, and a sufficient quantity of infusion of litmus added, to communicate to it a distinct blue colour, the acid is then poured gradually from the burette into the alkaline liquor, until the blue colour changes to distinct red, which it does by a very slight excess of sulphuric acid; the addition of the acid, when the point of saturation is nearly attained, must be made with great care, and the operator must be careful not to mistake the wine red colour, which the liquor assumes from the evolution of carbonic acid, for the distinct red produced by a slight excess of the sulphuric acid. As this mistake may, however, be made, it is better towards the close of the operation, after the addition of every drop of acid, to moisten a glass rod with the test liquid, and make a streak with it on blue litmus paper. As soon as an excess of sulphuric acid has been employed, the paper remains red after being dried, which is not the case if the reddening has been occasioned by carbonic acid; the test liquor being saturated, the quantity of acid which has been required to produce the effect is accurately observed: suppose it to be 90 measures, this then is the quantity equivalent to 170.1 grains of carbonate of soda, or 100 grains of soda. A standard acid is thus prepared, the precise strength of which is known, but as it is more convenient to have an acid 100 measures of which shall be equal to 100 grains of soda, every division of which on the burette represents therefore a grain of soda, the 90 measures are made up to 100 by the addition of 10 measures of water, and a stock of acid is then prepared, any vessel accurately divided into 100 equal parts serving for the purpose. When a sample of commercial soda has to be tested, 100 grains taken from different parts of the mass are carefully weighed out, dissolved in water, and filtered, if necessary, from any insoluble residue; the solution is then neutralized with the standard acid in the manner and with the precautions above described, and of course the number of measures required

Fig. 26.

represents in grains the quantity of carbonate of soda in the specimen: thus, suppose 47 measures of acid are required, the sample is at once seen to contain two ounces perfect of soda = 80.38 per cent. of carbonate; the same method may be employed in analyzing carbonate of potassa, and the different variety of pearl-ashes, but as the equivalent number of potassium is higher than that of sodium, a different calculation becomes necessary, though the same test acid may be used: thus, the equivalent number of sodium is 22.97, that of soda being 30.97, and that of carbonate of soda 52.97; the equivalent number of potassium is 39, that of potassa 47, and that of carbonate of potassa 59. The same quantity, therefore, of acid that is required to neutralize 30.97 grains of soda, would neutralize 47 grains of potassa; but as these numbers bear very nearly the ratio of two to three, the calculation becomes very simple: we have only to multiply the number of divisions of the burette required to saturate 100 grains of the potash specimen by three, and divide by two, to get the per centage amount of potassa with sufficient accuracy for most practical purposes: thus, suppose 30 measures of acid are required, the sample contains $\frac{30 \times 3}{2} = 45$ per cent. of potassa = 66 per cent. of carbonate.

There are, however, one or two circumstances, besides the unavoidable errors of manipulation, which prevent this method from attaining a high degree of accuracy. Both the soda and pearl-ash of commerce contain a variety of impurities; soda contains *sulphate of soda, chloride of sodium, sulphuret of sodium, basic silicate of soda, hydrate of soda, hyposulphite,* and sometimes *sulphite of soda:* of these *sulphuret of sodium,* which may be detected by the odour of sulphuretted hydrogen evolved on moistening the specimen with sulphuric acid, *silicate of soda, hyposulphite* and *sulphite of soda,* (which may be detected by dissolving a portion of the specimen in sulphuric acid, coloured with a few drops of chromate of potassa, the solution becomes green if either of the two latter salts are present,) all these salts interfere with the accuracy of the results. It is true that by heating the specimen with chlorate of potassa, the sulphuret of sodium, as well as the sulphite and hyposulphite of soda, becomes converted into sulphate, which is without any influence in the operation; but another source of inaccuracy is at the same time introduced, inasmuch as the hyposulphite of soda, if present, upon its conversion into sulphate, decomposes one equivalent of carbonate of soda, thus:—

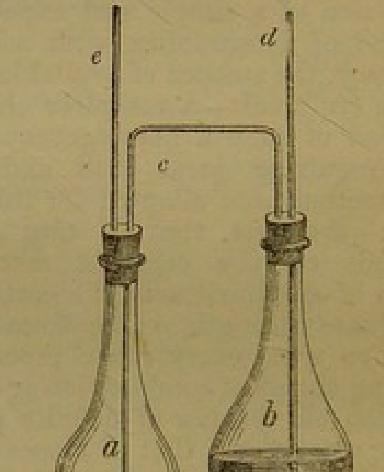
$$\mathrm{NaO, S_2O_2 + 4O + NaO, CO = 2(NaO, SO_3) + CO_2}$$

The carbonate under examination becomes then under-estimated, while the error arising from the presence of basic silicate of soda is without remedy. The method next to be described overcomes these difficulties, and is, moreover, after a little practice, more easy of execution.

2. *Method of Fresenius and Will.*—The alkalimetrical process above described seeks its object by determining the amount of *alkali,* calculating it from the measure of acid which it requires for its neutralization. In the method now to be described the result is obtained by determining the quantity of *carbonic acid* with which the alkali was combined.

The process is conducted as follows:[*]—

Fig. 27.



a and *b* are two flasks. Wide-mouth medicine bottles even may be employed. *b* must have a capacity of from 2½ to 2 ounces of water: it is advisable that *a* should be somewhat smaller, say of a capacity of about 1½ to 2 ounces. Both flasks are closed by means of doubly perforated corks: these perforations serve for the reception of the tubes, *c, d,*

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[*] A New Method of Alkalimetry, &c., by Drs. C. R. Fresenius and H. Will. Edited by J. Lloyd Bullock. 1844. Taylor and Walton.

and *e*. All these tubes are open at both ends; when operating, the end of the tube *d* is closed by means of a small piece of wax. The substance to be examined is weighed and projected into the flask *b*, into which water is then poured to the extent of one-third of its capacity. *a* is filled with common English sulphuric acid to about half its capacity. Both flasks are then corked, and the apparatus is weighed. The air in the whole apparatus is then rarefied by applying suction to the tube *e*; the consequence is, that the sulphuric acid contained in *a* ascends into the tube *c*, and thus a portion of it flows over into *b*; immediately upon its coming into contact with the carbonate contained in this flask the evolution of carbonic acid begins briskly. The peculiar construction of the apparatus compels the carbonic acid evolved to pass through the sulphuric acid contained in *a*, before it is permitted to escape through the tube *e*, this being the only aperture of the apparatus. It is obvious that this transmission through sulphuric acid will retain all the moisture with which the carbonic acid may be charged more completely than could be done in any other manner. Upon the influx of the sulphuric acid the fluid in *b* becomes heated, and expands together with the air contained in the flask: upon cooling, both acquire their original volume again, owing to which a new portion of sulphuric acid flows over into *b* as soon as the evolution of gas has ceased: the process is, however, expedited by applying suction to the tube *e* every time the evolution of gas ceases, and in this way the operation may be accomplished in a few minutes. When the carbonate is completely decomposed (which is immediately ascertained by no further evolution of gas taking place upon the influx of fresh portions of sulphuric acid into *b*), a somewhat larger quantity of the sulphuric acid contained in *a* is, by means of renewed suction, made to pass over into *b*: the fluid in this flask becomes hereupon heated to such an extent as to expel all the carbonic acid which it had absorbed in the course of the operation. As soon as the evolution of gas has completely ceased, the aperture of the tube *d* is opened by taking off the piece of wax and suction applied to the tube *e*, until all the carbonic acid still contained within the apparatus is replaced by air. The apparatus is then allowed to cool, wiped dry, and weighed. The loss of weight indicates, with the greatest possible exactness, the amount of carbonic acid which was contained in the test specimen. A common apothecary's balance, that will turn with one-sixth of a grain, is sufficiently delicate for weighing not only the whole apparatus, but the test specimen also; and it is not one of the least of the advantages of this method, that it enables the operator to experiment on a much larger scale than is possible in an ordinary analysis. The quantity of the sample employed is recommended by the author to be 6.29 grammes (= 97 grains) of potash, and 4.84 grammes (= 74.7 grains) of soda, these quantities containing in their state of purity exactly 2 grammes (= 30.88 grains) of carbonic acid; consequently, every 2 centigrammes (= .3088 grains) of carbonic acid that are given off, indicate *one* per cent. of carbonate; all trouble of calculation is thus avoided. Previous to submitting the sample to analysis, it must be thoroughly dried by exposure to heat over a lamp for about five minutes in a Berlin crucible, and allowed to cool with the cover on: it must also be ascertained whether any insoluble earthy carbonates are present, which is done by dissolving the specimen in water, filtering and well washing the residue: if the sample contain sulphuret, sulphite, or hyposulphite of the alkali, a tea-spoonful of *yellow chromate of potassa* is added to the solution in the flask, which decomposes both the sulphurous acid and the sulphuretted hydrogen at the moment of their liberation, all the products of the decomposition, viz., sulphate of chromium, water, and sulphur, remaining in the apparatus. The amount of caustic soda, and potassa, present in the specimen, the determination of which is of great importance, is found by comparing the quantity of carbonic acid evolved from a given weight of the alkali in its ordinary state with that evolved from a similar quantity after it has been mixed in a moist state with carbonate of ammonia, and dried at a high temperature, by which means all the caustic alkali becomes carbonated. Should any *bicarbonates* be present, they are converted into neutral carbonates, by the application of a gentle red heat: in order to ascertain their presence the solution to be examined is mixed with solution of chloride of calcium in excess, filtered, and ammonia added to the filtrate, a turbidity indicates the presence of bicarbonate.

The presence of free soda in the commercial article is detected by the alkaline reaction which the solution of the sample exhibits after the addition of chloride of barium in excess. Drs. Fresenius and Will apply the same method to the analysis of carbonates, the bases of which form insoluble compounds with sulphuric acid. The apparatus is, however, somewhat modified, in order to allow of the introduction of nitric acid in the place of sulphuric acid into the bottle *b*. For this purpose the tube *d* is expanded to a bulb in its upper part, and drawn out to a fine point at its lower end; it must be adjusted into the cork of *b* in such a manner as to allow of its being raised or depressed, still, however, preserving the bottle air-tight. It is filled with dilute nitric acid, and a wax stopper having been inserted into its upper aperture it is introduced into the cork, so that its point just reaches the surface of the water in *b*, through which the carbonate to be analyzed is diffused. The nitric acid is prevented from escaping from the tube by the wax stopper. The whole apparatus is weighed, the tube *d* is then cautiously depressed, so that its point nearly reaches the bottom of the flask, and by removing the wax stopper the nitric acid gradually escapes into *b*, occasioning the decomposition of the carbonate, the liberated carbonic acid escaping through the tube *c*, and becoming deprived of moisture by the sulphuric acid in *a*, previous to escaping through *e*. When the decomposition is complete, the carbonic acid which has been absorbed by the water in *b* is expelled by plunging the apparatus into hot water, air having been previously drawn through the flasks by suction at the tube *e*. As soon as the whole is cool the flasks are wiped dry and weighed. The loss indicates the amount of carbonic acid. It is scarcely necessary to say that nitric acid is here employed, in consequence of its forming soluble compounds with the bases of such carbonates as may require to be analyzed in this apparatus, viz., those of lime, strontia, and baryta.

It having been stated on the authority of the American chemists, *Messrs. Rogers*[*], that sulphuric acid is capable of absorbing a large amount of carbonic acid, and that the elegant alkalimetrical method of Drs. Fresenius and Will must in consequence be involved in serious errors, the author of this Treatise made and published[†] some experiments on the subject; the results being of a perfectly satisfactory character, he has thought it worth while to reproduce them here.

Carbonate of soda, prepared by igniting the pure bicarbonate, was first analyzed.

Ex. 1.—70 grains lost 28.99 grains of carbonic acid = 41.41 per cent.

Ex. 2—64.6 grains lost 26.8 grains = 41.48 per cent.

Theory requires 41.54 per cent.

Carbonate of potassa, prepared by igniting the pure bicarbonate.

Ex. 1.—79.24 grains lost 25.2 grains of carbonic acid = 31.81 per cent.

Ex. 2.—90.55 grains lost 28.84 grains = 31.84 per cent.

Theory requires 31.88 per cent.

Carbonate of strontia, analyzed by the method, with nitric acid, above described.

78.84 grains lost 22.75 grains of carbonic acid = 29.75 per cent.

Theory requires 29.8 per cent.

Some experiments were afterwards instituted, with the view of ascertaining whether there was, in fact, *any* absorption of carbonic acid by the sulphuric acid, and the result showed that if such were the case the quantity absorbed must be very trifling, and incapable of interfering in any way with the success of any experiment in which sulphuric acid is employed as a desiccating agent for carbonic acid.

Ammonium.

Ammonia is estimated as *chloride of ammonium*, and as double *chloride of platinum* and *ammonium;* in the analysis of organic substances it is sometimes determined from the volume of nitrogen gas which is produced by its decomposition.

Quantitative estimation as Chloride.—When the alkali exists in a solution, either in an uncombined state, or as carbonate, or combined with a weak volatile acid, or as chloride, it may be weighed in the form of the latter salt, for which purpose slight excess of hydrochloric acid is added to the solution, which is evaporated to dryness on the water bath, the residue being heated

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[*] Chemical Gazette, March 15th, 1848.

[†] Chemical Gazette, May 1st, 1848.

thereon till it ceases to lose weight; at this temperature the loss from volatilization is almost inappreciable. Its composition is

One equivalent of NH_4	18.0	33.65
One ditto of Cl	35.5	66.35
One ditto of NH_4 Cl	53.5	100

Quantitative estimation as double Chloride of Platinum and Ammonium.—Ammoniacal salts, soluble in alcohol, may be analyzed by converting the ammonium into a double salt, with bichloride of platinum; for this purpose the solution is super-saturated with hydrochloric acid, and an aqueous solution of bichloride of platinum added, the mixture is evaporated to dryness, and the residue treated precisely as the corresponding potassium salt; it is washed on a weighed filter, with alcohol, and dried at 212°, and its composition is

One equivalent of NH_4	18.00	8.06
One ditto of Pl	98.68	47.72
Three ditto of Cl	106.50	44.21
One do. $NH_4Cl+PlCl_2$	223.18	100

When this double salt is heated to redness it is entirely decomposed, metallic platinum in a fine spongy form alone remaining; this operation may therefore be performed on it in order to control the previous determination; the ignition must be carefully effected in a thin Berlin crucible; a gentle heat being first applied, and gradually increased until the organic matter of the filter is entirely destroyed. The crucible should be covered at first, but the cover must be removed towards the close of the operation, the crucible being then placed obliquely, in order to favour the access of air; every 100 parts of platinum correspond to 8.06 of ammonium, or 7.61 of ammonia.

Ammoniacal salts, insoluble in alcohol, are analyzed by igniting them with a mixture of caustic soda and hydrate of lime*; the ammonia is liberated from its previous combination, and is received into and condensed in hydrochloric acid; it is subsequently estimated as double chloride of platinum and ammonium, in the manner already described. The process is conducted as follows:—The salt to be analyzed having been thoroughly dried in the water bath, is weighed, and intimately mixed with a sufficient quantity of soda lime to one half fill a combustion tube of hard German glass, about 14 or 16 inches long, and half an inch internal diameter; in the operation of mixing, forcible pressure must be carefully avoided, or the ammoniacal salt will undergo partial decomposition, even in the cold; the combustion tube is drawn out to a point, and bent obliquely upward at its closed end, soda lime is first introduced so as to occupy about an inch of the end of the tube, this is followed by the mixture, the remainder of the tube is filled to within an inch of the top with soda lime that has served to rinse out the mortar, and, finally, a stopper of recently ignited asbestos is inserted; the tube is now laid in a horizontal position on the table, and a few smart taps given to it, in order to open a channel above the mixture for the passage of the ammoniacal gas. The condensing apparatus, containing a small quantity of hydrochloric acid, is now attached to the tube by means of a perforated cork, the combustion tube is placed in the furnace, and the whole apparatus having been proved to be air-tight, the tube is gradually heated with red hot charcoal, commencing at the interior portion, and proceeding gradually towards the closed end, until the tube is red hot throughout its whole length; when the evolution of ammonia has ceased, the point of the combustion tube is quickly broken off, and air drawn through the apparatus, so as to bring the whole of the ammonia into the hydrochloric acid. The only source of error to be apprehended in conducting this operation arises from the powerful affinity subsisting between hydrochloric acid and ammonia, in consequence of which the acid is apt to rush back with violence, and enter the combustion tube, thus spoiling the whole analysis. The inventors of the method, Drs. Will and Varrentrapp, recommend mixing the substance analyzed with an equal amount of sugar, which gives rise to the evolution of other and more permanent gases serving to dilute the ammonia. The accident may, however, be better prevented by employing a capacious condensing apparatus, provided with an extra bulb, as seen in *fig.* 28, which shows the disposition of the whole apparatus, and using

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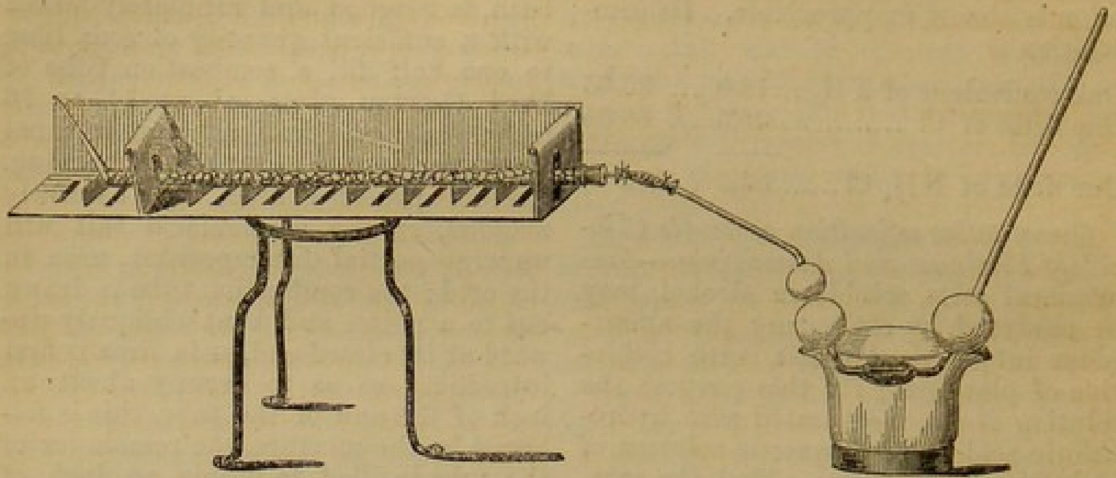
* Prepared by slaking a weighed amount of the best caustic lime with solution of soda of such a strength that there shall be about one part of hydrated soda to two of anhydrous caustic lime; the mixture is heated to feeble redness in a Hessian crucible, pulverized, and kept in a well-closed phial.

Fig. 28.



a moderate quantity of hydrochloric acid; or even better, by employing a condensing apparatus recommended by Mr. Warren de la Rue, and described in the memoirs of the Chemical Society, with which the recession of the acid into the combustion tube is rendered almost impossible. The operation being over, the contents of the condensing apparatus are transferred to an evaporating basin, and the apparatus repeatedly rinsed out with water; bichloride of platinum in excess is then added, and the remainder of the process conducted as has been already directed.

Separation of Ammonia from Potassa and Soda.—When all three alkalies are present in combination with the same volatile acid, the ammoniacal salt may be expelled from a weighed portion of the mixture by careful ignition, and the amount of ammonia calculated from the loss of weight. If the mixture contain ammonia in the form of chloride or carbonate, it may likewise be expelled by heat from the salts of the other alkalies, but if the ammonia be present in combination with a non-volatile acid, or if the mixture cannot be dried at a temperature insufficient to expel ammonia, it must be determined by combustion with soda lime, and the other alkalies must be estimated from a separate portion, having previously gently ignited it to expel all the ammonia. If no potassa be present, ammonia may be separated from soda by bichloride of platinum.

Lithium.

This metal is generally estimated in the form of *phosphate of soda* and *lithia*, the composition of which is

Two equiv. of NaO ...	61.94 ...	16.34
Two ditto of LiO	28.86 ...	7.61
Four ditto of PO_5	288.08 ...	76.05
	378.88	100

According to *Rammelsberg*, however, the double phosphate of soda and lithia is a salt of very variable composition, and perfectly useless for quantitative purposes. If there be no other base present, lithia may be estimated as sulphate, the composition of which is

One equivalent of LiO ...	14.43 ...	26.5
One ditto of SO_3............	40.00 ...	73.5
	54.43	100

Separation of Lithia from Potassa and Soda. — From an accurately weighed quantity of the mixture, the potassa is precipitated as chloride of platinum and potassium; the excess of platinum is removed from the filtered solution by sulphuretted hydrogen, or by evaporating to dryness and igniting the residue. According to *Rose*, the lithia is then precipitated as phosphate of soda and lithia, and the amount of soda is calculated from the loss sustained by the whole. *Rammelsberg*, however, considering the double phosphate of soda and lithia as unworthy of confidence in a quantitative determination, recommends to convert the soda and lithia into chlorides, and to digest them with a mixture of anhydrous alcohol and ether, equal parts of each, in which chloride of lithium is easily soluble, while a mere trace only of chloride of sodium is dissolved. An accurate method of quantitatively determining lithia in the presence of the other alkalies is, however, yet a desideratum.

GROUP 2ND.—*The Metals of the Alkaline Earths:—Barium, Strontium, Calcium, Magnesium.*

Barium.

Oxide of barium or *baryta* is weighed as *carbonate* and *sulphate*, most frequently as the latter, which is completely insoluble in water, and in all diluted acids.

Quantitative estimation as Sulphate.—To the solution containing the earth, heated to 212°, dilute sulphuric acid is added as long as precipitation is occasioned; the fluid is well agitated, poured into a beaker or a Phillips's precipitating jar, and allowed to stand till it is settled, and the supernatant fluid become quite clear: it is then transferred to a filter, the amount of ash yielded by which is known, and washed with hot distilled water until the wash water no longer produces any precipitate with chloride of barium, it is then dried and ignited, the heat being continued until the organic matter of the filter is completely destroyed, and the contents of the crucible perfectly white; when quite cold, it is weighed. Its composition is

One equivalent of BaO	76.64	65.7
One ditto of SO_3	40.00	34.3
One ditto of BaO, SO_3	116.64	100

Quantitative determination as Carbonate.—In certain cases the precipitation of baryta by sulphuric acid is inadmissible; it is then thrown down in the form of carbonate by carbonate of ammonia, mixed with a little caustic ammonia; the precipitate is allowed to settle in a warm place, and it is washed on the filter with water, rendered slightly alkaline by ammonia. It may be heated to redness, without losing carbonic acid.

Its composition is

One equivalent of BaO	76.64	77.69
One do. of CO_2	22.00	22.31
	98.64	100

Baryta is estimated as *carbonate* when it exists in combination with an organic acid: the salt is carefully ignited in a platinum crucible, first covered, and afterwards, with free access of air, the heat is continued till the residue is perfectly white; it is then allowed to cool, moistened with carbonate of ammonia, and again gently ignited.

Separation of Baryta from the Alkalies.—The compound is dissolved in water or in hydrochloric acid, if necessary; and the baryta precipitated as *sulphate*, the alkalies being in this case obtained also in the state of sulphates by evaporating the filtered solution; or as *carbonate*, in which case the alkalies may be obtained as chlorides, which is the most convenient form if they have subsequently to be separated from each other.

Strontium.

Oxide of Strontium.—*Strontia* is also weighed as *sulphate* and as *carbonate;* it is precipitated in the form of both salts precisely as baryta; but, as sulphate of strontia is not altogether insoluble in water, spirits of wine are added to the fluid, to diminish its solubility: when this is inadmissible, it is better to precipitate the earth as carbonate, washing the salt on the filter with water containing ammonia and carbonate of ammonia.

The composition of sulphate of strontia is

One equivalent of SrO	51.84	56.44
One do. of SO_3	40.00	43.56
One do. of SrO, SO_3	91.84	100

The composition of carbonate of strontia is

One equivalent of SoO	51.84	70.20
One do. of SO_2	22.00	29.80
	73.84	100

Separation of Strontia from Baryta.—The hydrochloric solution of the earths is mixed with excess of hydrofluosilicic acid, and allowed to remain at rest for some hours: the crystalline precipitate of silico fluoride of barium is collected on a weighed filter, washed and dried at 212°: the strontia in the filtrate is estimated either as sulphate or as carbonate.

The composition of silico-fluoride of barium is

One equivalent of Ba	68.64	46.98 = 52.45 BaO;
One do. of Si	21.35	14.60
Three do. of Fl	56.10	38.42
One do. of $(BaFl, SiFl_2)$*	146.09	100

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* According to *Berzelius* the formula of silico-fluoride of barium is $(3 BaFl, 2 SiFl_3)$.

Separation of Strontia from the Alkalies.—This is effected in the same manner as the separation of baryta.

Calcium.

Oxide of Calcium, or *Lime,* is estimated as *sulphate* and as *carbonate.* As sulphate of lime is soluble to a considerable extent in water, it is necessary to add to the solution about to be precipitated by sulphuric acid twice its volume of alcohol, and to wash the sulphate of lime on the filter with spirits of wine: it is ignited previous to weighing.

The composition of sulphate of lime is

One equivalent of CaO	28	...	41.17
One do. of SO_3	40	...	58.83
One do. of CaO, SO_3	68		100

Quantitative determination as Carbonate.—If the lime salt be soluble in water, and if the solution be perfectly neutral, oxalate of ammonia is added as long as a precipitate is produced; the oxalate of lime is allowed to settle completely, which usually requires some hours; the vessel (a beaker, or a Phillips' precipitating jar) being covered, and placed in a warm situation, it is then filtered, and the salt, having been thoroughly washed with hot water, is dried and exposed to a dull red heat for about twenty minutes; the oxalate of lime is by this means converted into carbonate; but, as it is possible that it may have lost carbonic acid during ignition, it is safer, before weighing, to moisten it with a few drops of solution of carbonate of ammonia, to evaporate to dryness on the water bath, and again expose it to a very gentle ignition.

The composition of carbonate of lime is

One equivalent of CaO	28	...	56
One do. of CO_2	22	...	44
One do. of CaO, CO_2	50		100

If, however, the lime salt can only be held in solution by a free mineral acid, or if it will not bear the addition of excess of ammonia without a precipitation taking place, as is the case with *phosphate of lime* for example, the lime is best estimated as sulphate, because, oxalate of lime being soluble in mineral acids, it would be impossible to precipitate it from a solution containing free nitric or hydrochloric acid; oxalate of lime is, however, insoluble, or nearly so in *acetic acid,* and likewise in *oxalic acid.* According to *Fresenius,* very accurate results may therefore be obtained by adding to the hydrochloric solution of the lime salt sufficient ammonia to occasion a slight precipitate, then a drop or two of hydrochloric acid to redissolve this precipitate, then oxalate of ammonia in excess, and finally, *acetate of potassa,* a portion of which becomes decomposed by the free hydrochloric acid, liberating a corresponding quantity of *acetic* or *oxalic* acid, in which, as before observed, oxalate of lime is almost entirely insoluble.

Separation of Lime from Baryta.—This is best effected by adding to the acid solution of the two earths very diluted sulphuric acid, as long as precipitation occurs; if the sulphuric acid be sufficiently diluted, no lime will be precipitated.

Separation of Lime from Strontia.—This is effected with some difficulty; the only good method is that recommended by *Stromeyer,* which is based on the complete solubility of nitrate of lime in absolute alcohol, and the insolubility of nitrate of strontia in the same menstruum. The two earths are converted into nitrates, excess of nitric acid being carefully avoided, the solution is evaporated to dryness in a flask that can be closed, and the residue digested for several hours with absolute alcohol: being frequently shaken, the mixture is then filtered, and the undissolved residue washed with alcohol; both earths are then estimated as sulphate.

Separation of Lime from Baryta and Strontia.—When all three earths are together in a solution, the baryta is first precipitated by hydrofluosilicic acid, the lime and the strontia are obtained from the solution filtered from the silico-fluoride of barium in the form of sulphates, by the addition of sulphuric acid and evaporation to dryness—the mixed sulphates are fused in a platinum crucible with three times their weight of mixed carbonates of potassa and soda: the fused mass is extracted with water, and the earths are thus obtained in the state of carbonates. They are next converted into nitrates, and separated by alcohol, as above directed.

Separation of Lime from the Alkalies.—The process for effecting this is very simple: the lime is separated by oxalate of ammonia with the usual precautions; the filtered solution is evaporated to dryness, and ignited to expel the ammoniacal salts; the residue is dissolved in water, and the alkalies determined according to the method already described.

Magnesium.

Oxide of magnesium or *magnesia* is weighed as *sulphate*, or *pyrophosphate*, and sometimes as pure *magnesia*.

Quantitative estimation as Sulphate.—The earth is determined in the form of this salt when no other fixed constituent is present; the solution containing it is mixed with excess of sulphuric acid, evaporated to dryness, and ignited in a platinum crucible; the residue is again treated with dilute sulphuric acid, evaporated to dryness, and again gently ignited; the residue is pure anhydrous sulphate of magnesia, the composition of which is

One equivalent of	MgO	20.67	34.07
One ditto	SO_3	40.00	65.93
One do.	$MgOSo_3$	60.67	100

Quantitative estimation as Pyrophosphate.—Muriate of ammonia is added to the solution, then ammonia in excess; should a precipitate hereupon occur, a fresh quantity of muriate of ammonia is added, by which the precipitate is redissolved; solution of phosphate of soda is then dropped into the mixture as long as precipitation takes place. The whole is well agitated, and allowed to repose for several hours: the precipitate is collected on a filter, the amount of ash furnished by which is known, and washed with water containing about one-eighth of ammonia, in which the *basic phosphate of magnesia* and *ammonia* ($PO_5 2MgO,NH_4O + 24$ aq.) is scarcely sensibly soluble; the washed salt is dried and carefully ignited, together with the filter; the latter requires considerable time for incineration, which is best effected by cutting in strips and burning it on the lid of the crucible. The composition of the ignited salt is

Two equivalents of	MgO	41.34	36.46
One ditto of	PO_5	72.02	63.54
One do. of	$2MgO,PO_5$	113.36	100

Separation of Magnesia from Baryta and Strontia.—The two latter earths are precipitated by carbonate of ammonia, a sufficient quantity of sal ammoniac having previously been added to the solution to prevent the precipitation of the magnesia: the precipitated carbonates of baryta and strontia are dissolved in hydrochloric acid, and the baryta separated from the strontia by hydrofluosilicic acid, the magnesia is determined in the filtrate as pyrophosphate; if no strontia be present, the baryta may be precipitated as sulphate.

Separation of Magnesia from Lime.—There are several methods of effecting this. 1st, by *oxalate of ammonia.*—Sal-ammoniac is added to the solution of the two earths, then slight excess of ammonia; the lime is then precipitated by oxalate of ammonia, with the proper precautions, and the magnesia in the filtrate determined as pyrophosphate. 2nd, by *sulphate of lime.* For this purpose the two earths must be in the state of sulphates: the mixture, having been ignited, is digested with a saturated solution of sulphate of lime, and the insoluble residue washed on a filter with the same salt; the whole of the sulphate of magnesia is thus removed, the sulphate of lime being quite insoluble in a saturated solution of sulphate of lime remaining on the filter: it is heated to redness and weighed; and from the difference in weight, before and after the operation, the amount of sulphate of magnesia is calculated. 3rd, by *chlorate of potassa.* The hydrochloric solution of the two earths is evaporated to dryness, and ignited in a platinum crucible: chlorate of potassa is then added in small quantities at a time, until the evolution of chlorine ceases. The mass on cooling is extracted with water, which dissolves the chloride of calcium, and leaves a residuum of pure magnesia, the chloride of magnesium having, under the influence of heat, aided by the chlorate of potassa, been completely decomposed: the lime is determined in the aqueous solution by oxalate of ammonia.

Separation of Magnesia from the Alkalies.—The best method is the following, recommended by *Berzelius:*—The bases are brought to the state of chlorides, to a concentrated solution of which finely powdered and perfectly pure red oxide of mercury is added in excess, mutual decomposition of the chloride of magnesium and of the oxide of mercury takes place, *chloride of mercury* being formed, which combines with the alkaline chlorides, forming a soluble double salt; and *magnesia*, which remains undissolved, on extracting the evaporated and ignited mass with water. The solution, filtered from the magnesia, is evaporated to dryness, and heated, to expel the chloride of mercury: the alkaline chlorides alone remain, which are separated from each other as directed (page 141); the *magnesia* may be contaminated with undecomposed oxide of mercury, from which, however, it is readily freed by heat. This method is well adapted for the analysis of *mineral waters, soils*, &c. The following method, proposed by Liebig, also gives accurate results; baryta water is added to the hydrochloric solution to alkaline reaction, magnesia is thereby precipitated, *baryta*, being a stronger base than *magnesia*, in consequence of which, it deprives it of its electro-negative element; to the solution, filtered from the precipitated magnesia, carbonate of ammonia, mixed with caustic ammonia, is added, the excess of baryta is thereby removed, and is filtered off; the alkalies are contained in the filtrate in the form of chlorides, and are separated from each other in the usual manner.

GROUP 3RD.—*Aluminum, Glucinum, Yttrium, Thorium, Zirconium, Chromium.*

Aluminum.

Alumina is precipitated from its solutions by ammonia, or carbonate of ammonia, sal-ammoniac having been previously added and heat applied. The precipitate, which is very bulky, requires long-continued washing with hot water, its ignition must be carefully performed in order to avoid loss by spirting. It shrinks very much in drying. Its composition is—

Two equivalents of Al	...27.38	... 53.29
Three ditto of O	.........24.00	... 46.71
One do. of Al_2O_3	...51.38	100

It is never weighed in any other form than as pure alumina.

Separation of Alumina from the Alkaline Earths and Alkalies.—To the hydrochloric solution of the mixture muriate of ammonia is added, then ammonia quite free from carbonic acid; the alumina is precipitated, carrying with it a little magnesia; it must be separated by filtration as rapidly as possible, the funnel being covered with a glass plate to prevent the access of carbonic acid, which would determine the precipitation of the earthy carbonates: the precipitate on the filter is well washed with hot water, it is then, while still moist, dissolved in hydrochloric acid, and boiled with excess of pure potassa; the small quantity of magnesia remains undissolved, and, having been separated from the alkaline ley by filtration, it is well washed, dissolved in a small quantity of hydrochloric acid, and added to the solution containing the alkaline earths and the rest of the magnesia. The potassa ley contains the whole of the alumina, which is precipitated by adding excess of hydrochloric acid, and, finally, supersaturating with ammonia: the alkaline earths and alkalies are separated from each other in the manner directed in the last section. The success of this process depends on the freedom of the ammonia from carbonic acid, and on the rapid filtering and careful washing of the precipitated alumina. If alumina has to be separated from baryta only, the latter earth may effectually be removed by sulphuric acid.

Separation of Alumina from Lime only.—The alumina is precipitated by ammonia free from carbonic acid, with the precautions just prescribed; and the lime in the filtrate is precipitated by oxalate of ammonia.

Separation of Alumina from Magnesia alone.—This may be effected by either of the following methods:—If the quantity of magnesia be small, the mixture of the two earths may be dissolved in hydrochloric acid, excess being avoided, and the solution boiled with excess of caustic potassa, by which the alumina is dissolved, magnesia remaining behind. If the quantity of magnesia be considerable, sal-ammoniac is added to the hydrochloric solution of the two earths, and the alumina is precipitated by ammonia; but, as it carries with it a small quantity of magnesia, it must be redissolved in hydrochloric acid and treated with caustic potassa as above; it is not safe to treat at once the hydrochloric solutions of the earths with excess of caustic potassa when the quantity of magnesia is considerable, it being in this case very difficult to separate them by an alkaline ley. The best method of separating *alumina* from *magnesia* is probably to precipitate the former by bicarbonate of potassa, and to estimate the magnesia in the filtrate as *pyrophosphate of magnesia:* the alumina precipitated in this manner carries with it a portion of potassa, which it is almost impossible to remove by washing; it must, therefore, be redissolved in hydrochloric acid and reprecipitated by carbonate of ammonia.

Glucinum.

Oxide of Glucinum.—Glucina, like *alumina*, is only weighed in its pure form as precipitated from its solution by *caustic* ammonia. Its composition is

Two equivalents of Gl ...	53.0 ...	68.83
Three ditto of O	24.0 ...	31.17
One do. of Gl_2O_3...	77	100

Separation of Glucina from Alumina.—Two methods have been proposed. The first depends on the solubility of *glucina* in carbonate of ammonia, and the insolubility of *alumina* in that reagent. The solution containing the two earths is mixed in a flask with a very considerable excess of a concentrated solution of carbonate of ammonia, the flask is closed, and occasionally shaken; when it is observed that the precipitate ceases to diminish in bulk, the *alumina* is separated by filtration, and the filtrate evaporated to dryness, and ignited to expel the ammoniacal salts; the residue, provided no other base or fixed acid be present, is pure *glucina:* or both the earths may be together precipitated by ammonia, and the precipitate digested with carbonate of ammonia till the glucina is entirely dissolved.

The second method is to dissolve both earths in a hot and concentrated solution of caustic potassa, to allow the ley to cool, and then to dilute it considerably with water, and again boil; the *glucina* is in this manner precipitated, while the *alumina* remains in solution.

The third method is that proposed by *Berthier*. The earths are dissolved in sulphuric acid, the solution concentrated, and sulphate of ammonia added, which causes the separation of the greater portion of the alumina in the form of an *alum:* to the decanted and diluted liquid *sulphate* of ammonia is added, and it is boiled until sulphurous acid ceases to be liberated; the alumina is entirely precipitated, and the glucina remains in solution, and may afterwards be precipitated by ammonia: or both earths may be together precipitated by ammonia, and, while moist, treated with sulphurous acid, which redissolves both, but on boiling the solution the alumina is completely precipitated.

The separation of glucina from *lime*, *magnesia*, and the *alkalies*, is effected in the same manner as the separation of alumina.

Yttrium.

Oxide of Yttrium, or *Yttria*, is weighed as the pure earth, in which state it is precipitated by caustic alkalies; it must, however, be observed, that when it is dissolved in nitric or in sulphuric acid, *potassa* must be the precipitant employed; in the latter case it is, according to *Wahler*, almost impossible to procure it free from sulphate of potassa. Its composition is

One equivalent of Y......32.2	... 80.09
One ditto of O 8.0	... 19.91
One do. of YO 40.2	...100

Separation of Yttria from Alumina and Glucina.—This is easily accomplished by digesting the mixture of the three earths in caustic potassa in which *yttria* is insoluble.

Separation of Yttria from Magnesia and the Alkalies.—From magnesia yttria is separated by caustic ammonia, sal-ammoniac having been previously added to the solution; from the alkalies it is separated precisely in the same manner as alumina.

Thorium.

Of *Oxide of Thorium*, or *Thorina*, little is known: from *alumina* it is distinguished by its insolubility in caustic potassa, and as it is completely precipitated from its solutions by ammonia, even in the presence of sal-ammoniac, it may thus be separated from *magnesia* and *lime*. *Thorina* forms, with sulphate of potassa, a double salt, quite insoluble in sulphate of potassa; this salt may, therefore, be employed to separate it from most other substances, but it must be concentrated and in excess; the double salt, after being washed, is dissolved in boiling water, and the *thorina* precipitated by caustic potassa. Its composition is

One equivalent of Th ...59.59	... 88.16
One ditto of O 8.00	... 11.84
One do. of ThO.........67.59	100

Zirconium.

Oxide of Zirconium, or *Zirconia*, is precipitated from its solutions by *am-*

monia and by *caustic potassa;* the latter is the best precipitant, the former often throwing down subsalts instead of the pure earth. Sulphate of potassa added in crystals and in sufficient quantity to saturate the liquid, which must be first completely neutralized by potassa, throws down the whole of the earth in the form of a double salt; it must be washed with water containing ammonia, and then boiled with caustic potassa, which leaves hydrate of *zirconia* in a pure state. Its composition is

Two equivalents of Zr	67.24	89.37
Three ditto of O	8.00	10.63
One do. of ZrO	75.24	100

The solubility of *zirconia* in bicarbonate of potassa affords a means of separating it from *alumina*, but an accurate method of separating it from *yttria* and *glucina* remains to be discovered.

Chromium.

Oxide of Chromium is usually estimated quantitatively in its pure state; the solution containing it is heated to the boiling temperature, and, ammonia being added in slight excess, it is boiled for about half an hour, or until the solution is perfectly colourless; the precipitate is collected on a filter, washed with boiling water, dried, and ignited. Its composition is

Two equivalents of Cr	56.30	70.11
Three ditto of O	24.00	29.89
One do. of Cr_2O_3	80.30	100

The ignition of this oxide must be performed with care, as at a particular temperature it suddenly becomes incandescent with a sort of explosion, whereby a portion may be projected from the crucible. The crucible should be closed with its cover.

When chromium exists in a solution in the form of chromic acid, it may be estimated as chromate of baryta, or chromate of lead, by adding respectively nitrate of baryta or nitrate of lead to the solution; it may also be precipitated by protonitrate of mercury, the resulting chromate being decomposed by ignition into mercury, oxygen, and oxide of chromium, from the weight of the latter the quantity of chromic acid may be calculated; it is better, however, to reduce the chromic acid to oxide of chromium in the solution previous to precipitating it, which is done by concentrating the solution and boiling it with excess of hydrochloric acid, mixed with alcohol, till the liquid assumes a pure green colour. The reduced oxide of chromium is precipitated by ammonia, after the excess of alcohol has been expelled by a gentle heat.

Estimation of Chromium in its compounds by Carbonic Acid.—This method has lately been proposed by *H. Vohl**, and is applicable to the determination of the metal whether occurring in the form of oxide or as chromic acid, but when the metal exists as oxide of chromium, it must in the first place be converted into chromic acid, the process depending on the conversion of oxalic into carbonic acid by the oxygen furnished by the reduction of chromic acid into oxide of chromium; thus

$$2\,(CrO_3) + 3\,(C_2O_3) = Cr_2O_3 + 6\,CO_2$$

for each equivalent of chromic acid, three equivalents of carbonic acid are formed, or 66 parts by weight for 50.31 parts of chromic acid. To determine the amount of carbonic acid, the author employs the alkalimetrical apparatus of Fresenius and Will (page 144). If merely the chromium has to be determined, any oxalate may be taken, but, if the alkalies are to be determined in the residuary liquid, oxalate of ammonia or baryta is employed. The analysis is very simple: when the chromium exists in the compound in the form of acid, the salt is taken then just as it is, and the process is precisely the same as in the analysis of manganese (to be described further on). If the salt is a chloro-chromate, before allowing the sulphuric acid to pass over, oxide of mercury must be mixed with the salt, to prevent the recrimination of chlorine or muriatic acid: after the operation the amount of chlorine can be determined from the perchloride of mercury by nitrate of silver, and the quantity of chlorochromic acid contained in the salt calculated from it.

The determination is less simple when the salt contains oxide of chromium. In the first place, the oxide must be converted into chromic acid, and this is best effected in the following manner:—The salt to be examined is dissolved in water, and caustic potassa added to it until the whole of the hydrated oxide of chromium has redissolved; upon which, keeping the solution cold, chlorine is passed into

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* Liebig's Annalen, Sept. 1847, and Chem. Gaz., Jan. 1st, 1848.

it until the green colour is changed into a yellowish red one: an excess of potassa is now added to this liquid, which is evaporated in the water-bath, and heated to faint redness in a platina crucible. The whole of the chlorate of potassa is decomposed, chromate of potassa and chloride of potassium remaining; these are dissolved, transferred with oxide of mercury into the apparatus, and the operation conducted as with chromates. The amount of oxide of chromium can be easily calculated from the quantity of carbonic acid which has escaped; 6 equivalents of carbonic acid are set free for each equivalent of oxide of chromium:—

$$Cr_2O_3 + O_3 = 2\,CrO_3$$

$$2\,(CrO_3) + 3\,(C_2O_3) = Cr_2O_3 + 6\,CO_2$$

In analyzing a salt in which both chromic acid and oxide of chromium occur, two determinations must be made. In the first place, the carbonic acid is determined, which the salt yields as it is, and the chromic acid calculated from the amount; upon which the liquid is treated as a salt of the oxide, the quantity of carbonic acid first obtained subtracted from that last obtained, and the amount of oxide of chromium calculated from the difference.

This method will, according to *M. Vohl*, render it possible for every one to submit to analysis those compounds of chromium which occur so frequently adulterated in commerce.

Separation of Oxide of Chromium from Alumina.—The usual method is to fuse the mixture of the two oxides with twice its weight of carbonate of soda, and twice and a half of its weight of nitre, the oxide of chromium becomes converted into alkaline chromate, which is extracted with water, and the alumina which remains undissolved is freed from alkali by dissolving in hydrochloric acid, and precipitating by ammonia. According to Dr. Schaffhaeutl, however, a portion of alumina in this process always dissolves along with the alkaline chromate; he therefore recommends to convey the precipitate obtained by adding ammonia to the solution containing the two oxides into a hot concentrated solution of caustic potassa, and to boil the whole down till near solidification; when quite cold, water is added, and the whole of the alumina dissolves without carrying with it a trace of oxide of chromium.

Separation of Oxide of Chromium from the rest of the Alkaline Earths.—This is also effected by fusing the mixture with carbonate of soda and nitre, the earths are thus obtained in the form of carbonates, and are separated from each other according to the instructions given (page 14).

Separation of Oxide of Chromium from the Alkalies.—The oxide of chromium is precipitated by ammonia, sal-ammoniac having previously been added to the solution. The alkalies are determined in the filtrate according to the directions given (page 14).

GROUP 4TH.—*Zinc, Nickel, Cobalt, Manganese, Iron.*

Zinc.

Oxide of Zinc is precipitated from its solutions, for the purpose of quantitative estimation, by carbonate of potassa or by hydrosulphuret of ammonia; in either case it is subsequently brought to the state of oxide, in order to be weighed.

Precipitation as Basic Carbonate.—Carbonate of potassa is added in excess to the solution, which is then boiled for some time; if, however, ammoniacal salts be present, a considerable excess of carbonate of potassa must be added, and the solution must be evaporated to dryness at the boiling temperature; in order to decompose the ammoniacal salts, the dry mass is well washed with hot water, and the residue, which is basic carbonate of zinc ($3\,HO, ZnO + 2\,ZnO, CO_2$), is strongly ignited, by which it becomes converted into oxide.

Precipitation as Sulphuret.—The solution, if it be acid, is first supersaturated with ammonia, the alkali being added in sufficient quantity to redissolve the oxide of zinc, which first precipitates; hydrosulphuret of ammonia is then added till it no longer occasions a precipitate, and the sulphuret of zinc, which is white, and very voluminous, is allowed completely to subside before filtration; the sulphuret is washed with water containing hydrosulphuret of ammonia, and then digested with concentrated hydrochloric acid until the solution ceases to smell of sulphuretted hydrogen; the resulting chloride of zinc is then precipitated as basic carbonate, and subsequently converted into oxide in the manner and with the precautions just described: it is to be observed, that it must not be neglected to examine whether the filtrate from the carbonate of zinc is free from *oxide of zinc*, which is done by adding to it a few drops of hydrosulphuret of ammonia; the formation of a white bulky precipitate indicates the presence of dissolved oxide of zinc, which must be collected and treated as above. The composition of *oxide of zinc* is

One equivalent	of Zn	...	32.52	... 80.25
One do.	of O	...	8.00	... 19.75
One do.	of ZnO	...	40.52	100

Separation of Oxide of Zinc from Oxide of Chromium.—The solution is mixed with tartaric acid, *excess* of potassa is then added, and the clear solution is precipitated with colourless sulphuret of potassium; the sulphuret of zinc is treated as above, the oxide of chromium is contained in the filtrate, and is obtained by evaporating it to dryness and fusing the ignited residue with nitre and carbonate of soda, the alkaline chromate thus obtained is treated as directed (p. 154); then both the oxides are combined with acids that form soluble salts with baryta, their separation can, according to *Fresenius*, be accomplished by digesting the acid solution for several hours with excess of artificially produced *carbonate of baryta:* the whole of the oxide of chromium is removed, and is mixed with the excess of carbonate of baryta, from which it is separated by dissolving in hydrochloric acid, and adding excess of sulphuric acid; the *oxide of zinc* remains in solution, and is precipitated by carbonate of potassa.

Separation of Oxide of Zinc from Alumina.—The solution containing the two oxides is supersaturated with ammonia, alumina is precipitated, and oxide of zinc remains in solution. If, to a solution of the mixed oxides, excess of *cyanide of potassium* be added, heat being avoided, alumina is precipitated, and oxide of zinc retained in solution. If to a solution of the two oxides in sulphuric acid, excess of *acetate of baryta* be added, and then sulphuretted hydrogen passed into the solution, sulphuret of zinc is precipitated, while alumina remains dissolved; the sulphuret of zinc is separated from the sulphate of baryta by digesting the mixture in hydrochloric acid, the oxide of zinc is then precipitated from the solution as basic carbonate, and the alumina is precipitated by ammonia.

Separation of Oxide of Zinc from Magnesia.—Sal-ammoniac is added to the solution, and then sufficient ammonia to retain both oxides in solution: the zinc is precipitated from the ammoniacal solution by hydrosulphuret of ammonia, and the magnesia in the filtrate determined in the usual manner. Another plan which has been proposed is to precipitate both oxides by carbonate of potassa; and then, having added a sufficient quantity of cyanide of potassium to dissolve the zinc, the whole is evaporated to dryness at a boiling temperature, a little more carbonate of potassa having first been added: on treating the dry mass with water, the magnesia remains undissolved, and the *zinco-cyanide of potassium* is held in solution.

Separation of Oxide of Zinc from the Alkalies and Alkaline Earths.—The bases are all brought into the state of acetates by adding *acetate of baryta* to the sulphuric acid solution as above described: the zinc is precipitated by hydrosulphuret of ammonia. To separate *oxide of zinc* from *lime*, *baryta*, and *strontia*, it has been recommended to treat the mixed solution with carbonate of potassa, until it acquires an alkaline reaction, then to add excess of cyanide of potassium, and apply heat: the earthy carbonates remain undissolved, while that of zinc is taken up. The solution is boiled with hydrochloric and nitric acids, until all hydrocyanic acid is expelled, and the oxide of zinc is then precipitated with carbonate of soda, those precautions being taken which are necessary when a salt of ammonia is present.

Nickel.

Oxide of Nickel is precipitated from its solutions either as *hydrated oxide* by caustic potassa, or as *sulphuret* by hydrosulphuret of ammonia: in either case it is converted into anhydrous *protoxide* to be weighed.

Precipitation as Hydrated Protoxide.—Pure solution of caustic potassa is added, and the solution heated to boiling; the voluminous apple-green precipitate, which is formed, requires protracted washing with hot water; after which it is dried and ignited: ammoniacal salts do not interfere with the precipitation of oxide of nickel by caustic potassa, but with carbonate of potassa it is not so complete.

Precipitation by Hydrosulphuret of Ammonia.—The complete precipitation of nickel in the state of sulphuret by hydrosulphuret of ammonia is not easy, in consequence of the partial solubility of sulphuret of nickel in that reagent. To insure success the hydrosulphuret of ammonia must be perfectly saturated and colourless, and not added in great excess; the vessel must be covered, and placed in a warm situation; the fluid above the precipitate should be free from colour; the sulphuret of nickel is washed on the filter with water, to which a few drops of hydrosulphuret of ammonia have been added; it is then dried, transferred to a beaker, and digested at a gentle heat, until completely dissolved with concentrated aqua regia; the filter is burnt, and its ashes added to the solution: this is better than digesting the filter, and precipitate together in aqua regia; since, as *Fresenius* observes, the presence of organic matter prevents the complete precipitation of oxide of nickel by caustic alkali: the solution filtered from the separated sulphur is precipitated by potassa, washed, dried, and ignited.

The composition of anhydrous protoxide of nickel is

One equivalent of Ni ...	29.57 ...	78.76
One ditto of O ...	8.00 ...	21.24
One ditto of NiO ...	37.57	100

Separation of Oxide of Nickel from Oxide of Zinc.—Several methods have been proposed:—1st. *Berzelius's Method.* The greater part of the oxide of zinc is first extracted by caustic potassa; the residue, after being well washed and heated, is mixed with pure *pulverized sugar*, and carefully carbonized in a porcelain crucible. The crucible is then surrounded with magnesia in a larger Hessian crucible, and heated for an hour in a blast furnace as strongly as possible. The oxides are reduced, and the zinc is driven off in vapour; the nickel is dissolved in nitric acid, evaporated to dryness in a platinum crucible, and ignited. The loss of weight gives the quantity of oxide of zinc. The principal point to be attended to is to extract all the potassa from the mixed oxides: the sugar must be perfectly pure, with which view it should be crystallized from an alcoholic solution.

2nd. *Ullgren's Method.*—The oxides are precipitated by carbonate of soda, the whole evaporated, and the residue gently heated, so that they remain perfectly insoluble when the mass is treated with water. The oxides are washed and dried, and then being placed in a tube, with a bulb, are reduced by hydrogen at a low red heat; the tube is allowed to cool, while a continuous current of hydrogen is passed through it; it is then closed at one end by fusion, filled with a concentrated solution of carbonate of ammonia, corked up, and placed in a warm situation for twenty-four hours; the *oxide of zinc*, which is not reduced, is dissolved in the carbonate of ammonia; the oxide of nickel *is* reduced, and the metal, after being well washed with carbonate of ammonia, is dried and weighed; the oxide of zinc is obtained from the ammoniacal solution by evaporation. The oxides must be finely pulverized before they are exposed to the action of hydrogen gas.

3rd. *Rose's Method.*—The mixed oxides, after having been ignited, are placed in the bulb of a reduction tube, which communicates on the one side with an apparatus, from which dry hydrochloric acid gas is liberated, and, on the other, with a flask containing a very dilute solution of ammonia. As soon as the air is expelled the bulb is gradually heated to redness, the oxides are converted into chlorides, the chloride of nickel remains in the bulb, and the volatile chloride of zinc passes into the solution of ammonia, in which it dissolves. The oxides are then determined in the usual manner. This method, though tedious and somewhat complicated, yields very accurate results.

4th. *Smith's Method.*—The oxides are converted into acetates; and, excess of acetic acid being added, sulphuretted hydrogen is passed through the solution, by which the whole of the zinc is precipitated as sulphuret, while the oxide of nickel remains in solution: this method, which is well adapted for the analysis of *German silver*, the constituents of which are *copper*, *zinc*, and *nickel*, has been found by *M. Louyet* to yield very accurate results.

Separation of Oxide of Nickel from Oxide of Chromium.—The mixed oxides are fused with nitre and carbonate of soda; the oxide of chromium is thus converted into *chromic* acid, and is dissolved on boiling with water as alkaline chromate.

Separation of Oxide of Nickel from Alumina.—Excess of cyanide of potassium is added, heat being avoided; alumina is precipitated, and oxide of nickel retained in solution: according to Berthier, on adding *sulphite of ammonia* to a solution of the two oxides, the alumina only is precipitated.

Separation of Oxide of Nickel from Magnesia.—This is effected in the same manner as the separation of oxide of zinc from the same earth.

Separation of Oxide of Nickel from Baryta, Strontia, and Lime.—Cyanide of potassium is added in excess, and then carbonate of potassa, the whole is boiled, and the insoluble carbonates separated by filtration from the *nickel cyanide.* The solution is boiled with hydrochloric acid until all the hydrocyanic acid is expelled; potassa in excess is then added, and the solution boiled till all the ammonia is liberated, the oxide of nickel is then precipitated by potassa.

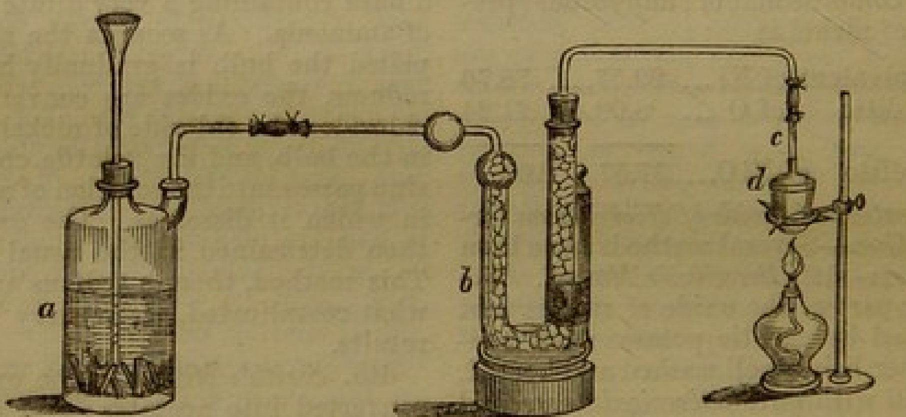
Cobalt.

This metal is precipitated from its solutions either by caustic potassa, or by hydrosulphuret of ammonia; it is weighed either as *oxide* or in the *metallic state;* when great or even moderate accuracy is required, it must be estimated in the latter form, as the ignited hydrated protoxide is of indefinite composition, varying according to the degree of heat employed.

Precipitation as Hydrated Protoxide.—The solution is boiled with excess of caustic potassa; the precipitate, which at first is blueish, becomes, after long boiling, of a dirty rose red colour; if ammoniacal salts are present, they must be decomposed, and the ammonia discharged by long-continued boiling, with great excess of caustic alkali; the precipitated hydrate requires long-continued washing with hot water, on being dried and ignited it turns black: in this state it is weighed; if the operator has determined on reducing it to reguline cobalt, he proceeds in the following manner.

Reduction of Oxide of Cobalt to Reguline Cobalt.—The small Berlin crucible *d, fig.* 29, having been carefully weighed, a certain known quantity of the previously weighed oxide is introduced, and the weight of the crucible again accurately noted; a stream of hydrogen gas, dried by passing through the U-shaped chloride of calcium, tube *b*, is then caused to flow through the apparatus, from the flask *a*, and a flame applied to the crucible containing the oxide; the heat must at first be gentle, but it must gradually be raised to full redness, this high temperature being necessary to prevent the reduced metal from acquiring a pyrophoric property, which would cause it to inflame on coming in contact with atmospheric air; the hydrogen reduces the metallic oxide, giving rise to a proportional amount of water, which escapes in the form of steam between the top of the crucible and its cover, and at the aperture through which the tobacco-pipe, *c*, enters. When it is seen that water no longer continues to form, the flame is removed from the crucible, and it is allowed to cool, while a stream of hydrogen still continues to pass over it; the crucible is then again weighed, and from the amount of reduced metal obtained the

Fig. 29.



quantity contained in the whole of the protoxide precipitated is calculated. If a sufficiently high temperature has not been employed, the reduced cobalt oxidizes at common temperatures, but if a full red heat has been employed it absorbs oxygen very slowly.

Precipitation as Sulphuret.—Sal-ammoniac is added to the solution, then slight excess of ammonia, and finally hydrosulphuret of ammonia as long as precipitation takes place; the resulting sulphuret of cobalt is washed with water, containing a little sulphuret of ammonium, then digested with aqua regia, and precipitated by potassa, precisely as sulphuret of nickel. The hydrated oxide, after being washed, dried, and ignited, is reduced by hydrogen in the manner just described. *Rose* recommends that, in the presence of ammoniacal salts, cobalt should always be precipitated by hydrosulphuret of ammonia.

Separation of Cobalt from Nickel.—Several methods have been proposed by different chemists, but until recently Phillips's process was the one generally preferred, which was as follows:—

1. *Method of Phillips.*—Both oxides are dissolved in an acid, and the solution supersaturated with ammonia, having previously added a sufficient quantity of sal-ammoniac, to prevent any precipitation from taking place; the solution, which has a sky-blue colour, is largely diluted with water, which should have been previously well boiled, to free it from atmospheric air: caustic potassa is added to the hot solution, and the vessel is closed with a cork; *oxide of nickel* is precipitated, and *oxide of cobalt* remains in solution; when the former has completely settled, the supernatant liquid, which should have a rose-red colour, is poured through a filter, and the oxide of nickel washed with hot water, ignited, and weighed; the oxide of cobalt in the filtrate is precipitated by hydrosulphuret of ammonia: the reason why it is necessary to dilute the solution of the two oxides with water, free from atmospheric air, is, that oxide of cobalt in an ammoniacal solution is converted into peroxide of cobalt, which, precipitating as a black powder, would contaminate the oxide of nickel. The more dilute the solution is, the less easily does the oxide of cobalt become oxidized. When a large quantity of ammoniacal salt is present, the quantity of caustic potassa required to precipitate the oxide of nickel is very considerable. According to Fresenius the separation by this method is not complete, the cobalt invariably containing traces of nickel, and the precipitated nickel often traces of cobalt.

2. *Liebig's Method.*—This is founded on the following considerations:—When any salt of cobalt is warmed with cyanide of potassium, and an excess of hydrocyanic acid, it is converted into the *percyanide of cobalt* and *potassium*, or *cobalticyanide of potassium*, $(Co_2Cy_6, K_3,)$ the aqueous solution of which does *not* undergo any decomposition by boiling with either of the mineral acids. On the other hand, the precipitate produced by cyanide of potassium in solutions of salts of nickel is redissolved by cyanide of potassium, but the solution *is* decomposed by dilute sulphuric acid, cyanide of nickel being precipitated. When, therefore, a mixture of a cobalt and a nickel salt containing free acid is treated with excess of cyanide of potassium, and slightly warmed, we obtain in solution the double cyanide of nickel and potassium, and cobalticyanide of potassium, $(Ni\,Cy + K\,Cy) + (CO_2\,Cy_6\,K_3,)$ and, on adding dilute sulphuric acid in the cold, three cases present themselves.

1st. If the cobalt and nickel exist in the solution in the proportion by weight of *two* cobalt to *three* nickel, we have in the solution, $3\,(Ni\,Cy,\ K\,Cy) + (Co_2\,Cy_6\,K_3,)$ and the three equivalents of nickel replacing the three equivalents of potassium, in the cobalticyanide of potassium, produce cobalticyanide of nickel, $(Co_2\,Cy_6\,Ni_3,)$ which is precipitated of a blueish white colour, leaving in the solution no trace of either cobalt or nickel.

2nd. If the solution contain *less* nickel than corresponds to the above proportions, a certain quantity of cobalticyanide of potassium remains in solution, while cobalticyanide of nickel is still precipitated.

3rd. If the solution contain *more* nickel than corresponds to the above proportions, cobalticyanide of nickel is still precipitated, together with the excess of cyanide of nickel, which, by long boiling with hydrochloric acid, is completely converted into chloride of nickel, which remains in solution.

Now cobalticyanide of nickel, though insoluble in hydrochloric acid, is decomposed by boiling with caustic potassa into protoxide of nickel, and cobalticyanide of potassium, thus, $Co_2\,Cy_6$

$Ni_3 + 3\,KO = Co_2\,Cy_6\,K_3 + 3\,NiO$, and chloride of nickel is also decomposed by caustic potassa into protoxide of nickel and chloride of potassium. Hence, the following method of analyzing mixtures of cobalt and nickel, which is applicable to all proportions.

Hydrochloric acid is added to the solution of the metals, and then cyanide of potassium in such excess that the precipitate at first formed is redissolved, the whole is boiled, adding from time to time hydrochloric acid, until hydrocyanic acid ceases to be evolved. Caustic potassa is then added in considerable excess, and the boiling continued until the hydrated protoxide of nickel is completely precipitated; it is then filtered, the filtrate contains the whole of the cobalt in the form of cobalticyanide of potassium; it is evaporated to dryness with excess of nitric acid, the residue fused, and treated with hot water: peroxide of cobalt remains, which is dissolved in hydrochloric acid, and the solution treated as already directed.

In analyzing ores of nickel, which contain small quantities only of cobalt, considerable excess of hydrochloric acid must be taken to precipitate the cyanides dissolved in cyanide of potassium, and the mixture must be continued in ebullition for a full hour.

Rose's Method. — This is founded on the greater tendency in the protoxide of cobalt than in the protoxide of nickel to pass to a higher degree of oxidation. Both metals are dissolved in hydrochloric acid; the solution must contain a sufficient excess of free acid: it is then diluted with much water; if 20 or 30 grains of the oxides are operated on, about 2 lbs. of water are added to the solution. As cobalt possesses a much higher colouring power than nickel, not only in fluxes, but also in solutions, the diluted solution is of a rose colour, even when the quantity of nickel present greatly exceeds that of the cobalt. A current of chlorine is then passed through the solution for several hours[*]; the fluid must be thoroughly saturated with it, and the upper part of the flask above the liquid must remain filled with the gas after the current has ceased. Carbonate of baryta in excess is then added, and the whole allowed to stand for 12 or 18 hours, and frequently agitated; the precipitated peroxide of cobalt and the excess of carbonate of baryta are well washed with cold water, and dissolved in hot hydrochloric acid; after the separation of the baryta by sulphuric acid, the cobalt is precipitated by hydrate of potassa, and, after being washed and dried, is reduced in a platinum or porcelain crucible by hydrogen gas, in the manner shown in *fig.* 53. The fluid filtered from the superoxide of cobalt is of a pure green colour; it is free from any trace of cobalt. After the removal of the baryta by means of sulphuric acid, the oxide of nickel is precipitated by caustic potassa. To insure accurate results, it is indispensably necessary to wait a considerable time, at least 12, or even better, 18 hours after the addition of the carbonate of baryta, as the superoxide of cobalt is precipitated very slowly.

Another Method.—The two oxides are covered with prussic acid, and then potassa added till a portion remains undissolved. The solution is kept boiling for a quarter of an hour, moist hydrated oxide of mercury is then added till a portion remains undissolved; a green precipitate occurs containing all the nickel, with the excess of oxide of mercury. By ignition, pure oxide of nickel remains. Acetic acid is added to the filtrate to aid reaction; it is then precipitated with blue vitriol. The blue precipitate contains all the cobalt; this is dried, ignited, redissolved in hydrochloric acid; the copper, precipitated by sulphuretted hydrogen, and then from the filtrate the cobalt by potassa. The method depends upon the fact, that *nickelo*-cyanide of potassium is decomposed by oxide of mercury, while *cobalto*-cyanide of potassium experiences no change.

Separation of Oxide of Cobalt from Oxide of Zinc.—The above method may, according to Rose, be employed for the separation of these two oxides; and also for that of other oxides from oxide of cobalt, which are strongly basic, and which are not converted into superoxides: oxide of zinc may, likewise, be separated from oxide of cobalt by *Liebig's* process with cyanide of potassium, cobalticyanide of zinc is gradually dissolved in boiling hydrochloric acid, and a clear solution is obtained: on the addition of caustic potassa and boiling, both the cobalt and the zinc are retained in solution, the former as cobalticyanide of potassium, and the latter

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[*] Mr. Henry employs a solution of *bromine* till the solution smells strongly of it; he finds this to answer equally well with the chlorine, and the process is rendered less tedious and unpleasant.

as oxide; and, from the solution, zinc is precipitated by sulphuretted hydrogen: the methods of *Berzelius* and *Ullgren*, for the separation of oxide of nickel from oxide of zinc, may likewise be employed for the separation of oxide of cobalt.

Separation of Oxide of Cobalt from Oxide of Chromium.—This is effected in the same manner as the separation of oxide of nickel from oxide of chromium.

Separation of Oxide of Cobalt from Alumina.—Cyanide of potassium is added, heat being avoided; the cobalt is dissolved as cobalticyanide of potassium, and the alumina precipitated; according to *Berthier*, the separation may likewise be effected by sulphite of ammonia.

Separation of Oxide of Cobalt from the Alkaline Earths.—This is effected in the same manner as the separation of the oxide of nickel.

Manganese.

This metal is quantitatively estimated as *protoxide*, as *red oxide*, or as *protosulphate*.

Quantitative estimation as Protoxide.—*Ebelman* prefers reducing the higher oxides of manganese to the state of protoxide for the purpose of weighing. To perform the experiment, he introduces the oxide into a small platinum crucible, the lid of which has a small platinum tube in the centre, through which a current of dry hydrogen gas is conveyed by means of a green glass tube, of a diameter nearly equal to that in the crucible cover (see *fig.* 53), heat is applied by means of a spirit-lamp; the reduction is complete after a few minutes, and a rapid current of gas is passed into the crucible while cooling; the oxide obtained is quite pure; it dissolves in hydrochloric acid without rendering it black, and without disengaging chlorine. Its composition is

One equivalent of Mn.	27.67	77.57
One ditto of O	8.00	22.43
One do. of MnO	35.67	100

Quantitative estimation as Red Oxide.—The solution is heated to boiling with excess of carbonate of soda. Should ammoniacal salts be present, the solution must be treated in the same manner as in the precipitation of carbonate of zinc, under similar circumstances: the precipitate is thoroughly washed, dried, and ignited, by which it is decomposed into the red oxide (manganoso—manganic oxide); sometimes the solution is precipitated with caustic potassa, and the hydrated protoxide thus formed is converted into red oxide by strong ignition; it must be remembered, however, that hydrated protoxide of manganese is soluble in sal-ammoniac. It is sometimes convenient also to precipitate manganese as sulphuret, by adding coloured hydrosulphuret of ammonia to the solution to which sal-ammoniac and ammonia have been added, the precipitate, having been washed with water containing hydrosulphuret of ammonia, is digested with hydrochloric acid, and the solution precipitated by carbonate of ammonia.

The composition of red oxide of manganese is

Three equivalents of Mn	83.01	72.17
Four ditto of O	32.00	27.83
One ditto of $MnO+Mn_2O_3$	115.01	100

Quantitative estimation as Sulphate.—Oxide of manganese is converted into protosulphate in the same manner and with the same precautions as magnesia: the salt must be ignited very feebly, or it will lose sulphuric acid. Its composition is

One equivalent of MnO	35.67	47.13
One ditto of SO_3	40.00	52.87
One do. of MnO,SO_3	75.67	100

Separation of Oxide of Manganese from Oxides of Cobalt and Nickel.—*Rose's* original method, which, though complicated, gives very accurate results is the following:—The metals are first precipitated together as oxides by caustic potassa, they are then ignited, weighed, and converted into chlorides by introducing them into a bulbed tube, and transmitting over them a current of dry hydrochloric acid gas, a moderate heat being at the same time applied: it requires a long time thus to convert the oxides completely into chlorides; when the conversion is complete, dry *hydrogen gas* is passed through the apparatus, the bulb containing the chlorides being strongly heated, the hydrogen displaces the chlorine from the chlorides of cobalt and nickel, forming with it hydrochloric acid gas; and the operation must be continued as long as white clouds are formed, on holding a glass rod that has been dipped in ammonia at the end of the apparatus where the excess of gas escapes: the hydrogen is allowed to pass through the tube till it is quite cold, the chloride of manganese, which has not been decomposed by the process, is dissolved out by water; the reduced cobalt and nickel are washed with very dilute hydrochloric acid, and, finally, with water; the two metals are then separated from each other by one of the methods above given, and the manganese is precipitated from the solution of the chloride, to which has been added the washings from the cobalt and nickel by carbonate of soda.

Rose states that *nickel* may be conveniently separated from manganese in the same manner as cobalt, namely, by chlorine and carbonate of baryta. A method of separating oxide of cobalt from oxide of manganese was proposed by *Barreswil:* it consists in adding carbonate of baryta to the solution, and then passing a current of sulphuretted hydrogen through it, by which, according to *Barreswil*, cobalt only is precipitated; this method has not, however, been found successful by other chemists. A plan for the separation of oxides of cobalt and nickel from oxide of manganese was proposed by *Wakenroder*, and has obtained the approval of *Rose:* it is based on the fact that, although nickel and cobalt are not precipitated from their acid solutions by sulphuretted hydrogen, their sulphurets precipitated by hydrosulphuret of ammonia are *not* dissolved by very dilute hydrochloric acid. The acid solution of the three oxides is made ammoniacal, and the metals are precipitated by hydrosulphuret of ammonia: the solution is then rendered slightly acid by dilute hydrochloric acid; the sulphuret of manganese is dissolved with facility, small portions also of the sulphuret of cobalt and nickel may also be dissolved, but they may be removed by reprecipitating the solution with ammonia and hydrosulphuret of ammonia, and treating it anew with dilute hydrochloric acid.

Manganese from Cobalt (*Liebig's Method*).—The metals are precipitated by cyanide of potassium, an excess of which redissolves the cyanide of cobalt, and a part also of the protocyanide of manganese, while another portion remains undissolved, this is filtered off and washed: the filtrate is heated to ebullition, a few drops of hydrochloric acid, insufficient, however, to acidify the solution, are added from time to time, and the manganese and cobalt are separated from one another in the same manner as nickel is separated from cobalt.

Ebelman has recently proposed to separate manganese from cobalt or nickel, by exposing the mixture of the oxides to a current of dry sulphuretted hydrogen, at a temperature a little below redness. The oxides are converted into sulphurets, the sulphuret of manganese is dissolved by very weak hydrochloric acid, in the cold. The smallest quantity of cobalt may, he says, be detected in this manner. He applies the same process to the separation of arsenic from tin.

Separation of Oxide of Manganese from Oxide of Zinc.—The oxides are dissolved in excess of acetic acid, and the zinc is precipitated by sulphuretted hydrogen; the solution must be acid, and contain no other acid but acetic.

Separation of Oxide of Manganese from Oxide of Chromium.—This is effected in the same manner as the separation of oxide of zinc from oxide of chromium.

Separation of Oxide of Manganese from Alumina.—Caustic potassa is added in excess to the solution, which is then boiled; the alumina, which is at first precipitated with the oxide of manganese, is redissolved, and is determined in the filtrate in the usual manner; the oxide of manganese is dissolved in hydrochloric acid, and precipitated as carbonate. According to *Berthier*, alumina may be separated from oxide of manganese by boiling with *sulphite of ammonia.*

Separation of Oxide of Manganese from Magnesia.—Muriate of ammonia is added in sufficient quantity to the solution, and the manganese is precipitated as sulphuret by hydrosulphuret of ammonia; the filtrate contains the whole of the magnesia; it is acidulated with hydrochloric acid, and boiled, to decompose the excess of hydrosulphuret of ammonia, filtered to separate the sulphur, and the magnesia determined in the filtrate as sulphate (provided no other base be present), or as double phosphate of ammonia and magnesia.

Separation of Oxide of Manganese from Lime.—When the quantity of oxide of manganese present is small, the solution is mixed with muriate of ammonia, and, oxalate of ammonia having been added, the solution is quickly filtered; the lime is thus separated as oxalate, and is determined in the usual manner: the oxide of manganese in the filtrate is precipitated by hydrosulphuret of ammonia, but, if the quantity of oxide of manganese be considerable, this method will not be successful, as a portion of that metal would be precipitated both as oxide and as oxalate, together with the lime; in this case, the solution having been mixed with muriate of ammonia and caustic ammonia, the manganese is precipitated by hydrosulphuret of ammonia, and filtered quickly, both funnel and receiving vessel being covered, to prevent the formation of carbonate of lime; the filtrate is digested with hydrochloric acid, to destroy the excess of hydrosulphuret of ammonia, then supersaturated with ammonia, and the lime precipitated as oxalate.

Separation of Oxide of Manganese from Alumina, Magnesia, and Lime.—When all three earths are contained in a solution, together with oxide of manganese, the method of separation depends on the quantity of the latter present; if it be small, the alumina is first precipitated by caustic ammonia, sal-ammoniac in sufficient quantity having been previously added to the solution; the alumina carries with it small quantities both of magnesia and of lime, from which it is separated by digestion with caustic potassa; in filtering the alumina care must be taken to guard both funnel and receiving vessel as much as possible from the air, to prevent the precipitation of carbonate of lime; the filtrate from the alumina is mixed with oxalate of ammonia, by which the lime is separated. The oxide of manganese and the magnesia are contained in the filtrate from the oxalate of lime, and are separated from each other as above directed; the small quantities of magnesia and oxide of manganese which had been precipitated with the alumina, and which remain undissolved in the alkaline ley, are dissolved in hydrochloric acid, and added to the filtrate from the oxalate of lime. When the quantity of oxide of manganese is considerable, it is separated from the filtrate from the alumina, by hydrosulphuret of ammonia, the solution filtered from the sulphuret of manganese is boiled with hydrochloric acid, to decompose the excess of hydrosulphuret of ammonia; ammonia added, and the lime precipitated as oxalate. The solution filtered from the oxalate of lime contains the magnesia which is precipitated, and estimated in the usual manner. The small quantities of magnesia and oxide of manganese which have been precipitated, together with the alumina, having been removed by caustic potassa, are dissolved in hydrochloric acid, and estimated separately.

Examination of Commercial Oxide of Manganese, to ascertain its practical value.—Several methods have been proposed.

First Method. — By estimating the amount of chlorine evolved during the solution of the ore in hydrochloric acid, the value of the oxide being in exact proportion to the quantity of chlorine produced. Three methods of estimating the chlorine have been employed.

1 (*a*). By noting the quantity of protosulphate of iron which it peroxidizes. If the oxide of manganese be perfectly pure, 43.67 parts (one equivalent) will produce 35.5 parts (one equivalent) of chlorine, which will peroxidize 278 parts (two equivalents) of crystallized protosulphate of iron, thus:—

$$\mathrm{Mn\,O_2 + 2\,H\,Cl = Mn\,Cl + 2\,H\,O + Cl},$$

$$\text{and } \mathrm{2\,(Fe\,O, S\,O_3) + H\,O + Cl = Fe_2O_3, 2\,S\,O_3 + H\,Cl}.$$

Hence 25 grains of pure oxide of manganese yield chlorine sufficient to peroxidize 159 grains of protosulphate of iron; 25 grains of the powdered specimen are weighed out, and a quantity not less than 359 grains of crystallized protosulphate of iron. The oxide of manganese is thrown into a flask containing about one ounce of strong hydrochloric acid slightly diluted, and a gentle heat applied. The protosulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved, and the addition of that salt continued till the liquor, after being heated, gives a *blue* precipitate with *red prussiate of potassa*, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess; by weighing what remains of this salt, the quantity that has been added is ascertained, say *m* grains. If the whole of the specimen consisted of peroxide, it would require 159 grains of protosulphate of iron, and that quantity would therefore indicate 100 per cent. of peroxide; but, if a *portion* of the manganese only is peroxide, a proportionally smaller quantity of the protosulphates will be consumed, and that quantity will give the real proportion of peroxide, by the proportion, as 159 : 25 :: *m* to the quantity required.

1 (*b*). The chlorine evolved is passed through water in which *lime* is diffused; *chloride of lime* is formed; a certain quantity of protosulphate of iron is dissolved in water, and the solution of chloride of lime is added thereto, until the iron liquor ceases to strike a blue colour with a drop of solution of red prussiate of potash: then, comparing the quantity of the solution of chloride of lime required with the quantity that was produced, the quantity of chlorine generated, and hence the total quantity of available oxygen, is known. The theory of the process may be expressed as follows:—

$$MnO_2 + 2\,HCl = MnCl + 2\,HO + Cl$$

the liberated chlorine combines with the lime, forming CaO, Cl, and

$$CaO, Cl + 2\,(FeO, SO_3) = \\ CaCl + Fe_2O_3, 2\,SO_3$$

1 (*c*). *Baumann* conveys the chlorine into a solution of nitrate of silver, and calculates the amount of real peroxide of manganese in the specimen from the quantity of chloride of silver formed.

Second Method.—By converting *oxalic acid* into carbonic acid, by means of the second atom of oxygen which the peroxide of manganese contains. $Mn\,O_2 + C_2\,O_3$, producing $Mn\,O$, and $2\,CO_2$, 100 grains of the specimen are introduced into a weighed flask, and 150 grains of oxalic acid dissolved in 500 grains of water are poured upon it; to this 350 grains of oil of vitriol are to be added, and the orifice of the flask closed by a cork, through which passes a tube containing fragments of recently fused chloride of calcium, the weight of this cork and tube are to be included in the tare of the flask. On the addition of the oil of vitriol, a brisk effervescence takes place, owing to the escape of carbonic acid, which passing over the fragments of chloride of calcium in the tube is dried, so that the gas alone passes off. When the action slackens, a gentle heat may be applied, until all the oxide of manganese has dissolved; the small quantity of a light brownish sediment, which generally falls, is easily distinguished from the particles of black oxide. As soon as the action is quite over, the flask is allowed to cool, and as it still contains a quantity of carbonic acid gas, this is removed by taking out the cork, and blowing air gently into the flask by a glass tube; the cork is then to be replaced, and the flask with its contents weighed; the difference of weight represents the amount of carbonic acid evolved; *one-fourth* of the oxygen of which had been derived from the peroxide of manganese by its conversion into protoxide, which remains combined with sulphuric acid in the liquor, and the quantity of peroxide in the 100 grains of the one are thus directly found. *Example.*—Suppose the flask and the materials together to weigh 1876 grains, and after the action has terminated 1816.5 grains: the loss, 59.5 grains, is carbonic acid, consisting of 16.3 grains of carbon, and 43.2 grains of oxygen; the oxygen derived from the mineral is therefore $\frac{43.2}{4} = 10.8$, which represents 59 grains of pure peroxide of manganese in 100 grains of the substance experimented upon.

3rd. *Method of Fresenius and Will**.—This is founded on the same principle. A certain weighed quantity of finely powdered manganese is projected into B (see *fig.* 27), and about $2\frac{1}{2}$ parts of *neutral oxalate of potash*, prepared by saturating the common binoxalate with carbonate of potash and crystallizing, or two parts of neutral oxalate of soda, and as much water added as will fill about one-third of the flask; the apparatus is then prepared as directed in p. 144, B is then closed, the apparatus weighed, and, by sucking the tube *e*, some sulphuric acid is made to pass from *a* into *b*. The evolution of carbonic acid commences immediately, and in a very uniform manner: as soon as it stops, some more sulphuric acid is sucked over from *a* into *b*, and the operation thus continued till all the manganese is completely decomposed: this operation will require from six to ten minutes: its completion is ascertained not only by no further evolution of carbonic acid taking place upon a further influx of sulphuric acid into *b*, but also by no black powder remaining at the bottom of the flask: some more sulphuric acid is then sucked over into *b*, in order to heat the fluid contained therein, so as completely to expel all

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* New Method of Alkalimetry, by Drs. Fresenius and Will, edited by J. Lloyd Bullock, page 116, *et seq.*

the carbonic acid evolved during the course of the operation; the wax stopper is then removed from *a*, and the tube *d* sucked until the air no longer tastes of carbonic acid; the apparatus is then allowed to cool and weighed. The entire examination may thus, according to the authors, be performed in a quarter of an hour; from the loss of weight of the apparatus, (the amount of carbonic acid expelled,) the amount of available oxygen is found, or what, in fact, is the same, the amount of peroxide contained in the manganese under examination, according to the following arrangement. *Two* equivalents of carbonic acid stand to *one* equivalent of peroxide of manganese in the same proportion as the amount of carbonic acid found stands to x, x being the quantity of real peroxide contained in the specimen. Let us suppose that our experiment had been made with four grammes (61.76grs.) of manganese, and that we had obtained 3.5 grammes (54.03 grs.) of carbonic acid. The arrangement would be

$$4 : 43.67 :: 3.5 : x$$
$$x = 3.47.$$

Thus, four grammes of the manganese containing 3.47 grammes of peroxide, 100 parts of the same substance must contain 86.7 parts. To render, however, this calculation unnecessary, we need only ascertain what amount of manganese must be taken to make the number of centigrammes of carbonic acid obtained immediately indicate the per centage amount of peroxide. The calculation must, therefore, be

$$4 : 43.67 :: 100 : x$$
$$x = 0.993.$$

Thus, if we take 0.993 grammes (15.33 grains) of the specimen, the number of centigrammes of carbonic acid expelled will indicate the per centage amount of peroxide. But as the quantity of carbonic acid obtained would be too minute to admit of a direct determination of its weight, it is advisable to take a multiple of 0.993 grammes, and to divide the number of centigrammes of carbonic acid obtained by the same number, which has served as a multiplier. The multiple by 3, *i. e.* 2.98 grammes, is deemed by the authors the quantity best adapted for the examination. Should the manganese contain carbonated alkaline earths, which is sometimes the case, it must undergo a preliminary process previous to the examination. To ascertain the presence or absence of carbonate of lime or baryta in the manganese under examination, it is sufficient to moisten a sample powder with dilute nitric acid; their presence is certain if any effervescence take place. The specimen, in that case, is treated as follows:—2.98 grammes of the specimen is projected into *b*, covered with very dilute nitric acid, one part acid to twenty parts of water, and allowed to stand at rest for a few minutes; the supernatant fluid is then poured upon a small paper filter, the manganese remaining in the flask is repeatedly washed with water, as well as the solid particles on the filter, (the supernatant water being always poured on the filter,) and the latter then thrown into *b*, taking care not to lose a particle of manganese; the further operation is conducted as usual. The neutral oxalate of potash is preferable to free oxalic acid, or to binoxalate of potash, since, when employing the former substance, the evolution of carbonic acid commences only upon the influx of sulphuric acid into *b*, whilst free oxalic acid, or binoxalate of potash, begin to evolve carbonic acid immediately upon coming into contact with manganese and water; and this would, of course, interfere with the correctness of the results, rendering it almost impossible to determine the exact weight of the apparatus before the commencement of the operation. Such is the method of examining ores of manganese proposed by the German chemists: the results are most accurate, and the manipulation is so simple, that it will no doubt entirely supersede all the other methods that have been described. It will be observed that, from the almost absolute identity of the equivalent number of carbonic acid multiplied by 2, $22 \times 2 = 44$, with that of peroxide of manganese, 43.67, the calculation of the quantity of real peroxide in a specimen of manganese becomes a problem of the utmost simplicity; and that, if we take 100 grains of the specimen, the loss of weight in *grains* will denote the per centage proportion of pure peroxide. One atom of peroxide of manganese, $MnO_2 = 43.67$, contains one atom of oxygen, separable by sulphuric acid, and capable of converting one atom of oxalic acid into two atoms of carbonic acid. Thus:—

Oxalic acid $C_2O_2 + O = 2(CO_2)$
" " $36 + 8 = 44$

Dr. Ure recommends 250 grains of oxalate of potash to 100 grains of the sample.

Iron.

This metal is, under all circumstances, weighed as sesquioxide; if it exist in the solution in the form of a protosalt, it must be peroxidized by heating with nitric acid as long as fumes of nitrous vapour are discharged: ammonia is the precipitant employed, as the oxide precipitated by potassa or soda is always contaminated by a certain quantity of the alkali, from which it is almost impossible to free it by washing: the hydrated sesquioxide shrinks greatly on drying, and, by ignition, loses all its water. Iron is sometimes precipitated as sulphuret by hydrosulphuret of ammonia: the solution must not contain free acid: it must be well washed on the filter with water, to which a few drops of hydrosulphuret of ammonia have been added, the funnel being protected from the air with a glass plate to prevent a portion of the sulphuret from becoming oxidized into sulphate, which would dissolve and be carried through the filter: the washed sulphuret is, together with the filter, digested with dilute hydrochloric acid, filtered, and the filtrate peroxidized by nitric acid and precipitated by ammonia. When iron has to be separated from other bases, it is sometimes precipitated by *succinate of ammonia:* the solution must be very exactly neutralized by ammonia, the alkali being added in drops in a very diluted state until the small quantity of sesquioxide of iron which it precipitates is not redissolved by applying a gentle heat, the supernatant liquid possessing a red colour; the neutral succinate of ammonia is then added, upon which succinate of peroxide of iron of a brown colour is precipitated; it is filtered when quite cold, and washed first with cold water, and, finally, with a warm solution of ammonia, in order to remove a portion of the succinic acid: it is then dried and ignited in a current of air, in order thoroughly to peroxidize the iron. The sesquioxide of iron is—

Two equivalents	of Fe	... 56	... 70
Three do.	of O	... 24	... 30
One do.	of Fe_2O_3	80	100

Separation of Peroxide of Iron from Protoxide of Iron.—This is attended with very great difficulties, and can only be accomplished when the compound is soluble in acids. When no other base but iron is present, as, for example, in native magnetic iron ore, *Rose* directs that a weighed quantity of the substance should be dissolved in hydrochloric acid, and, having boiled with nitric acid to peroxidize the whole of the iron, it is to be precipitated by ammonia; the increase of weight is owing to the acquisition of oxygen, which has combined with the protoxide of the compound, and is *half as much in quantity* as the oxygen previously existing in the protoxide, for the protoxide of iron, on being fully converted into peroxide, acquires one-half more oxygen than it already possessed.

$$2(FeO) + O = Fe_2O_3$$

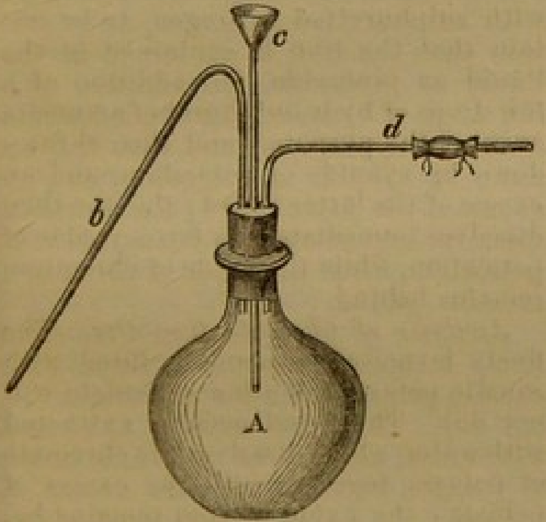
Thus, then, finding first the quantity of oxygen gained by the substance operated on, we find next the quantity of oxygen belonging to the protoxide existing in the compound, and from this it is easy to calculate the quantity of the protoxide. When this is found, the quantity of peroxide contained in the substance is learned from the difference in weight between the quantity of the compound submitted to analysis and the quantity of protoxide made out by calculation. It is easy, however, to see that, as the proportion of protoxide of iron is generally very small in comparison with that of peroxide, the greatest accuracy in experimenting is necessary, in order to arrive at correct results, a very trifling error becoming a very considerable one in the subsequent calculation of the quantity of protoxide.

Another method, given by *Rose*, for determining the quantity of oxygen in a compound consisting merely of protoxide and peroxide of iron, is by converting the oxides into metallic iron by igniting them in a current of dry hydrogen gas, and determining not only the quantity of iron revived, but also the weight of the water formed.

To determine experimentally the quantity of peroxide of iron in a soluble compound of peroxide and protoxide, a weighed quantity of the pulverized mixture is introduced into a flask, the whole of the atmospheric air from which is then expelled by a current of carbonic acid gas; hydrochloric acid sufficient to dissolve the compound is then added, and the flask quickly and securely closed. Solution being effected, recently prepared perfectly clear sulphuretted hydrogen water is added in excess, and the flask again closed, and allowed to remain at rest for some days; the peroxide of iron is reduced to protoxide by the sulphuretted hydrogen, and a proportional quantity of sulphur is deposited; this is carefully collected on a small weighed filter, washed and dried at a gentle heat; the filter must be protected from the atmosphere during the process of filtration; from the weight of the sulphur the quantity of oxygen that has entered into combination with the hydrogen of the decomposed sulphuretted hydrogen is found this oxygen was derived from the peroxide of iron; and, by multiplying it by three, the whole quantity of oxygen that was present in the substance in the form of sesquioxide of iron is found. Every sixteen grains of sulphur that are deposited indicate the abstraction of three grains of oxygen, and the presence of seventy grains of sesquioxide in the specimen.

Another method of analyzing a mixture of the two oxides is the following, given by *Fresenius*:—A known quantity of the finely divided substance is introduced into the flask A (*fig.* 30), which is then filled with carbonic acid through the tube *d*; hydrochloric acid, not in great excess, is then added through the funnel *c*, and the solution of the compound assisted by heat; a stream of carbonic acid passing all the time through the apparatus, hot water is next added, and the solution boiled and allowed to cool; pure recently precipitated carbonate of baryta is now mixed into a milky fluid, and poured into the flask through the funnel till it predominates; the whole mixture is then digested at a very gentle heat. The flask is filled with boiling water nearly up to the end of the tube *b*, which, being depressed as far as necessary into the liquid, the clear fluid is drawn off; the tube is then raised, and the flask again filled with boiling water; when the precipitate has settled, the clear fluid is again drawn off by the syphon *b*; the flask is then rinsed out with boiling water, and the precipitate thrown on a filter, and well washed with boiled water, as much as possible out of access of air: the amount of peroxide of iron in the washed precipitate is then determined. The liquid is drawn off by the syphon, and the filtrate from the precipitate contains the whole of the dissolved protoxide of iron; the solution is concentrated, the iron peroxidized, and, finally, precipitated after the removal of the *baryta*.

Fig. 30.



Indirect Method of determining the quantity of Protoxide of Iron in a mixture of Protoxide and Peroxide.—*Rose's Method.*—A weighed portion of the substance is dissolved in hydrochloric acid in a flask, which has previously been filled with carbonic acid gas; the solution being effected, solution of *chloride of gold* and *sodium* is added in excess, and the flask closed; reduction takes place, and metallic gold is precipitated, which is collected, washed, ignited, and weighed; from the quantity obtained, the quantity of oxygen, which was necessary to convert the protoxide of iron into peroxide, is ascertained by calculation, thus:—

$$6\,FeCl + AuCl_3 = 3\,Fe_2Cl_3 + Au$$

one equivalent of precipitated gold corresponds to six equivalents of protochloride or protoxide of iron.

Fuch's Method.—A weighed portion of the substance is dissolved, as in *Rose's* method, in hydrochloric acid, in a flask which has previously been filled with carbonic acid gas; a weighed slip of clean copper is introduced, and the flask, having been filled nearly to the brim with boiled water, accurately closed; the mixture is digested until the fluid becomes colourless, or nearly so; the slip of copper is then removed from the flask, dried, and weighed; the diminution in weight indicates the amount of chlorine consumed to convert the original protochloride of iron into perchloride, every equivalent of copper corresponding to an equivalent of chlorine, and every one equivalent of chlorine converting *two* equivalents of protochloride of iron into perchloride $2\ FeCl + Cl = Fe_2\ Cl_3$; it follows that every equivalent of dissolved copper corresponds to two equivalents of perchloride of iron in the solution, or, what amounts to the same, to two equivalents of peroxide of iron present in the analyzed substance. The quantity of iron actually present in the specimen must be determined by peroxidizing a solution of a weighed quantity, and precipitating by ammonia. The method is founded on the fact that, when air is excluded, hydrochloric acid is incapable of dissolving copper; but that on the addition of peroxide of iron, or when that substance is already present in the mixture, the acid dissolves a quantity of copper corresponding thereto.

Separation of Iron from Manganese.—The iron in the solution is first brought to the state of sesquioxide, and is then precipitated by succinate or benzoate of ammonia, a sufficient quantity of sal-ammoniac having previously been added; the precipitated succinate is treated in the manner already described, and the manganese in the filtrate is precipitated by carbonate of soda. Another method of separation is by digesting the solution of the two metals with excess of recently precipitated carbonate of baryta, which throws down the iron as basic carbonate of peroxide; the washed precipitate is dissolved in hydrochloric acid, the baryta separated by sulphuric acid, and the iron precipitated by ammonia; the filtrate from the basic carbonate of peroxide of iron contains the manganese, together with a soluble baryta salt; the latter is removed by sulphuric acid, and the manganese precipitated by carbonate of soda.

Separation of Iron from Cobalt and Nickel.—The iron is peroxidized, and precipitated by succinate or benzoate of ammonia, and the cobalt and nickel in the filtrate separated and estimated by one of the methods described (page 159).

Separation of Iron from Zinc.—The iron in the solution is peroxidized by nitric acid, the solution is evaporated to dryness, and all excess of acid removed; the residue is dissolved in acetic acid; free acetic acid is added, and the zinc precipitated by sulphuretted hydrogen; the precipitated sulphuret of zinc should have a pure white colour.

Separation of Iron from Chromium.—*Rose's Method.*—To the solution of the two metals a sufficient quantity of tartaric acid is added, to prevent the precipitation of either of the metals by potassa*; that alkali is then added, and the iron precipitated by sulphuret of potassium; the solution filtered from the sulphuret of iron contains the oxide of chromium: it is evaporated to dryness, ignited, fused with carbonate of soda and nitre, and the chromium in the alkaline chromate thus formed determined as directed (page 154).

Berthier's Method.—The oxides are precipitated by ammonia or carbonate of ammonia; and, while still moist, digested with slight excess of sulphurous acid; the whole of the iron dissolves, and also a certain quantity of the oxide of chromium, while the remainder of this latter metal is converted into pure subsulphite. The solution is boiled until it is decolourized, when it only contains iron. To precipitate this metal, the sulphurous acid is expelled, either by sulphuric acid or by aqua regia; an alkali or an alkaline carbonate is then added, or the iron is precipitated by an alkaline hydrosulphuret without expelling the sulphurous acid.

Liebig's Method.—A mixture of the two metals in solution is first saturated with sulphuretted hydrogen, to be certain that the iron is contained in the liquid as protoxide, (an addition of a few drops of hydrosulphuret of ammonia answers the purpose,) and then thrown down by cyanide of potassium, and an excess of the latter added; the iron then dissolves immediately as ferrocyanide of potassium, while the oxide of chromium remains behind.

Analysis of Chromic Iron Ore.—The finely levigated mineral is fused with caustic potassa (alkaline carbonate will not do). The fused mass is extracted with water, which dissolves the chromate of potassa, together with the excess of potassa; the oxide of iron remains behind, together, perhaps, with a small quantity of the undecomposed ore, which is separated from the sesquioxide of iron by hydrochloric acid: from the hydro-

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* Rose directs ammonia to be added, and the iron to be precipitated by hydrosulphuret of ammonia; but, according to Fresenius, tartaric acid does not prevent the precipitation of oxide of chromium by ammonia.

chloric solution the iron is precipitated by ammonia, and the chromic acid in the aqueous solution is reduced to sesquioxide of chromium by hydrochloric acid and alcohol: if the mineral contained alumina, it will be found in the aqueous solution with the alkaline chromate, and will be precipitated together with the oxide of chromium, from which it is separated in the manner described (at page 155).

Separation of Iron from Yttria.—Scherer's Method.—To a neutral solution, oxalate of potassa is added: a white crystalline precipitate, consisting of the double oxalate of yttria and potassa, is gradually formed, which, by ignition, is converted into yttria and carbonate of potassa; the mixture is dissolved in hydrochloric acid, diluted with much water, and the yttria precipitated by caustic of ammonia: it must be well washed with boiling water, after which it may be ignited and weighed.

Berthier's Method.—The moist hydrates are boiled with sulphurous acid, the yttria is deposited, and the iron remains in solution; to prevent the formation of an ochreous deposit from the action of the air, the solution should be boiled in a flask with a long neck, and when no more sulphurous acid is disengaged, it should be filled with boiling water and corked: when it has become cold the liquid is decanted on to a filter replaced by boiling water, and finally filtered and edulcorated.

Separation of Iron from Alumina.—The solution containing the two oxides (the iron being in the state of sesquioxide) is concentrated by evaporation, and digested with excess of caustic potassa, in which the alumina alone dissolves. *Dr. Knop* recommends the addition of a suitable quantity of hydrosulphuret of ammonia to the alkaline ley, or, when practicable, the direct precipitation of the two oxides with hydrosulphuret of ammonia, the precipitate being washed with water containing hydrosulphuret of ammonia, and the alumina subsequently extracted with potassa, to which a few drops of hydrosulphuret of ammonia have been added, in order to obtain at once a perfect precipitation and separation of these two bodies. According to *Berthier*, the method above described for separating iron from yttria may also be applied for separating the same metal from alumina.

Separation of Sesquioxide of Iron from Magnesia.—Muriate of ammonia is added to the solution, then caustic ammonia; the iron is precipitated, carrying with it a small portion of the magnesia, from which it is freed by again dissolving in hydrochloric acid; and, after exactly neutralizing with ammonia, precipitating by succinate or benzoate of ammonia, the magnesia in the filtrate from the first and second operations is determined as pyrophosphate.

Separation of Sesquioxide of Iron from Protoxide of Manganese, Magnesia, Alumina, Lime, and Fixed Alkali.—Muriate of ammonia is first added to the solution, the *sesquioxide of iron* and *alumina*, together with small portions of protoxide of manganese and magnesia, are precipitated by ammonia; it is filtered as quickly and with as little exposure to the air as possible. The precipitate, after being well washed, is dissolved in hydrochloric acid, excess being avoided. The solution is supersaturated with caustic potassa, and digested. Alumina dissolves, and is precipitated from the alkaline ley in the manner directed (at page 152). To the filtrate from the first precipitate by ammonia oxalate of ammonia is added, by which the lime is separated. The filtrate from the oxalate of lime contains the greater part of the magnesia, and protoxide of manganese, and the alkali; the residue, insoluble in caustic potassa, consists of sesquioxide of iron, together with small quantities of protoxide of manganese and magnesia. After being well washed it is dissolved in hydrochloric acid, diluted with water, neutralized with ammonia, and the sesquioxide of iron precipitated by succinate of ammonia. The filtrate is added to the filtrate from the oxalate of lime, concentrated by evaporation, and the protoxide of manganese precipitated by hydrosulphuret of ammonia; the filtrate from the sulphuret of manganese containing the magnesia and the alkali is warmed to decompose the excess of hydrosulphuret of ammonia. It is filtered from the sulphur, and evaporated to dryness with sulphuric acid; the magnesia and alkali are hereby converted into sulphates. The mixture is ignited in a platinum crucible with a fragment of carbonate of ammonia, in order to convert the bisulphates into neutral sulphates: the mixture is weighed, dissolved in water, and acetate of baryta added in sufficient quantity to remove all the sulphuric acid in the form of sulphate of baryta. The mixture is warmed, and the sulphate of baryta filtered off. The filtrate contains acetates of magnesia and alkali, together with the excess of acetate of baryta: it is evaporated to dryness and ignited in a platinum capsule; by this treatment the acetates are converted into carbonates; the carbonate of the alkali present being soluble is easily removed by hot water, the solution may be evaporated to dryness, and the alkali converted into and weighed as *sulphate*. The carbonates of baryta and magnesia remain undissolved; they are dissolved in hydrochloric acid, the baryta separated by sulphuric acid, the filtrate evaporated to dryness, and the magnesia estimated as sulphate. This method of separating magnesia from alkalies given by Rose is very tedious, and requires considerable dexterity in manipulation in order to yield accurate results; it is, therefore, far preferable, instead of converting the magnesia and alkali into sulphates, to convert them into chlorides, and to treat the solution with red oxide of mercury, as directed, (p. 151).

Quantitative determination of Iron in Iron Ores.—The method proposed by *Fuch* has already been alluded to, (p. 167.) The specimen is dissolved in strong and pure hydrochloric acid and peroxidized, either by cautiously adding crystals of chlorate of potassa, or by passing a current of chlorine through the liquor, till a drop of it let fall into a solution of red prussiate of potash gives no tinge of blue. It is then to be boiled for a few minutes, to expel the excess of chlorine, and a weighed quantity of pure copper introduced; the boiling is to be continued without intermission till the liquor passes off to a pale yellow green. When no further change of colour is observed to take place, the flask must be filled up with hot water, and the copper removed, washed in cold water, dried, and weighed. This method requires great care to give results at all approaching to accuracy, and is altogether inapplicable in the presence of arsenic acid. The method which has generally been resorted to consists in performing, on a small scale, the operations carried on in the blast furnace for the production of the metal, namely, by mixing the ore with fluxes varying with the nature of the ore, and exposing it in a crucible lined with charcoal to an intense long-continued heat. The button of cast iron thus obtained indicates the richness of the ore: but as the flux may occasionally retain appreciable quantities of iron, which may also be disseminated throughout the ores, and, moreover, as the metallic button obtained may be contaminated by *carbon, silicium, phosphorus, arsenic,* and *manganese,* it is evident that no great dependence can be placed on the result of this process.

Method of Marguerite.—This is based on the employment of a normal test solution, and on the reciprocal action of the salts of *protoxide of iron* and *permanganate of potassa* (chameleon mineral), whereby a quantity of the latter is decomposed exactly proportionate to the quantity of iron. The ore is dissolved in hydrochloric acid, and the metal brought to the minimum of oxidation, which is done by treating the solution with *sulphite of soda,* and boiling to expel the excess of sulphurous acid; the solution of permanganate of potassa is then added cautiously until the pink colour appears, and the number of divisions of the burette required for the purposes accurately noted. The theory of the process is as follows:—

$$Mn_2O_7, KO = 2\,MnO + O_5 + KO$$

$$2\,MnO + O_5 + KO + 10\,FeO = 2\,MnO + KO + 5\,Fe_2O_3$$

one equivalent of permanganate of potash is equal to two equivalents of protoxide of manganese, one of potassa, and five of oxygen, and these five equivalents of oxygen suffice to peroxidize ten equivalents of protoxide of iron. There must be a sufficient quantity of free acid present, to keep in solution the peroxide of iron formed, as also the potassa and protoxide of manganese. The whole of the iron must be at the *minimum* of oxidation, and the excess of sulphurous acid must be expelled; if the latter precaution be neglected, an erroneous result will be obtained, as the sulphurous acid will itself take oxygen from the permanganic acid, and thus react in the same manner as iron. The author found that the only two metals that interfered with the process are *copper* and *arsenic,* which, if present as arsenic acid and peroxide of copper, might, by the action of the sulphurous acid, become reduced to *arsenious acid* and *protoxide of copper,* which would afterwards withdraw oxygen from the permanganic acid; but, by a slight modification of the general process, both of these sources of error may be obviated. The operation is carried on as usual, except that, after having boiled the solution to expel the excess of sulphurous acid, a piece of pure laminated *zinc* is added, which, acting upon the hydrochloric acid, disengages hydrogen; arsenic and copper are hereby reduced to the metallic state. When the solution of the zinc is complete, the precipitated particles of arsenic and copper are removed by filtration, and the clear liquor proceeded with as before.

To prepare the permanganate of potassa, 7 parts of chlorate of potassa, 10 parts of hydrate of potassa, and 8 parts of peroxide of manganese, are intimately mixed; the manganese must be in the finest possible powder, and the potash, having been dissolved in water, is mixed with the other substances, dried, and the whole heated to very dull redness for an hour. The fused mass is digested in water, so as to obtain as concentrated a solution as possible, and dilute nitric acid added, till the colour becomes of a beautiful violet; it is afterwards filtered through asbestos, in order to separate the oxide of manganese which it holds in suspension. The solution must be defended from the contact of organic matter, and kept in a glass-stoppered bottle. To convert the solution into a test liquor of known value, a certain quantity, say 10 grains, of pure iron, such as harpsichord wire, is dissolved in pure hydrochloric acid; after the disengagement of hydrogen has ceased, and the solution is complete, the liquor is diluted with about half a pint of cold water, and the solution of the permanganate of potassa added, until a slight pink colour becomes manifest, and the number of divisions of the burette necessary to produce this effect carefully noted; this number is then employed to reduce into weight the result of an analysis of ore.

Separation of Phosphoric Acid from Iron.—Berthier's Method.—The compound is dissolved in hydrochloric acid, and sulphurous acid, *sulphite of ammonia*, and *alum* in sufficient quantity added; the solution is then boiled, the alumina of the alum is precipitated, carrying with it the phosphoric acid. If arsenic be present, it remains wholly in solution, in the state of arsenious acid.

Determination of the amount of Carbon in Cast Iron.—The specimen is pulverized in a steel mortar, mixed with a sufficient quantity of oxide of copper, and burned, as in the method for determining the carbon in organic substances; the combustion is perfect, and the results are accurate.

Determination of Sulphur in Iron.—Dr. Bromeis employs an apparatus similar to that of Will and Varrentrap (*fig.* 148) for nitrogen analyses. Instead, however, of two bulbs there are four, in order that the sulphuretted hydrogen evolved during the solution of the iron in dilute sulphuric, may be completely absorbed by the *ammoniacal solution of silver* with which the bulbs are filled. The silver is estimated in the form of sulphuret of silver.

Uranium.

This metal is generally precipitated from its solutions by caustic ammonia. The precipitate, which is yellow, is washed on the filter with a dilute solution of muriate of ammonia; it is then dried and heated, by which it is converted into the green oxide, the composition of which is

One equivalent	of Ur	60	88.23
One do.	of O	8	11.77
One do.	of Ur O	68	100

M. Ebelmen has published the following remarks on the determination of this metal*. The tendency of the oxide of uranium to combine with bases, gives rise to its frequently carrying down along with it, in its precipitation by ammonia, bases which are not precipitated when alone by that reagent, such as barytes and lime. If the liquid contains much potash, a considerable quantity is often found in the precipitate, which is easily recognised by the orange yellow colour perceptible at various parts of the heated precipitate. Sulphuretted hydrogen separates uranium from a great number of metals. The oxide may be separated very easily from the peroxide of iron by means of carbonate of ammonia; but those metals whose oxides dissolve in part or wholly in carbonate of ammonia, such as *manganese*, *zinc*, *cobalt*, and *nickel* have been regarded difficult of separation from uranium. The use of the carbonates of soda and of potash affords a very exact and simple means of effecting their removal; for uranate of potash is not

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* Ann. de Chim. et de Phys., Juin, 1842; and Chem. Gaz., vol. i. p. 207.

soluble in the subcarbonate of potash, but it dissolves completely, and in very little time, in a liquid saturated with a bicarbonated alkali. When a solution of a salt of uranium is precipitated with a slight excess of carbonate of potash, and the liquid diluted with water, the whole of the uranium is dissolved, and imparts to it a yellow colour. In both cases the double salt of potash is formed. The carbonate of *zinc, cobalt*, and *manganese* are, on the contrary, insoluble in carbonate of potash. To effect their separation the solution may be thrown down, either by potash, the precipitate edulcorated and digested with bicarbonate of potash, which will only dissolve the oxide of uranium, or by slight excess of carbonate of potash, the precipitate being collected on a filter, and washed as long as the liquor which passes through is coloured. On adding to a solution of the phosphate or arseniate of uranium, in an excess of carbonate of potash, a known quantity of sesquioxide of iron dissolved in nitric acid, those two acids may be completely separated from the uranium, and their proportion determined by the increase in weight of the peroxide of iron. The oxide of uranium may also be separated by potash, and the phosphoric and arsenic acids left in solution.

To separate the oxide of uranium in solution, it may be saturated with hydrochloric acid, boiled to expel the carbonic acid, and the uranium precipitated by ammonia; but as the liquor contains much potash the precipitate retains a certain quantity, and is not entirely converted into the state of green oxide, which makes it necessary to redissolve it, and precipitate again with ammonia.

To extract uranium with great precision from the uranate of potash dissolved in hydrochloric acid, the whole is evaporated to dryness in a platinum crucible gradually heated, and a current of dry hydrogen conveyed into it as long as the gas which is given off possesses an acid reaction. The double chloride of potassium and uranium is converted into uranium (so called) in the form of a black powder, which is separated by washing from the chloride of potassium.

Separation of Uranium from Nickel, Cobalt, and Zinc.—When the oxide of uranium in its preparation from *pitchblende* is so far purified as to be dissolved in carbonate of ammonia, *Wohler* directs to mix hydrosulphuret of ammonia with the solution as long as a black precipitate falls; in this way the nickel, cobalt, and zinc are entirely separated, no uranium being precipitated. According to *Berthier*, *uranium* is completely separated from *iron*, *manganese*, *cobalt*, *nickel*, and *zinc*, by boiling the solution after the addition of sulphate of ammonia.

Analysis of Pitchblende.—Of the various methods which have been employed by different chemists, the following, adopted by *Arfwedson*, seems on the whole the best. The mineral is reduced to fine powder, and digested with boiling aqua regia; the solution is evaporated on a water bath, to expel the excess of acid, then diluted with water, and precipitated by sulphuretted hydrogen, sulphurous acid being previously added to reduce the arsenic acid to arsenious acid: *arsenic*, *copper*, *lead*, and *bismuth* are in this manner precipitated. The solution is filtered, the excess of sulphuretted hydrogen expelled by boiling, and ammonia added; the precipitate thereby formed is washed and dissolved, while yet moist, in carbonate of ammonia, peroxide of iron remains undissolved, and is separated by filtration. The solution is evaporated till the ammonia is volatilized, whereupon the peroxide of uranium is rendered insoluble; it is washed, dried, and calcined in a platinum crucible, by which it becomes converted into *urano-uranic oxide* of a green colour. The uranates of lime, zinc, cobalt or nickel, which may have been present in the solution, are not decomposed by the calcination; they are readily dissolved, however, by dilute hydrochloric acid, which acid serves, therefore, to separate them from the urano-uranic oxide, which is thus obtained pure. It is washed first with dilute acid, and then with distilled water.

From the metallic uranates in solution in hydrochloric acid oxide of uranium may be obtained. For this purpose the solution is precipitated by ammonia, the dried precipitate is reduced by hydrogen gas, and treated immediately with hydrochloric acid, which dissolves all the foreign metals, leaving protoxide of uranium insoluble.

Group 5th.—*Lead, Silver, Mercury, Bismuth, Cadmium, Copper, Palladium.*

Lead.

This metal is completely precipitated

from its acid solutions by *sulphuretted hydrogen;* it is also precipitated by *sulphuric acid*, by *carbonate of ammonia*, by *oxalate of ammonia*, and by *hydrochloric acid*, and it may, therefore, be weighed as *sulphuret*, *sulphate*, *chloride*, and as *oxide*, the latter being produced by igniting with free access of air the carbonate and oxalate.

Precipitation as Sulphuret.—A stream of washed sulphuretted hydrogen gas is transmitted through the solution, rendered slightly acid with nitric acid until it is completely saturated, a gentle heat is then applied, and the precipitated sulphuret is filtered as quickly and with as little access of air as possible, in order to avoid the decomposition of a portion of the sulphuretted hydrogen, which would occasion a precipitation of sulphur; as it is difficult, even with great care to prevent this, it is better to convert the washed sulphuret of lead into sulphate, which is done by transferring it, filter and all, into a beaker, and pouring on it concentrated and fuming nitric acid, the sulphur becomes hereby oxidized into sulphuric acid; a gentle heat is applied to assist the action, the mixture is carefully transferred into a small Berlin crucible, and a few drops of sulphuric acid being added, it is evaporated to dryness and ignited. The composition of sulphate of lead is

One equivalent of PbO	111.56 ...	73.61
One ditto of SO_3.........	40.00 ...	26.39
One ditto of PbO,SO_3	151.56	100

With respect to the precipitation of lead by sulphuretted hydrogen, the following observations have been made by *Dr. Vogel.* In precipitating lead with sulphuretted hydrogen it is usual to warm the liquid, to prevent any of the precipitate from passing through the filter, but this may give rise to considerable loss. If sulphuretted hydrogen be passed through a moderately strong solution of acetate of lead, until the filtered liquor contains no more metal, and is consequently not rendered turbid either by sulphuretted hydrogen or by sulphuric acid, and if the liquor be now warmed, a further precipitate is produced by sulphuretted hydrogen after filtration; the liberated acetic acid evidently decomposes the sulphuret of lead. The same is the case with nitrate of lead, and remarkably so with the chloride. This is of considerable importance where lead has to be separated from chlorides, and where it cannot be precipitated by sulphuric acid. With *mercury* and *bismuth* no such decomposition of the sulphuret occurs, and only in a slight degree with *antimony.* The above behaviour may even be employed for the separation of some metals. If, for example, sulphuretted hydrogen be passed into a liquid containing *nitrate of bismuth* and *nitrate of lead*, until no further precipitate occurs, and the whole be then heated to boiling, the sulphuret of lead is entirely redissolved, while the sulphuret of bismuth is not attacked. The lead may then be precipitated from the solution by sulphuric acid.

Precipitation of Lead by Sulphuret of Sodium.—A method of estimating lead by means of a normal solution of sulphuret of sodium has been proposed by *Domonté*, and is described by him as simple, quick, and accurate, and well adapted for the examination of *white lead* and *acetate of lead*, substances which, as met with in commerce, are often greatly adulterated. To prepare the normal solution of sulphuret of sodium, about 300 grains are dissolved in a pound of water, a certain known quantity of lead is dissolved in nitric acid, precipitated, and redissolved by caustic potassa; the solution of sulphuret of sodium placed in a graduated burette is added carefully to the alkaline solution, which is maintained at a temperature near to ebullition. Each addition of the sulphuret produces a black precipitate of sulphuret of lead; from time to time the liquid is boiled, and the precise point at which a drop of the reagent produces no further precipitate is carefully observed. The number of divisions of the burette which have been required represents the value of the lead employed in the experiment: thus, suppose 10 grains of lead to have been used, and 30 burette divisions of the alkaline sulphuret have been continued, then, in all analyses of commercial products, for every 30 divisions of the burette that are required the operator may infer that 10 grains of lead are present.

The author does not find the success of the experiment to be interfered with by the presence of *tin*, *antimony*, *arsenic*, *iron*, *cobalt*, *nickel*, or *zinc.* The first three metals are not precipitated by an alkaline sulphuret; in the presence of excess of free alkali, *zinc* is precipitated *after* the lead, but the colour of the sulphuret being white, renders its presence rather an advantage than otherwise;

copper complicates the process. It is necessary in the first place to determine this metal by the method of *Pelouze* (to be described hereafter). *Domontè* then makes a synthetic assay on a mixture formed of a weight of copper equal to that found by experiment, and of lead equal in weight to that employed in preparing the standard solution. This assay shows by how many divisions the plumbimetric liquor ought to be diminished on examining the alloy. The number is, in fact, the difference between the results of the assay of pure lead, and those of the assay of the mixture of lead and copper. This being done, he examines the alloy in the ordinary way. *Bismuth* cannot be separated from lead in this way, but, commercially speaking, it is not likely that this metal will be found to occur as a contamination, its higher price being a guarantee.

Quantitative estimation as Sulphate.—When lead is to be weighed in the form of this salt, the solution is precipitated by dilute sulphuric acid, and then mixed with twice its volume of alcohol, sulphate of lead not being altogether insoluble in water; it is collected on a filter, on which it is washed with spirits of wine. Its composition has been given above.

Quantitative estimation as Oxide.—*(a.) Precipitation as Carbonate.*—Carbonate of ammonia, mixed with a little caustic ammonia, is the precipitant employed, and the solution is heated; it is washed on the filter with pure water, and afterwards ignited in a porcelain crucible, by which it is converted into protoxide of lead. The precipitate is removed as completely as possible from the filter, and the latter is ignited alone, the residue being afterwards mixed with the ignited precipitate; the object of this is to prevent the reduction of a portion of the protoxide of lead by the organic matter of the filter. The same observation applies to the sulphate.

(b.) Precipitation as Oxalate.—*Rose* prefers *oxalate of ammonia* as the precipitant of oxide of lead from its solutions, which must be either neutral or weakly ammoniacal. The precipitated oxalate of lead is converted into prótoxide by ignition in an open porcelain crucible, having, as in the two former cases, been removed as much as possible from the filter, the latter being ignited alone.

The composition of protoxide of lead is

One equivalent of Pb	103.56	92.82
One ditto of O.	8.00	7.18
One ditto of PbO	111.56	100

Quantitative estimation as Chloride.—The solution is precipitated by excess of hydrochloric acid, concentrated by evaporation in the water bath, and the residue washed with absolute alcohol, mixed with ether. As chloride of lead is volatilizable, it must not be ignited, but dried at a high temperature, at a gentle heat. Its composition is

One equivalent of Pb	103.56	74.47
One ditto of Cl.	35.50	25.53
One ditto of $PbCl$	139.06	100

Lead is completely separated from all the metals that have hitherto been treated of by means of sulphuretted hydrogen; the solution must be acidified with nitric acid, and considerably diluted.

Silver.

This metal is weighed as *chloride*, as *sulphuret*, as *cyanide*, or in its pure *metallic* state.

Quantitative estimation as Chloride.—To the solution contained in a long-necked flask, and acidified with nitric acid, hydrochloric acid is added in excess; the whole is then well agitated, and allowed to remain for several hours in a warm place: the clear fluid is carefully separated by decantation from the precipitated chloride, which is then washed with water acidulated with hydrochloric acid. It is then transferred to a weighed porcelain crucible, in which the washing is continued with distilled water till all traces of acid are removed, the various washings are collected in a beaker, and, if the whole be not perfectly clear, it must be allowed to stand in a warm place for several hours, and the precipitate, if any should form, must be added to the contents of the porcelain crucible. The chloride of silver, having been perfectly washed, is heated to incipient fusion, and weighed; it may afterwards be completely removed from the crucible by reducing it by means of dilute sulphuric acid and zinc. Should the quantity of chloride obtained in the experiment be small, it may be advisable to collect it on a filter, from which it should, after washing, be removed as completely as possible, and the filter, with the residue remaining on it, burnt, on the cover of the crucible, the ashes mixed with the bulk of the chloride, which is then heated to incipient fusion in a counterpoised porcelain crucible as before. According to *Rose*, it is not admissible to precipitate silver by the *chlorides of potassium, sodium*, or *ammonium*, as these salts, particularly the latter, are capable of retaining traces of silver in solution. In cases where the presence of much chloride of ammonium is unavoidable, *Gay Lussac* and *Liebig* recommend to evaporate the solution filtered from the chloride of silver nearly to dryness, and to treat the residue with nitric acid; on exposing the whole to heat, the alkaline chlorides are converted into nitrates, while the small quantity of chloride of silver remains unaltered, and does not dissolve when the mixture is diluted.

The composition of chloride of silver is—

One equivalent	of Ag	108.0	76.26
One do.	of Cl	35.5	24.74
One do.	of $AgCl$	143.5	100

Quantitative estimation as Sulphuret.—Washed sulphuretted hydrogen gas is transmitted through the solution as long as a precipitate continues to form; the whole is then warmed, and allowed to settle; it is finally collected on a weighed filter, washed as rapidly as possible out of contact of air, and dried at 212°. Silver may likewise be precipitated as sulphuret from neutral and alkaline solutions by hydrosulphuret of ammonia; but, as in this case the precipitated sulphuret is invariably accompanied by sulphur, it is necessary to convert it for weighing into chloride, by digesting it with nitric acid, and then precipitating it with hydrochloric acid.

The composition of sulphuret of silver is

One equivalent	of Ag	108	87.09
One do	of S	16	12.91
One do.	of AgS	124	100

Quantitative estimation as Cyanide.—Cyanide of potassium is added in sufficient quantity to redissolve the precipitate which is at first formed, dilute nitric acid is then added, and a gentle heat applied, by which the whole of the cyanide of silver is reprecipitated. It is washed, and dried at 212°.

The composition of cyanide of silver is

One equivalent	of Cy	26	19.4
One do.	of Ag	108	80.6
One do.	of $AgCy$	134	100

Silver, when combined with organic acids, is estimated in the metallic state, to which it is reduced by igniting the salt in a porcelain crucible. The heat should be gentle at first and the cover on, to prevent loss during the ignition. The lid is afterwards removed, and a strong heat applied for a considerable time, in order to effect complete combustion of the carbon of the organic acid. *Silver* is completely separated from all the metals of the first four groups by sulphuretted hydrogen. The solutions must in all cases be acid. From *lead* it may be separated by hydrochloric acid, the solution having previously been largely diluted with water to prevent the precipitation of chloride of lead; or by heating the solution containing both metals with *cyanide of potassium*, which precipitates the lead in the state of carbonate, retaining the silver in solution, as *argento cyanide of potassium*. The silver is subsequently precipitated in the form of cyanide of silver by the addition of nitric acid.

Estimation of Silver in Alloys by a Standard Solution of Common Salt.—This method, which was introduced several years ago by *Gay Lussac*, and which is extensively employed in France, consists in dissolving a certain known weight of the alloy in pure nitric acid, and in determining the exact quantity of a standard solution of common salt, which is required completely to precipitate the silver, the proportion of silver is determined by the volume of the standard solution used. A burette, similar to that shown in *fig*. 26, is employed for measuring the volume of the test liquor, which is added drop by drop to the nitric solution of the alloy, until no further precipitation takes place. The number of divisions of the burette required to precipitate a certain weight of pure silver is previously determined. The presence of *copper* and *lead* does not, in the least, interfere with the accuracy of the process; there is, however, one metal which may introduce error, though its presence in silver alloys is very rare, viz., *mercury*, which might be precipitated by the test solution, together with the chloride of silver, in the form of calomel. To avoid this inconvenience, *M. Levol* supersaturates the nitric solution of the alloys with caustic ammonia, he then adds the normal test liquor, and supersaturates the excess of ammonia with acetic acid; he states that by this modification he is able, either with the presence or absence of copper, to estimate accurately silver containing a tenth part of its weight of mercury. The presence of mercury in the precipitate of chloride of silver is rendered evident by its non-coloration under the influence of light. *M. Gay Lussac* simplifies this process, by adding to the nitric solution of silver the ammonia and acetic acid at one and the same time, but in sufficient quantity to saturate the whole of the nitric acid, both that in combination with the silver and that in the free state. He finds acetate of soda to answer quite as well as acetate of ammonia. In preparing the standard solution of salt, it is convenient in practice to have it of such a strength that 100 divisions of the burette shall correspond exactly to 10 grains of pure silver; or, if the operator prefer the continental system of weight and measure, it should be of such a strength that 100 cubic centimetres are required to precipitate 1 gramme of pure silver, and the burette employed should be divided into 1000 parts, so that each division may correspond with a thousandth part of the saline solution. All trouble of calculation is thus dispensed with, since the number of divisions required to effect the complete precipitation indicates an equal number of thousandths of silver in the alloy operated upon. In preparing the saline solution, *Gay Lussac* dissolves common culinary salt in a certain quantity of water, and then determines with the greatest care the quantity required to precipitate 1 gramme of pure silver; this being determined, he dilutes the solution with pure water, and brings it to such a strength that 100 cubic centimetres shall be equivalent to 1 gramme of silver; then, suppose 28 cubic centimetres of the first solution are required, this is mixed with $\frac{72}{28}$ of its volume of distilled water to form the standard liquor; and he finds it convenient in practice to dilute a portion of this normal liquor still further with 9 times its volume of water, so that, when the solution of the alloy is nearly precipitated, it may be completed with a more diluted saline solution, an excess of a few drops of which could do no harm, and 10 cubic centimetres of which correspond with one of the first solution. In these determinations by volume, *temperature* exercises an influence on the result which ought not to be neglected; the dilatation of the two liquors for every variation of temperature may, however, be ascertained once for all, and *Gay Lussac* has calculated and published tables on the subject, which show the changes of volume for each degree above and below + 15° centigrade, as the normal temperature; he has also described a convenient apparatus for the whole analytical process*. *Berzelius* remarks that this method is susceptible of greater accuracy than that of cupellation; it effects, moreover, a great saving of time, since several assays may be made at once. On the other hand, it is not so applicable to the determination of small quantities of silver as the process of cupellation; its use is, therefore, confined in a great measure to the examination of large ingots and silver coin. It may be observed that the correctness of the results depends not only on the dexterity of the operator, but also upon the exact observation of the moment when the complete precipitation has been effected.

Among the various other methods of separating *silver* from *copper*, *two* may be specially noticed. *The first* consists in fusing the argentiferous copper with 2½ parts of lead, and cooling the fused mass in thick round cakes. These cakes are then introduced into a furnace of peculiar construction, and the heat is raised sufficiently high to fuse the alloy of silver and lead, but not to fuse the copper. On cooling, the whole of the silver is found combined with the lead, from which it is separated by cupellation. *The second Method* consists in dissolving the argentiferous copper in sulphuric acid, in a platinum vessel, and in precipitating the silver from the solution by means of plates of copper; the precipitated copper, which is in the form of a gray metallic powder, is washed and fused with a mixture of nitre and borax; it is thus purified from the copper which may have been precipitated with it. The method has two advantages; *first*, the copper is recovered in a marketable form (that of blue vitriol); and *second*, the gold, amounting to from $\frac{1}{1000}$ to $\frac{1}{1200}$th part, is saved, this metal remaining undissolved by the sulphuric acid.

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* Ann. de Chim. et de Phys. vol. lviii. p. 218; and vol. lxiii. p. 334.

Analysis of Alloys of Silver by Cupellation.—This method, which is the one usually adopted at the mint, and by refiners, and which, as above observed, is well adapted for the examination of very small quantities of silver alloys, where no very great accuracy is required, consists essentially in this. The noble metals *silver*, *gold*, and *platinum* are capable of withstanding the action of the air, even at high temperature; the base metals, on the other hand, become, under similar circumstances, oxidized. It is not possible, however, entirely to remove the oxidable metals from silver by heat alone, in consequence of the protective action of the latter, the alloy is therefore mixed with a certain quantity of pure lead, and heated in a small vessel formed of bone earth, called a *cupel;* now the oxide of lead is fusible, and possesses the property of dissolving the oxides of the base metals. On heating the mixture, therefore, to bright redness, the foreign metals present in the alloy become oxidized, are dissolved by the fused oxide of lead, and absorbed by the cupel; while, if the operation has been carefully conducted, a button of pure silver remains.

The *cupel*, which is best made of a mixture of finely levigated ashes of birch wood and calcined bones, is thus prepared:—The ash, slightly moistened, is laid in a brass mould somewhat deeper than that of the cupel intended to be made; in this is placed a curved and polished steel pestle, which is then struck smartly with a hammer. The operator must be careful to put as much ash into the mould as is required to make the cupel *at once*, it is otherwise apt to separate in layers when it comes to be heated. The little vessel thus made is dried with great care, and heated to redness before it is used. One part, by weight, of the cupel, absorbs during the process of cupellation, the oxide formed by two parts of lead. The assayist is thus furnished with a guide to the size of the cupel required for any particular experiment. In mixtures of lead and *copper*, only one part of copper is reduced to scoriæ by six parts of lead; but when the copper is alloyed with silver, a much larger quantity of lead is required. The quantity of lead necessary for different proportions of copper and silver has been determined. The results of the experiments made on this subject are thus given by *Berzelius**; 1 part of copper alloyed with 30 parts of silver, requires 128 parts of lead; with 15 parts of silver, 96 of lead; with 7 of silver, 64 of lead; with 4 of silver, 56 of lead; with 3 of silver, 40 of lead; with 1 of silver, 30 of lead; with $\frac{1}{3}$ of silver, 20 of lead; and with $\frac{1}{15}$ of silver, 17 of lead. It is scarcely necessary to mention that the lead employed in assaying must be perfectly free from silver, or, if it does contain any of that metal, the quantity must previously be determined with the greatest care.

The alloy to be examined is beat to a thin leaf by a polished hammer on a polished anvil, and being cut into small square pieces and accurately weighed, it is enveloped in a piece of thin lead, the weight of which is also known. The muffle (*fig.* 28, "Qualitative,") is placed in one of the apertures of the furnace (see *figs.* 25, 26, 27, Part I.), and as soon as one half of the bottom is red hot, the empty cupel is introduced, and advanced gradually into the muffle till it is itself red hot; a weighed piece of lead is then introduced, and, when it is melted, the assay, enveloped in its covering of lead, is carefully introduced; the heat is then somewhat diminished, taking care, however, not to reduce it below the melting point of the vitrified lead, all the imperfect metals are gradually dissolved, and the fluid glass, which they form with the oxide of lead, soaks into the cupel, producing an appearance called circulation, by which the operator judges whether the process be going on well. As soon as a play of colours is perceived on the melted metallic button, the mouth of the muffle is partially closed with a piece of charcoal, until it is perceived that the surface of the molten globule is clear and brilliant. It is allowed to remain for some minutes in the cupel, in order that the whole of the oxide of lead, &c., may be absorbed by the bone ash, after which it is allowed gradually to solidify; it is then removed, and, having been cleansed from all adhering oxide of lead, is weighed. The loss of weight indicates of course the quantity of copper and other oxidable metals originally present in the alloy. The instant of the disappearance of the last traces of the oxidable metals is known by the melted silver globule becoming suddenly whiter, or flashing,

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* Traité de Chimie, vol. ii. p. 483.

as it is technically termed. In this manner the silver which accompanies the lead in galena is extracted; but, previous to submitting the sample to the operation of cupellation, advantage is taken of the remarkable fact, that the quantity of silver may be concentrated in a comparatively small quantity of lead by crystallization. It has been ascertained that the silver is not diffused uniformly through all the lead, but combined in atomic proportions with a certain quantity of it forming an alloy, which is then mixed with an excess of lead. This alloy is more fusible than lead, so that when a large basin of lead containing a small quantity of silver is melted, and allowed to cool very slowly, so as to crytallize, the portions which first solidify are pure lead; and these portions being removed with iron colanders, all the silver remains in the mother liquor. The process must be stopped, however, before this begins to congeal. By a succession of crystallizations of this sort, the great excess of lead is gradually got rid of, and the quantity to be oxidized at the cupel diminished in a corresponding degree*.

Mercury.

This metal is in general most conveniently weighed in its *metallic state*. It may also be estimated in the form of *calomel* (subchloride); and as *sulphuret*.

Quantitative Estimation as Metallic Mercury.

1. *Reduction by the dry way.*—The solid mercurial compound is heated in a tube of hard glass, with an excess of soda lime, precisely in the same manner and with the same precautions as are observed in the analysis of ammoniacal salts (see page 147). The open end of the combustion tube is drawn out, and bent at a somewhat obtuse angle, in order that it may be inserted into a flask containing water, into which the mercury is received; when the analysis is over, the fluid metal is collected into one large globule, by agitating the flask, it is then decanted into a porcelain capsule, and the adhering water having been removed by blotting paper, it is dried in vacuo over sulphuric acid, without the application of heat.

In their experiment for the determination of the atomic weight of mercury, *Erdmann* and *Marchand* adopted the following somewhat complicated method of reducing the oxide, their object being the attainment of the greatest accuracy*. A combustion tube about 3 feet long was drawn out in front to an open point, from 9 to 10 inches in length, and curved downwards. A loose stopper of copper shavings, which had been first oxidized by heating them while exposed to the air, and then reduced in a current of hydrogen, was introduced through the other end, and thrust forward to near the point. This copper was followed by a stratum five to six inches in length, of small fragments of strongly ignited sugar-charcoal, from which every trace of dust had been carefully removed by sifting, and then the oxide (which had previously been strongly ignited in a current of air so as to remove every trace of mercurial vapour) was introduced. To advance to the front every trace of oxide which might have remained adherent to the hinder portions of the tube, it was finally rinsed with pulverulent copper: the tube, thus arranged, was treated precisely in the same manner as in organic analysis, and then placed in a long furnace. To the hinder extremities a broad tube, filled with chloride of calcium, was fixed by means of a caoutchouc tube; to this was applied a Liebig potash apparatus, filled with sulphuric acid, and at last a large gasometer filled with carbonic acid. The point in front of the tube was connected by a caoutchouc tube with a weighed recipient, destined to receive the mercury, and in the arm proceeding from the last bulb of the latter there was placed some gold leaf, to retain any trace of mercurial vapour which had not been condensed in the bulb. A gentle stream of the dry carbonic acid gas was first allowed to pass from the gasometer through the apparatus, the tube was then immediately surrounded with incandescent charcoal, proceeding from the front towards the hinder part in the same manner as in an organic analysis. The carbon in the anterior portion of the tube is seen to burn at the expense of the liberated oxygen, and the mercury, which distils over in the current of carbonic acid, collects perfectly bright in the recipient. On the combustion of the charcoal some water is formed,

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* Kane's Chemistry.

* Journal für Praktische Chimie, xxxi. p. 385.

which passes over along with the mercury. This water is entirely removed, as well as the carbonic acid contained in the apparatus, by a current of atmospheric air at the close of the operation. By this mode of analysis these chemists obtained from four experiments the following numbers:—92.594,92.596,92.598, and 92.596, the mean of which, 92.596, gives as the equivalent number of mercury the figure 100.07.

A modification of this process, consisting in the employment of a current of hydrogen gas to assist in the reduction of the mercurial compound, has been adopted by *M. Millon**.

Hydrogen gas, he observes, is more easily obtained in a regular current than most other gases, and it greatly facilitates the decomposition of all mercurial compounds: it favours the expulsion of the water which accompanies the reduction, and likewise the condensation of the mercury in the expansion of the tube in which it is to be collected and weighed. The process is conducted as follows:—The dry gas is passed through a tube containing copper turnings heated to redness—a plan which was found the most efficacious for preserving the perfect metallic lustre of the mercury, while it also insured the purification of the hydrogen. On leaving the tube with the copper turnings, the gas enters the tube containing the mercurial salt. This tube should be from fourteen to sixteen inches long and of the diameter of an ordinary tube for organic analysis. At a small distance from its free extremity it is contracted, and then again contracted and drawn out at the point and curved upwards: it thus presents a space of from three to four inches between the two contractions.

A little asbestos is first placed in the tube next the first contracted part; then caustic lime in small fragments to the extent of from six to eight inches: the mercurial compound is next introduced, the quantity of which may vary from 15.5 to 62 grains, and then the tube is filled with caustic lime similar to the other. The tube is now placed in the furnace used for organic analysis: it receives the current of hydrogen at its wider and uncontracted extremity, and heat is applied in the usual manner. The ignited charcoal is gradually approached to the part of the tube containing the mercurial compound, and then a few pieces are placed behind it to prevent the condensation of the metal there. The water is first seen in the portion of the tube between the contractions: it is dissipated by gently heating it. This part of the tube is then allowed to cool, and the mercury now makes its appearance, condensing in its turn without any difficulty. At the end of the operation the part of the tube containing the mercury is separated by slightly moistening the heated tube; the portion of the tube is weighed with the mercury it contains: the metal is then poured out, the tube is rinsed out by nitric acid; it is then washed, dried, and weighed again. The difference between the two weights gives the weight of the mercury. The author states that by this mode of operating he has been able to propel 45 to 60 grains of mercury from one extremity of the tube to the other, condensing it between the contracted parts without the smallest loss. Two analyses of chloride of mercury yielded 73.87 and 73.82 per cent. of mercury, figures which give as the atomic weight of mercury 100.07, the same as that obtained by *Erdmann* and *Marchand*.

2. *Reduction in the Moist Way.*—The best reducing agent for this purpose is *protochloride of tin.* The process is conducted as follows:—The mercurial compound, if a solid, is digested with strong hydrochloric acid, a concentrated solution of protochloride of tin, which has been rendered perfectly clear by the addition of a few drops of hydrochloric acid, is then added. The whole is boiled, but only for a few minutes, to avoid the risk of the volatilization of a portion of the mercury in company with the aqueous vapours. On cooling, the mercury is usually found deposited in the form of a black precipitate, the supernatant fluid is removed by a syphon, and the precipitate is boiled with hydrochloric acid, on which it generally loses its pulverulent appearance, and becomes converted into running globules. It is washed, first with very dilute hydrochloric acid, and finally with distilled water; it is then received into a porcelain crucible, dried, first with bibulous paper, and lastly over sulphuric acid in the manner already directed. When mercury has to be estimated in a liquid containing nitric acid, it is necessary to destroy this acid before a correct determination can be made: this is done by

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* Ann. de Chim., 1846.

adding hydrochloric acid gradually to the solution and concentrating by evaporation. The nitric acid is thus destroyed, free chlorine being at the same time disengaged, and the addition of the hydrochloric acid must be continued as long as the odour of chlorine is perceptible: protochloride of tin is then added, and the remainder of the operation is conducted in the manner already described. It is very difficult to obtain correct results when the solution contains much nitric acid. Wherever it is admissible, therefore, it is advisable to precipitate the mercury as sulphuret by sulphuretted hydrogen, or colourless hydrosulphuret of ammonia, having previously nearly neutralized the solution with potassa, and mixed it with excess of cyanide of potassium.

Other reducing agents, such as *phosphorous* or *sulphurous* acids, may be employed in the place of protochloride of tin, and *Rose* remarks, that the former would be preferable to the tin salt, could it be procured easily in sufficient quantities. It may be added at once to a mercurial solution containing nitric acid, which it destroys, with the aid of heat, more effectually than hydrochloric acid. It is moreover easier to obtain mercury in large globules by these acids than when protochloride of tin is employed.

Quantitative estimation as Subchloride.—This method, which is extremely tedious, and which is only employed in certain cases where other methods are inadmissible, is directed by *Fresenius* * to be applied in the following manner:—The solution of the mercurial compound is mixed with hydrochloric acid in excess, potassa is then added until the excess of acid is nearly neutralized, and then excess of *formiate of soda*, after which it is allowed to remain for four days at rest at a temperature of from 140° to 176°. It is then collected on a filter which has been dried at 212°, and weighed. The filtrate is again allowed to stand for twenty-four hours, and should any fresh precipitate form, it is added to the first; the same process is repeated until the filtrate remains perfectly clear. The whole is then washed, dried at 212°, and weighed. Care must be taken to confine the temperature to 170°, since otherwise metallic mercury might separate; should this be the case, the precipitate will exhibit a grayish appearance, and the experiment must, under such circumstances, be considered a failure.

The composition of subchloride of mercury is

Two equivalents of Hg	200.14 ...	84.92
One ditto of Cl	35.50 ...	15.03
One ditto of Hg_2Cl ...	235.64	100.00

Quantitative estimation as Sulphuret.—A stream of washed sulphuretted hydrogen is transmitted through the acid solution of the salt; in solutions of the *suboxide* the precipitate formed is black at once; but, when a compound of *oxide* of mercury is under examination, in the beginning of the experiment white-coloured compounds of mercurial salts, with sulphuret of mercury, are produced: the addition of larger quantities of the gas causes the precipitate to assume various colours, but it ends in becoming pure black. If the whole of the mercury exists in the original solution as *oxide*, it may be determined in the state of *sulphuret*, with which view the precipitate, occasioned by sulphuretted hydrogen, is received on a weighed filter, quickly washed with cold water, dried at 212°, and weighed; but if the mercury, or any portion of it, existed as *suboxide*, it is inadmissible to estimate it as subsulphuret, because it is liable to be partly decomposed, even by a gentle heat, into sulphuret of mercury and metallic mercury; and as the latter may be partly volatilized by a very gentle heat, an error of greater or less amount would be introduced (Rose). The sulphuret containing a *minimum* of sulphur must therefore undergo further treatment, as follows:—It is collected on a filter, and transferred, filter and all, into a wide-mouthed flask, capable of being closed by a glass stopper. A small quantity of dilute hydrochloric acid is then poured into the flask, and a slow current of chlorine conducted into the solution; the sulphuret is hereby decomposed into *chloride*, *sulphuric* acid, and *free sulphur*, as soon as the latter is observed to have a clear yellow colour; the stream of chlorine is stopped, and the flask is exposed to a gentle heat to expel the free chlorine; it is then filtered off from the sulphur, and the mercury in the filtrate is estimated by protochloride of tin.

Mercury may also be separated from neutral or alkaline solutions by hydrosulphuret of ammonia; an excess of the

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* Quantitative Analysis, p. 212.

precipitant does not dissolve the precipitate in the cold; the sulphuret must, subsequently, be treated with chlorine, and the metal estimated in the manner just described. It must be observed that, in the presence of *sesquioxide of iron* or of *chromic acid*, oxide of mercury cannot safely be weighed as sulphuret, in consequence of the free sulphur with which it would be accompanied: it must be treated with chlorine and protochloride of tin, and estimated in the metallic state.

The composition of sulphuret of mercury is

One equivalent of Hg	100.07	86.21
One do. of S	16	13.79
One do. of $Hg\,S$	116.07	100

Separation of Oxides of Mercury from Oxide of Lead.

1. *By Sulphuretted Hydrogen Gas.*—The two metals are first precipitated together as sulphurets from a diluted solution; the mixed sulphurets are dried, and introduced into a bulb blown in a tube of hard glass, the weight of which, before and after the introduction of the sulphurets, is accurately taken. The tube is connected with an apparatus for generating chlorine, and a stream of the gas, dried by passing through a tube filled with chloride of calcium, is sent through the tube. When the whole apparatus is filled with chlorine, the bulb containing the sulphurets is gently heated, upon which the chloride of mercury volatilizes, and is completely separated from the chloride of lead. The sublimed chloride of mercury is driven forward by the flame of a small spirit lamp, and received in a vessel containing water. As soon as all appearance of sublimation ceases, the tube leading from the bulb to the receiver is cut off with a file, and any crystals which may have collected in it are washed into the flask. The chloride of mercury dissolved in the receiver is precipitated by protochloride of tin, and the chloride of lead remaining in the bulb is determined by first weighing it together with the bulb, and then dissolving it out and weighing the bulb alone.

2. *By Cyanide of Potassium.*—This method, which is far more simple and easy of execution than the one just described, is conducted as follows:—The diluted solution of the two oxides is mixed with carbonate of soda, and then heated with excess of cyanide of potassium; the whole of the lead is precipitated in the state of carbonate, while the mercury remains in solution in the form of double cyanide of mercury and potassium. The solution is filtered off from the insoluble lead salt and precipitated by sulphuretted hydrogen.

3. *By Hydrochloric Acid.*—All the mercury present in the compound must be in the form of *oxide*. The dry mixture is treated with hydrochloric acid, and evaporated to dryness at a gentle heat. Alcohol, mixed with ether, is added to the residue, and the whole is digested: chloride of mercury alone dissolves. The insoluble chloride of lead is received on a filter, washed with alcohol, dried, and weighed. The alcoholic solution of chloride of mercury is evaporated to expel the alcohol and ether, and the mercury is then precipitated by protochloride of tin.

4. *By Sulphuric Acid.*—The solution is concentrated, and mixed with excess of sulphuric acid: after the lapse of several hours it is filtered. The precipitated sulphate of lead is washed first with dilute sulphuric acid, and then with alcohol. The mercury in the filtrate is precipitated by protochloride of tin.

Separation of Oxides of Mercury from Oxide of Silver.

1. *By Hydrochloric Acid.*—For this purpose the mercury must be in the state of *oxide*, suboxide of mercury being precipitated by hydrochloric acid. To insure this the compound is digested with nitric acid, hydrochloric acid is then added in slight excess, and the precipitated chloride of silver is collected and weighed with the precautions prescribed (page 174). The mercury in the solution is precipitated by protochloride of tin, the nitric acid having been previously destroyed by chlorine.

2. *By Cyanide of Potassium.*—The solution is nearly neutralized with potassa; excess of cyanide of potassium is then added, by which the precipitate which first forms is entirely redissolved, and the solution contains the double cyanides of silver and potassium, and of mercury and potassium. On adding nitric acid the cyanide of potassium is decomposed, the silver is precipitated in the form of cyanide of silver, while the cyanide of mercury remains in so-

lution; the former is separated by filtration, and from the filtrate the mercury is precipitated by sulphuretted hydrogen.

3. *By Chlorine.*—This is effected precisely in the same manner and with the same apparatus as is employed in the separation of oxide of mercury from *oxide of lead;* chloride of silver remains in the bulb, in which it is weighed, the bent tube, through which the volatilized chloride of mercury makes its escape into the receiver having been cut off. The fused chloride of silver must, after weighing, be removed from the bulb by zinc and sulphuric acid, in order that the weight of the latter may be taken.

Separation of Suboxide of Mercury from Oxide of Mercury.—The solution is diluted considerably with water, and the suboxide is precipitated as subchloride by hydrochloric acid: heat must be avoided. The subchloride, after standing for some time, is received on a weighed filter, and dried at a gentle heat. The oxide of mercury in the filtrate is precipitated by protochloride of tin. If the substance be a solid and insoluble, it is acted upon at a low temperature, with diluted nitric acid, until it is completely dissolved: hydrochloric acid is then added as before.

Analysis of Amalgams.—If the metal or metals with which the mercury is combined be not volatile, or oxidizable by heat with excess of air, the amount of mercury in the amalgam may be ascertained in the simplest manner by igniting it in a porcelain crucible. If, however, the metals are liable to alteration by exposure to heat in an open vessel, the ignition must be performed in a retort, the neck of which, after the volatilization of the mercury, must be closed up by the blowpipe, while the retort is still ignited.

Bismuth.

This metal is almost invariably weighed as oxide. It is precipitated from its solution in nitric acid by carbonate of ammonia; the solution should be diluted, and it should be heated nearly to boiling for a few minutes before it is filtered, otherwise a portion of the oxide will be retained in solution by the precipitant. Neither carbonate of potassa nor carbonate of soda can be substituted for carbonate of ammonia; a portion of the former is carried down with the precipitate, and is not easily removed by subsequent washing, and the latter fails to effect a perfect precipitation. The carbonate of bismuth, having been washed, is separated from the filter and ignited in a porcelain crucible, by which it loses carbonic acid and becomes converted into protoxide of a yellow colour. The filter is burnt on the cover of the crucible, and its ashes added to the oxide.

The composition of protoxide of bismuth is

One equivalent of Bi...	70.95
One do. of O ...	8
One do. of $Bi\,O$	78.95

In the presence of sulphuric or hydrochloric acids bismuths cannot be effectually precipitated by carbonate of ammonia, as in the former case a basic sulphate, and in the latter a basic chloride, is at the same time precipitated, and neither of these salts can be subsequently decomposed even by protracted digestion with excess of carbonate of ammonia. In such cases it is necessary, in the first place, to mix the solution of the bismuth salt with acetic acid (water will not do, as it would cause the formation of an insoluble basic salt), and then to precipitate the bismuth in the form of sulphuret by sulphuretted hydrogen, or by hydrosulphuret of ammonia, having previously rendered the solution alkaline by the addition of caustic ammonia. The precipitated sulphuret, having been washed, is decomposed by digesting it, filter and all, with nitric acid; the solution is diluted with weak acetic acid, filtered, the filter washed with the same diluted acid, and the filtrate finally precipitated by carbonate of ammonia.

Separation of Oxides of Bismuth from Oxides of Lead.

1. *By Sulphuric Acid.*—An excess of sulphuric acid is added to the solution containing the two oxides, and heat is applied till the sulphuric acid begins to volatilize: it is then quickly filtered, and the sulphate of lead is washed with water acidulated with sulphuric acid. The sulphate of bismuth in the filtrate is precipitated by carbonate of ammonia. The results are not very accurate, since sulphate of lead is not altogether insoluble even in dilute sulphuric acid.

2. *Ullgren's Process.*—The two oxides

are together precipitated with carbonate of ammonia, and redissolved in acetic acid. A strip of *clean lead*, of known weight, is then put into the solution, so that the whole of it is covered. The vessel is closed, and allowed to stand for some hours. The bismuth is separated in the metallic state, and that which remains on the strip of lead is washed off, and the strip dried and weighed. It is brought on a filter and washed with water that has been boiled and allowed to cool; it is then dissolved in nitric acid, evaporated to dryness, ignited, and the oxide weighed. The solution of lead is precipitated with carbonate of ammonia, and the weight of the oxide determined from this is to be deducted, the oxide corresponding to the loss which the strip of lead has suffered during the operation.

3. *By Heat.*—The process is the same as that employed for the separation of *silver* from *mercury* and *lead* from *mercury*, namely, by converting the metals into chlorides by heating them in an atmosphere of chlorine, and expelling the volatile chloride of bismuth by heat. Too high a temperature must be avoided, otherwise a portion of the chloride of lead may be also volatilized. The proportion of bismuth may be calculated from the loss of weight which the compound under examination experiences.

4. *Liebig's Method.*—To a cold solution of the nitrates of the two oxides *carbonate of lime* is added, which precipitates the bismuth, but not the lead.

5. *By Caustic Potassa.*—To the nitric solution caustic potassa is added; both oxides are precipitated; but on adding excess of the caustic alkali the oxide of lead is redissolved.

Separation of Oxide of Bismuth from Oxide of Silver.

1. *By Hydrochloric Acid.*—Nitric acid is added to the solution, and then hydrochloric acid, which precipitates the silver as chloride. The bismuth in the filtrate is precipitated by sulphuretted hydrogen, the sulphuret decomposed by nitric acid, and, finally, precipitated by carbonate of ammonia.

2. *By Cyanide of Potassium.*—This reagent is added to the solution of the two oxides, whereupon the bismuth is precipitated as carbonate; the silver remains in solution as double cyanide of silver and potassium; it is separated by filtration from the carbonate of bismuth, and is, finally, precipitated as cyanide by the addition of nitric acid.

Separation of Oxide of Bismuth from Oxide of Mercury.—This also is effected by cyanide of potassium; the soluble argento-cyanide of potassium is decomposed by sulphuretted hydrogen, and the mercury may be determined as sulphuret.

Cadmium.

This metal may be quantitatively estimated as *oxide* or as *sulphuret*.

Estimation as Oxide.—The solution under examination is precipitated by carbonate of potassa, and the resulting white carbonate of cadmium is decomposed by ignition into carbonic acid and water which escape, and oxide of cadmium which remains behind in the form of a brown powder. Ammoniacal salts interfere with the complete precipitation of oxide of cadmium by alkaline carbonates; carbonate of ammonia cannot, therefore, be employed as the precipitant. In precipitating oxide of cadmium by carbonate of potassa in the presence of ammoniacal salts, the same precautions must be taken as in the precipitation of carbonate of zinc under similar circumstances.

The composition of oxide of cadmium is

One equivalent of Cd. …	55.74 …	87.45
One do. of O. …	8 …	12.55
One do. of Cd O ………	63.74	100

Precipitation as Sulphuret.—This may be effected either by sulphuretted hydrogen, or by hydrosulphuret of ammonia; in acid solutions the former reagent is employed. It should be largely diluted, and the gas allowed to pass slowly through the liquid for a long time; the resulting sulphuret is of a yellow or orange colour, according as the solution has been more or less diluted. It is collected on a weighed filter, washed with distilled water, and dried at 212°.

The composition of sulphuret of cadmium is

One equivalent of Cd. …	55.74 …	77.78
One do. of S …	16 …	22.22
One do. of Cd S ………	71.74	100

When hydrosulphuret of ammonia is employed as the precipitant, the sulphuret should be decomposed by digestion with hydrochloric acid, and the solution precipitated with carbonate of potassa. It has been observed by *Dr. H. Reinsch*[*], that when a salt of cadmium is dissolved in hydrochloric acid, and then treated with sulphuretted hydrogen, no precipitate takes place till after the gas has been passed through the solution for a long time, and that then the precipitate is a combination of sulphuret of cadmium with chloride. On edulcorating with water the chloride is dissolved, and the yellow sulphuret is left on the filter. This observation shows the necessity of diluting the solution before passing the gas through it. I have observed, also, that in precipitating a hydrochloric solution containing copper, lead, bismuth, and cadmium by sulphuretted hydrogen, the three former metals are completely thrown down before the chloride of cadmium is at all decomposed; the filtered liquor gives no traces of either of the three first metals, but on continuing to pass the gas slowly through it for a long time the cadmium is precipitated of its characteristic yellow colour.

Separation of Oxide of Cadmium from Oxides of Lead.

1. *By Cyanide of Potassium.*—The diluted solution of the two oxides is first rendered slightly alkaline by carbonate of soda; cyanide of potassium is then added, and heat applied. The lead is precipitated as carbonate, the cadmium remains in solution as double cyanide of cadmium and potassium, and may be precipitated from the filtered solution by sulphuretted hydrogen.

2. *By Sulphuric Acid.*—The solution is concentrated, and excess of dilute sulphuric acid added; sulphate of lead precipitates, which is received on a filter and washed, first with dilute sulphuric acid, and, finally, with alcohol; the cadmium in the filtrate is precipitated by carbonate of potassa; the former method with cyanide of potassium gives the best results, in consequence of the partially solubility of sulphate of lead, even in dilute sulphuric acid.

Separation of Oxide of Cadmium from Oxide of Silver.

1. *By Hydrochloric Acid.*—To the diluted solution nitric acid is added, and then slight excess of hydrochloric acid, the liquor filtered from the precipitated chloride of silver contains the cadmium, and is precipitated by carbonate of potassa.

2. *By Cyanide of Potassium.*—The nitric solution of the two metals is rendered neutral by the addition of potassa; cyanide of potassium is then added in such quantity that the precipitate, which is at first formed, is entirely redissolved. To the clear solution excess of nitric acid is next added, whereupon the whole of the silver is precipitated as cyanide: the cadmium remains in solution, and may either be precipitated by hydrosulphuret of ammonia, having previously rendered it slightly alkaline by the addition of potassa, or the hydrocyanic acid may be expelled by evaporating with sulphuric acid, and the cadmium precipitated as carbonate by carbonate of potassa.

Separation of Oxide of Cadmium from Oxide of Mercury.—This may be effected by *formiate of soda*, but the process is tedious, and requires considerable care. Hydrochloric acid is added to the solution, which is then nearly saturated with potassa; excess of formiate of soda is then added, and the solution is set aside for some days at a temperature not above 170°. The mercury precipitates in the form of calomel: the solution filtered from the subchloride of mercury contains the cadmium, which is then precipitated by carbonate of potassa. Cyanide of potassium may also be employed to separate these two oxides in the following manner:—The clear solution is rendered neutral by potassa, and an excess of cyanide of potassium is then added. To the solution of the two cyanides very dilute nitric acid is added, and the whole is boiled; the mercury salt is not decomposed: the cyanide of cadmium, on the other hand, is converted into nitrate, and may, consequently, be decomposed by carbonate of potassa: the filtrate, from the carbonate of cadmium, containing the oxide of mercury, may be precipitated by sulphuretted hydrogen.

Separation of Oxide of Cadmium from Oxide of Bismuth.—This likewise is effected by cyanide of potassium, an excess of the cyanide is added, and heat applied, the whole of the bismuth is separated as carbonate, and the cadmium is precipitated either by sulphuretted hydrogen, or by carbonate of potassa, having previously boiled the

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[*] Jahrb für Prakt. Pharm., xiii. p. 72; and Chem. Gaz., vol. v. p. 167.

solution, filtered from the carbonate of bismuth, with hydrochloric acid.

Copper.

In whatever manner copper may be precipitated from its solutions, it is invariably weighed as oxide. If the salt to be examined be soluble in water or in nitric acid, provided no organic substance be present, it is best precipitated by *caustic potassa*. The solution is considerably diluted, and raised to the boiling temperature in a capacious porcelain basin, and the caustic alkali gradually added as long as a brownish black precipitate is produced; the boiling is continued for a few minutes, and the precipitated oxide is then received on a filter, and washed with boiling water. The greater part of it is then removed from the filter and transferred to a platinum crucible, in which it is ignited. The filter, with its adhering oxide, is dried, burnt on the cover of the crucible, and the ashes added to the main bulk of the oxide. As oxide of copper absorbs moisture rapidly from the atmosphere, it must be weighed as soon as it is sufficiently cold to be placed in the scale of the balance, and it is advisable to allow the crucible to cool underneath a receiver by the side of a vessel containing concentrated sulphuric acid. If the solution be not dilute, the precipitation by caustic potassa is incomplete, as is rendered evident by the filtrate becoming discoloured when mixed with sulphuretted hydrogen water, the same is the case if any organic matter be present; in either of these cases the filtrate must be concentrated by evaporation, precipitated by sulphuretted hydrogen, and the precipitate treated as will be presently described. The oxide on the filter must be well washed with boiling water, to remove all traces of the alkali which is invariably carried down in company with the oxide during its precipitation.

The composition of oxide of copper is

One equivalent of Cu ...	31.66 ...	79.73
One do. of O	8 ...	20.27
One equiv. of Cu O	39.66 ...	100

Precipitation as Sulphuret.—The solution is acidified with hydrochloric acid, diluted with water, and a stream of washed sulphuretted hydrogen gas passed through it till it is perfectly saturated. The precipitated sulphuret is received on a filter and washed as quickly as possible with water impregnated with sulphuretted hydrogen, it is removed as completely as possible, from the filter, which is then dried and ignited, and its ashes mixed with the bulk of the precipitate. The copper cannot be estimated as sulphuret, as that salt becomes partially oxidized during drying; it is therefore decomposed by digestion with dilute nitro-hydrochloric acid, and, the sulphur being separated, the solution is evaporated with sulphuric acid until the nitric acid is entirely expelled; a large quantity of water is then added, and the oxide is precipitated by caustic potassa at the boiling temperature. If the solution be neutral or alkaline, hydrosulphuret of ammonia may be employed as the precipitating agent.

Lovel's Method of determining Copper.—This is a modification of the method proposed by *Fuch* for the quantitative estimation of iron (see page 167). The cupreous solution is introduced into a flask that can be accurately closed with a glass stopper, ammonia is added till the liquid assumes a transparent blue colour, and the flask is then filled with water, from which all atmospheric air has been expelled by boiling; a clean and accurately weighed slip of copper is introduced into the bottle, which is immediately closed; when the liquor has become perfectly colourless, the slip is removed, washed, dried, and weighed, the diminution in weight which it has undergone indicates the amount of copper originally present in the solution. The result which, when properly conducted, is very accurate, depends on the abstraction of one equivalent of copper from the slip by every equivalent of oxide of copper in the solution to form an equivalent of suboxide of copper which forms with ammonia a colourless solution, thus

$$CuO, + Cu = Cu_2O$$

It requires a considerable time to complete the process, which is obviously altogether inapplicable in the presence of foreign metals, which are capable of being precipitated by copper.

Cassaseca's Method.—This consists in dissolving the copper compound in an acid, adding an excess of ammonia to the solution, and comparing the tint furnished by this solution with those which a known weight of pure copper yields likewise in the state of ammoniuret.

Pelouze's Method of Estimating Copper

by Standard Solutions[*].—This mode of analysis was suggested to the author, by the accuracy and rapidity with which alloys of silver are analyzed by the process discovered by *M. Gay Lussac* (page 175). He succeeded in effecting his object in several different ways, all based principally on the phenomena of precipitation and simultaneous decoloration. The following was the mode of proceeding which he finally adopted: a certain quantity of very pure copper is dissolved in nitric acid, the solution is diluted with water and excess of ammonia added; a deep blue solution is obtained. On the other hand, some sulphuret of sodium (colourless crystallized hydrosulphate of soda of commerce) is dissolved in water and poured into a tube graduated and divided into tenths of cubic centimetres, the ammoniacal solution is heated to boiling, and the solution of the sulphuret gradually added. If we suppose that it required 31 cubic centimetres to decolorize 1 gramme of copper, we have a standard solution of known strength. To apply this to the analysis of copper alloys, a certain known weight is dissolved in aqua regia, the solution is supersaturated with ammonia, heated to boiling, and the standard solution of the sulphuret added until it is decolorized, taking care to add from time to time a little dilute ammonia to replace that which is evaporated. The decrease in the depths of the blue tint points out that the end of the experiment is more or less near, and when it is requisite to add the last portions of the sulphuret in drops. When the operation is supposed to be finished the number of divisions employed for the decoloration is read off and compared with the number required to decolorize an equal weight of pure copper. It must be remarked that the ammoniacal liquor from which the copper has been precipitated does not long remain colourless, but gradually becomes blue in consequence of the sulphuret of copper becoming partially converted into sulphate, by the absorption of oxygen. This mode of operating is not, according to the author, liable to an error amounting to more than five or six thousandths, though still greater accuracy is obtained by completing the decoloration of the blue liquid with a very weak solution of sulphuret, precisely in the manner recommended by *Gay Lussac* in his Analysis of Silver Alloys by Standard Solutions of Common Salt. Neither *tin*, *zinc*, *cadmium*, *lead*, *antimony*, *iron*, *arsenic*, nor *bismuth*, in any way interfere with the success of this process, not being in the least affected by the sulphuret of sodium while a trace of copper remains to be precipitated; indeed the author found that when the sulphuret of zinc, cadmium, tin, lead, bismuth and antimony are placed in contact with an ammoniacal solution of sulphate of copper, they decolorize it, some in the cold, others with the assistance of heat, which proves very evidently that these sulphurets cannot exist, except perhaps, for an instant, in a solution of copper. Their formation subsequently to the decoloration has no influence on the result of the analysis, as the termination of this is judged of by the decoloration of the liquid, without paying the least attention to the precipitates which subsequently form; or, if any attention *is* paid, it is only with a view to obtain some knowledge of the nature of the metals which accompany the copper. Thus, if any alloy consists of copper, lead, tin, and zinc, the presence of *zinc* is readily detected by the white precipitate which succeeds the black precipitate of sulphuret of copper, the lead and tin being precipitated at the outset by ammonia. *Cadmium*, like zinc, is precipitated immediately after the copper. The very moment the liquid is observed to be decoloured, a beautiful pure yellow precipitate of sulphuret of cadmium is formed if the addition of sulphuret be continued. If the alloy contains *silver*, that metal is previously precipitated from the nitric solution by hydrochloric acid. In this method of estimating copper, an important property of the ammonia, besides that of heightening the colour, is that it prevents the salts of copper being precipitated by *sulphites* and *hydrosulphites*, without which it would probably have been impossible to estimate the copper by means of solutions of the alkaline sulphurets, since these salts almost always occur in the alkaline sulphurets, and are, moreover, produced from them by contact with the air. A solution of sulphuret of sodium becomes weaker by contact with the air, but the alteration is very slow, nor is it necessary to change the liquid as long as any remains in the flask in which a quantity has been prepared. The only precaution to be taken—and it is one which

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[*] Comptes Rendus, Feb. 2, 1846.

applies to all standard solutions—is to determine previous to *each assay* the actual strength of the sulphuret with a known weight of pure copper. *M. Pelouze* states, in conclusion, that this method applied to the analysis of copper ores, yields results of the greatest accuracy, and that he entertains no doubt that it will render great services in the administration of the Mint, the government foundries, and other metallurgical works.

Separation of Oxide of Copper from Oxide of Lead.

1. *By Cyanide of Potassium.*—To the diluted solution of the two oxides carbonate of soda is added in slight excess, and then cyanide of potassium, and heat applied. The lead precipitates as carbonate; the copper remains in solution in the form of double cyanide of copper and potassium: it is evaporated with sulphuric acid till all the hydrocyanic acid is expelled, then largely diluted with water, and precipitated at the boiling temperature by caustic potassa.

2. *By Sulphuric Acid.*—The solution is concentrated, and the oxide of lead precipitated by dilute sulphuric acid, the sulphate of lead is collected on a filter, and washed first with dilute sulphuric acid, and then with spirits of wine. The filtrate is boiled for some time, to drive off the alcohol, and finally precipitated by caustic potassa.

Separation of Oxide of Copper from Oxide of Silver.

1. *By Hydrochloric Acid.*—Nitric acid is added to the solution, the silver is then precipitated as chloride by hydrochloric acid, and the oxide of copper is thrown down from the filtrate by caustic potassa.

2. *By Cyanide of Potassium.* — The solution is neutralized with potassa, cyanide of potassium is then added till the precipitate which is first formed is entirely redissolved. To the clear solution nitric acid is added, which precipitates the silver completely as cyanide. The filtrate is evaporated with sulphuric acid till all the hydrocyanic acid is expelled, and the copper is finally precipitated by caustic potassa. *Fresenius* gives another method of treating the solution of the oxides of these two metals in cyanide of potassium. Sulphuretted hydrogen is passed into the solution, which precipitates only the silver, provided sufficient cyanide of potassium be present. The solution filtered from the sulphuret of silver is heated to expel the excess of sulphuretted hydrogen; cyanide of potassium is again added, and then, having completely decomposed this salt by evaporating with a mixture of sulphuric and nitric acids, the copper is precipitated by caustic potassa.

For the methods of assaying alloys of silver and copper, see "*Silver.*"

Separation of Oxide of Copper from Oxide of Mercury.

1. *By Cyanide of Potassium.*—This is effected in the same manner as the separation of oxide of silver from oxide of copper; the solution of the two oxides in cyanide of potassium is treated with sulphuretted hydrogen, by which mercury alone is precipitated.

2. *By Formiate of Soda.* — Hydrochloric acid is added to the solution, which is then nearly neutralized with potassa, and the mercury precipitated as subchloride by formiate of soda, in the manner directed in treating of the separation of oxide of mercury from oxide of cadmium.

Separation of Oxide of Copper from Oxide of Bismuth.

1. *By Carbonate of Ammonia.*—On adding this reagent to the solution of the two oxides, in considerable excess, oxide of bismuth alone is precipitated; it is allowed to remain at rest for some time in a warm place, and then filtered, the oxide of bismuth being washed on the filter with carbonate of ammonia. The filtrate is gently evaporated to expel the excess of carbonate of ammonia, caustic ammonia is then added, and the oxide of copper is finally precipitated by caustic potassa. This method is not to be recommended, it being difficult to remove all traces of oxide of copper from the precipitated oxide of bismuth, even by protracted washing with carbonate of ammonia.

2. *By Cyanide of Potassium.*—Carbonate of soda is first added in slight excess to the solution, the oxide of bismuth is then precipitated in the form of carbonate, by heating with cyanide of potassium; the copper in the filtrate is determined by precipitating it by caustic potassa, having previously expelled the hydrocyanic acid by evaporating with sulphuric acid.

3. *By Chlorine.*—The solution of the two metallic oxides is precipitated by

sulphuretted hydrogen, and the mixed sulphurets, having been washed and weighed, are introduced into a bulb, blown in a tube of hard glass, connected with an apparatus for generating chlorine. A stream of this gas is transmitted through the tube, which at the same time is heated by a spirit lamp, first gently, and then to redness; the sulphurets are thus converted into chlorine, and the chloride of bismuth, being volatile, is gradually expelled; it may be received into a vessel containing water impregnated with hydrochloric acid, or the amount of oxide may be estimated by the loss of weight sustained by the analyzed substance. The apparatus employed may be the same as that used for separating mercury from lead, mercury from silver, or bismuth from lead. The chloride of copper remaining in the bulb is washed out with a little dilute nitric acid, evaporated with sulphuric acid, and finally precipitated by caustic potassa.

Separation of Oxide of Copper from Oxide of Cadmium.

1. *By Carbonate of Ammonia.*—This reagent is added in excess to the solution of the two oxides; carbonate of cadmium is precipitated, while oxide of copper remains in solution.

2. *By Cyanide of Potassium.*—This reagent is added until a clear solution is obtained, sulphuretted hydrogen is then passed through the mixture, by which the *cadmio-cyanide* is completely decomposed, sulphuret of cadmium being precipitated, while the whole of the sulphuret of copper remains in solution. The excess of sulphuretted hydrogen is expelled by heat, and a little more alkaline cyanide added. The copper may then be precipitated as sulphuret by the addition of an acid, or the double cyanide may be decomposed by evaporating with sulphuric acid, and the metal precipitated as oxide by caustic potassa.

Separation of Oxide of Copper from Oxide of Zinc.—Analysis of Brass.—Although oxide of zinc is, when alone, completely soluble in caustic potassa, this reagent cannot safely be employed to separate zinc from copper, since the oxide of copper invariably carries down with it a greater or less quantity of oxide of zinc. Sulphuretted hydrogen is, however, an effectual reagent for this purpose. The alloy, being dissolved in nitric acid, is treated with a current of the gas; sulphuret of copper alone precipitates, and from the filtrate the oxide of zinc may be completely thrown down, by boiling with carbonate of potassa, or by evaporating it to dryness, and igniting in a platinum crucible.

Analysis of Phosphate or Arseniate of Copper.—*Berthier's* method is to dissolve the compound in hydrochloric acid, and to boil the solution with *sulphite of ammonia*, whereupon the copper is thrown down as a *red subsulphite*, a minute trace only remaining in the solution. The same chemist has also proposed sulphite of ammonia as a means of separating oxide of copper from the oxides of iron, manganese, nickel, and zinc; he adds excess of this salt, and boils; copper alone is precipitated. In analyzing brass he first separates the copper in this manner, and then precipitates the zinc by hydrosulphuret of ammonia.

Palladium.

This metal is remarkable for its great affinity for *cyanogen*, on which property is founded a method of separating it from its solutions; *cyanide of mercury* is added, the solution having previously been neutralized with soda; a bright yellow precipitate is produced, which, by drying, becomes yellowish gray, and by ignition is decomposed, metallic palladium of a blue colour remaining in the crucible. From all metals which are not precipitated by sulphuretted hydrogen, palladium may be separated by that reagent; the resulting sulphuret is converted by heat into basic sulphate, which, being dissolved in hydrochloric acid and neutralized with soda, is precipitated by cyanide of mercury.

Separation of Palladium from Copper.—In crude platinum ores palladium occurs in combination with copper. *Berzelius* gives the following process for separating these two metals[*]. Both metals are precipitated from an acid solution by sulphuretted hydrogen. The precipitated sulphurets are exposed to heat, while still moist, and roasted as long as they give off sulphurous acid; they are thereby converted into basic sulphates of oxides. These salts are dissolved in hydrochloric acid, the solution is mixed with chloride of potassium and nitric

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[*] Poggendorf's Annalen, B. xiii. p. 561; and Rose's Manual of Analytical Chemistry, translated by Griffin, p. 135.

acid, and then evaporated to dryness. The dark saline mass thus produced contains chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium. The first two of these salts are to be extracted by alcohol, specific gravity 0.833; the palladium salt, being insoluble therein, remains behind. It is brought on a weighed filter, and washed with alcohol; it is then dried and weighed; it contains 28.84 per cent. of palladium. The saline mass may also be dissolved in water, and precipitated with cyanide of mercury. The alcoholic solution of the copper salt is evaporated to expel the spirit, the saline mass is redissolved in water, and the copper precipitated by caustic potassa.

Palladium has of late years been imported into this country from Brazil, alloyed with gold, some specimens containing 5 or 6 per cent. of palladium. The operation of refining is thus described by *Mr. Cock*[*]. The gold dust is fused, in charges of about 7 lbs. troy, with its own weight of silver, and a certain quantity of nitre; the effect of this fusion is to remove all earthy matter, and the greater part of the base metals contained in the gold dust and in the silver melted with it. The fused mixture is cast into ingot moulds, and when cooled the flux or scoria is detached. Two of the bars thus obtained are then remelted in a plumbago crucible, with such an addition of silver as will afford an alloy, containing one-fourth its weight of pure gold, and which, first being well stirred to insure a complete mixture, is poured through a perforated iron ladle into cold water, and thus very finely granulated. It is then ready for the process of parting. For this purpose about 25 lbs. of the granulated alloy is placed in a porcelain jar upon a heated sand bath, and subjected to the action of about 25 lbs. of pure nitric acid, diluted with its own bulk of water; after the action of this quantity of acid, the parting of the gold is very nearly effected; but, to remove the least portions of silver, &c., about 9 or 10 lbs. of strong nitric acid are boiled upon the gold for two hours. It is then completely refined, and, after being washed with hot water, is dried and melted into bars containing 15 lbs. each.

The nitric acid gas, and the vapour of nitric acid arising during the above process, are conducted by glass pipes (connected with the covers of the jars) into a long stoneware pipe, one end of which slopes downwards into a receiver for the condensed acid, the other end being inserted into the flue for the purpose of carrying off the uncondensed gas.

The nitrate of silver and palladium, obtained as above, is carefully decanted into large pans, containing a sufficient quantity of solution of common salt to effect the precipitation as chloride of the whole of the silver, the palladium and copper remaining in solution in the mother liquor, which is drawn off, and, when clear, run off, together with the subsequent washings from the chloride of silver, into wooden vessels, and the metallic contents are then separated in the form of a black powder, by precipitation with sheet zinc, assisted by sulphuric acid. The chloride of silver, when washed clean, is reduced by the addition of granulated zinc and dilute sulphuric acid, washed on the filter with boiling water, dried and melted in plumbago crucibles without the addition of any flux. From the black powder obtained as above, the palladium is extracted by resolution in nitric acid and supersaturation with ammonia, by which the oxides of palladium and copper are first precipitated and then redissolved, while those of iron, lead, &c., remain insoluble. To the clear ammoniacal solution, hydrochloric acid in excess is then added, which occasions a copious precipitation of the yellow ammonia—chloride of palladium, from which, after sufficiently washing it with cold water and ignition, pure metallic palladium is obtained. The mother liquor and washings contain all the copper and some palladium, which are recovered by precipitation with iron.

Rhodium.

This metal is, according to Berzelius[*], best estimated by the following process:—The solution is mixed with excess of carbonate of soda, and evaporated to dryness; the dry residue is then ignited in a platinum crucible. Upon dissolving the mass in water, peroxide of rhodium remains behind, which is brought upon a filter and washed, first with hydrochloric acid, and finally

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[*] Proceedings of the Chemical Society, vol. i. p. 162.

[*] Poggendorf's Annal., B. xiii. p. 454; and Rose's Manual of Analytical Chemistry, translated by Griffin, p. 131.

with water. It is then ignited with the filter, and subsequently reduced by hydrogen gas. The reduction is so easily effected that it is scarcely necessary to assist the action of the gas by the application of heat.

Separation of Rhodium from Copper.—*Berzelius* directs to pour the solution into a flask which is furnished with a glass stopper, and to saturate it with sulphuretted hydrogen gas. The flask is then closed and allowed to remain for twelve hours in a warm situation. The sulphuret of copper is, in that time, fully, and the sulphuret of rhodium, for the most part, precipitated. The solution is filtered, and, being heated and evaporated, yields a fresh portion of sulphuret of rhodium, which is added to the other sulphurets. These are placed, while still moist, in a platinum crucible, and roasted as long as sulphurous acid exhales. When the roasting is finished, the mass is subjected to the action of concentrated hydrochloric acid, peroxide of rhodium remains undissolved, and is reduced by hydrogen gas, the copper in the solution is precipitated by caustic potassa.

Rhodium exists together with *iridium, palladium, osmium,* &c., in platinum ores. It is extracted from the liquor from which the palladium has been precipitated by cyanide of mercury by the following process. Hydrochloric acid is added, and the solution is evaporated to dryness, the excess of cyanide of mercury is decomposed, and transformed into chloride. The dry saline mass is reduced to a very fine powder and washed with alcohol, sp. gr. 0.837. The double chlorides of sodium and platinum, sodium and iridium, sodium and copper, and sodium and mercury, are dissolved, but the double chloride of sodium and rhodium remains behind in the form of a fine red powder. It is washed with alcohol and decomposed by gently heating in a current of hydrogen gas, by which the chloride of rhodium is reduced, and the metal is subsequently separated from the chloride of sodium by water. Another method of treating the saline mass is to mix it with about twice its weight of carbonate of potassa, and to calcine the mixture. The residue is treated with water, and the copper dissolved out by hydrochloric acid. The residual mass is next mixed carefully with five times its weight of anhydrous bisulphate of potassa and heated to redness in a well-covered platinum crucible; the heat is continued till the mixture is about to solidify. The oxide of rhodium dissolves in the bisulphate of potassa. The saline mass is extracted with boiling water, and the process is repeated with fresh bisulphate as long as the salt continues to receive colour; excess of carbonate of soda is poured into the aqueous extract, the whole is evaporated to dryness, and the residue is calcined; the residue is again treated with boiling water. Oxide of rhodium remains undissolved, and is then in a state to be reduced by hydrogen gas.

Osmium and Ruthenium.

The first of these metals, which is found in combination with *iridium* in platinum ores, is extracted by the following process*. The grains of *osmium-iridium,* which are exceedingly hard, are reduced to a very fine powder, which is then digested with hydrochloric acid, to remove the iron which has become rubbed from the mortar during the operation of trituration: it is then dried, mixed with nitre, and heated gradually to redness in a porcelain retort connected with a receiver containing caustic ammonia. During this operation both metals become oxidized, and a portion of the oxide of osmium, or osmic acid, which is volatile, is carried forward with the nitric oxide gas, and condensed in the ammonia, to which it communicates a yellow colour. Another portion is condensed on the sides of the receiver in the form of a crystalline mass. All disengagement of gas having ceased, the apparatus is allowed to cool, the receiver containing the ammonia is then removed, and the mass which remains in the retort is dissolved in water. The solution is of a deep brown colour, and contains a combination of the two oxides with potassa. It must not be filtered, since the organic matter of the paper decomposes it. It is therefore at once distilled, at a gentle heat, in a retort connected with a receiver, and the greater part of the liquor drawn over. This liquor, which is colourless, and possessed of a strong and disagreeable odour, contains the osmium in the form of *osmic acid.* The following method of extracting *iridium* and *osmium*

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* Berzelius's Traité de Chimie.

† Berzelius's Traité de Chimie.

from the pulverulent residue, after digesting platinum ore with aqua regia, was proposed by *Wöhler*. The residue is mixed with an equal weight of dry and finely pulverized common salt, heated to redness in a long glass tube, and a stream of chlorine sent through, as long as it continues to be absorbed. In this operation, the *titanate of iron* is not attacked, but there are formed compounds of iridium and osmium with chloride of sodium; much osmic acid is also disengaged, being expelled with the aqueous vapour introduced with the chlorine gas; this is condensed in a receiver containing ammonia, which is adapted to the tube. When no more chlorine is absorbed, the contents of the tube are treated with water, which dissolves the double salts of iridium and osmium. The solution has a deep red-brown colour. The titanate of iron and other matters remain undissolved. The solution is then distilled, by which much osmic acid, arising from the decomposition of the chloride of osmium, is removed, and is condensed in a receiver containing ammonia; when no more osmic acid passes over, the distillation is stopped, and the residual liquor, after being filtered, is mixed with excess of carbonate of soda, evaporated to dryness, and the residue feebly calcined. It consists of a mixture of suboxide of iridium with chloride of sodium; the latter is dissolved out by water. The suboxide of iridium is not, however, pure, it still contains a notable quantity of iron and of osmium; the former is removed by reducing the oxide to the metallic state in a current of hydrogen gas, and then acting on the residue with concentrated hydrochloric acid. Under this treatment the platinum residue loses in general from 25 to 30 per cent. of its weight: it is not, however, exhausted; and, by a second treatment with chloride of sodium, a farther amount of 5 or 6 per cent. of a mixture of osmium, iridium, and iron may be extracted. From the residue a small quantity of platinum may generally be dissolved out by aqua regia: it not unfrequently, also, contains chloride of silver, which may be separated by ammonia.

The following modification of this process has been recommended by *Fritzsche*[*]. Equal portions of caustic potassa and chlorate of potassa are melted together in a very spacious porcelain crucible over a spirit lamp, and into the fused mass is conveyed about three times its weight of osmium-iridium, without first reducing it to powder. As soon as, on farther heating, the chlorate of potassa liberates oxygen, the fused mass begins to act on the osmium-iridium. The mass froths violently, so that the heat must be moderated when it becomes more tenacious; the action at last proceeds without any further heating, the mass becomes nearly black, and the operation is discontinued as soon as the frothing has ceased. During the whole operation not a trace of osmium vapours is perceptible, but a slight evolution commences on the solidification of the mass, which is increased by farther heating; this, however, is unnecessary, so that there is scarcely any trouble with the vapours of osmic acid. Six hundred grammes of osmium-iridium may be fused with ease in a porcelain crucible capable of holding 2 lbs., with 100 grains of caustic potassa and chlorate of potassa, over a spirit lamp. The operation scarcely lasts an hour, and at least 50 grains are decomposed. On treating the fused mass with water, an orange-coloured solution, containing *osmium* and *ruthenium*, is obtained, and a blackish blue precipitate, which may very easily be separated by suspension from the undecomposed *iridium-osmium*.

By the above process of *Berzelius* iridium cannot be completely separated from osmium, for, on heating the former while exposed to the air, vapours of osmic acid are always disengaged. In order to complete the separation of these two metals the following method is employed by *Fremy*[†]: 100 grammes of the residue of the platinum workings are mixed with 300 grammes of nitre; the mixture is introduced into a large crucible and kept for an hour at a red heat in a wind furnace. After this calcination the mass is poured out on a metallic plate, which operation should be performed in the open air, and it is even indispensable to cover the face, for without this precaution the vapours of osmic acid would act violently on the skin. During the calcination with nitre, a certain quantity of osmic acid is lost, but it was found that the proportion of this

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[*] Journ. für Prakt. Chem., xxxvii. p. 483; and Chem. Gaz., vol. iv. p. 319.

[†] Comptes Rendus, Jan. 22, 1844; and Chem. Gaz., vol. ii. p. 107.

acid which might be condensed would never repay the inconveniences of calcining in a porcelain crucible. The decanted mass, which contains the osmiate and iridiate of potassa, is treated in a retort with nitric acid, which liberates the osmic acid, which is condensed in a concentrated solution of potassa. The residue is treated with water which removes the nitre, and it is then acted upon with hydrochloric acid which dissolves the oxide of iridium. In this manner the osmium is obtained in the state of osmiate of potassa, and the iridium in that of soluble chloride. Into the solution of osmiate of potassa *Fremy* pours a small quantity of alcohol; the liquid becomes heated, acquires a red tint, and deposits a crystalline powder of *osmite* of potassa; in this case the osmium is frequently precipitated entirely from solution. The salt may be washed with alcohol, which does not dissolve it, and it then may be preserved without alteration. All the compounds of osmium may be prepared from it. On treating it with a cold solution of sal-ammoniac, it dissolves at first, and is then decomposed, giving rise to a new yellow salt, scarcely soluble in cold water. This salt, which is so easily prepared, affords, on calcination in a current of hydrogen, osmium perfectly pure.

To extract the *iridium*, *Fremy* treats the chloride obtained as above with sal-ammoniac, a reddish brown precipitate is formed, consisting of a combination of the bichlorides of osmium and iridium with sal-ammoniac. To separate these two double salts a stream of *sulphurous acid* is passed into the water in which they are suspended, the double salt of iridium is decomposed, chloride of iridium is formed, which is very soluble in water; the double salt of osmium undergoes no change, it remains in the state of a red salt. The soluble salt of iridium crystallizes in large brown prisms out of solutions in sal-ammoniac; it is therefore easy to purify it when calcined in a current of hydrogen; it affords metallic iridium in a state of purity.

Besides *iridium* and *osmium* another metal has been found in the platinum residues by *Professor Clauss*[*]. It is called by its discoverer *ruthenium*. He prepared it in the following manner:—The residue, which had been once fused with nitre and extracted with water and acids, was mixed with an equal quantity of nitre, and kept at a white heat in a Hessian crucible for two hours. The mass was taken out while still red hot with an iron spatula, and, after cooling, was reduced to a coarse powder, which was extracted with distilled water, leaving it to stand with it till it became clear; the perfectly clear liquid, which was of a dark yellow colour, was then decanted. It could not be filtered, since it was decomposed by the action of the organic matter of the paper. It contained *rutheniate*, *chromate*, and *silicate* of potassa, not a trace of either *rhodium* or *iridium*, and only a very minute trace of *osmiate of potassa*. Nitric acid was cautiously added to this solution, until the alkaline reaction of the liquid had disappeared: oxide of ruthenium and potassa, and some silicate acid, were hereby precipitated in the form of a velvet black powder, while chromate of potassa remained undissolved. After edulcoration the oxide of ruthenium and potassa was dissolved in hydrochloric acid, and the solution was evaporated till the silica separated as a gelatinous mass. It was then diluted with water and filtered. It could not be evaporated to dryness for the more complete separation of the silica, because the chloride of ruthenium was thereby decomposed into an insoluble protochloride. The filtered solution, which is of a beautiful orange yellow colour, was evaporated down to a very small volume, and mixed with a concentrated solution of chloride of potassium, when the salt $K\,Cl_2 + Ru\,Cl_4$ separated in reddish brown crystals. A further quantity was obtained by evaporating the liquid decanted from the crystals. The salt was further purified by recrystallization. *Clauss* has hitherto only been able to obtain the metal as a blackish grey powder, which is considerably lighter than *iridium*: the aqueous solution of its chloride is precipitated in the form of a black oxide by ammonia, by which it is distinguished from all the other platina metals, none of which are precipitated by ammonia at the ordinary temperature. If a slip of zinc be inserted in a solution of the orange-coloured chloride acidified with hydrochloric acid, a black metallic powder is after a time deposited, the liquid acquires a dark indigo blue colour, but

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[*] Bullet. de la Classe Physico-Math. de l'Acad. de St. Petersburg, t. iii. p. 311; and Chem. Gaz., vol. iii. p. 49.

subsequently, after the whole of the metal is deposited, becomes colourless.

Analysis of a mixture of Oxides of Lead, Bismuth, Silver, Copper, Mercury, and Cadmium.—To a diluted solution carbonate of potassa is first added and then excess of cyanide of potassium; the oxides of *lead* and *bismuth* are precipitated in the form of carbonates, they are received in a filter, washed, dissolved in nitric acid, and the oxide of lead separated from the oxide of bismuth by dilute sulphuric acid, as directed (p. 182). The washing from the precipitated carbonates being mixed with the filtrate, excess of diluted nitric acid is added, the silver is precipitated as cyanide, in the form of which salt it is estimated. The filtrate from the cyanide of silver, together with the washings, are again neutralized by carbonate of potassa, a fresh quantity of cyanide of potassium is added, and a stream of sulphuretted hydrogen gas is passed through the solution, the *mercury* and the *cadmium* are precipitated as sulphurets: the whole of the sulphuret of copper is retained in solution by the cyanide of potassium, provided a sufficient quantity of that reagent has been added; to insure this, it is advisable to add a fresh portion after the action of the sulphuretted hydrogen. The precipitated sulphurets of mercury and cadmium, after being well washed on the filter, are decomposed by digestion with aqua regia, the solution is filtered off from the sulphur, nearly neutralized with potassa, and the mercury estimated as subchloride by formiate of soda, as directed p. 180. The cadmium in the solution, filtered from the subchloride of mercury, is precipitated by carbonate of soda. The sulphuret of copper, which remains dissolved in the cyanide of potassium, is mixed with nitric acid and evaporated with the addition of sulphuric acid, until the whole of the hydrocyanic acid is expelled, the sulphate of copper retained in solution is finally precipitated at a boiling temperature by caustic potassa.

Group 6th.—*Antimony, Arsenic, Tin, Platinum, Iridium, Gold, Selenium, Tellurium, Tungsten, Vanadium, Molybdenum.*

Antimony.

This metal is quantitatively estimated as *sulphuret*, as *antimonious acid*, and as *pure metal.*

Precipitation as Sulphuret.—The solution is diluted with water, and sufficient tartaric acid added to redissolve any basic salt which the addition of water may have precipitated. A stream of washed sulphuretted hydrogen gas is then conducted through the solution until it smells strongly of it, it is allowed to remain at rest for some time in a moderately warm situation till the excess of sulphuretted hydrogen has been expelled. If the solution under examination contain antimony in the state of oxide only, the precipitated sulphuret may be then collected on a weighed filter, washed thoroughly with distilled water, dried at 212°, and weighed. Its composition is

One equivalent of Sb	129.03	72.88
Three ditto of S	48	27.12
One ditto of SbS_3	177.03	100

But if any of the higher oxides of antimony are also present, which will always be the case when the compound under examination is dissolved in aqua regia, correct results cannot be obtained by simply weighing the precipitated sulphuret, its composition being variable. In this case the sulphuret must be decomposed by nitric acid, and the amount of sulphur present determined by converting it into sulphuric acid in the following manner:—The sulphuret is collected on a filter, dried at 212°, and its weight, filter included, accurately determined; a portion is then removed for analysis, the weight of this portion is noted; it is digested in a flask with fuming nitric acid, carefully added at first, the action generally being very energetic; hydrochloric acid is then added, and heat applied and continued for some time if a clear solution be obtained; it is diluted with water, tartaric acid being added to redissolve any basic salt which may be thereby precipitated. The sulphuric acid formed by the oxidation of the sulphur is precipitated in the form of sulphate of baryta by chloride of barium: it is received on a filter, well washed with boiling distilled water, ignited, and weighed: from the weight obtained the amount of sulphur is calculated, which, being deducted from the weight of the sulphuret of antimony operated on, gives the quantity of metal; should it happen that a portion of the sulphur escaped oxidation by the nitric acid, the solution will not be clear; in this case, the solution, having been diluted with water with the requisite addition of tartaric acid, is passed through a weighed filter, and the weight of the separated sulphur, after being well washed and dried on the filter at 212°, is added to that calculated from the sulphate of baryta. It may be observed, that it is easy to see whether sulphuret of antimony precipitated the from the original solution by sulphuretted hydrogen is the sulphuret corresponding to $Sb\,O_3$: a small weighed portion of it is boiled in a test tube with hydrochloric acid, if a clear solution is obtained the sulphuret is $Sb\,S_3$, and the remainder may at once be weighed and calculated, but if it does not completely dissolve it contains a mixture of one or more of the higher sulphurets, and the residue must be treated as above directed. Two other methods have been proposed for treating the mixed sulphurets: one is to decompose them at a gentle heat in a current of dry hydrogen gas, by which operation the sulphur is removed partly as sulphur and partly as sulphuretted hydrogen, metallic antimony being left behind; the other is to heat the mixture in a small retort out of contact of air, by which all the higher sulphurets are converted into the lowest; neither of these methods, however, gives such correct results as the first. When the reduction process is adopted, it is impossible to regulate the heat so as to prevent the volatilization of a small portion of the antimony, and, in the process of heating the sulphurets out of contact of air, a portion of $Sb\,S_3$ is volatilized, and another portion is reduced to oxide, which is sublimed together with the sulphur.

Quantitative estimation as Antimonious Acid.—The compound under examination is evaporated with nitric acid, and the residue ignited as long as it continues to lose weight. Its composition is

One equivalent of Sb	129.03	80.12
Four do. of O	32	19.88
One do. of $Sb\,O_4$	161.03	100

Separation of Antimony from Manganese, Iron, Zinc, Cobalt, Cadmium, Lead, Bismuth, Copper, Silver, and Mercury.—This may be effected by hydrosulphuret of ammonia, in which the sulphuret of antimony *alone* is soluble. The concentrated solution of the oxides is first saturated with ammonia, and, disregarding the bulky precipitate which is thereby produced, hydrosulphuret of ammonia, containing excess of sulphur, is added, and the whole digested at a gentle heat: water is then added, and it is allowed to cool, the vessel being closed. When quite cold, it is filtered; the whole of the antimony is contained in the filtrate, from which it may be precipitated by hydrochloric acid. If the compound to be analyzed be a solid, it may frequently, according to *Fresenius*, be analyzed by fusing it with sulphuret of potassium, and treating the fused mass with water, when sulphuret of antimony alone will be dissolved. It is necessary, however, to observe, that sulphuret of mercury is not altogether insoluble in sulphuret of potassium, neither is sulphuret of copper altogether insoluble in hydrosulphuret of ammonia.

Arsenic.

This metal, whether in the form of *arsenious acid* or in that of *arsenic acid*, may be quantitatively estimated by combining it with *protoxide of lead;* when in the form of arsenious acid, it is generally most conveniently weighed as *sulphuret.*

Quantitative estimation by Protoxide of Lead.—To insure the metal being in the state of arsenic acid, the compound under examination (which must contain no other acid) is digested with aqua regia, and carefully evaporated to dryness; the residue, after being somewhat more strongly heated in a platinum crucible, is dissolved in water, and a known weight of recently ignited and pure protoxide of lead added; the mixture is carefully evaporated to dryness, and gently ignited: the amount of arsenic acid present is learned from the increase in weight, and from this the quantity of arsenic is calculated.

Estimation as Sulphuret.—For this purpose the arsenic must be in the form of *arsenious acid,* to insure which the solution of the compound should be mixed with a concentrated aqueous solution of *sulphurous acid,* and gradually heated to gentle ebullition in a flask; the heat must be maintained till the whole of the excess of sulphurous acid is expelled; hydrochloric acid is now added, and a stream of washed sulphuretted hydrogen is conducted through the liquid, till it smells strongly of it. It must not be immediately filtered, because the sulphuretted hydrogen liquor may hold in solution a portion of sulphuret of arsenic. It is set aside in a warm place, until the excess of sulphuretted hydrogen gas is expelled. *Fresenius* recommends that this be done by transmitting through the solution a stream of washed carbonic acid gas. The liquid, being freed from sulphuretted hydrogen, is passed through a weighed filter, washed with hot distilled water, dried at 212°, and weighed. Its composition is

One equivalent of As ...	75 ...	60.97
Three ditto of S ...	48 ...	39.03
One ditto of $As_2 S_3$	123	100

Should the process of treating the solution with sulphurous acid not have been adopted, and if there is reason for supposing that a portion of the arsenic may have been in a higher state of oxidation than that of arsenious acid, and if, moreover, there should be present certain other substances capable of decomposing sulphuretted hydrogen, such as *chromic acid*, *peroxide of iron*, &c., then the sulphuret of arsenic cannot be weighed for the purpose of estimating the metal, until after the excess of sulphur has been removed: this is done precisely in the same manner as has been directed in the case of sulphuret of antimony, with excess of sulphur, viz., by converting the free sulphur into sulphuric acid, and determining its amount in the form of sulphate of baryta.

Levol's Method of estimating Arsenic in the Copper and Tin of Commerce, and in Bronzes.—The arsenic is thrown down, in company with peroxide of tin, by nitric acid, and the arseniferous oxide of tin thus produced is reduced by hydrogen gas. The author found the reduction to take place readily at a dark red heat, the greater part of the arsenic being separated by sublimation, the small quantity still remaining with the tin is received by hydrochloric acid. The arseniuretted hydrogen yields on decomposition the whole of the arsenic retained by the tin. The best state for employing the tin for the purpose of collecting the arsenic appeared to be that of a solution in cold weak nitric acid; the protoxide which is thus formed remaining dissolved readily comes into contact with the molecules of the arsenic; and, when the temperature is raised to convert it into peroxide, it seizes on the arsenic and carries it down with it. Arsenic and antimony oxidized with nitric acid likewise enter into combination, but the product is not entirely insoluble. *M. Levol* has also published a method for the quantitative separation of the *arsenic* and *arsenious* acids; it is founded on the insolubility of the bibasic arseniate of ammonia and magnesia ($2\,NH_3$, $2\,MgO$, $AsO_5 + 10$ Aq.), a salt corresponding to the double ammonio-phosphate of magnesia, and which he obtained in the same way as the latter, viz., by adding a soluble ammonio-magnesian salt to the liquid containing arsenic acid, having previously rendered it ammoniacal; it is deposited in the form of very minute crystals on the sides of the vessel; its solubility is such that one part of arsenic acid, diluted with 56818 parts of water rendered ammoniacal, is made apparent shortly after the addition of a few drops of the concentrated solution of ammonio-sulphate of magnesia. Arsenious acid does not yield an insoluble double salt with ammonia and magnesia. The precipitate, on being dried and ignited, becomes $2\,MgO$, $AsO_5 = 55.74$ per cent. of the new salt which represents 41.02 per cent. of arsenic acid. M. Levol suggests the use of ammonio-magnesian salts in cases of poisoning by arsenic acid. The separation of *arsenious* from *arsenic* acid may also, according to *Fresenius*, be effected satisfactorily in the following indirect manner:—The solution containing the two acids is divided into two equal portions; in one the arsenic acid is reduced to arsenious acid by sulphurous acid, and the whole then precipitated by sulphuretted hydrogen: the precipitated sulphuret of arsenic is washed, dried at 212°, and weighed. The arsenious acid in the other half of the solution is converted into arsenic acid by chlorine, for which purpose it is mixed with hydrochloric acid and solution of indigo, added till the fluid acquires a blue colour. Chloride of lime, containing a known amount of chlorine, is then added from a weighed solution, until the blue colour disappears: from the quantity consumed the amount of chlorine used is calculated. This operation depends on the circumstance that every equivalent of arsenious acid requires two equivalents of chlorine to convert it, in the presence of water, into arsenic acid: thus

$$AsO_3 + 2\,Cl + 2\,HO = AsO_5 + 2\,HCl.$$

By calculating the resulting quantity of arsenious acid upon sulphuret of arsenic, and subtracting the weight of this from the total weight obtained from the first portion of the analyzed solution, the amount of arsenic, and originally contained in the latter, is found.

Separation of Arsenic from the Metals of the 5th Group.—This may be effected by hydrosulphuret of ammonia, having first precipitated the solution by sulphuretted hydrogen, the sulphuret of the metals of the 5th Group being insoluble in hydrosulphuret of ammonia. The dissolved sulphuret of arsenic is precipitated from its alkaline solution by acetic acid; but it must be remembered, that in this case it contains free sulphur, which must be removed and estimated in the manner already described. The separation of arsenic from the members of the 5th Group may likewise be effected by fusing the mixture with twice its weight of carbonate of soda and twice and a half its weight of nitre; the arsenic is hereby converted into arsenic acid, which combines with the alkali, and may thus be dissolved out from the remaining metallic oxides; from lead arsenic acid is separated by dissolving the compound in nitric acid and precipitating the lead by sulphuric acid, with the addition of alcohol.

Separation of Arsenic from Antimony.—When the compound of the two metals is in the reguline state, the arsenic may be expelled by heating out of contact of air; when, however, other metals are also present, this process cannot be adopted, since most other metals retain a part of the arsenic when at a red heat. In this case several methods have been proposed:—

1. The substance is dissolved in aqua regia, tartaric acid is added, and the antimony and arsenic are together precipitated by sulphuretted hydrogen: the sulphurets are intimately stirred together, collected on a filter, dried at a very gentle heat, and weighed. From a weighed portion the amount of sulphur is determined by dissolving it in aqua regia, and having added tartaric acid and diluted with water, precipitating the sulphuric acid formed by chloride of barium. Another weighed portion of the mixed sulphurets is heated in a tube, through which a stream of hydrogen gas is passing; the excess of sulphur and the sulphuret of arsenic are expelled, leaving the sulphuret of antimony, which may then be weighed. This method, when carefully performed, is capable, according to *Rose*, of affording a result only about a half per cent. from truth: the proportion of arsenic present is calculated from the loss, the united weight of both metals having by the first experiment been determined in the state of sulphuret.

2. *Behren's Method.*—The arsenic and antimony are combined into sulphurets, and to the mixture is added, while still moist, an equal volume of neutral *nitrate of lead*, and about as much water. The mass is boiled in a porcelain dish, being stirred without interruption, and, the water which evaporates being renewed until the whole has acquired a dark brown colour, it is then filtered. The residue contains the entire amount of antimony, and a portion of the arsenic. The solution contains the arsenic in the state of arsenious acid, nitric acid, and oxide of lead; it is heated with carbonate of ammonia as long as a precipitate is formed. To the liquid filtered from the carbonate of lead some hydrochloric acid is added, until it has an acid reaction; sulphuretted hydrogen gas is then transmitted through the solution, and the sulphuret of arsenic thus obtained has no trace of antimony. To separate the arsenic contained in the state of sulpho-arseniuret of lead, in the mass which remained on the first filtration, *M. Behren* digests it at a gentle heat with caustic ammonia, which converts the sulpho-arseniuret of lead into sulphuret of lead and sulphuret of arsenic, which latter dissolves in ammonia. To the filtered solution hydrochloric acid is added, and the sulphuret of arsenic precipitated is added to that first obtained.

Fresenius objects to the precipitation of the lead in the solution containing the arsenic of carbonate of ammonia, he prefers separating the two metals by hydrosulphuret of ammonia, or by evaporating the solution to dryness, and fusing the residue with carbonate of soda and nitre.

3. *Antimony* and *arsenic* in alloys may, according to *Fresenius*, be separated, though not in a very accurate manner, by heating the mixture covered with common salt and carbonate of soda, in a glass tube, through which a current of dry carbonic acid gas is passing: the tube is heated gently at first, but the heat is gradually increased to the highest degree of intensity; by this

means the arsenic is driven off, while the volatilization of the antimony is prevented by the common salt and carbonate of soda.

4. The method proposed by *Fresenius*, to distinguish between the metallic mirrors formed by antimony and arsenic, under similar circumstances, and which has already been described*, may be employed in the quantitative estimation of these two metals; when carefully performed, it yields results which are tolerably accurate.

Rose has recently† described a method of separating the acids of arsenic and antimony, as likewise that of the peroxide of tin from bases by the use of *chloride of ammonium*. Great inconveniences, he observes, are attached to the method generally employed for analyzing these compounds, particularly such as are sparingly soluble in water and in hydrochloric acid; all these difficulties may, however, in many cases be avoided, by adopting the following process:—Suppose we have a salt of one of these metallic acids, with an alkaline base to examine; after having ignited and weighed it, it is to be mixed in a finely pulverized state with from five to eight times the quantity of finely powdered chloride of ammonium, and heated in a small porcelain crucible, which may be covered with a concave platinum lid, over an argand lamp, until the whole of the chloride of ammonium is volatilized. The alkali is left behind in the state of chloride, the quantity of which may be with great accuracy determined. So long as chloride of ammonium continues to be volatilized, the temperature is so low that none of the alkaline chloride can escape. As soon as the ammoniacal salt is driven off, the temperature is moderated, so that the residue in the porcelain crucible does not fuse. After weighing, it is mixed with a fresh quantity of chloride of ammonium, and again heated, in order to see whether the weight of the residue remains constant or is diminished; in which latter case, the treatment with chloride of ammonium must be repeated. Sometimes, owing to the access of air, the platinum lid is covered with a film of the metallic acid, especially with peroxide of tin when *stannates* are examined. In this case, the lid, in the subsequent ignition, is covered with a little of the ammoniacal salt. The use of chloride of ammonium in analytical chemistry is not, *Rose* observes, restricted to the compounds here mentioned, but is capable of considerable extension, as he purposes hereafter to point out.

Tin.

This metal is weighed as *peroxide:* it has also been attempted to estimate it by a *normal solution of iodine.*

Quantitative estimation as Peroxide.—The compound under examination is evaporated nearly to dryness, at a boiling heat, with strong nitric acid to insure the whole of the metal being in the state of peroxide; if any hydrochloric acid be present, it must be completely decomposed and expelled. The peroxide of tin, which by the action of the nitric acid has become converted into the insoluble modification, is filtered, washed, ignited, and weighed. Its composition is

One equivalent of Sn ...	58.82	78.61
Two do. of O ...	16	21.39
One do. of SnO_2 ...	74.82	100

Tin may also be precipitated from its acid solution, whether in the state of a proto-salt or of a persalt, by sulphuretted hydrogen; in the former case the resulting sulphuret is brown, in the latter case it is yellow; the gas must be passed through the solution till it smells strongly of it, and a gentle heat must afterwards be applied, by which a small quantity of sulphuret, which is dissolved in the saturated liquor, becomes again deposited; the sulphuret of tin must not be weighed as such, but converted into peroxide, which may be done by heating it, first gently and then intensely, in a porcelain crucible, till all the sulphur is removed in the form of sulphurous acid, the expulsion of which is facilitated by adding a small fragment of carbonate of ammonia. *Rose* recommends to convert the sulphuret of tin into peroxide by nitric acid, observing that, when the quantity of sulphuret is at all considerable, its conversion into peroxide takes place by heat alone with extreme slowness.

Quantitative estimation of Tin by Volume.—This method was proposed by *M. Gaultier de Claubry*‡. As a normal solution, he employs 1 grm. (about 15

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* *See* Part I. p. 52.

† Chem. Gaz., April 15th, 1848.

‡ Comptes Rendus, July 13, 1846; and Chem. Gaz., vol. iv. p. 455

grs.) of *iodine* dissolved in a *decilitre* (about 6 cubic inches) of alcohol, sp. gr. 0.932, and the solution of tin is prepared with one gramme of this metal dissolved in hydrochloric acid, and diluted with water freed from air, so as to form a litre (61 cubic inches). By means of a graduated pipethe, a demi-decilitre (about 3 cubic inches) of the tin solution is measured off, and the burette, divided into tenths of a cubic centimetre, is filled with the normal solution ; the latter is poured into the first until it is no longer decolorized ; half a decilitre of the tin solution, containing 5 decigrammes (about 7.5 grs.) of tin, decolorizes 100°, or 10 cubic centimetres of the normal solution. If the tin ore under examination is soluble in hydrochloric acid, the operation is perfectly simple ; if it does not dissolve in it, it is acted on with aqua regia, containing much hydrochloric acid ; and, when the tin is become converted into perchloride, an excess of hydrochloric acid is added, and it is then boiled with some *iron*, by which it becomes reduced to protochloride ; the process is now conducted in the same manner as in the preceding case. If it happens to be an alloy containing only 20 per cent. of lead, hydrochloric acid will dissolve it; beyond that, however, only imperfectly ; but, as *aqua regia* scarcely acts on the compounds of lead, the alloy must be dissolved in nitric acid, evaporated to expel the excess of acid, and then treated with hydrochloric acid and iron. *Stannic acid*, especially when it has not been dissolved, is readily converted into protochloride in the presence of an excess of hydrochloric acid and protochloride of iron, so that the assay is brought to the same state as when the product could be acted upon immediately with hydrochloric acid. When the compound to be analyzed contains *arsenic, antimony, bismuth, copper*, or *lead*, the iron precipitates it, and again reduces the assay to the state of a tin solution. To precipitate the whole of the copper, and not to leave any of the protochloride of that metal in solution, a considerable excess of hydrochloric acid must be employed, and the boiling with iron continued for some length of time. The analysis of a salt of tin can be made with the same ease, and if a mixture of a per and proto-salt is examined, or any of the corresponding haloid compounds, the relative proportions can be determined by analyzing the substance itself, and then making a second analysis of the product boiled with hydrochloric acid and iron. *Zinc* and *iron* do not interfere with the analysis by iodine, while the protosalts of iron and the corresponding haloid compounds decolorize the sulphate of indigo, which *M. Pelouze* had attempted to employ for the estimation of tin, and renders this process impracticable.

Iodine may, according to the author, be used to determine the quantity of tin in a solution containing various metals; but if there be present an *arsenite, sulphite*, or *hyposulphite, phosphite*, or *hypophosphite*, the normal solution will be decolorized as with protochloride of tin. It will be requisite, therefore, to oxidize these salts by nitric acid or by chlorine, and to reduce the tin to protochloride by means of iron.

Separation of protoxide of tin from peroxide of tin.—Rose's method is the following :—The solution is divided into two portions; in one the amount of the metal is determined by precipitating it by sulphuretted hydrogen, and then converting it into peroxide in the manner described above. The other portion is dropped into solution of chloride of mercury, and the subchloride of mercury precipitated is filtered, washed, dried at a gentle heat, and weighed. From this weight it is easy to calculate how much protoxide or protochloride of tin was contained in the solution, since the quantity of chlorine contained in the subchloride of mercury is the same as that contained in the protochloride of tin, by which it was precipitated; or, on the other hand, the quantity of chlorine in the subchloride of mercury is equivalent to the quantity of oxygen in the protoxide of tin, which acted as a precipitant.

Separation of Oxides of Tin from the Members of the Fifth Group.—This may be effected by supersaturating the concentrated solution with ammonia, and then precipitating by hydrosulphuret of ammonia the sulphuret of tin retained in solution, while the sulphurets of the other metals remain undissolved. From most other metals tin may also be separated by nitric acid ; the alloy is boiled with the acid, which oxidizes all the metals, and dissolves everything but tin, which remains in the form of insoluble peroxide.

To separate *tin* from *iron Berthier* employs *sulphite of ammonia*, which he adds to the hydrochloric solution; having previously diluted it with water and neutralized with ammonia, the whole of the tin is precipitated, while the iron remains in the liquid.

Analysis of Alloys of Tin and Copper.—The process of *M. Cottereau*[*] is founded on the principle that copper is precipitated from its solutions by *zinc* before *tin*. The alloy is reduced to a fine powder, a certain quantity weighed off and digested with boiling hydrochloric acid. Into the resulting solution of the protochlorides of copper and tin a plate of zinc is introduced. By a previous assay of the copper contained in the alloy by the cuprometric process of *M. Pelouze* (p. 186), the quantity of copper is determined, and consequently an equivalent amount of zinc may be added to the solution; or the plate of zinc may be immediately introduced into the solution, and left there until a bright iron blade does not acquire a red tint on being immersed in the liquor. The strip of zinc is then removed, and the precipitate collected on a filter. Whichever plan be adopted, the filtered liquor is acted on just as if it were pure protochloride of tin. The protochloride of zinc formed does not in the least interfere with the reaction.

Separation of Tin from Antimony.—This is attended with very great difficulties. The following methods have been proposed:—

1st. *Berthier's Method.*—The two metals being dissolved in concentrated hydrochloric acid, tartaric acid is added to the solution, which is then diluted with water, *sulphite of ammonia* added, and the whole boiled. The tin is precipitated while the antimony remains dissolved.

2nd. *Levol's Process*[†].—The alloy being reduced to a thin plate is heated with hydrochloric acid; after some minutes' boiling a saturated aqueous solution of chlorate of potassa is added in small quantities at a time, until the alloy entirely disappears. The two metals are then thrown down together by means of a bar of distilled zinc; the precipitate is removed from the zinc with the greatest care, a quantity of concentrated hydrochloric acid, about equal to what was employed at first, is added, and the whole is boiled so as to re-dissolve the tin without previously removing the chloride of zinc; when the action has terminated, that is, when nothing remains but the antimony, which is always the case after an hour's boiling, this metal then forms a very fine blackish powder: it is collected on a weighed filter, and the tin may now be immediately obtained from the liquors by sulphuretted hydrogen.

According to *Dr. L. Elsner*[‡] the above process has no claim to accuracy. He found, on repeating the experiment with a mixture of 7½ grains of tin and as much antimony, exactly according to the directions given by *Levol*, that the acid liquid filtered from the black powder, on being treated with sulphuretted hydrogen, yielded a precipitate which consisted evidently of two differently coloured layers; the inferior layer was clearly the orange-red precipitate of sulphuret of antimony, above which was the chocolate-brown protosulphuret of tin. It is certain, therefore, that some antimony had dissolved with the tin. *Dr. Elsner* convinced himself that antimony is partly dissolved on being boiled with hydrochloric acid, and that, consequently, no quantitative method of separating it from tin can be founded on its insolubility in that acid.

Rose's Method[§].—Strong nitric acid is cautiously poured upon the metals, and when the violent oxidation has ceased the whole is evaporated at a gentle heat, and the dry powder of the oxides fused in a silver crucible over an argand lamp with an excess of hydrate of soda. The fused mass is softened with a large quantity of water, gently warmed, and the antimoniate of soda allowed to subside. When perfectly cold, the clear solution is passed through a filter: if this is done while it is still warm, the solution will contain some antimoniate of soda. The insoluble salt is again treated once or twice with water, allowed to settle and cool, and the liquid, when perfectly clear, passed through the filter. When the whole of the stannate of soda has been dissolved in this manner, the liquid which has been warmed with the antimoniate of soda remains opalescent; it must not be poured on the filter, as it would pass through turbid. A small quantity of a dilute solution of carbonate of soda may be added to it, which renders it clear;

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[*] Comptes Rendus, June 29th, 1846; and Chem. Gaz., vol. iv. p. 348.

[†] Ann. de Chim. et Phys., Jan., 1845; and Chem. Gaz., vol. iii. p. 52.

[‡] Journ. für Prakt. Chem., vol. xxxv. p. 313.

[§] Chem. Gaz., vol. v. p. 313.

but the edulcoration must not be continued for any length of time, as otherwise some antimoniate would be dissolved.

The moist antimoniate of soda is now treated in a beaker with a mixture of hydrochloric and tartaric acids, in which it readily dissolves; and the filter, upon which mere traces of the salt should have collected, washed with the same mixture. The antimony is then precipitated from the solution by sulphuretted hydrogen, and the amount of antimony estimated from the quantity of sulphuret obtained. *Rose* reduces the sulphuret of antimony by hydrogen in a porcelain crucible, through the lid of which a thin porcelain tube passes (see *fig.* 29). A gentle heat is carefully applied, until the crucible no longer decreases in weight. After the reduction the inner side of the lid is coated with metallic antimony, which, however, in no way interferes with the accuracy of the experiment.

The solution of stannate of soda is acidified with hydrochloric acid. It is not necessary to add so much acid that the whole of the eliminated oxide of tin is again re-dissolved. It is merely necessary that the solution should strongly redden blue litmus paper. Upon this, sulphuretted hydrogen is passed into it. The sulphuret of tin is converted by roasting into oxide. When it has been dried, it frequently decrepitates, which, by want of care, may occasion a very considerable loss. It is, on this account, preferable to place it with the filter, while still moist, in a porcelain crucible, and to heat it for a long time very gently, and with access of air, in order to expel the sulphur at the lowest possible temperature. If a strong heat be given at the commencement, white fumes of oxide escape, especially when the air has free access. The higher sulphuret of tin has the property of subliming somewhat at certain temperatures; the vapours are oxidized by contact with the air, and form oxide of tin. This is also the cause of a white sediment of oxide of tin being formed upon the charcoal, when sulphuret of tin is heated on charcoal before the blowpipe. A strong heat should not be applied until there is no longer any perceptible odour of sulphurous acid. After being strongly ignited, a piece of carbonate of ammonia is placed in the crucible, and, after its volatilization, a strong heat applied, with access of air, in order to expel the whole of the sulphuric acid formed; a small decrease of weight will be perceived.

The oxide of tin thus obtained never appears perfectly white; and the sulphuret of tin, precipitated by sulphuretted hydrogen, does not possess a purely yellow colour, which *Rose* attributes to melting the metallic oxides with hydrate of soda in the silver crucible, traces of oxide of silver being removed by the alkaline solution. The results do not attain the highest degree of accuracy. Although stannate of soda containing an excess of hydrate of soda does not become turbid by boiling, as stated by *Fremy*, and the solution may even be evaporated until crystals separate, which, on the addition of water, entirely dissolve, yet the antimoniate of soda contains a small quantity of oxide of tin. Consequently the sulphuret precipitated by sulphuretted hydrogen from the acid solution of the antimoniate of soda contains a small amount of sulphuret of tin, which does not part with the whole of its sulphur at the temperature at which the sulphuret of antimony is reduced by hydrogen. For this reason a somewhat smaller amount of tin, a larger quantity of antimony, and a slight excess, is found in the analysis.

Separation of Tin from Arsenic.—The following process is given by *Fresenius**. The solution is perfectly freed from nitric acid by evaporating it to dryness at a gentle heat, with the addition of hydrochloric acid. A weighed portion of the dry mass is digested with hydrochloric acid, and solution of chlorate of potassa added until it is completely dissolved. The solution is introduced into a flask, together with a strip of clean zinc; the flask is provided with a bent tube, through which the disengaged hydrogen is conveyed, first through a bottle half full of water, and then into a Liebig's potash apparatus (*fig.* 31) filled with a solution of neutral nitrate of silver. As soon as the evolution of gas has ceased the apparatus is taken asunder, the zinc is removed from the flask and carefully washed, the washings being added to the contents of the flask, the precipitate in which is allowed to subside, and the clear supernatant fluid cautiously decanted. The flask contains the whole of the tin, it may also contain a portion of the arsenic, but the greater

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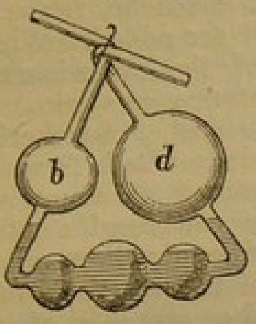
* Instruction in Quantitative Analysis, p. 341.

part of the latter metal will have been volatilized in the form of arseniuretted hydrogen, and have become condensed in the solution of nitrate of silver in the state of *arsenious acid*. The precipitated metal in the flask is treated with hydrochloric acid ; if it completely dissolves, it is free from arsenic, and may at once be precipitated as sulphuret of tin by sulphuretted hydrogen, but, if a black powder remains, it consists of metallic arsenic, and must be separated, washed, dried, and weighed, and the weight added to that of the arsenic found in the silver solution. This method is troublesome, but it appears to be the best known of separating these two metals.

Fig. 31.



When *antimony*, *tin*, and *arsenic* have to be separated from one another, the process just described is adopted ; the greater portion of the antimony and arsenic is transferred to the silver solution, and, if the metal precipitated by the zinc does not completely redissolve in hydrochloric acid, the insoluble residue may contain both antimony and arsenic : it is separated by filtration from the tin solution, and after having been well washed, first with dilute hydrochloric acid and then with pure water, it is submitted to one of the processes already described for the separation of antimony from arsenic. The tin in the filtrate is precipitated by sulphuretted hydrogen. The contents of the potash apparatus are filtered, the insoluble antimoniuret of silver is collected upon a filter washed, and the antimony determined by nitric acid. The weight found is added to that obtained from the insoluble black powder. The arsenic which remains in the solution, filtered from the antimoniuret of silver, is separated from the silver by hydrochloric acid, and finally precipitated, with the proper precautions, by sulphuretted hydrogen. The following equations, given by *Fresenius*, illustrate the nature of the decompositions and transpositions in this process :

$$6\,(AgO,NO_5) + AsH_3 =$$
$$6\,Ag + AsO_3 + 3\,HO + 6\,NO_5$$
$$3\,(AgO,NO_5) + SbH_3 =$$
$$Ag_3Sb + 3\,HO + 3\,NO_5$$

Six equivalents of nitrate of silver and one of terhydride of arsenic react in such a manner as to produce six equivalents of silver, one of arsenious acid, three of water, and six of nitric acid ; again, three equivalents of nitrate of silver and one of terhydride of antimony, give rise to one equivalent of antimoniuret of silver, three of water and three of nitric acid.

Platinum.

In whatever form this metal may be precipitated, it is invariably weighed in the reguline state. It may be precipitated from its solution as *ammonio-chloride of platinum*, as *potassio-chloride of platinum*, and as *sulphuret of platinum*.

1. *Precipitation as Ammonio-Chloride of Platinum.*—The acid solution is concentrated ; it is then mixed with a concentrated solution of muriate of ammonia, and a sufficient quantity of spirits of wine added to effect the complete precipitation of the double salt : the precipitate is allowed to subside perfectly ; it is then collected on a filter and washed with spirits of wine till the fluid passes through quite colourless, dried, and ignited, by which it is completely decomposed, metallic platinum, in the form of a grey spongy powder, remaining in the crucible. The ignition requires to be performed with great care : the dried double salt is transferred, filter and all, into a weighed platinum crucible, and is heated gently, the cover of the crucible being laid loosely on, as long as fumes of sal-ammoniac are seen to escape ; the cover is then removed, and a stronger heat applied till the organic matter of the filter is consumed ; the crucible is finally exposed to an intense heat. The reason why a gentle heat must be applied at first is, because a portion of the undecomposed double salt might otherwise be carried off with the fumes of the sal-ammoniac.

Precipitation as Potassio-Chloride of Platinum.—The solution is mixed with chloride of potassium in excess, and alcohol added ; the precipitated double salt is collected on a filter, dried at 212°, and weighed. It would not be safe, however, to estimate the platinum from the weight of the double salt, and, indeed, after ignition, it is not completely decomposed into metallic platinum and chloride of potassium; where accuracy is required, therefore, a known portion of the double salt dried at 212° must be introduced into a weighed bulbed tube, and heated to redness, while a stream of dry hydrogen gas passes through it. It thus becomes completely reduced, hydrochloric gas being evolved; when this has ceased, which is known by white fumes ceasing to be formed on bringing a glass rod or a feather dipped in ammonia water near the end of the tube, the apparatus is allowed to cool, the chloride of potassium is then dissolved out with water, and the reduced platinum well washed. It is then again heated to low redness in a stream of hydrogen gas, and weighed; the weight obtained calculated upon the whole precipitate on the filter gives the result.

Precipitation as Sulphuret.—This is sometimes practised to separate platinum from such metals as are not precipitated from their acid solutions by sulphuretted hydrogen, as well as from others whose sulphurets are insoluble in alkaline sulphurets; in the former case, the gas is passed into the acid solution. No precipitation frequently takes place till heat is applied, when the solution turns brown, and sulphuret of platinum is precipitated; it is not weighed as such, but after being washed is ignited, by which it becomes reduced, and is then estimated in its metallic state: in the latter case, the solution is rendered either neutral or alkaline, and hydrosulphuret of ammonia added in excess, in which the sulphuret of platinum dissolves.

Separation of Platinum from Antimony, Arsenic, and Tin.—This is readily effected by taking advantage of the volatility of the chlorides of the three last metals; all four are first precipitated together by sulphuretted hydrogen; the mixed sulphurets are introduced into a bulbed tube, and heated in a stream of chlorine gas. Platinum alone remains.

Separation of Platinum from the Metals which accompany it in its Ores, namely, Iridium, Osmium, Rhodium, and Palladium.—Berzelius directs to proceed as follows*:—The mineral is introduced into a tubulated retort connected with a receiver, and gently heated with hydrochloric acid, to which a little nitric acid has been added; as the action slackens, fresh portions of nitric acid are added. When the acid is saturated, the liquor is evaporated to the consistence of syrup. It is then allowed to cool, diluted with a little water, and decanted from the undissolved residue. The product of the distillation contained in the receiver has generally a yellow colour, in consequence of the spirting over of a portion of the contents of the retort. Spangles of osmium-iridium are also sometimes found there. The distillate is returned to the retort, and the greater portion redistilled. If the mineral is not now decomposed, a fresh quantity of aqua regia must be added. It frequently happens that a residue still remains, which, on examination, is found to consist of grains of osmium and iridium, which had escaped detection before submitting the ore to the action of the acid, or of brilliant plates of the same alloy or of iridium itself in a black and pulverulent state; fragments of hyacinth, quartz, chrome, iron, titanium, iron, &c., &c., are also frequently formed in the insoluble residue. The acid from the second distillation should be colourless. Should it not be so, it must be a third time distilled. This distillate contains *osmic acid*, the method of separating which has been already described. The solution in the retort has usually a deep red colour; if it disengages an odour of chlorine, it is a proof of the presence of *bichloride of palladium*, which must be decomposed into chloride by boiling. Into the clear liquor a saturated solution of chloride of potassium is poured as long as a precipitation takes place. This precipitate, the colour of which varies from a clear yellow to a cinnabar red, consists of the double chloride of platinum and potassium, mixed with a greater or less quantity of the double chloride of iridium and potassium, to which it owes its red colour. It is received on a filter and washed with a dilute solution of chloride of potassium until the wash liquor ceases to strike blue with ferrocyanide of potassium. The filtrate contains *rhodium*, *palladium*, a little *platinum and iridium*, *iron* and *copper*. The double salt on the filter is dried, intimately mixed with double its weight of carbonate of potassa, and heated gradu-

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* Traité de Chimie, vol. ii. p. 429, *et seq.*

ally till the mass begins to fuse in a platinum crucible. The carbonate of potassa decomposes the double platinum salt, chloride of potassium is formed, the platinum is reduced to the metallic state, while the iridium remains in the state of suboxide. The mass is washed first with water, then with warm hydrochloric acid; the residue is finally digested, first with dilute, and then with concentrated aqua regia, in which the suboxide of iridium is insoluble. The solution contains the whole of the platinum, still, however, mixed with a certain quantity of iridium. It is, therefore, again precipitated with chloride of potassium, and the precipitate decomposed as before by ignition with carbonate of potassa; should the solution in aqua regia still have a red tinge, it must undergo a third treatment. The solution of platinum, when pure, has a pure golden yellow colour. It is necessary to bear in mind, however, that there exists a chloride of platinum the aqueous solution of which has a dark brown colour, though this is only formed by evaporating and gently heating the bichloride, during which chlorine is disengaged. It cannot, therefore, be formed by dissolving the chloride of platinum directly. Into the solution of pure chloride of platinum, solution of chloride of ammonia is poured; a clear yellow precipitate is formed, consisting of double chloride of platinum and ammonium; this precipitate furnishes, by gentle ignition, pure metallic platinum. For details of the processes for converting the metal as thus obtained, in what is termed its *spongy form* into a malleable state, works on general chemistry must be consulted.

Gold.

This metal, like the preceding, is always weighed in the metallic state, in which it is precipitated from its solutions by *protosulphate of iron* or by *oxalic acid*. A method of estimating the metal indirectly by means of standard solutions has also been published by *O. Henry*. Gold may also be precipitated from its acid solution by sulphuretted hydrogen. The sulphuret is readily reduced by heat alone.

Precipitation by Protosulphate of Iron.—If the solution contains nitric acid, it must be evaporated nearly to dryness, with the addition of successive portions of hydrochloric acid, the residue is dissolved in water, acidulated with hydrochloric acid, and mixed with an excess of a clear solution of protosulphate of iron. It is set aside for some time in a warm place till the reduced gold has completely subsided in the form of a fine brown powder, which is then filtered, gently ignited, and weighed. The object in expelling the nitric acid is to prevent the formation of aqua regia, which might redissolve a portion of the precipitated gold. Solution of *protonitrate of mercury* may be employed in the place of protosulphate of iron; the latter, however, is preferable as the reducing agent.

Reduction by Oxalic Acid.—In certain cases it is not convenient to introduce another metal into the solution from which gold is to be precipitated, *oxalic acid* is then employed as the reducing agent. The solution as before is freed from nitric acid, and oxalate of ammonia added; if the solution does not already contain free hydrochloric acid, a quantity is next added, and the mixture set aside in a warm place; the whole of the gold is deposited in the form of yellow scales, which are collected on a filter, washed, gently ignited, and weighed. In cases where gold is the only fixed substance present, its quantity may be estimated by simply evaporating the solution to dryness and igniting the residue, and, when in combination with other substances which are incapable of precipitating from acid solutions by sulphuretted hydrogen, gold may be separated by that reagent, and the resulting sulphuret decomposed by ignition in a platinum crucible.

The rationale of the reduction of terchloride of gold by protosulphate of iron is this:

$$\mathrm{Au\,Cl_3 + 6\,Fe\,O, S\,O_3 = 2\,(Fe_2O_3, 3\,S\,O_3) + Fe_2Cl_3 + Au}$$

One equivalent of terchloride of gold and six of protosulphate of iron give rise to two equivalents of persulphate of iron, one of sesquichloride of iron and one of gold.

The rationale of the reduction by oxalic acid is as follows:

$$\mathrm{Au\,Cl_3 + 3\,(H\,O, C_2O_3) = Au + 3\,H\,Cl + 6\,CO_2}$$

One equivalent of terchloride of gold and three of oxalic acid give rise to one equivalent of gold, three of hydrochloric acid, and six of carbonic acid.

M. Henry's Method of estimating

Gold by Standard Solutions[*].—This process, which was devised by the author in consequence of the difficulty which he experienced in appreciating very minute quantities of gold, either by weighing or by cupellation, in certain investigations in which he was engaged relative to the new processes of gilding and silvering of *Elkington* and *Ruolz*, is founded on the principle, that in a mixture of terchloride of gold, a basic salt, and copper, a quantity of the latter metal, equivalent to that of the gold, separated either in powder or upon the object to be gilt, is dissolved. When the amount of gold upon a gilt object, or in a bath which has been, or is to be employed in gilding has to be ascertained, the following plan may be adopted. The objects, weighed with care, are digested with hot pure nitric acid; as soon as the copper forming the basis is dissolved, the solution is diluted with distilled water, and the gold is soon seen to settle at the bottom of the vessel in small brilliant scales. These are collected, and, after washing, dissolved in aqua regia, the solution evaporated with great precaution nearly to dryness, so as to obtain a ruby red product, soluble in water; this is terchloride of gold with a little acid. This product is now dissolved in distilled water, and mixed with five or six times its weight of pure bicarbonate of potash or soda, dissolved in distilled water; the mixture is heated, conveyed into a ground-stoppered flask, and a somewhat large amount of finely divided copper, which has been previously heated in a current of hydrogen, added to it; the mixture is now and then shaken, and after about an hour the liquid assayed. A very minute quantity of the liquid is poured upon a watch glass and treated with protosulphate of iron; if the liquid does not yield a black or gray precipitate, it is a sign that it contains no gold in solution; should the contrary occur, more copper must be added and again agitated. When the whole of the gold has been precipitated upon the copper, the liquid is carefully saturated with pure sulphuric acid so as to be *slightly acid*. By this means all the copper precipitated in the state of *carbonate* is dissolved without the gold or *metallic copper* being at all acted upon. It is filtered, and a solution of pure *ferrocyanide of potassium* of known strength carefully added by means of a graduated barette, until a precipitate ceases to be formed; the number of divisions of the instrument employed to precipitate the copper is noted, and in this manner the quantity of the metal dissolved in the liquid is ascertained.

When it is a solution which is to be, or has been, used for gilding, the author advises to precipitate the diluted acid solution by a current of sulphuretted hydrogen, to collect the precipitate and strongly calcine it after washing. The sulphuret of gold being reduced to the metallic state, the calcined residue is redissolved in nitric acid, and the gold which has remained unattacked, dissolved in aqua regia, and treated as above described.

The use of the ferrocyanide of potassium, to determine the amount of copper which represents the gold in a compound, is founded on the fact, that this reagent is still very sensitive when sulphuret of sodium has no longer any perceptible action. The conditions requisite for the success of the operation are: 1st, to take care that the copper employed is perfectly *free* from oxide; 2nd, to be certain that, after contact with the copper, no gold remains in solution; 3rd, to saturate the mixture exactly with pure sulphuric acid after the reaction; 4th, to mix as quickly as possible, at a gentle heat, the copper and the bicarbonate to the solutions of the terchloride of gold; 5th, to add to the test liquid, which has been made shortly before use with precaution, and only by drops, when but a slight chestnut or dark red precipitate is produced.

M. Henry quotes a number of experiments, the results of which prove the exactness of the process, as well as the ease and quickness with which it may be performed.

Separation of Gold from Platinum.—The alloy is boiled in aqua regia, and the gold reduced by oxalic acid; from the filtered solution the platinum may be thrown down in the metallic state by by formic acid; or the platinum may first be precipitated from the hydrochloric solution by chloride of potassium, and the gold in the filtrate may then be reduced by protosulphate of iron.

Separation of Gold from Antimony, Tin, and Arsenic.—This may be effected in the same manner as the separation of

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[*] Journ. de Pharm., Jan., 1847; and Chem. Gaz., May 15th, 1847.

platinum from these metals, viz., by heating the mixed sulphurets in a stream of chlorine gas. The chlorides of tin, antimony, and arsenic distil over, while the gold remains behind. *Dr. Elsner* employs metallic zinc as the precipitant for gold, which he finds to remove the metal from a solution of its chloride more effectually than protosulphate of iron. For the quantitative determination of gold, however, in a mixture of platinum, gold, and tin, he prefers protosulphate of iron, on account of the greater simplicity of the operation. He first precipitates the platinum by a concentrated solution of chloride of ammonium, and afterwards the gold from the filtrate by a recently prepared solution of protosulphate of iron. He found that, when an excess of this reagent was employed, the filtrate from the precipitate still gave a beautiful dark red colouring with protochloride of tin, though no precipitate was observed.

Analysis of Alloys of Gold.—Several methods are employed. In the first place, an approximation to the relative proportions of the constituents is obtained by the touch-stone and the assay-needle: the former is a black and polished basalt; black flint and pottery will serve the same purpose. The assay-needles are small fillets of gold, alloyed with different and known quantities of silver or copper: the sets may consist of pure gold; pure gold, 23½ carats, with half a carat of silver[*]; 23 carats of gold, with one carat of silver; 22½ carats of gold, with 1½ carat of silver, and so on till the silver amounts to four carats, after which the additions may proceed by whole carats. Other needles may be made in the same manner, with copper instead of silver, and other sets may have the addition, consisting either of equal parts silver and copper, or such proportions as the occasions of business require. When a specimen of gold is about to be examined, it is rubbed on the touch-stone, and the colour which it leaves is compared with that communicated to the stone by the assay-needles taken successively; that which leaves a mark most nearly resembling that produced by the specimen is in composition most nearly allied to it, and, as the composition of the needle is known, so the operator is enabled to judge of the quantity of silver necessary to be added for the *quartation* proof. The alloy is next cut into small thin plates, and fused in the cupel (see *Silver*), with 3½ times as much pure silver as it contains gold, and with three or four times its weight of lead. After the operation, the gold and the silver remain, the oxide of copper being absorbed with the oxide of lead by the cupel. This process is termed *quartation*, because the gold forms one-fourth part of the cupelled alloy, a proportion which admits of the complete subsequent extraction of the silver by the action of nitric acid. The alloy of gold and silver is next reduced to thin plates, weighed, and gently heated with nitric acid, diluted, and quite free from nitrous and hydrochloric acids; the silver dissolves, the gold remaining untouched. The acid being saturated, a stronger acid is added, and the solution is gradually brought to boil, by which the perfect separation of the silver is accomplished, the gold retaining still the form of the original plate. It is, therefore, easily weighed; previous to which, however, it must be washed with distilled water, as long as any traces of silver appear, by the test of common salt, and then heated to redness. The loss which the mass experiences by the process of cupellation indicates the quantity of copper contained in the alloy, and the proportion of silver is afterwards found by the action of the nitric acid. It must particularly be borne in mind, that if the nitric acid be not free from nitrous acid, and especially from hydrochloric acid, a portion of the gold, sufficient to affect seriously the result of the assay, may be dissolved.

Purification of Gold by Cementation.—The alloy is reduced to a thin plate, and surrounded in a crucible with a pulverulent mixture of four parts of brick-dust, one of calcined vitriol, and one of common salt. It is then exposed for 16 or 18 hours to a strong red heat. The vapours of hydrochloric and sulphuric acids which are formed attack the metals mixed with the gold, and the mass is prevented from fusing by the brick-dust. If the first cementation has not been found sufficient to purify the gold, the operation is repeated, but, in the place of common salt, nitre is used. The same method is employed to refine the surface of gold articles after they

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[*] In estimating or expressing the fineness of gold, the whole mass spoken of is supposed to weigh twenty-four carats of twelve grains each, either real or merely proportional like the assayers' weights; and the pure gold is called fine. Thus, if gold is said to be twenty-three carats fine, it is to be understood that, in a heap weighing twenty-four carats, the quantity of pure gold amounts to twenty-three carats.—*Dr. Ure's Chemical Dictionary.*

are polished. The cementation here produces the same effect as tartar and salt, in which silver goods are boiled to give them a white colour.

Purification by Fusion with Sulphuret of Antimony.—Some borax is fused in a crucible, so that the walls become lined with the vitrified flux; a mixture of two parts of sulphuret of antimony and one of the gold to be assayed is then introduced. The sulphur combines with the foreign metals, and the antimony unites with the gold; the alloy being removed, the scoriæ are a second time fused, with the addition of two parts more of sulphuret of antimony, and, when the whole of the gold is extracted, the various alloys are mixed together and heated in an open vessel, with two parts of sulphur. The sulphuret of antimony volatilizes, leaving the gold pure; to increase the action, a current of air from a pair of bellows may be directed on the surface of the melted mass, or, what is perhaps still better, the mixture of the two metals may be fused in a large crucible, with three times its weight of nitre, by which the antimony becomes oxidized and dispersed, the gold remaining untouched. Another method is to fuse the gold alloy with a mixture of *oxide of lead* and *sulphur*, and to add to the fused mass charcoal in the state of fine powder; the gold is thus obtained alloyed with the lead only, from which it may be separated by cupellation.

Selenium.

When existing in solution in the form of *selenious acid*, it is reduced by sulphite of ammonia, which separates selenium in the form of a cinnabar red powder, which, if boiled, becomes black; it is collected on a filter, and dried at a very gentle heat: nitric acid, if present in the solution, must be decomposed and expelled by hydrochloric acid, previous to the addition of the sulphite of ammonia. When, however, selenium is contained in a solution, as *selenic acid*, it must first be reduced to selenious acid by boiling with hydrochloric acid, if it be intended to precipitate it by sulphite of ammonia. As, however, it is difficult entirely to convert *selenic* into *selenious acid* by hydrochloric acid, *Rose* recommends that the estimation of selenic acid be effected by precipitating it in the form of seleniate of baryta, by nitrate of baryta, which, when washed, dried, and ignited, has the following composition:

One equivalent of SeO_3	63.57 ...	45.34
One ditto of BaO	76.64 ...	54.66
One ditto of BaO, SeO_3	140.21	100

As selenium is precipitated from its solution when in the form of selenious acid by sulphuretted hydrogen, it may thus be separated from all those substances which are not precipitated by that reagent. *Selenic acid* does not, however, possess the property of being precipitated by sulphuretted hydrogen; when selenium, therefore, exists in this state, and has to be separated from other substances, it must either be precipitated as seleniate of baryta, or reduced to selenious acid. From the metals of the Fifth Group selenious acid may be separated by hydrosulphuret of ammonia, in which sulphuret of selenium is soluble; and from the other metals of the Sixth Group it may be separated by converting it into selenic acid, which remains, as before observed, unaltered by sulphuretted hydrogen gas.

Analysis of Seleniate of Lead.—It is reduced to a fine state of division, and diffused in water, through which a current of sulphuretted hydrogen is passed; the liquor filtered from the sulphuret of lead is boiled, to expel the excess of sulphuretted hydrogen, and the selenic acid precipitated as seleniate of baryta; in this way selenic acid may be separated from other metals which are capable of precipitation by sulphuretted hydrogen.

Tellurium.

Like *selenium*, this metal is best precipitated from its solution when in the state of oxide, by sulphite of ammonia; the precipitation must be effected at a boiling temperature, and the solutions should contain free hydrochloric, but not nitric acid. From those oxides which are not precipitated by sulphuretted hydrogen, it may be separated by that reagent. The sulphuret of tellurium is decomposed by digestion with aqua regia, and subsequently reduced by sulphite of ammonia. From the metals of the Fifth Group, tellurium is separated by hydrosulphuret of ammonia. From gold and platinum it may be separated by ignition in a glass tube through which a stream of chlorine is passing. Chloride of tellurium is volatilized, and may be received into a vessel containing very dilute hydrochloric acid, in which it dissolves, and out of which it may be precipitated by sulphite of ammonia. From arsenic, tellurium may, according to *Berzelius*, be separated by distillation, reguline tellurium remaining behind.

Tungsten.

The method proposed by *Berzelius*, for quantitatively estimating tungstic acid, was to precipitate it from its neutral or alkaline solution in the form of sulphuret of tungsten by hydrosulphuret of ammonia, and then to add excess of the reagent, by which the sulphuret is dissolved; from this solution it is reprecipitated by nitric acid, and, having been washed and dried, it is roasted by a gentle heat, whereby it becomes converted into tungstic acid, in which state it is weighed. The composition of tungstic acid is

One equiv. of W (Wolfram)	94.64	79.77
Three do. of O	24.00	20.23
One do. of WO_3	118.64	100

A method of determining the quantity of tungstic acid in neutral salts, by nitrate of mercury, has also been described by *Berzelius*. The following is the plan proposed by *M. Marguerite*[*]. He recommends it as being very simple and perfectly exact.

The salt to be analyzed is placed in a small platinum crucible, and several times its weight of pure concentrated sulphuric acid added. At first a gentle heat is employed, and then the temperature is gradually raised to a red heat. After calcination, the residue is composed of an acid sulphate and of free tungstic acid. It is thrown on a filter, washed with water, charged with sal-ammoniac, which prevents the tungstic acid from combining with water, and from passing through the filter, which frequently happens, even when it has been ignited. When the last washings no longer precipitate chloride of barium, the residue is ignited to drive away the sal-ammoniac, and a few drops of nitric acid added to obviate any error that might arise from a slight reduction which the tungstic acid may have undergone, and to insure the perfect combustion of the last traces of charcoal of the filter. In this way the tungstic acid may be directly determined.

Analysis of Insoluble Tungstates.—They are fused with carbonate of potassa in a platinum crucible, by which operation tungstate of potassa is formed, which salt, being soluble in water, may be treated with hydrosulphuret of ammonia as above directed.

Analysis of Wolfram.—This mineral, which is a double tungstate of iron and manganese, is best analyzed, according to *Wöhler*, by mixing it in a finely divided state with two parts of dry chloride of calcium and fusing in a platinum crucible. The melted mass is treated with water, which dissolves out the chlorides of manganese and iron, and leaves the tungsten in the form of insoluble tungstate of lime.

Molybdenum.

This metal is weighed in the form of the gray bisulphuret. It is precipitated from its solution in hydrosulphuret of ammonia by hydrochloric or acetic acid. The compound thus precipitated is the tersulphuret, which may, indeed, be converted by ignition into molybdic acid (MO_3); but it would not be safe to estimate the metal in this form, because, at the temperature necessary to decompose the tersulphuret, a portion of molybdic acid would be volatilized. *Rose*, therefore, directs the precipitate occasioned by adding hydrochloric or acetic acid to the solution of tersulphuret of molybdenum in hydrosulphuret of ammonia to be gently ignited in a small weighed retort, by which it loses one of its atoms of sulphur, leaving the bisulphuret, which has the following composition:

One equivalent of MO	47.88	59.94
Two do. of S	32	40.06
One do. of MOS_2	79.88	100

From all the metallic oxides, the sulphurets corresponding to which are not soluble in hydrosulphuret of ammonia, *molybdenum*, like *tungsten*, may be separated by that reagent. For this purpose, the compound is dissolved in excess of hydrochloric acid; should *lead* or *silver* be present, the chlorides thus formed are removed by filtration, excess of hydrosulphuret of ammonia containing excess of sulphur is added, and the mixture digested for an hour. It is then filtered, the filtrate containing the tersulphuret of molybdenum is supersaturated and digested with acetic or hydrochloric acid, and the precipitate treated as above directed.

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[*] Comptes Rendus, Feb. 3, 1845; and Chem. Gaz., vol. iii. p. 183.

ACIDS.

1. *Acids of Sulphur.*

Quantitative estimation of Sulphuric Acid.—This is always effected by converting it into *sulphate of baryta.* If the substance to be examined be dissolved in water, it must be acidified with pure hydrochloric acid heated nearly to ebullition, and chloride of barium or nitrate of baryta gradually added till no further precipitation occurs. The sulphate of baryta formed usually subsides quickly and completely, but it must be allowed to settle thoroughly before it is filtered ; it is washed on the filter repeatedly with boiling distilled water, dried, and ignited, the weight of the ash left by the filter, which has been determined by a previous experiment, being deducted : for the composition of sulphate of baryta, see page 149. If the substance analyzed be dissolved in nitric acid, it must be well diluted with distilled water before it is precipitated by a baryta salt, otherwise nitrate of baryta may be thrown down, which would afterwards require long-continued washing to remove ; in all cases, the operator must be careful to wash the precipitate on the filter till the washings no longer give any cloudiness when dropped into dilute sulphuric acid. Should the substance under examination be insoluble in water and in hydrochloric acid (sulphates of baryta, strontia, lime, or lead, for example), it must be fused in a platinum crucible (porcelain in the case of lead) with about four times its weight of a mixture of carbonate of soda and carbonate of potassa, the whole having been previously well mixed by trituration in a mortar ; the mass should be kept in a state of fusion for some time, to insure complete decomposition, and, when cool, transferred to a dish, and digested with distilled water repeatedly, till all the soluble matter is removed ; this consists of the whole of the sulphuric acid of the compound analyzed, in combination with soda and potassa, together with the excess of the alkaline carbonates ; the base or bases with which the acid had been previously in combination remain in the form of insoluble carbonates, and are to be determined in the manner directed in the preceding pages. The sulphuric acid is precipitated from the solution by nitrate of baryta or chloride of barium, having previously supersaturated the liquid with hydrochloric acid, or with nitric acid if lead be present ; the precipitant in that case being nitrate of baryta.

Estimation of Sulphurous Acid.—The precipitate which this acid forms with barytic salts is soluble in hydrochloric acid, by which it is at once distinguished from sulphate of baryta ; when a soluble sulphite, or a salt of any of the other lower acids of sulphur is presented for analysis, it is converted into sulphate by careful and protracted digestion with nitric acid, or with aqua regia : dry *sulphites, hyposulphites,* and *hyposulphates* may also be converted into sulphates by fuming nitric acid. When a mixture of a sulphate and a sulphite has to be examined, two different portions of the compound are analyzed ; in one the quantity of *sulphuric* acid is determined in the ordinary manner, namely, by precipitating it from its hydrochloric solution by chloride of barium or nitrate of baryta ; the other portion is digested with nitric acid or with aqua regia, and, the sulphite being thus converted into sulphate, the solution is also precipitated by a barytic salt. The difference in the two quantities of sulphuric acid found furnishes the data for calculating the proportion of *sulphite* in the compound. The same method may be adopted for analyzing mixtures of sulphates with salts of any of the other lower acids of sulphur.

*MM. Fordos and Gelis' method of analyzing a mixture of the different compounds of Sulphur with Oxygen**.—The process is founded on the different action which chlorine and iodine exert on the acids of sulphur†. Thus, nei-

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* Journ. de Pharm., June, 1843; and Chem. Gaz., July 15th, 1843.

† Six of these compounds have been well made out, and the existence of several others is probable; the six well-defined acids have the following composition : — SO_3, SO_2, S_2O_2, S_2O_5, S_3O_5, S_4O_5, and they have been thus classified by Berzelius :—

Monothionic	SO_3, SO_2,	Sulphuric and sulphurous acids.
Dithionic	S_2O_3, S_2O_5	Hyposulphurous and hyposulphuric acids.
Trithionic	S_3O_5	Sulphyposulphuric acid of *Langlois.*
Tetrathionic	S_4O_5	Bisulpho-hyposulphuric acid of *Fordos* and *Gelis.*

Besides these, a new series of acids of sulphur has been announced by Plessy (Comptes Rendus, Aug., 1845), to which he assigns the following composition :—S_5O_6, S_5O_7, S_6O_7, S_8O_{10}; and M. Wackenroder, and MM. Fordos and Gelis, have each described an acid having the composition S_5O_5.

ther of these bodies exerts any action on sulphuric or hyposulphuric acids, while they rapidly convert sulphurous into sulphuric acid. On passing a current of chlorine into a dilute solution of a hyposulphite, sulphur is precipitated, and sulphurous acid disengaged; and, on passing the gas into a solution of the sulphyposulphuric acid of *Langlois*, or the bisulphyposulphuric acid of *Fordos* and *Gelis*, the whole of the sulphur becomes converted into sulphuric acid; again, iodine, though without any action on the sulphohyposulphates exerts an action of a peculiar nature on solutions of the hyposulphites. *MM. Fordos* and *Gelis* apply these facts to the analysis of mixtures of salts of the different acids of sulphur. Thus, suppose the solution to contain a sulphate, a sulphite, a hyposulphite, a hyposulphate, and a bisulpho-hyposulphate. The liquid is divided into two equal portions.

1. The sulphuric acid is determined by chloride of barium, the precipitated sulphate of baryta being washed first for some time with boiling distilled water, and then with water rendered slightly acid with hydrochloric acid; the solution must not be acid previous to adding the chloride of barium, or a partial oxidation of the sulphurous acid may take place, thus occasioning too large an amount of sulphate of baryta.

2. Another portion is mixed with a considerable quantity of carbonate of magnesia, and saturated with iodine, the quantity required being carefully noted; the amount of sulphuric acid contained in the liquid is again determined by chloride of barium; the quantity of sulphate of baryta obtained will be greater than in the first experiment, and the increase will indicate the quantity of sulphurous acid and the weight of iodine which it was necessary to employ in order to convert it into sulphuric acid; when this point is attained, it is easy, without having recourse to any other experiment, and by a simple subtraction, to procure all the elements necessary for the determination of the amount of hyposulphurous acid. The quantity of iodine which had been required to convert the sulphurous acid into sulphuric is subtracted from the total amount employed; the difference will have been absorbed by the hyposulphurous acid: *two* equivalents of this acid absorb *one* of iodine. In treating the liquid with iodine, an alcoholic solution of known strength is employed, or small fragments of iodine are added by degrees to the liquid from a flask, the weight of which has been previously determined. The solution is very rapid, and the point of saturation is easily ascertained. As soon as the liquor acquires a yellow colour, no more should be added. The change of colour is very striking, and it is quite useless to add starch or any other foreign body to the solution. The necessity of adding carbonate of magnesia to the liquid previous to the addition of the iodine arises from the fact, that water is decomposed by the *sulphite*, which is also in solution; it becomes sulphate, taking oxygen from the water; at the same time the iodine takes the hydrogen, and hydriodic acid is formed; but this acid would, if at the moment of its production it did not find a base to saturate it, act on the undecomposed portion of the sulphite or on the hyposulphite, which the liquid likewise contains, and there would be a loss of sulphurous acid and a deposit of sulphur.

3. This portion of the liquid is employed to determine the amount of bisulpho-hyposulphuric acid. It is saturated with iodine, without, however, keeping any account of the quantity employed. The iodine forms as before a sulphate at the expense of the sulphite, and a bisulpho-hyposulphate at the expense of the hyposulphite. This quantity will go to increase that already contained in the solution. This being done, about 100 parts of water are added to the liquid under examination, through which a current of chlorine is then passed. This gas will bring to the state of sulphate the whole of the sulphur of the bisulpho-hyposulphate, without attacking that of the ordinary hyposulphite. When the saturation is complete, chloride of barium is added to the solution; the weight of the sulphate of baryta obtained will represent the sulphur of the sulphate, of the sulphite, of the hyposulphite, and of the bisulpho-hyposulphite. As the operations made with the first and second portions of the liquid will have indicated the quantity of sulphur contained in the three first, the difference between the two weights will serve to determine the amount of sulphur contained in the latter, and consequently its entire amount.

4. There will now only remain the hyposulphuric acid. To determine this it will suffice to know the total amount

of sulphur in the mixture analyzed; for then, after having assigned to the four other acids the amount pertaining to them, the difference must of course belong to the hyposulphuric acid. The solution is evaporated to dryness, a small quantity of caustic soda being added, to retain the sulphurous gases; the solid residue is treated in the usual manner with fuming nitric acid, and the amount of sulphur determined by chloride of barium.

Quantitative estimation of Hydrosulphuric Acid (Sulphuretted Hydrogen).—The best precipitant is *arsenious acid;* if the acid be in solution in water, as, for example, in certain mineral springs, the water is mixed with a clear solution of arsenious acid in hydrochloric acid, and the precipitate which forms allowed to subside; it is then collected on a filter, washed with cold water, dried at 212°, and weighed: for the composition of sulphuret of arsenic see page 195. If the hydrosulphuric acid is evolved in the gaseous form, the substance from which it is expelled is heated in a flask, and the gas received into a vessel containing a solution of arsenious acid in caustic potassa: the last traces of the gas are removed from the flask by pouring into it solution of bicarbonate of potassa. The operation being completed, the alkaline ley is supersaturated with hydrochloric acid, and the sulphuret of arsenic thereby precipitated collected, dried, and weighed.

Analysis of Compounds of Sulphur with Bases.—Sulphur is readily detected in sulphurets and in sulphates by fusing the sample with soda upon charcoal before the blowpipe; a hepar is thus obtained, which, on being moistened, is easily recognised by means of silver; as, however, it may still be uncertain whether the sulphur existed in the compound in the form of a sulphate or of a sulphuret: *Von Kobell* has suggested the following simple method of solving the question: The finely pulverized sample is boiled with caustic potassa in a porcelain crucible, and heated till the potash begins to melt, or the sample is fused with hydrate of potassa in a platinum spoon before the blowpipe. The mass is then dissolved in a little water, and filtered; a bright strip of silver is placed in the solution; and, if the sample contains a sulphuret, the hepatic reaction is frequently immediately perceptible, but sometimes only after a few hours. With very small quantities the platinum spoon, with the flux, may be placed in a small glass with some water, and the silver introduced. The silver is easily restored to brightness by rubbing it with leather and a little caustic lime: sulphates after such treatment have no reaction on the silver.

Separation of Sulphur from the Alkalies and Alkaline Earths.—If the compound be soluble in water, its solution may be mixed with a solution of *chloride of copper*, upon which sulphuret of the latter metal is precipitated. The precipitate is collected on a filter as quickly as possible, to prevent the oxidation of a portion of the sulphuret, and then treated with red fuming nitric acid, by which the sulphur is brought into the state of sulphuric acid, and may then be precipitated with the proper precautions by a soluble salt of baryta. The weight of the sulphate of baryta obtained furnishes data for calculating the amount of sulphur present in the substance analyzed. If the sulphuret to be examined be not readily soluble in water, it may be decomposed in a flask by dilute sulphuric or hydrochloric acid, the hydrosulphuric acid evolved being conducted through a series of Wolfe's bottles (*Fig.* 49, Part I.), about two-thirds filled with a neutral solution of chloride of copper; three bottles may be employed, the latter containing, in addition to the metallic chloride, a little caustic ammonia, to insure the complete absorption of the hydrosulphuric acid gas. The gas remaining in the flask at the end of the operation must be driven forward into the bottles by a current of carbonic acid gas. This is effected by pouring into the flask through its funnel a solution of carbonate of ammonia, not, however, sufficient to neutralize the acid, because it may happen that a portion of sulphur has been deposited in the generating flask during the decomposition, which it would of course be necessary to collect on a tared filter, wash, dry, and weigh; but if the liquor were rendered alkaline, supposing the sulphuret of an alkaline earth to have been under examination, an insoluble carbonate would be precipitated, which would render the collection of the sulphur difficult.

Metallic sulphurets may be analyzed in the dry way by mixing them with thrice their weight of dry carbonate of soda and an equal quantity of nitre, to which must be added a considerable quantity of pure and dry common salt;

if the sulphuret loses sulphur by heat, the mixture is kept for some time in fusion in a porcelain crucible; by this operation the sulphur is separated from the metal with which it was originally combined, and is transferred in the form of sulphuric acid to the alkali; a soluble sulphate is thus produced, which may be precipitated by nitrate of baryta, and the quantity of sulphur calculated from the weight of the sulphate of baryta formed.

Dr. Geo. Kemp[*] applies this method to the analysis of copper ores in the following manner:—A portion of the ore is carefully mixed with about three times its weight of pure *chlorate of potassa*, previously fused, and the mixture is introduced into a Bohemian glass tube about six inches in length; another portion of chlorate is used to remove the last portion of the mixture from the mortar, finishing the contents of the tube by adding another small quantity of perfectly pure chlorate in powder. The tube is thus nearly one-third filled. Having provided a passage for the gas given off in the usual way[†], the tube is exposed to the heat of a Berzelius's spirit lamp, commencing at the upper part of the mixture and proceeding downwards; in the course of a few seconds the oxidation is complete, and the contents of the tube, when cold, carefully washed out with nitro-hydrochloric acid into a small digesting flask, and placed on the sand bath; after a few minutes' digestion a clear solution is obtained, containing all the *copper*, *iron*, and *sulphate of potassa*, while the silica remains as a precipitate. Having diluted the solution, the metals and the sulphur are precipitated and estimated in the usual way.

Determination of Sulphur in Iron.—*Dr. Bromeis*[‡] passes the gas obtained by acting on the iron, with dilute sulphuric acid, through an ammoniacal solution of silver, contained in an apparatus similar to that employed by *Will* and *Varrustrap* for nitrogen analyses; the whole of the hydrosulphuric acid is absorbed, and is determined as sulphuret of silver.

Determination of Sulphur in Sulphuret of Lead.—The sulphur is converted into sulphuric acid by digesting the ore in fuming nitric acid; the sulphate of lead produced is dissolved in hot caustic potassa, the alkaline solution is filtered from the insoluble matters, and the lead again precipitated as sulphuret by sulphuretted hydrogen; it is received on a filter, washed, dried, and digested in a weighed platinum capsule with fuming red nitric acid; it is thus again converted into sulphate, in the form of which salt it is weighed.

Sulphuret of silver and *sulphuret of bismuth* must be decomposed by pure nitric acid; the substances should be reduced to as fine a state of division as possible, and projected into a flask capable of being closed with a stopper, and containing the very strongest fuming nitric acid; the bottle must be closed the moment the sulphuret is introduced, and occasionally agitated; when the action slackens, a gentle heat may be applied. In the case of *sulphuret of silver*, should any of the sulphur have escaped oxidation, it may be dissolved by adding, in small portions, chlorate of potassa; but, in the case of *sulphuret of bismuth*, the unoxidized sulphur must be collected on a tared filter, washed with acetic acid, dried, and weighed; from the clear filtrate the bismuth is precipitated by sulphuretted hydrogen, and from the filtrate from the precipitated sulphuret of bismuth, the sulphuric acid is precipitated by a salt of baryta, having first acidified it with hydrochloric acid.

Separation of Sulphur from Metals by Chlorine Gas.—This method is applicable to the analysis of compound sulphurets of those metals, the chlorides of which are not volatile at a low red heat. The substance is introduced into a bulbed tube connected with an apparatus by means of which a stream of dry chlorine gas may be passed through it. The disposition of the apparatus is seen in *fig.* 32; *a* is the flask containing the materials for generating chlorine gas, which is dried by passing first through the Wolfe's bottle *b*, containing concentrated sulphuric acid, and then through the siphon-shaped tube *c*, containing chloride of calcium; the sulphuret to be analyzed is weighed, and carefully introduced into the bulbed tube *d*, bent at right angles, and dipping into water contained in the bottle *e*. If the process cannot be conducted under a flue, it may be advisable to close the mouth of the bottle

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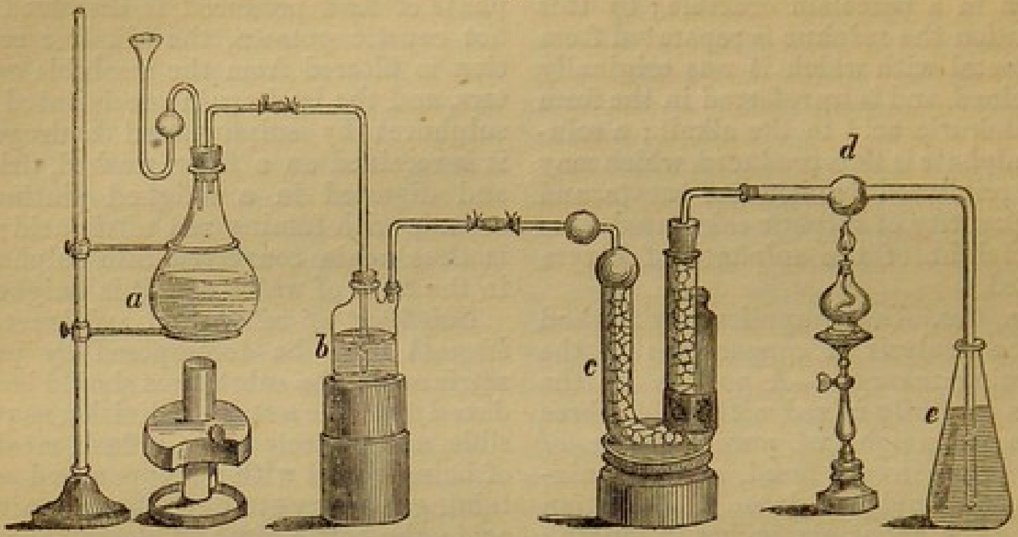
[*] Chem. Gaz., vol. ii. p. 215.

[†] This operation will be minutely described further on.

[‡] Ann. der Chem. und Pharm., Sept., 1842; and Chem. Gaz., vol. i. p. 160.

Fig. 32.



e with a cork, through which a tube is inserted which may convey the excess of chlorine into another bottle, containing milk of lime or potash, thus preventing annoyance to the operator by the escape of the irritating gas into the apartment. The whole apparatus is first filled with chlorine, which is made evident by the yellow green colour of the space above the water in the bottle *e*, a very gentle heat is then applied to the bulb, the sulphuret is decomposed, its metallic base or bases combining with the chlorine, while the sulphur is driven forward into the bottle *e* in the form of *chloride of sulphur*, which is immediately decomposed by the water into hyposulphurous acid, hydrochloric acid, and sulphur; the former, by the action of the chlorine, passes into sulphurous acid and finally into sulphuric acid, so that the last result of decomposition is sulphuric acid, hydrochloric acid, and a greater or less quantity of free sulphur. When the action is over, the bulb is heated towards the bend, so as to force the whole of the chloride of sulphur into the bottle *e;* the tube is then cut off under the bend, and the separated end thrown into the bottle. The excess of chlorine is expelled from *e* by the application of a gentle heat, it is allowed to remain at rest for some hours till the sulphur has completely solidified, it is then collected on a tared filter, washed, dried, and weighed, and the sulphuric acid is lastly precipitated by nitrate of baryta or chloride of barium.

Rose applies the above method to the analysis of mixed sulphurets of those metals the chlorides of which are either partly or wholly volatile at the temperature employed. For example, in the analysis of the mixed sulphurets of *antimony, iron,* and *zinc;* in such a case, the water in the bottle *e* must be mixed with tartaric acid and a small quantity of hydrochloric acid; and the chloride of antimony which distils over into the bottle *e* is precipitated by sulphuretted hydrogen, after the free sulphur has been removed by filtration, and the sulphuric acid by a soluble salt of baryta. If the heat employed has not been too great, the whole of the chloride of zinc, and the greater part of the perchloride of iron, will be retained in the bulb; a certain portion of the latter, however, will have been volatilized, and will have found its way into the liquid in the bottle *e*, from which, together with any chloride of zinc which may also have distilled over, it must be precipitated after the removal of the antimony, by hydrosulphuret of ammonia.

The methods of separating sulphur from organic substances will be described further on.

2. *Acids of Phosphorus.*

1. *Phosphoric Acid.*—In a solution which contains nothing but phosphoric acid, the amount of that acid may be estimated by evaporating to dryness with the addition of a known weight of recently ignited protoxide of lead; the residue, after being heated to redness, is weighed, the increase of weight indicates the amount of phosphoric acid.

The presence of nitric acid does not interfere with the accuracy of this method.

The quantitative determination of phosphoric acid, when in combination with bases and in the presence of other acids, is frequently attended with considerable difficulties, especially when it exists in small quantities only. The following are the principal methods at present in use.

Estimation as Pyrophosphate of Magnesia.—Chloride of ammonium, ammonia, and sulphate of magnesia are added to the solution, which is then well agitated, or stirred with a feather; a glass rod should not be used for the purpose, as the crystalline double salt which is precipitated adheres so firmly to those parts of the sides of the beaker which have been touched by the glass rod that it cannot afterwards be readily removed. The mixture is allowed to remain at rest for several hours; it is then filtered, and the precipitate washed with water containing a little ammonia, in which it is almost insoluble; the washing must not be continued too long, but stopped immediately it is found that a few drops of the filtrate, when evaporated on platinum foil, leave no residue; it is then ignited, first gently and afterwards strongly: for the composition of the ignited salt, see p. 151. This method does not apply to the analysis of phosphates after they have been ignited, without a previous preparation, as has been shown by *Weber**; the reason is, that they are converted by heat from tribasic into bibasic salts, and bibasic or pyrophosphoric acid forms with magnesia a salt which is much more soluble in water than tribasic or common phosphoric acid. By the action of acids it is true that pyrophosphoric acid is converted into the tribasic acid, but Weber found that the transformation was not perfect, even when the compound was treated for a considerable time with concentrated sulphuric acid. In order to ascertain which of these two phosphoric acids we have under examination, the following test may be applied. The compound is dissolved in nitric acid and reprecipitated by ammonia; the precipitate, after long standing, is collected on a filter; to the filtrate, nitrate of silver is added, and the ammoniacal liquid is then carefully neutralized with nitric acid; the appearance of a white turbidness, or the formation of white flakes, indicates the presence of pyrophosphoric acid. When the phosphoric acid in a phosphate is to be separated and determined by magnesia, and is not contained in the solution as the tribasic compound, the phosphate must be fused with excess of carbonate of soda. This can be done in all cases when the phosphoric acid is combined with the alkalies or those metals which are completely decomposed by fusion with carbonate of soda; but it does not succeed in converting the phosphoric acid into the tribasic compound in its combinations with the alkaline earths, as these are only imperfectly decomposed. The only way to reprecipitate entirely the pyrophosphate of magnesia from its solutions by ammonia is to heat it for some time with concentrated sulphuric acid, when, on solution, it can be almost entirely precipitated by ammonia.

The precipitates which the tribasic and bibasic phosphoric acids produce with magnesia differ essentially from each other in their external properties. The first is granular, crystalline, and soon subsides, especially when warmed; the latter is voluminous and flocculent, and remains long suspended in the liquid. Small quantities of pyrophosphoric acid cannot be separated or even detected by magnesia.

Estimation by a Standard Solution of Permanganate of Potash.—Raewsky's Method.—This process consists in bringing the acid to the state of pure perphosphate of iron, which is collected, and the amount of iron in it determined. The author has ascertained, by numerous experiments, that the perphosphate of iron in the state in which it is obtained in this experiment has a uniform composition, viz., $Fe_2O_3\,PO_5$, the relation of the oxygen of the base to the oxygen of the acid being as 3 to 5. The process is conducted as follows. The phosphoric acid compound is dissolved in acetic acid: should it be in combination with bases which yield salts insoluble in acetic acid, it must be separated from them; to the solution is added an excess of a solution of peracetate of iron, or, as this salt is not permanent, it may be made by double decomposition at the very moment it is called into action, with which view 1500 grains of iron alum are dissolved in about a quart of water, and an equal quantity (or rather less) of acetate of soda in another quart of water, equal quantities of each are added

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* Chem. Gaz., vol. v. p. 450.

to the solution. The phosphate of iron immediately separates in the form of slightly yellowish light flakes, the precipitate is collected and carefully washed. The excess of iron passes off in the washing, and the pure phosphate is left on the filter. Hydrochloric acid is then dropped on the filter so as to dissolve the whole; the salt of iron is reduced by means of sulphite of soda, and the amount of iron determined by converting it into peroxide with a solution of mineral chameleon of known strength, according to the method of, and following the precautions indicated by, *M. Marguerite*, see page 170. Having determined the quantity of iron by a simple calculation, and knowing the composition of the perphosphate, the proportion of phosphoric acid is readily found. Thus, supposing phosphate of soda to be the subject of analysis, and that having operated on 0.466 gramme (7.2 grains), 15 divisions of the normal solution have been employed, the strength of which is 54.4 divisions for every 0.250 gramme (3.86 grains) of iron, the iron is then found by the proportion :—

As $54.4 : 0.250 :: 15 : X = 0.069$ of iron.

On the other hand, the composition of the phosphate of iron being known, we have the proportion:—

As $56\,(Fe_2) : 72\,(PO_5) :: 0.069\,(Fe) : X =$ 0.0887 phosphoric acid. Now, in 1 of phosphate of soda there is 0.191 phosphoric acid; consequently we have the proportion :—

$$\text{As } 0.191\,(PO_5) : 1\,(2\,NaO, HO, PO_5) :: 0.0887 : X$$

$X = 0.464$ phosphate of soda, the quantity submitted to analysis was 0.466 gramme.

M. Raewsky found that the same process was applicable to the determination of pyrophosphoric acid, with this difference, that, instead of using the neutral acetate of iron, the solution must be precipitated by a solution of ammoniacal iron alum.

Separation of Phosphoric Acid from Sulphuric Acid.—This is very easily effected by means of chloride of barium, the solution being dilute and acidified with hydrochloric acid.

Separation of Phosphoric Acid from Bases.—This is frequently attended with very great difficulties; wherever it is admissible the quantity of the base is determined, the amount of phosphoric acid in combination therewith being calculated from the loss. When it is necessary to make a direct determination of the acid, it may be done in the following manner.

1. *Separation of Phosphoric Acid from the Alkalies.*—A very accurate method is to add to the solution of the alkaline phosphate a known quantity of solution of pure iron, and then to precipitate with ammonia; the quantity of phosphoric acid present is ascertained by the increase of weight in the precipitate above that which the known quantity of iron should yield. A certain weighed quantity of pure iron (harpsicord wire) is dissolved in nitric acid, and added to the solution under examination; ammonia in excess is then added, which should produce a voluminous red brown precipitate; if it has a white tinge, it is a proof that sufficient iron has not been added: this precipitate is collected on a filter well washed with hot water, dried, ignited, and weighed. It consists of peroxide of iron *plus* a certain quantity of basic perphosphate of iron; suppose, for example, that 10 grains of iron dissolved in nitric acid had been added, and that the ignited precipitate weighed 20.36 grains, we obtain the amount of phosphoric acid by simply subtracting 14.286, the amount of sesquioxide of iron, which 10 grains of metallic iron yield from 20.36, and we find that the phosphate under analysis contains 6.074 grains of phosphoric acid. The alkalies in the filtrate from the precipitate are determined as directed in page 141.

Tribasic alkaline phosphates are very conveniently analyzed by precipitating their aqueous solutions with neutral nitrate of silver. The composition of the ignited precipitate which is yellow is

Three equiv. of AgO ...	348 ...	82.85
One ditto of PO_5 ...	72 ...	17.15
One equiv. of $3AgO, PO_5$	420	100.

Alkaline phosphates containing one equivalent of basic water give, after ignition, when dissolved in water, a white precipitate with neutral nitrate of silver, the composition of which after ignition is

Two equivalents of AgO	232	76.31
One ditto of PO_5	72	23.69
One do. of $2AgO,PO_5$	304	100.

Indirect Determination of Phosphoric Acid by Oxide of Lead.—Acetate of lead is added in slight excess to an aqueous solution of the substance under examination; a precipitate is produced containing all the phosphoric acid in combination with oxide of lead; but, as this compound is not of invariable composition, it must be analyzed in order to ascertain the amount of phosphoric acid which it contains: with this view it is collected on a filter, washed, dried, ignited, and weighed, it is then dissolved in as small a quantity of nitric acid as possible, and sulphuric acid and alcohol added, the latter for the purpose of preventing the solution of any trace of the sulphate of lead: the sulphate is collected on a filter, washed with dilute alcohol, ignited and weighed; from the weight obtained the equivalent of oxide of lead is calculated, and, this being deducted from the weight of the mixture analyzed, the amount of phosphoric acid is obtained.

Separation of Phosphoric Acid from the Alkaline Earths.—The compound is dissolved in a small quantity of hydrochloric acid, perchloride of iron is next added, and then acetate of soda in excess, the precipitate must have a reddish brown colour; if it has a white tinge, more perchloride of iron must be added; the whole is now heated to ebullition for ten minutes in an evaporating basin, a bulky precipitate subsides, provided a sufficient quantity of alkaline acetate has been added; this is basic phosphate and basic peracetate of iron. It is collected on a filter, and well washed with boiling water. The amount of phosphoric acid which it contains may be determined in two ways.

a. It is dissolved in hydrochloric acid, and, tartaric acid having been added (to prevent the precipitation of peroxide of iron), it is treated with excess of ammonia; a clear transparent yellow liquid is obtained, in which the phosphoric acid is determined as pyrophosphate of magnesia, in the manner already directed.

b. The mixture of basic phosphate and basic peracetate of iron, after being well washed, is ignited with free access of air. To insure the whole of the iron being in the maximum state of oxidation, a few drops of nitric acid are added to the residue in the crucible, which is again ignited, and this is repeated as long as the least increase of weight is observed. It is now digested, crucible and all, with strong hydrochloric acid, and, a perfect solution having been obtained, water is added, then tartaric acid, ammonia in excess, and finally hydrosulphuret of ammonia; a gentle heat is applied, and the mixture is allowed to remain at rest in a warm situation, covered with a glass plate, until the sulphuret of iron has completely subsided, the supernatant liquor having a clear yellow colour; the sulphuret is transferred to a filter, and washed uninterruptedly with as little access of air as possible, with water, to which a few drops of hydrosulphuret of ammonia have been added. The object in keeping the funnel covered with a glass plate during the filtration is to prevent a portion of the sulphuret of iron from being oxidized into sulphate, which, being soluble, would pass through the filter, thus occasioning a serious loss. The sulphuret of iron, having been washed, is dissolved in hydrochloric acid; the solution is peroxidized by the addition of nitric acid, and finally precipitated by ammonia; the weight of the ignited oxide obtained subtracted from that of the original mixture of perphosphate and peroxide gives the amount of phosphoric acid.

This method, which gives very accurate results, is adopted by *Will* and *Fresenius* in the analysis of soils and ashes.

Separation of Phosphoric Acid from Alumina.—This may be effected in two ways: First, the compound is dissolved in nitric or hydrochloric acid, and having added tartaric acid and ammonia, the phosphoric acid is estimated as pyrophosphate of magnesia: in this case the filtrate from the precipitate by sulphate of magnesia will contain magnesia and alumina, which must be separated from each other as directed page 152. Secondly, the phosphate of alumina is heated to intense ignition for half an hour in a platinum crucible, with a mixture of 1½ parts of artificially prepared silicic acid and six parts of carbonate of soda. The ignited mass is digested with bicarbonate of ammonia in excess, and the solution filtered from the insoluble silicate of soda and alumina: the phosphoric acid in the filtrate is determined by adding a known quantity of iron dissolved in nitric acid, and precipitating by ammonia in the manner already described.

Another method of separating alumina from phosphoric acid, recommended by *Fuch*, is to dissolve a known weight of the compound in caustic potassa, and to precipitate the alumina in the form of double silicate of alumina and potassa by a solution of silicate of potassa. The solution filtered from this precipitate contains all the phosphoric acid; it is supersaturated with hydrochloric acid and evaporated to dryness: the residue is dissolved in water, the solution rendered alkaline by ammonia, and the phosphoric acid determined as pyrophosphate of magnesia. The precipitate, consisting of double silicate of potassa and alumina, having been washed, is digested in hydrochloric acid and evaporated to dryness, the residue is moistened with hydrochloric acid, allowed to stand for half an hour, and then treated with water, whereupon the chloride of aluminum dissolves, leaving the silicic acid in its insoluble form, the alumina is finally precipitated from the filtered liquid by carbonate of ammonia.

Separation of Phosphoric Acid from Magnesia, Oxide of Cobalt, and Oxide of Nickel. Von Kobell's Method.—To the nitric or hydrochloric solution of the compound, perchloride of iron is added; it is then precipitated with carbonate of lime; the whole of the phosphoric acid is found in the precipitate, the supernatant liquid containing no traces of it.

Separation of Phosphoric Acid from Oxide of Uranium. Ebelmen's Method.—The phosphate, as precipitated from its solution by ammonia, is dissolved in a solution of bicarbonate of potash; on the addition of caustic potash the oxide of uranium is precipitated in the form of uranate of potash, while the phosphoric acid remains in the alkaline solution. Or the phosphoric acid may be first separated from the solution by the addition of a known quantity of peroxide of iron dissolved in nitric acid, the bicarbonate being in excess; a precipitate falls consisting of the whole of the peroxide of iron and phosphoric acid, the increase of weight of which represents the amount of phosphoric acid. The peroxide of uranium is afterwards estimated in the usual manner.

Analysis of Phosphites and Hypophosphites.—They are converted into phosphates by evaporating to dryness with nitric acid and igniting the remainder. When treated in this manner, the neutral phosphites yield neutral phosphates, while the neutral hypophosphites yield acid phosphates (*Rose*).

The following method of separating phosphoric acid from phosphorous and hypophosphorous acids is likewise given by *Rose:* The solution is poured gradually and in small quantities into a solution of chloride of mercury which must be fully saturated; a precipitate of subchloride of mercury, exhibiting the splendour of mother-of-pearl, is determined, but its complete separation requires gentle digestion for several days: the subchloride of mercury is collected on a filter, dried by exposure to a gentle heat, and weighed. From its weight it is easy to calculate how much oxygen has been taken up by the phosphorous or hypophosphorous acid to effect its conversion into phosphoric acid: hence the quantity of either of these acids is readily inferred. This quantity of oxygen is equivalent to the quantity of chlorine contained in the subchloride of mercury, since the chloride of that metal, on being converted into subchloride, loses exactly one-half of its chlorine. Another quantity of the solution to be analyzed is treated with nitric acid and a weighed quantity of oxide of lead in the manner already described, the object being to determine the whole quantity of phosphoric acid, both that originally contained in the solution and that formed from the phosphorous or hypophosphorous acid, at the expense of the oxygen of the nitric acid. Now, it is learnt by the first operation how much phosphoric acid is produced by the phosphorous or hypophosphorous acid of the solution, and, by deducting this from the whole quantity obtained by the second operation, the actual proportion of phosphoric acid in the solution analyzed is known.

According to *Wohler*[*] phosphorous acid is converted into phosphoric acid by being heated with sulphurous acid, sulphuretted hydrogen being formed and sulphur separated. In this manner he states that phosphorous acid may easily be detected in phosphoric acid: when arsenious acid is present at the same time, the sulphuret of arsenic is immediately formed on treatment with

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[*] Ann. der Chem. und Pharm., xxix. 252; and Chem. Gaz., vol. i. p. 127.

sulphurous acid. Phosphorous acid in phosphoric acid may also be detected by Marsh's apparatus, from the phosphuretted hydrogen which is disengaged. The gas burns with a whitish flame, and when held close to a surface of porcelain a ring of green light is observed in the expanded flame similar to that afforded by phosphorus when burnt in chlorine gas or with an insufficient access of atmospheric air.

Boracic Acid.

Quantitative Estimation of Boracic Acid.—As this acid does not form with any base a compound perfectly insoluble in water, it cannot be determined by direct precipitation, neither can it be estimated even when existing alone in solution by evaporating to dryness, because, although it is one of the most fixed of all substances at an intense heat, it possesses the property of volatilizing with the vapour of water or of alcohol. Boracic acid may be determined by adding to the solution an accurately weighed quantity of pure oxide of lead, evaporating to dryness, igniting, and weighing the residue, and calculating the amount of boracic acid from the increase of weight. The quantity of this acid, in its salts, is best found by determining the quantity of the base accurately and subtracting the amount from the weight of the substance analyzed.

Separation of Boracic Acid from Phosphoric Acid.—The phosphoric acid may be precipitated by sulphate of magnesia, and determined as pyrophosphate, or by *Von Kobel's* method, by the addition, first, of perchloride of iron, and then of carbonate of lime; not a particle of boracic acid is precipitated, but the separation of the phosphoric acid is complete.

Separation of Boracic Acid from the Alkalies.—The alkalies are converted into sulphates by heating for some time with excess of sulphuric acid; the boracic acid is removed by agitating the evaporated mass repeatedly during a considerable time with absolute alcohol, the flask being kept closed.

Separation of Boracic Acid from those fixed Bases with which it forms Compounds decomposable by Sulphuric Acid.—The following method was proposed by *Arfwedson.* A known weight of the compound is reduced to a fine powder, and mixed in a platinum crucible with four parts of pure pulverized fluor spar. It is then moistened with sulphuric acid and heated, first gently, and gradually to redness, at which temperature it is maintained as long as fumes continue to be evolved. The whole of the boracic acid is thus driven off in the form of fluoride of boron ($BO_3 + 3\,FlH = BFl_3 + 3\,HO$). The bases, together with gypsum, remain behind in combination with sulphuric acid; they are separated from each other according to the directions which have been given in the preceding pages, and the amount of boracic acid is calculated from the loss sustained by the original substance after deducting from it the quantities of the different bases found; these determinations must therefore be made with great care, since the whole loss falls on the boracic acid.

When the bases with which boracic acid is combined are precipitable by sulphuretted hydrogen or by hydrosulphuret of ammonia, these reagents are employed to separate them; their quantities must be accurately determined and deducted from the weight of the compound submitted to analysis; the difference of weight is the quantity of boracic acid.

From the alkaline earths boracic acid is separated in the same manner as phosphoric acid, the amount of acid being calculated from the loss.

Determination of Boracic Acid in Silicates undecomposable by Acids (Axinite, Tourmalines).—No methods leading to accurate results are at present known; the following process adopted by *Gmelin*, and given by *Rose*, is the best. The mineral is finely levigated, and heated strongly with carbonate of baryta. The ignited mass is treated with a sufficient quantity of hydrochloric acid to decompose it, and evaporated to dryness on the water bath. The silica is separated from the residual mass in the usual manner, and the baryta precipitated from the filtered solution by carbonate of ammonia. The clear liquid is again evaporated to dryness and gently ignited; it is then weighed and treated with alcohol and hydrochloric acid. The alcohol is inflamed, and in this way the boracic acid is got rid of; the residue is once more ignited and weighed, and the quantity of boracic acid is indicated by the loss of weight. Another method, recommended by the same chemist, is to ignite the pulverized mineral with carbonate of soda, and to treat the ignited mass with water. The solution having been digested with carbonate of ammonia, to remove the small portions of silica and alumina which the water had dissolved, is evaporated to dryness, the dry mass treated with sulphuric acid, and the boracic acid dissolved by digestion with alcohol. The solution is finally saturated with ammonia, and the residue, which consists of boracic acid, is ignited and weighed.

Silicic Acid.

This acid is always converted from its soluble to its insoluble condition, for the purpose of estimation. The conversion is effected by evaporating the solution to dryness with hydrochloric acid, or any other volatile acid. The silicic acid is, generally, first obtained in a gelatinous state; but, by continuing the heat, it loses the whole of its water, and is brought to the condition of a dry powder. The evaporating mass must be constantly stirred with a glass rod during its exsiccation, to prevent spurting. The bases with which the silicic acid was combined are separated by dilute acid, and the silicic acid, having been thoroughly washed and dried, is ignited in a platinum crucible and weighed, when cold, with the cover on, the dry powder absorbing moisture rapidly from the air. For the properties of silicic acid, see Part I. p. 65. Its composition is—

One equivalent of Si	..	21.35	47.08
Three do. of O	..	24.00	52.92
One do. of SiO_3	..	45.35	100.

Separation of Silicic Acid from Bases.—Quantitative Analysis of Natural Silicates.—In the first part of this Treatise* it was remarked that the great natural family of silicates may be arranged in three classes:—1st, those easily decomposable by hydrochloric acid; 2nd, those only decomposable by prolonged digestion with concentrated acid; and, 3rd, those which absolutely resist the action of acids, even after prolonged digestion. We now extract from Rose's Treatise on Analysis† a list of the names and composition of a series of interesting minerals belonging to each of these classes:—

1. *Silicates decomposable by Hydrochloric Acid in the Cold.*

	Combination of.
1. Apophyllite	Potassa, silica, lime, and water.
2. Natrolite	Silica, soda, and water.
3. Scolezite	Silica, alumina, lime, soda, and water.
4. Mesolite	Ditto . . ditto . . ditto.
5. Mesole	Ditto . . ditto . . ditto.
6. Analcime	Silica, alumina, soda, and water.
7. Laumonite	Silica, alumina, lime, and water.
8. Potash harmotone	Silica, alumina, baryta, potash, and water; sometimes lime.
9. Leucite	Potassa, silica, and alumina.
10. Eleolite	Silica, alumina, lime, potassa, soda, and water.
11. Brewsterite	Silica, alumina, strontia, baryta, lime, and water.
12. Sodalite	Soda, silica, and alumina, with a small quantity of hydrochloric acid.
13. Cronstedtite	Silica, oxide of iron, and water.
14. Ilvaite	Silica, protoxide of iron, and lime.
15. Gehlenite	Silica, alumina, lime, and oxide of iron.
16. Wernerite	Silica, alumina, lime, and soda.
17. Tabular spar	Silica and lime.
18. Nepheline	Soda, silica, and alumina.
19. Cancrinite	Soda, silica, and lime.
20. Mellinite	Silica, magnesia, lime, and oxide of iron.
21. Chabasite	Silica, alumina, lime, and water, with a little potassa.
22. Pectolite	Silica, lime, soda, potash, oxide of iron, and water.
23. Okenite	Silica, lime, soda, potash, oxide of iron, oxide of manganese, and water.
24. Davyne	Silica, alumina, lime, iron, and water.
25. Sodolenite	Yttria, silica, glucina, oxides of cerium, and iron.

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* Page 24, "Qualitative Analysis of Natural Silicates."

† Translated, with Notes and Additions, by A. Normandy.

	Combination of.
26. Allophane	Alumina, silica, and water.
27. Helvine	Silica, glucina, alumina, protoxide of iron and of manganese.
28. Datholite	Silica, boracic acid, lime, and water.
29. Botryolite	Differs from the preceding in containing one atom more water.
30. Haüyne	Potash or soda, silica, alumina, lime, and sulphuric acid.
31. Nosian	Sesquisilicate of alumina and soda (Klaproth).
32. Lazulite	Silica, alumina, lime, oxide of iron, magnesia, soda, and sulphuric acid.
33. Eudialite	Silica, soda, zirconia, lime, oxides of iron and manganese, hydrochloric acid, and water.
34. Orthite	Silica, alumina, oxides of iron, cerium, lauthanum, and manganese; lime, yttria, magnesia, and a small quantity of water.
35. Electric Calamine	Oxide of zinc, silica, and water.
36. Sidéroschisolite	Protoxide of iron, silica, alumina, and water.
37. Hisingerite	Silicate of protoxide and sesquioxide of iron + six atoms of water.
38. Dioptase	Silicate of copper and water.
39. Meerchaum	Magnesia, carbonic acid, silica, water, a little alumina, and traces of manganese and lime.
40. Copper, Malachite	Carbonate and silicate of copper and water.

The above minerals, when finely pulverized, form a jelly when hydrochloric acid is poured upon them. The next nine do not form a jelly, and some of them are only decomposed by protracted digestion with hot hydrochloric acid. Nearly all of these minerals resist altogether the action of acids after being ignited.

1. Stilbite	Silicate of alumina, lime, and water.
2. Epistilbite	Ditto . . . ditto.
3. Heulandite	Tersilicate of alumina and lime.
4. Anorthite	Silica, alumina, lime, and magnesia.
5. Sphene or Pitanite	Tersilicate of lime and titaniate of lime.
6. Pyrosmalite	Lime, tersilicate of oxide of iron and of manganese.
7. Cerite	Hydrated silicate of peroxide of cerium.
8. Cerine or Allanite	Silicate of alumina and of cerium, of iron and of lime.
9. Potchblende	Uranium ore, containing from two to five per cent. of silica, probably in a state of mechanical, not chemical, combination.

Silicates only decomposable by fusion with Carbonate of Potassa or Soda.

1. Felspar.
2. Albite.
3. Rhiacolite.
4. Petalite.
5. Spodumene (Soda Spodumene.)
6. Oligoclase.
7. Labradorite.
8. Barytic harmotone.
9. Olivine.
10. Prehnite.
11. Carbonated Manganese.
12. Mica.
13. Lepidolite.
14. Talc.
15. Chlorite.
16. Pinite.
17. Achmite.
18. Amphibole.
19. Anthrophyllite
20. Pyroxene.
21. Diallage.
22. Chaloyant or Schiller Spar.
23. Epidote.
24. Idocrase.
25. Garnet.
26. Dichroite.
27. Emerald.
28. Euclase.
29. Phenakite.
30. Tourmaline.
31. Axinite.
32. Topaz.
33. Chondrodite.
34. Picrosmine.
35. Carpholite.
36. Steatite.
37. Serpentina.
38. Pumice stone.
39. Obsidian.
40. Pitch stone.

To this class belong also the different species of false gems and artificial glass.

Silicates which resist the action of Acids and fusion with Alkaline Carbonates, but which are decomposed by ignition with pure Potash.

1. Zircon.
2. Cyanite.
3. Cymophane.
4. Staurolite.
5. Andalusite.

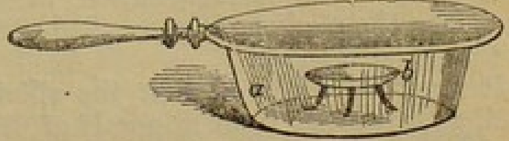
1. *Decomposition of Silicates by Acids.*—The mineral is reduced to the finest

possible powder, according to the instructions given, page 94, Treatise I., without, however, employing the elutriating process. It is dried at 212°, avoiding a higher temperature, because many of these compounds contain water and other volatile matters, which must not be expelled ; and because, moreover, an elevated temperature might interfere with the readiness with which the silicate is decomposed by acids. The pulverized mineral, having been deprived of its hygrometric water, is weighed in a platinum or porcelain dish, and digested at a gentle heat, until complete decomposition has taken place, which is known by rubbing a glass rod against the bottom and sides of the vessel ; if it produce a grating noise, it shows that the decomposition is not complete, and the digestion must be continued till the end of the rod glides smoothly over the bottom of the dish. The separated silicic acid does not, in all cases, assume the same appearance, as was remarked above: sometimes it separates in a bulky gelatinous state, in other cases no jelly is formed, the acid being liberated in the form of a fine powder: some silicates, again, are decomposed almost instantaneously, while others require long-continued digestion. The operator must bear all these facts in mind ; and, above all, he must assure himself of the complete decomposition of the mineral, or all his time and labour will have been expended in vain. The decomposition being complete, the mass is evaporated to dryness on the water bath, and the residue heated until all moisture is expelled ; the dry mass is then digested with hydrochloric acid, which dissolves out all the bases, leaving the silicic acid in its insoluble modification: it is collected on a filter, washed with boiling distilled water, dried, ignited, and weighed. The filtrate and the washings are quantitatively examined for bases, according to the instructions given in the last chapter. *Rose* objects to the evaporation of the silicate to dryness after its decomposition by hydrochloric acid, partly on the grounds that the whole of the silica is not thereby rendered insoluble, and that portions have still to be separated in the course of the analysis, but chiefly because it is possible that during the evaporation certain volatile constituents of the compound may be expelled, and thus escape detection, which, he says, has happened with many chemists who have pursued this method. Compounds which are easily decomposed by hydrochloric acid should never, according to this eminent chemist, be exposed to heat, but digested with cold acid, only employing heat when the decomposition will not proceed without it. In cases where the silicic acid is separated in the gelatinous form, *Rose* treats the mass with water, and thus separate the silicic acids in light flocks. Most chemists, however, prefer the method of evaporating the whole mass at once to dryness: it is the simplest, and, on the whole, the least troublesome ; and, if the mass has been thoroughly exsiccated, there is very little fear of any of the silicic acid finding its way again into the solution. In the case of those minerals which contain volatile constituents, their nature will generally be made known by the preliminary examination, and the course of analysis will be shaped accordingly : it is evident, however, that these particular cases cannot come within the limits of a description of a general method, to which the above instructions must be understood to apply.

Decomposition of Silicates by Fusion with Alkaline Carbonate.—The mineral reduced to the finest possible state of division, by elutriation, if necessary, is mixed in a platinum crucible with from three to four times its weight of pure anhydrous carbonate of soda, or with an equal quantity of well-dried and previously pulverized carbonate of potash, or, which perhaps is still better, with a mixture of the two carbonates in the proportion of single equivalents, such as is obtained by calcining Rochelle salt, (tartrate of potash and soda), lixiviating the calcined mass in water, and evaporating the solution to dryness. The mixing of the pulverized mineral with the alkaline carbonate is made by a rounded glass rod : it must be very intimate, and all portions adhering to the rod must be carefully wiped off into the crucible. The cover is placed on the crucible, and it is buried in calcined magnesia contained in a good Hessian crucible, which is then placed in the furnace. The heat must be gentle at first, but gradually raised to intense ignition, at which it must be maintained from thirty minutes to an hour ; at the end of this time the mass will be either completely fused or in a state of semi-fusion, according as the mineral contains more or less silicic acid. The crucible is removed from its bed of magnesia when cold, and its contents transferred to a beaker, which can be covered with a glass plate. When the mass has only been in a state of semifusion, it is generally easily removed by bending and pressing the sides of the crucible; but, when the fusion has been complete, it is sometimes not very easy to remove it without having recourse to hydrochloric acid: in the event of this being necessary, the crucible should be placed in a large beaker before the acid is poured on it, in order to avoid loss by the sudden evolution of carbonic acid. The contents of the crucible being safely lodged in the beaker, the mass is drenched with water, and hydrochloric acid added cautiously, to prevent too violent an effervescence; it is then covered with its plate and exposed to a gentle heat, until perfect solution has taken place, or until only slight flakes of silica are seen floating in it, by which it is known that the decomposition of the mineral has been complete. If, on the other hand, a heavy gritty powder should subside to the bottom of the vessel, the operator hereby learns that, either from the mineral not having been in sufficiently fine a state of division, or from the heat not having been sufficiently intense or long continued, or from some other cause, the mineral has not been entirely decomposed; and the powder must be carefully collected, washed, dried, and weighed, and the weight deducted from the quantity originally taken; or, which is always best, the whole experiment must be recommenced with a fresh portion of substance. Supposing, however, the decomposition to have been successfully performed, the silica is separated by evaporation to dryness on the water bath, and the analysis proceeded with precisely in the same manner as in the case of a silicate, decomposable by simple digestion with hydrochloric acid.

Decomposition of Silicates by Fusion with Caustic Potash.—The finely pulverized mineral is mixed in a silver crucible, with four or five times its weight of caustic potash; the cover is placed on the crucible, and it is carefully heated over a lamp to dryness, and the dry mass is subsequently heated to redness; a far better method, however, of decomposing these silicates, which refuse to yield to alkaline carbonate, is to subject them to the action of hydrofluoric acid, as first recommended by *Berzelius*, and afterwards adopted by *Brunner*. With this view, the finely powdered mineral is placed in a shallow platina dish *b*, supported on a leaden tripod, standing in the centre of a leaden dish *a* (*fig.* 33), about six inches in diameter.

Fig. 33.



The bottom of this leaden vessel is covered to the depth of from one-eighth to one-fourth of an inch, with a mixture made to the consistence of paste of powdered fluor spar and sulphuric acid. The dish is provided with a flat cover, made of the same metal. The mineral to be decomposed is moistened with a little water, and, the cover having been placed on the dish, the latter is gently heated over the sand bath underneath a flue; hydrofluoric acid gas is liberated, by means of which from twenty to thirty grains of silicious mineral may be completely decomposed in the course of an hour and a half. During the process the powder must be twice moistened with a few drops of water; if it is well spread out on the platina dish, it is unnecessary to stir it. When the operation is finished, concentrated sulphuric acid is added, drop by drop, to the powder as long as hydrofluosilicic acid is given off; a gentle heat is at the same time applied, and finally the excess of sulphuric acid is driven off by continued heat and evaporation to dryness. The dry residue, after being moistened with hydrochloric acid, is boiled in water, and further examined in the usual way. This method is particularly applicable to the examination of such minerals as contain alkalies; another method of analyzing such silicates, proposed by *Abich*, is to fuse them with hydrate of baryta or with carbonate of baryta, using from four to six parts of the carbonate to one of the mineral; the most intense heat is required, no action taking place till a state of fusion has been induced; but, when once the action has commenced, it goes on rapidly and energetically, and the operation is finished in a quarter of an hour; no silicate has yet been found to withstand the action of this agent, but the most powerful heat, attainable in a wind furnace of the best construction, is required. When hydrate of baryta is employed, the operation may be conducted in a silver crucible over a good spirit lamp; from four to five parts of the hydrate, deprived of its water of crystallization, are mixed intimately with one of the powdered mineral, and the mixture is then covered with a layer of carbonate of baryta. The decomposition being complete, the analysis is proceeded with in the usual manner.

It must be observed that the silicic acid, as separated from minerals of difficult decomposition, may contain a considerable quantity, 12 or 15 per cent. of *alumina*, and still form a transparent glass when fused with soda. It is always necessary, therefore, to examine the silica obtained from such minerals very carefully for that earth; with which view it is fused with carbonate of potash, the melted mass treated with hydrochloric acid, and the solution evaporated to dryness. The dry mass is moistened with hydrochloric acid, and afterwards treated with water. The acid solution, filtered from the undissolved silicic acid, is now supersaturated with ammonia. If the solution give no precipitate, the silicic acid may be considered to have been pure; but, if a precipitate is formed, this can only arise from an impurity, which, in most cases, will prove to be alumina.

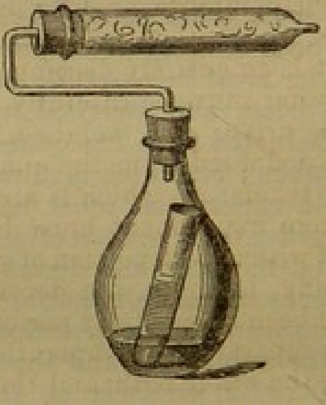
Carbonic Acid.

Determination of Carbonic Acid in a free state in aqueous Solution.—This is very conveniently effected by adding to a weighed or measured quantity of the solution a clear mixture of chloride of calcium and excess of ammonia; the latter absorbs the carbonic acid, and carbonate of ammonia is formed, which, reacting with the chloride of calcium, gives rise to chloride of ammonium and carbonate of lime: the latter is precipitated. It is collected on a filter and washed with water, to which ammonia has been added; the funnel must be carefully protected from the air during filtration, otherwise carbonic acid might be absorbed, which would increase the amount of carbonate of lime. The amount of carbonic acid in the precipitate may be estimated by gently igniting it, and estimating it as carbonate of lime (for the composition of which see page 150), or it may be determined in the apparatus of *Fresenius* and *Will*, *fig.* 27, using that modification of the apparatus recommended for the analysis of carbonates, the bases of which form insoluble compounds with sulphuric acid, and described page 145.

Estimation of Carbonic Acid in the gaseous State.—The volume of gas is first accurately measured in a graduated tube standing over mercury; a small piece of moistened caustic potassa, attached to a piece of ignited harpsicord wire, is then passed through the mercury into the tube; when the absorption has ceased, the potassa is withdrawn, and the volume of the unabsorbed gas accurately determined: the difference in the two measurements indicates the quantity of carbonic acid. When the volume of the gas is large, and contained in a receiver which is not graduated, it is sometimes determined by the increase in weight of a piece of caustic potash passed into the receiver, and allowed to remain for some time in contact with the gas.

Analysis of Carbonates.—We have already described at some length the method which is easiest of execution, and which, on the whole, gives the most satisfactory results, viz., that of *Fresenius* and *Will* (page 144). *Fig.* 34 shows a little apparatus that may sometimes be conveniently employed. It consists of a small thin-bottomed flask, capable of containing about four ounces of water. It is fitted with a cork, through which is inserted a bent tube adapted to another wide tube, containing fragments of dried chloride of calcium: the extremity of this tube is drawn out to a capillary orifice. The small tube seen inside the flask is intended to hold the sulphuric or hydrochloric acid, with which it is proposed to decompose the carbonate. It is made somewhat too long in the figure; it should rest against the side of the flask at an angle of about 45° from the bottom, so that by inclining

Fig. 34.



the flask the whole of the acid can be made to flow out. The carbonate to be analyzed is accurately weighed and projected into the flask, which should contain about an ounce of water; and, the chloride of calcium tube having been fixed air-tight into its place, the whole apparatus is accurately weighed. Great care must be taken that none of the acid in the tube runs in contact with the carbonate before the operation is commenced. Everything being ready, the flask is inclined so as to allow a portion of the acid to flow out of the tube; effervescence immediately takes place, carbonic acid is expelled, and escapes through the orifice of the chloride of calcium tube, being thoroughly dried during its passage through the lime salt. As soon as the effervescence has ceased, a fresh portion of acid is caused to flow out of the tube, and the operation is repeated until no farther escape of carbonic acid gas is perceived.

The flask is now placed in a vessel of boiling water, where it is allowed to remain for some time in order to expel all the carbonic acid in the liquor, and in the upper part of the flask aqueous vapour is prevented from escaping by the chloride of calcium. On cooling, atmospheric air finds its way into the flask, which is thus brought to the same condition it was in previous to commencing the experiment. It is now weighed; the loss of weight indicates the amount of carbonic acid. This is a very convenient little apparatus for the analysis of limestones and marls.

In *Silliman's Journal* for April 1844, *Professor Rogers*, of the University of Virginia, having given an account of some new instruments and processes for the analysis of carbonates*; their object being to attain a higher degree of accuracy than they found possible by any of the methods in ordinary use, which, though fitted for ordinary analysis, were not as they considered adapted for that higher description of research involved in the investigation of the atomic weights of lime, magnesia, potash, &c., &c.

The method of the American chemists is, like those already described, the *indirect* method, the amount of carbonic acid being calculated from the loss of weight after the operation is concluded. They also take account of the amount of carbonic acid contained in the liquid, which they found too considerable to be overlooked. They separate and measure this portion of absorbed carbonic acid in the following manner. A tube of thin glass, twenty-four inches long and one-fourth of an inch in diameter, is graduated at its closed extremity to fiftieths of a cubic inch. Mercury is poured into the tube until the vacant space above is not much more than sufficient to contain all the liquid in the bottle in which the analysis has been made; this liquid is then poured on the mercury gently, so as to produce as little agitation as possible, and the tube is then completely filled with mercury. The tube thus filled is inverted in a bowl of mercury, and supported in an inclined position; the part containing the solution is then heated to the boiling point by the flame of a spirit lamp. Bubbles of carbonic acid rapidly ascend, and the gas continues to be disengaged, even after the commencement of ebullition, so that, to insure its entire separation, this temperature should be maintained for two or three minutes. The tube placed in an erect position may now be brought to the temperature of the apartment by a moist cloth.

The mercury in the bowl is now covered with a saturated solution of common salt, and the tube is raised a little, so as to allow this liquid to ascend and take the place of the mercury in the tube; after which the instrument is transferred to a deep narrow jar, filled also with the saturated solution, and is depressed to the proper level for measuring the volume of included gas. As this volume always includes a minute quantity of common air, disengaged from the liquid by boiling, the tube is now transferred to a large cistern of water, when, by continued agitation for a minute or two, all the carbonic acid will be absorbed, and thus its volume made known by subtraction. These processes being conducted at or near the temperature of the room, or the volume being corrected for expansion, should the temperature be much higher, the height of the residuary carbonic acid is given with sufficient accuracy by estimating each length of a cubic inch as equivalent to 0.047 gr.

Direct determination of Carbonic Acid in saline Compounds. Brunner's Method.—Deeming it advisable to exchange the negative method of determining carbonic acid in saline compounds for a positive method, in which the liberated acid should itself be brought into the balance

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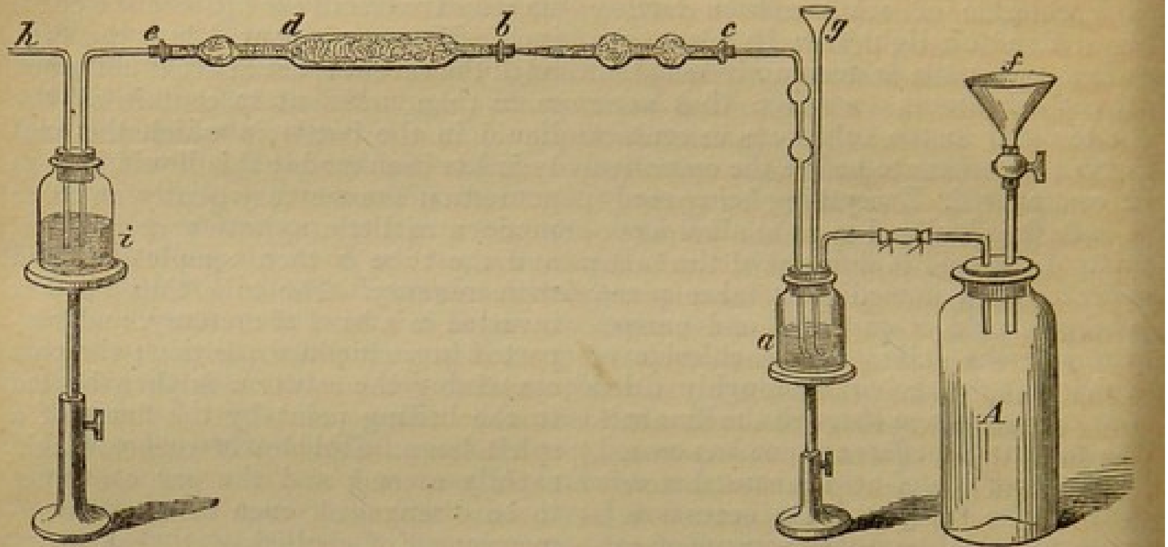
* *See* Chem. Gaz., vol. ii. page 305, *et seq.*

Fig. 35.



Brunner invented the apparatus shown in *fig.* 35*. The substance to be examined is placed in the little flask *a*, and a suitable quantity, for instance an ounce of water, poured over it; upon which the flask is closed with a tight-fitting cork provided with three tubes, and when necessary coated with cement. The straight tube terminates above in a small funnel *g*, through which the sulphuric acid is poured. The second, provided with two bulbs, is connected by its rectangular bend with a tube *b c*, from a third to half an inch wide, and in order to gain space, likewise furnished with two expansions, containing asbestos, moistened with sulphuric acid. The third is bent twice, and terminates in the large empty flask *a*. To adapt it more easily, it may be cut anywhere in the middle, and the two parts connected by caoutchouc.

The two tubes dipping in the liquid of the bottle *a* are drawn out at their lower lengths into fine somewhat laterally curved points; the tube *be* contains, in the expanded portion *b d*, which is from three quarters to one inch in width, well-burnt lime, which may be readily moistened with water; from *d* to *e* asbestos or fragments of pumice-stone, drenched with sulphuric acid, and separated from the lime by a tight stopper of asbestos: the small Wolfe's flask contains lime water.

The analysis is now performed in the following manner. A small quantity of sulphuric acid is poured into the flask *a* through the funnel tube, the stop-cock of *f* being closed: as this will not descend of itself, it is made to do so by drawing gently with the mouth at *h*. The evolution of gas, which is made perceptible by the ascending bubbles and by the air passing through the lime water in *i* is now waited for; another portion of acid is then added, and this continued until it may be assumed that a tolerable excess of acid has been introduced. This being done, some water containing a little caustic potash in solution is allowed to flow into the flask *A* by opening the stopcock of *f*, whereby a current of air is passed through the vessel *a*, which carries the carbonic acid contained partly in the liquid, partly in the upper space of the vessel, into the tube *b e*; but, since this would never be completely effected without the application of heat, the vessel *a*, towards the end of the experiment, is immersed in a small dish filled with water, which is kept warm over a small lamp as long as is found requisite.

It is best to regulate the current of air, so that about two bubbles of gas pass through the lime water in a second. It will, however, never be found to become in the least degree turbid. It is scarcely necessary to observe that the object of the sulphuric acid in *b c* is to retain the moisture carried by the gas from *a*; also that the potash added to the water which flows into the large flask is to absorb the carbonic acid of the atmospheric air; and lastly, that the increase in the weight of *b e* yields the result sought for. Several analyses made by the author according to this method yielded very satisfactory results.

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* Poggendorff's Annalen, No. 6, 1846; and Chem. Gaz., vol. iv. p. 367.

The analysis of a great many solid carbonates may be very simply effected by simply igniting them, and estimating the amount of carbonic acid from the loss of weight; it is, of course, indispensable that the substance shall contain no other volatile constituents, which may be expelled by the ignition, together with the carbonic acid. It is also necessary that the substance from which the carbonic acid is expelled shall not itself undergo any alteration whereby it may be either increased or diminished in weight. The carbonates of certain metallic oxides are in this condition; as, for example, the carbonates of protoxide of iron and of manganese, and of oxide of cobalt. The analysis of these salts may be performed by igniting them in a bulbed tube of hard glass, through which a stream of dry carbonic acid gas is passing. Carbonates which contain water are analyzed by the same process which is adopted in determining the carbon and hydrogen in organic substances, and which will be fully described hereafter.

The decomposition of carbonates by heat is greatly facilitated by mixing them with about four times their weight of finely powdered borax, as was first pointed out by *Count F. Schaffgotsch*[*]. He did not find anhydrous boracic acid so convenient for the purpose, since by long melting this acid decreases slowly but constantly in weight. The anhydrous biborate of soda, or glass of borax, is, however, absolutely fixed, and is well adapted for the purpose, from the ease with which it decomposes the carbonates in fusing, and from its causing no ebullition on account of its thick fluidity.

Separation of Carbonic Acid from Sulphurous Acid.—For this purpose *Persoz* introduces into a graduated tube containing the mixed gases a glass rod covered with paste, and coated with powdered iodate of potash of soda; the sulphurous acid is hereby converted into sulphuric acid, and as soon as no further decrease in the quantity of the confined gas is perceptible the glass rod is removed, and the residual gas immediately measured. Before, however, the carbonic acid can be considered as free from sulphurous acid, another glass rod must be introduced, which is also covered with the paste made with starch and a dilute solution of iodate of potash; if the least trace of sulphurous acid exist in the gas, the rod is instantly coloured blue. This method is, therefore, well adapted for the detection of minute traces of sulphurous acid.

Separation of Carbonic Acid from all other Acids.—As carbonic acid is readily removed from its combinations by heating with stronger acids, its separation from most other electro-negative bodies is attended with but little difficulty. The carbonic acid is determined in one portion of the compound, and the other acids in another portion. If the substance under examination contains fluorides, the carbonic acid is expelled by one of the weak non-volatile acids, such as tartaric or citric acids; since, if sulphuric or hydrochloric acid were employed, hydrofluoric acid would, at the same time, be discharged. When there occurs in the course of an analysis a mixed precipitate of fluoride of calcium and carbonate of lime, *Fresenius* directs the separation of the two substances to be effected by pouring acetic acid over the mixed precipitate, adding alcohol, filtering, and, finally, washing the residue with alcohol.

Separation of Carbon from Nitre and Sulphur. Analysis of Gunpowder.—The sample intended for analysis (from 20 to 30 grains) is finely pulverized and dried, either in the water bath, or in vacuo over sulphuric acid, in the manner shown in *fig.* 17. It is then digested for some time with boiling distilled water, and the insoluble portion thrown on a filter, the weight of which is known. It is repeatedly washed while on the filter with hot water. The filtrate and the washings are evaporated to dryness, and the dry mass estimated as nitre; or, after having weighed the residue, it may be redissolved in water, and tested for common salt by nitrate of silver, and, if any notable quantity is thereby indicated, the silver salt must be added as long as any precipitation takes place, and the resulting chloride of silver calculated into its equivalent of chloride of sodium, and the amount deducted from the dry salt. The substance remaining on the filter is dried and weighed; it consists of carbon and sulphur. To determine the proportion of these two elements, a fresh quantity, from 15 to 20 grains, of the finely powdered sample, is intimately mixed with an equal amount of pure anhydrous carbonate of soda; the mass is thus mixed with about eight parts of nitre and six of common salt. The whole is

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[*] Poggendorf's Annalen, No. 10, 1842, p. 263.

strongly heated in a platinum crucible: the sulphur becomes hereby oxidized into sulphuric acid at the expense of the oxygen of the nitric acid, and the acid thus formed unites with the potash of the decomposed nitre, forming sulphate of potash. As soon as the mass becomes white, it is dissolved in water, acidified with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium; from the weight of sulphate of baryta obtained the amount of sulphur is calculated.

Marchand modifies the above (*Gay Lussac's*) method of estimating the sulphur in gunpowder in the following manner. A mixture of 1 part of nitrate and 3 parts of carbonate of baryta is intimately mixed with a twelfth part of the powder, and heated in a tube closed at one end. A layer from 3 to 4 inches in length of baryta salt is inserted in front of the mixture, and the whole is heated in the combustion furnace, beginning at the anterior portion. The mixture which does not fuse is easily removed from the tube, which is rinsed with dilute hydrochloric acid, in which the ignited mass is then dissolved. The liquid is retained in a beaker for several hours near 212°, and the sulphate of baryta is then collected on a filter. The amount of sulphur may likewise be determined accurately in the moist way. From 30 to 40 grains of the powder are treated in a flask with concentrated nitric acid, with the addition of a few grains of chlorate of potassa; the mass is kept gently boiling, until at last a colourless liquid is obtained, which is diluted with a large quantity of water, and precipitated while hot with chloride of barium.

The charcoal is estimated indirectly by deducting the weights of the moisture, nitre, and sulphur from the original weight of the powder analyzed.

The amount of nitre in gunpowder may, according to *Marchand*, be ascertained with great precision by determining the quantity of nitrogen in the powder. For this purpose a portion of the sample is weighed off, reduced to a fine powder, and intimately mixed with oxide of copper; the mixture is transferred to a combustion tube, the sealed end of which is charged with carbonate of lead, and then with oxide of copper; oxide of copper and metallic copper are placed in front. The details of the process will be given hereafter.

Separation of the Sulphur from the Charcoal.—For this purpose *Marchand* adopts *Wöhler's* method, which is as follows. An indefinite quantity of the mixture as dry as possible is brought into the bulb of a weighed reduction tube; the tube is filled with metallic copper, it is heated in a current of dry hydrogen gas, which drives the sulphur into the copper; the tube is then weighed, and likewise after shaking out the residuary charcoal. In this way the relative quantity of sulphur and charcoal is obtained. The heat which must be applied to remove the whole of the sulphur from the charcoal is, in general, greater than that at which the charcoal had been prepared, and there is generally observed during the expulsion of the sulphur a strong odour of humic acid, carbonic acid, carbonic oxide, and water. Instead of distilling the sulphur from the charcoal, it may be removed by solvents. *Marchand* employs for this purpose *sulphuret of carbon*. After exhausting the gunpowder with water, which he effects in a displacement apparatus of the form of an ordinary chloride of calcium tube, from 7 to 8 inches long, the bulb being stopped with asbestos, he treats it with absolute alcohol, which displaces the water, upon which sulphuret of carbon, which has been rectified over oxide of lead, is poured over it until what passes through leaves no sulphur on evaporation; the powder is then finally treated with alcohol. It is still better to use the sulphuret of carbon mixed with absolute alcohol. As soon as the charcoal is washed, a current of dry air is drawn through the tube by means of an aspirator, the tube itself being confined in an air bath at 248°. The dry charcoal is weighed accurately in the tube.

The sand, &c. contained in the powder may be determined with tolerable accuracy by trituration and suspension. *Marchand* gives the following as the composition of the so-called *Bernese* sporting powder:—

Nitre	79.16
Sulphur	9.72
Charcoal	10.99
	99.87

Oxalic Acid.

The quantitative estimation of this acid may be effected by precipitating it from its solutions in the form of oxalate of lime, and determining the latter as carbonate, or by ascertaing the amount of carbonic acid yielded by its decomposition.

Quantitative Estimation of Oxalic Acid by Precipitation.—The acid, if in a free state, is neutralized as exactly as possible with ammonia diluted with water, and chloride of calcium mixed with acetate of soda added; the precipitated oxalate is well washed, dried, and ignited, with the precautious prescribed page 150, by which it is converted into carbonate; and the quantity of oxalic acid is calculated from the weight of the latter, every equivalent of oxalic acid yielding two of carbonic acid, thus

$$C_2O_3 + O = 2\ CO_2$$

There are two ways of estimating the amount of carbonic acid yielded by the decomposition of oxalic acid; one is by burning it with oxide of copper, according to the ordinary method of organic analyses; and the other, which is by far the most convenient and expeditious, is by neutralizing it with ammonia, and bringing it into contact with peroxide of manganese and sulphuric acid, in the manner fully described, under the head of MANGANESE, page 164. 9 parts of oxalic acid require theoretically 11 parts of manganese, but an excess of the latter does no harm. Both of these latter methods are applicable to the determination of oxalic acid in the oxalates. When the oxalate is soluble in water, the amount of oxalic acid may be determined by precipitation, as carbonate of lime, and the base or bases with which it was combined determined in the filtrate by appropriate methods. Many of the insoluble oxalates may be analyzed by simple ignition, the bases being left either as pure metals, or as oxides or as carbonates. Oxalates, the bases of which are precipitated by carbonate of potash, may be decomposed by boiling for some time with that alkali; oxalic acid is thus brought into a soluble state in the form of oxalate of potash, and may be precipitated by a neutral solution of lime.

Oxalic acid, as met with in commerce, frequently contains *tartaric acid* and *sulphate of potash.* The former is detected by digesting a portion of the acid in a test tube with concentrated sulphuric acid; it should remain colourless; but if tartaric acid is present it turns black, that acid being decomposed. The presence of sulphate of potash is indicated by a precipitate insoluble in nitric acid, produced on adding to a solution of the suspected acid a few drops of chloride of barium.

Hydrofluoric Acid.

When this acid exists in aqueous solution, it is quantitatively estimated, by rendering the liquid alkaline by ammonia, and precipitating the hydrofluoric acid in the form of fluoride of calcium by the addition of chloride of calcium; the precipitate, which is gelatinous, is washed on the filter with hot distilled water, and then with acetic acid, to remove any carbonate of lime which may have formed during the process of filtration. The composition of the ignited salt is

One equiv. of Ca……	20.0……	51.68
One do. of Fl……	18.7……	48.32
One do. of CaFl……	38.7 …	100.

The fluorine in soluble fluorides may be determined in the same manner, the bases being estimated in the filtrate according to the usual rules. Insoluble fluorides may be analyzed in two ways.

1. *Decomposition by Sulphuric Acid.*—The fluorine in this process is estimated *indirectly.* A weighed quantity of the fluoride, finely pulverized, is heated in a platinum capsule with concentrated sulphuric acid; the fluorine escapes in the form of hydrofluoric acid gas, and the excess of sulphuric acid is finally expelled by raising the heat to ignition. From the weight of the resulting sulphate the quantity of metal in the base is calculated; that of the fluorine is indicated by the loss of weight. Should the substance analyzed contain more than one base, the resulting sulphates must be submitted to further analysis, before a calculation can be made of the amount of fluorine present in the substance.

2. *Conversion of the Fluorine into Fluoride of Silicium. Wöhler's process*.*—The weighed substance is intimately mixed with pure silica, unless it already contains some; the mixture is placed in a small flask, which can be weighed on the balance; very concentrated sulphuric acid, which has been boiled, is added, and the flask quickly closed with a cork, through which a small tube, filled with fused chloride of calcium, and drawn out to a fine point, passes. The whole

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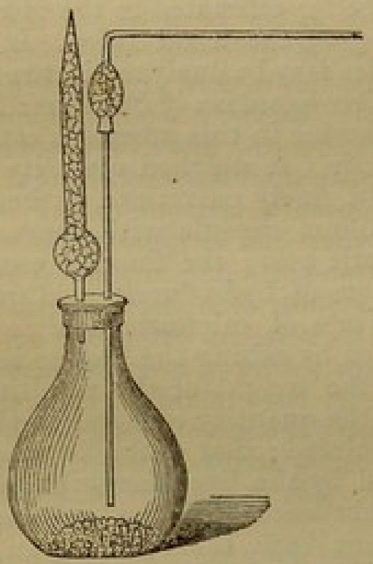
* Poggendorff's Annalen, vol. xlviii.; and Chem. Gaz., vol. iii. p. 504.

apparatus is now weighed, and then exposed to a proper heat, as long as gaseous fluoride of silicium is evolved. The last portions are removed by exhaustion under the air-pump. The loss of weight which it experiences is fluoride of silicium, from which the amount of fluorine is calculated. 1.395 parts of fluoride of silicium are formed for each part of fluorine. To test this method, the author estimated the amount of fluorine in fluor spar, and the results were accurate to the first decimal place. To avoid the use of the air-pump, *Fresenius* modifies the apparatus by adding a second tube, closed with a waxed stopper, the lower end reaching nearly to the bottom of the flask; the last traces of gas may, with this arrangement, be removed from the flask by simple suction: for which purpose a suction tube is applied, filled with dry cotton at the lower end, and with moist cotton in the centre. *Fig.* 36 shows the apparatus arranged for this purpose. The above process is well adapted for the separation of fluorine from the silicates. Another method, proposed by *Berzelius* and modified by *Regnault*, is the following: the finely levigated powder is kept for some time in a state of fusion, with four times its weight of carbonate of soda: it is then extracted with boiling water, and the filtered solution is mixed with a solution of carbonate of zinc in ammonia, and evaporated to dryness. By digesting the dry residue with boiling water, a solution is obtained which contains the whole of the fluorine in the form of fluoride of sodium, in conjunction with carbonate of soda. It is carefully neutralized with hydrochloric acid, and the carbonic acid completely removed by allowing it to stand for some hours under a bell jar by the side of a vessel containing solution of caustic potassa. The hydrofluoric acid is finally precipitated and estimated in the form of fluoride of calcium.

Fig. 36.



Where the fluoride to be analyzed contains water, the amount of that substance cannot be estimated by simply heating the fluoride, since the simultaneous action of the air and the water sometimes effects a partial decomposition of the fluoride, and a portion of hydrofluoric gas escapes along with the vapour of water. In such cases the analysis is performed as follows. The joint amount of water and fluoride is first determined by heating a known weight of the substance with concentrated sulphuric acid in the manner above described; a fresh portion of the compound is then mixed in a little glass retort with about six times its weight of finely pulverized and recently ignited protoxide of lead; the mixture is covered with a layer of oxide of lead, the retort is weighed, and heat is then applied, gentle at first, but gradually increasing to redness; aqueous vapour, unaccompanied with the slightest trace of hydrofluoric acid gas, escapes. The retort is allowed to cool; it is then weighed again, and the amount of water calculated from the loss which it has sustained. By the first operation the joint amount of water and fluorine has been learnt; and we have only now to deduct from that amount the quantity of water, indicated by the second experiment, to find the quantity of fluorine in the substance under examination.

Separation of Fluorides from Phosphates.—The process of *Berzelius* as modified by *Regnault*, which we have described above, for separating fluorides from silicates, may also be employed when phosphates also are present. In this case the solution filtered from the silicic acid will contain phosphate of soda in addition to fluoride of sodium and carbonate of soda. It is analyzed as follows: it is rendered ammoniacal, and mixed in a glass flask which can be closed air-tight with a solution of chloride of calcium; the precipitate which is produced consists of fluoride of calcium and phosphate of lime. It is washed with the proper precautions, dried, ignited, and weighed; it is then treated in a platinum crucible with concentrated sulphuric acid, and heated until the whole of the hydrofluoric acid is expelled. The residue is treated with alcohol in which sulphate of lime is insoluble, and the phosphoric acid dissolved in the alcohol is precipitated and estimated as pyrophosphate of magnesia. The amount of fluorine originally present in the mixed precipitate of fluoride of calcium and phosphate of soda is learnt by the loss of weight sustained by the action of the sulphuric acid.

Hydrochloric Acid.

The quantitative determination of this acid is effected by precipitating its chlorine in the form of chloride of silver; for the composition of this salt, and for the precautions to be observed in its precipitation, the student is referred to p. 137–8. If hydrochloric acid alone is present in aqueous solution, it may be estimated in the form of sal ammoniac by adding ammonia in excess, evaporating the solution to dryness, and performing the exsiccation of the residue in the water bath.

Soluble chlorides are analyzed by first precipitating the chlorine by nitrate of silver, and then, after removing the excess of the silver salt from the filtrate by hydrochloric acid, estimating the amount of base or bases by the ordinary processes.

The analysis of the compounds of chlorine with *tin* and *antimony* is performed in a somewhat different manner. If a solution of nitrate of silver were added to a solution of perchloride of tin, there would be precipitated, besides chloride of silver, a compound of peroxide of tin with oxide of silver, which would vitiate the result. It is necessary, therefore, to remove the base from the solution before attempting to precipitate the electro-negative element; this is done by passing through the solution, contained in a flask which can be corked, a stream of sulphuretted hydrogen, and, when it is saturated, allowing it to repose for a considerable time; the sulphuret of tin is filtered off as soon as it is completely subsided, and the excess of sulphuretted hydrogen removed from the filtrate by mixing it with a solution of sulphate of copper;—this is indispensable; otherwise, on the addition of nitrate of silver, a precipitate both of chloride and of sulphuret of silver would take place. The excess of sulphuretted hydrogen being removed, the solution is precipitated by nitrate of silver in the usual manner. In the case of chloride of antimony, it is unnecessary to remove the base previous to determining the chlorine; but the precaution must be taken of mixing the solution with a sufficient quantity of tartaric acid to prevent the formation and precipitation of a basic salt.

Such chlorides as are insoluble, or only sparingly soluble, in water, but soluble in nitric acid, are dissolved in the latter menstruum, the solution diluted with water, and precipitated by nitrate of silver in the usual manner.

Analysis of Chlorides insoluble in Water and in Nitric Acid.—This may be performed in three ways:—1st, by reducing them to the metallic state by ignition in a stream of dry hydrogen gas; 2nd, by fusion with alkalies; and 3rd, by digestion with caustic potash.

1st. *By Reduction.*—The apparatus, *fig.* 29, p. 158, may be employed. The chloride to be analyzed (chloride of lead for instance) is accurately weighed in the little porcelain crucible *d*, a stream of dry hydrogen gas from the bottle *a* is conducted over it, and the crucible is then heated to redness by means of a spirit lamp, the heat required being somewhat greater than in the reduction of oxides. When hydrochloric acid gas ceases to be disengaged, which is known by fumes ceasing to be produced when a feather or glass rod moistened with ammonia is held near the tube of the crucible cover, the crucible is allowed to cool and again weighed; the loss of course indicates the amount of chlorine.

2nd. *By Fusion with Alkalies.*—The chloride to be analyzed (chloride of silver for instance) is mixed in a porcelain crucible with three parts of a mixture of carbonates of potash and soda, and heated till the mass enters into fusion and effervescence ceases; it is then allowed to cool, and the mass treated with water. The silver remains undissolved in a state of very fine division. It is filtered, washed, ignited, and weighed. The chlorine in the filtrate, representing that in the compound analyzed, is determined as chloride of silver. *Gmelin* decomposes chloride of silver in the following manner:—He fills a crucible almost to the top with an intimate mixture of three parts of the chloride and seven of *colophony;* he then exposes it to a gentle heat, when the resin burns with a green flame, owing to the hydrochloric acid generated from the chlorine of the chloride and the hydrogen of the resin; a stronger heat is then given to fuse the silver, a little borax is added, and the crucible tapped gently once or twice to facilitate the union of the silver. This process was first proposed by *Mohr.*

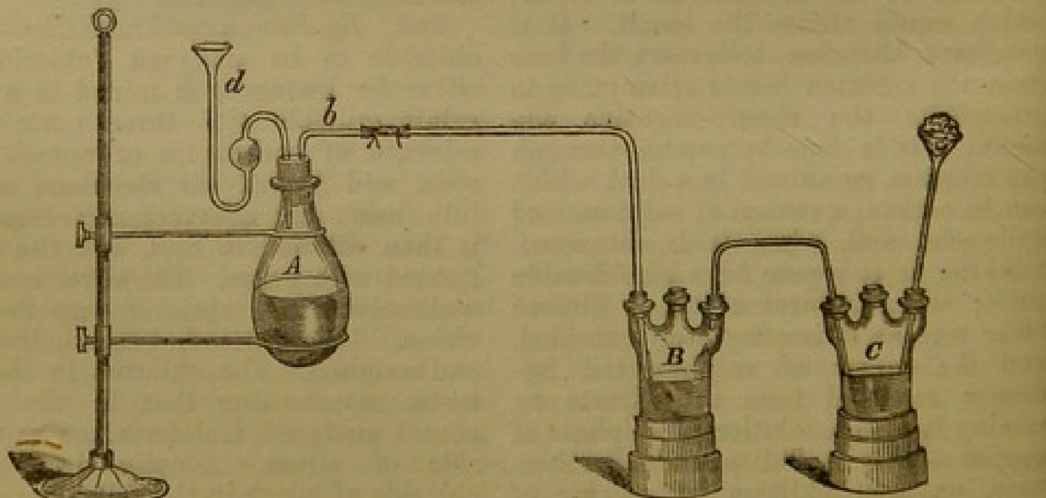
3rd. *By Digestion with Caustic Potash.*—This method is particularly applicable to the analysis of *protochloride of mercury.* The solution filtered from the metallic protoxide is acidulated with nitric acid, and precipitated with nitrate of silver. The protoxide of mercury may be dissolved in aqua regia, and determined by one of the methods described page 187; or a fresh portion of the protochloride may be taken and treated with hydrochloric acid and protochloride of tin, as directed page 179. *Dr. Gregory*[*] decomposes chloride of silver by digestion with caustic potassa, and has recommended it as a convenient method of preparing pure oxide of that metal. His method is to mix well the moist chloride with a sufficient quantity of caustic potash, specific gravity 1.25, and to boil for about ten minutes, or until the chloride has become converted into a jet black powder. If any white specks are observed, the mixture must be rubbed in a mortar, and again boiled. When the decomposition appears complete, the oxide is to be carefully washed by decantation with hot water until all the saline matter has been removed; it is thus obtained as a heavy black powder. It is worthy of remark that, if the chloride of silver has once been dried, it is only decomposed by boiling for a long time with caustic potash, and then with great difficulty. According to *Dr. Meurer*[†], the above process does not succeed when the experiment is made on several ounces.

Levol modifies the process thus:—He places the chloride in a solution of caustic potassa, in which some *sugar* is dissolved, and then boils. The silver is quickly reduced by the sugar, carbonic acid being evolved, and is brought to the state of fine powder, which is easily washed.

The amount of chlorine in many metallic chlorides may be determined *indirectly* by converting them into sulphates, for which purpose the compound is treated with concentrated sulphuric acid and heated till all the hydrochloric acid gas and the excess of sulphuric acid are expelled; the amount of chlorine is inferred from the loss of weight.

Quantitative Estimation of Free Chlorine.—Since chlorine gas is absorbed both by water and mercury, it cannot be estimated by the ordinary methods of measuring gases without very great difficulty. The determination of the gas is best effected by leading it into ammonia, a portion of which it decomposes, muriate of ammonia being formed, and nitrogen gas set free. The operation is conducted as follows:—The substance from which the gas is to be liberated is introduced into the flask A, *fig.* 37. This flask is provided with a

Fig. 37.



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[*] Proceedings of the Chemical Society, No. 4.
[†] Archiv. de Pharmacie.

well-fitting cork, through which two tubes are inserted, one of which, *b*, communicates with a Wolfe's bottle, B, containing a sufficient quantity of ammonia to absorb all the chlorine that can be evolved; the other tube, *d*, is a safety tube, and is surmounted by a funnel, through which any required liquid may be poured into the flask. The Wolfe's bottle, B, is connected with a second bottle, C, also containing ammonia, further to prevent the possibility of any chlorine escaping absorption. This second bottle is provided with a long tube, surmounted by a funnel, in which, during the operation, there is placed some cotton moistened with ammonia. Heat is applied to the flask A, and, when the disengagement of chlorine has ceased, all the gas with which the flask is filled, as well as that in the connecting tubes, is expelled, and conducted into the ammonia, by pouring through the funnel of the safety tube (which during the experiment is filled with a strong solution of common salt) a concentrated solution of bicarbonate of potash until it is filled. The extremity of the tubes leading from the flask to the first Wolfe's bottle, and from the first Wolfe's bottle to the second, must not quite reach the surface of the ammonia, to avoid the danger of a sudden absorption, and the consequent rushing of the ammonia into the evolution flask. The operation being ended, the ammonia and the moistened cotton are transferred to a beaker acidulated with nitric acid, and the amount of chlorine condensed determined by the nitrate of silver. The disengagement of the chlorine throughout the experiment must be very slow, otherwise a complete decomposition of the ammonia might not take place, and a portion of chlorine may be liberated in company with the nitrogen. If the chlorine is in aqueous solution, it may be determined by the same decomposition, for which purpose it is only necessary to add excess of ammonia and proceed with the solution in the usual manner. According to *Buchner**, the amount of chlorine in chlorine water may be determined by agitating it with a weighed amount of metallic mercury, taking care to use such an excess, that a portion of the fluid metal separates in the free state, in order that the whole of the chlorine shall be in the form of the insoluble subchloride; the quantity of chlorine is found by collecting, drying, and weighing the calomel and unaltered mercury, and comparing the weight with that of the metal when introduced into the solution. The same method may be employed to test a solution of chlorine for hydrochloric acid, the chlorine being so entirely removed, that the presence of hydrochloric acid may be ascertained by the acid reaction of the liquid, and its amount determined in the usual manner.

Chlorimetry, or Determination of the Value of Chloride of Lime.

1. *Modification of the Method of Gay Lussac.*—This is founded on the conversion of calomel into chloride of mercury by the chlorine set free from the bleaching powder. A fluid is prepared holding in suspension a known quantity of subchloride of mercury; into this a measured quantity of the solution of chloride of lime to be tested is poured until the liquid becomes perfectly clear, the quantity of chlorine consumed, and, consequently, the value of the bleaching powder is calculated from the number of divisions of the burette which have been required to render the turbid mixture clear.

Preparation of the Standard Mercurial Test Liquor.—It is based on the following considerations:—

Every 236.64 grains of subchloride of mercury require 35.5 grains of chlorine to convert them into chloride; every 58.47 grains of common salt (which is the chloride most convenient for the purpose) contain 35.5 grains of chlorine, or 164.7 grains contain 100 grains of chlorine.

Let 50 measures of a solution of a protosalt of mercury, the protonitrate, for example, be introduced into the graduated burette, *fig.* 26, and then poured off into a beaker and diluted with 4 or 5 ounces of water; then let 82.35 grains of common salt be dissolved in water and introduced into the burette so as to fill exactly 100 measures. Let this solution be poured gradually into the solution of the protonitrate, which during the time should be kept warm by immersion in a basin of hot water, until the last drop added no longer produces a precipitate. Let us suppose that 20 measures have been required; now, as 100 measures of the saline solution contain 82.35 grains of chloride of sodium = 50 grains of chlorine; the

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* Buchner's Report, xxxi. p. 164.

20 measures must contain 16.47 grains = 10 of chlorine. We consequently arrive at the conclusion that 50 measures of the protonitrate of mercury require 10 grains of chlorine to convert the salt into subchloride, and if the 50 measures are increased to 100 by dilution with water a solution is obtained, every 10 divisions of which are equivalent to 1 grain of chlorine, and every single division of which represents one-tenth of a grain; any quantity of the test liquor may thus be easily prepared.

Method of testing the Bleaching Powder.—100 grains of the specimen, selected from different parts of the sample, and well mixed together, are rubbed in a mortar with a little water, and transferred to a tube graduated into 200 equal parts, each part corresponding with a division of the burette; the mortar is rinsed out with a little more water, the washings transferred to the graduated tube, the whole well agitated, and the mark at which the solution stands in the tube is accurately noted. Suppose the whole to occupy 150 measures. The burette is now filled to 100 with the mixture. Next, 100 measures of the standard protonitrate of mercury are poured into a beaker and diluted with water, excess of common salt is added to the solution, which is then acidified with pure hydrochloric acid. The well-agitated solution of chloride of lime is then dropped gradually into the newly formed calomel in the beaker, until it is perfectly clear, by which it is known that the whole of the calomel has been converted into corrosive sublimate. It must be constantly stirred while the bleaching solution is being added, and it is essential that it should remain acid during the whole time. Now, from what has been explained above, it is evident that the number of divisions of the bleaching solution that have been consumed in rendering the turbid mercurial salt clear, must correspond with 10 grains of chlorine. Suppose 65 measures were required, then the value of the specimen is found very simply by the following proportion:—

$$\text{As } 65 : 10 :: 150 : x$$

$x = 23.07 =$ the quantity of chlorine in 100 grains of the bleaching powder.

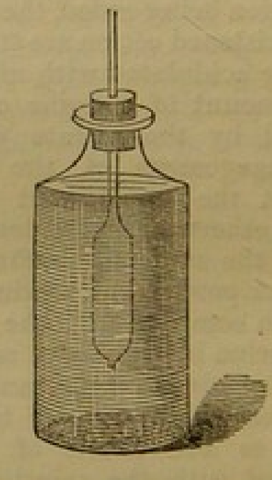
It is evident that any other proportions than those here given may be employed, both in making the standard mercurial solution and in performing the analytical process. The above must be regarded as merely an illustration of the principles of the operation. This method is found to yield very accurate results: there is, perhaps, one disadvantage attending it, which is, that the solution of protonitrate of mercury is somewhat liable to change, and give rise to the formation of an insoluble basic salt, which would, of course, interfere with its accuracy as a test. From this objection the methods next to be described are free.

2. *Gay Lussac's Method by Arsenious Acid.*—When arsenious acid, water, and chlorine are brought into contact with each other, a reaction takes place, the result being the formation of hydrochloric and arsenic acids, thus:—

$$AsO_3 + 2\,HO + 2\,Cl = AsO_5 + 2\,HCl$$

every equivalent (or 99 parts) of arsenious acid requires two equivalents (or 71 parts) of chlorine; 100 parts of chlorine are therefore required to peroxidize 140 parts of arsenious acid. To prepare a standard solution of this acid 280 grains are dissolved in hydrochloric acid, the quantity employed being exactly 20 times the capacity of a large dropping tube; which, therefore, when immersed into the bottle containing the solution, as shown in *fig.* 38, will remove just 14 grains of arsenious acid = 10 grains of chlorine: a mark is made in the neck of the dropping tube to regulate the quantity of solution admitted. When the chlorimetric assay is about to be made, 50 grains of the bleaching powder are prepared in the manner already described, and the burette is filled to the 100th division with the solution. A measure of the arsenious solution is then taken from the bottle with the

Fig. 38.



dropping tube, transferred to a beaker, diluted with water, and coloured blue by the addition of a few drops of solution of indigo. The bleaching liquid is then gradually and carefully dropped into the arsenical solution, which is all the time well stirred, until the blue tinge is entirely destroyed. This shows that the conversion of the arsenious into arsenic acid is complete, and, consequently, that 10· grains of chlorine have been consumed, and, as before, the value of the bleaching powder is ascertained by the rule of simple proportion; thus, suppose 90 measures have been consumed, then

$$\text{As } 90 : 10 :: 100 : x$$

$x = 11.11 =$ the quantity of chlorine in 50 grains of the bleaching powder, or 22.22 per cent.; or still more simply, as each measure of the burette corresponds with half a grain of bleaching powder, and as the number of measures consumed contain 10 grains of chlorine, we find at once the per centage amount of chlorine in the example by dividing 2000 by the number of measures required; thus $\frac{2000}{90} = 22.22$.

3. *Otto's Method by Protosulphate of Iron.*—When protosulphate of iron, water, chlorine, and free sulphuric acid are brought into contact, a reaction takes place, resulting in the formation of hydrochloric acid and persulphate of iron; thus

$$2\,FeO,SO_3 + 2\,SO_3 + HO + Cl = Fe_2O_3,3\,SO_3 + HCl$$

every two equivalents, or 152 parts of anhydrous, or 278 parts of crystallized protosulphate of iron, require one equivalent, or 35.5 parts of chlorine; 100 grains of chlorine are therefore required to convert 783.1 grains of crystallized protosulphate of iron into persulphate. To prepare the iron salt for these experiments, *Fresenius* directs that iron nails free from rust be dissolved in dilute sulphuric acid, finally with the application of heat; the solution is filtered while still warm, into about twice its volume of spirits of wine; the precipitate which is produced consists of protosulphate of iron with 7 equivalents of water. It is collected on a filter, edulcorated with spirits of wine, spread upon a sheet of blotting paper, and allowed to dry in the air until it has completely lost the smell of spirits of wine: the dry salt must be kept in a well-closed bottle. To perform the chlorimetric assay, 78.3 grains of the protosulphate are dissolved in about two ounces of water, and the solution strongly acidulated with sulphuric acid; 50 grains of the bleaching powder are then prepared as before directed, and the burette filled with the solution, which, after being well agitated, is added drop by drop to the solution of the iron salt until complete peroxidation has taken place; this is known by solution of red prussiate of potash no longer striking a blue precipitate. The best way of testing the solution from time to time, is to cover a large white plate with drops of the red precipitate, and, as the operation draws towards an end, to convey a minute drop from the solution, at the end of a small stirring rod, to one of the drops; the process is complete when prussian blue ceases to be formed, a green colour being produced in its stead. The number of divisions of the burette which have been consumed is now noted; this corresponds with 10 grains of chlorine, that being the quantity required for the peroxidation of 78.3 grains of crystallized protosulphate of iron. The calculation is precisely the same as in the last method.

4. *By Yellow Prussiate of Potash.*—When ferrocyanide of potassium is brought into contact with free chlorine, a reaction takes place, resulting in the production of *ferricyanide* of potassium and chloride of potassium. Thus

$$2\,(K_2Cfy) + Cl = K_3Cfy_2 + KCl$$

every two equivalents, or 368 parts of anhydrous, or 422 parts of crystallized ferrocyanide of potassium require one equivalent, or 35.5 parts of chlorine; 100 grains of chlorine, therefore, are required to convert 1188.7 grains of crystallized yellow prussiate of potash into red prussiate, or 118.87 grains correspond to 10 grains of chlorine. The experiment is conducted in precisely the same manner as before, and as soon as the whole of the ferrocyanide is converted into ferricyanide, the mixture ceases to give prussian blue with a solution of peroxide of iron*.

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* This method, which is given by Mr. Parnell, *see* "Elements of Chemical Analysis," p. 416, is ascribed to Mr. J. Mercer, of Oakenshaw. This gentleman also avails himself of the oxidizing powers of a mixture of ferricyanide of potassium and caustic potash, in effecting the bleaching of indigo. The manner of applying the discharge may be arranged to suit the conditions of the calico-printer; but the experiment for illustration may conveniently be made by impregnating indigo blue calico with a so-

5. *By a Standard Solution of Sulphate of Indigo.*—This method is now very rarely employed, in consequence of the alteration which the indigo solution undergoes by keeping, and of the complex nature of the action which chlorine exerts on the colouring principle. The indigo solution was prepared by dissolving indigo of commerce in Nordhausen sulphuric acid, and diluting the deep blue compound formed until a certain volume was exactly decoloured by an equal volume of dry chlorine. This was effected by filling a bottle with dry gas, perfectly pure, and causing it to be absorbed by a dilute solution of caustic potassa; the indigo solution was then diluted till 100 measures were exactly decolourized by 100 measures of the chlorinated potash. The method being now but little used, further details may be dispensed with. From all the acids which have hitherto been treated of, hydrochloric acid is easily separated by nitrate of silver; the compound to be examined should be dissolved in nitric acid, the whole of the chlorine is thus obtained in the form of chloride of silver, and the other acids may, generally speaking, be determined in the filtrate by the usual methods.

Hydrobromic Acid.

When present in a solution in the form of hydrobromic acid, bromine is determined by precipitating it in the form of bromide of silver, precisely in the same manner as chlorine. Like the chloride, the bromide of silver is insoluble in water and in nitric acid: it is yellowish white when precipitated, but it changes colour when exposed to the light. It is decomposed by chlorine, bromine being separated. When heated it fuses, solidifying, on cooling, into a yellow horny mass. Its composition is

One equivalent of Br.	78.26	...	42.01
One ditto Ag.	108.00	...	57.99
One ditto of Ag Br.	186.26		100

The analysis of bromides may be effected in the same manner as that of the corresponding chlorides. The indirect method is, in many cases, the most convenient: a weighed quantity of the compound is decomposed by heating it in a porcelain capsule, with concentrated sulphuric acid; the amount of metal is calculated from the weight of the resulting sulphate, and that of the bromine from the loss sustained. The analysis of those bromides, the bases of which are capable of being precipitated by sulphuretted hydrogen, may be performed by that reagent. Free bromine, in aqueous solution, is determined in exactly the same manner as free chlorine.

Separation of Bromine from Chlorine.—Two methods of performing this analysis are known, a *direct* and an *indirect* method. The former is based on the solubility of bromide of barium in absolute alcohol, and the insolubility of chloride of barium in the same menstruum. The two substances are precipitated together out of their solution, by nitrate of silver; the precipitates, after having been washed and dried, are reduced by being brought into contact with zinc and dilute sulphuric acid, there are thus formed bromide and chloride of zinc, which are dissolved in the acid liquor; on the addition of excess of baryta water the zinc is precipitated, together with sulphate of baryta in the form of hydrated oxide; the filtered solution contains bromide and chloride of barium, it is evaporated to dryness, and the dry mass treated with absolute alcohol, which, as above stated, dissolves only the bromide of barium. The bromine is separated from the barium in the alcoholic solution, and the chlorine from the barium in the solution obtained on treating the residual mass with water, by one of the methods already given.

This method does not give absolutely accurate results. The *indirect* method is based on the decomposition of bromide of silver by chlorine gas. The bromine and chlorine are, as before, precipitated together by a solution of nitrate of silver, and the precipitate having been washed, dried, fused, and very accurately weighed, is introduced into a bulbed tube of hard glass, the ex-

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lution of the red prussiate, and dipping it into a weak solution of the alkali. The nature of the reaction is as follows:—

One equivalent of *Ferricyanide* of Potassium, K_3Cfy_2, differs from two equivalents of *Ferrocyanide* $2(K_2Cfy)$, by containing one atom less potassium. When potash is presented to the former, this deficient atom of potassium is supplied; but the affinity is not strong enough to liberate the oxygen. When, however, a second body, having an affinity for oxygen, such as litharge or indigo, is presented to the potash and ferricyanide; this second affinity, acting in a different direction, withdraws the oxygen, and allows the potassium to unite with the compound radical ferrocyanogen, thus

$$K^3Cfy_2 + KO + PbO = 2(K_2Cfy) + PbO_2;$$

the decomposition being of the same kind when any organic matter is substituted for the oxide capable of further oxidation, soda and ammonia may be substituted for potash in the above decomposition, producing the oxidation, or discharging the indigo. —*Mem. Chem. Soc.*, Part 21.

act weight of which has also been noted. The tube is connected with an apparatus for evolving chlorine, and a current of that gas dried by passing through chloride of calcium is caused to traverse the tube, to which heat is at the same time applied sufficient to keep the mixed silver salts in a state of fusion. After the operation has been continued for about half an hour, the tube is allowed to cool, and the chlorine in its interior having been replaced by atmospheric air it is again weighed; the process is again repeated, and the tube a second time weighed: should the second weight correspond with the first, the analysis is complete; if not, the process must be again repeated till the two last weighings are absolutely alike.

The amount of bromine originally present is calculated from the diminution in the weight of the mixture, the bromide of silver being now replaced by chloride of silver. The calculation is made thus:—Suppose the weight of the mixed chloride and bromide to have been 100 grains, and, after the experiment, suppose the weight to have decreased 5 grains. The equivalent of bromide of silver is 186.26, that of chloride of silver 143.5; then, as 42.76 (the difference between the respective equivalents of bromide and chloride of silver) : 186.26 (the equivalent of bromide of silver) : : 5 (the difference in weight found in the experiment) : x; $x = 21.78 =$ the quantity of bromide of silver in the mixture analyzed.

Hydriodic Acid.

Iodine when present in a solution in the form of hydriodic acid, and in the absence of bromine and chlorine, is best precipitated in the form of iodide of silver by solution of nitrate of silver. This salt, which when newly precipitated is of a bright yellow colour, has many properties in common with the corresponding chlorine and bromine compounds. Thus, it is insoluble in water and in dilute nitric acid, and soluble, though with great difficulty, in ammonia; like bromide of silver, it is decomposed by chlorine; it also blackens when exposed to the light, and, when heated, it fuses into a horny mass, without undergoing decomposition. Its composition is

One equivalent of	I	126.36 ...	53.91
One ditto	Ag	108.00 ...	46.09
One ditto	AgI	234.36	100

In the presence of hydrobromic and hydrochloric acids, iodine may be very accurately estimated in the form of *protiodide of palladium*, by means of protochloride of palladium. The precipitate, which is of a deep brown black colour, is allowed to settle for some hours; it is then collected in a tared filter, dried at a temperature below the boiling point of water, or, what is still better, in vacuo, over sulphuric acid, and weighed. Its composition is

One equivalent of	I ...	126.36 ...	70.34
One ditto	Pd ...	53.27 ...	29.66
One ditto	Pd I ...	179.63	100

Iodine may also be estimated by the process recommended by *M. Duflos*, viz., by precipitating it in the form of protiodide of copper by a solution of sulphate of copper in concentrated sulphurous acid; the precipitate may either be collected on a filter, washed, and determined as protiodide of copper, or it may be dissolved in dilute nitric acid, precipitated by nitrate of silver, and weighed as iodide of silver. This method is well adapted to the separation of iodine from chlorine, in cases where the presence of chlorine is immaterial. *M. Sarphati*[*] recommends a solution of perchloride of copper in dilute hydrochloric acid; a solution composed of 1 part of crystallized sulphate of copper, and 2½ of crystallized sulphate of iron.

Iodine is sometimes determined by the *indirect* method, viz., by converting the base or bases with which it is combined into sulphates, by digestion with sulphuric acid in a porcelain capsule, and calculating the quantity of iodine from the loss. Metallic iodides, which are insoluble in water, may be decomposed by ignition with carbonates of soda, iodide of sodium is obtained on treating the fused mass with water, from which the iodine may subsequently be precipitated by nitrate of silver. The base or bases are found in the insoluble residue either as carbonates or oxides. Metallic iodides may also be decomposed by boiling with caustic potash.

Iodine in a free state, in aqueous solution, cannot be determined in the same manner as chlorine and bromine, viz., by the decomposition of ammonia, since the contact of iodine with ammonia gives rise to the formation of

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[*] Ann. der Chem. und Pharm., xxxix. p. 254.

iodide of nitrogen, which is not decomposed by excess of ammonia. In order to estimate the iodine under these circumstances, it is dissolved in excess of caustic potash, the solution, which must be colourless, treated with nitric acid, and precipitated by nitrate of silver; the washed and dried precipitate is ignited, by which the small quantity of iodate of silver formed is converted into iodide.

Separation of Iodine from Chlorine.—Of all the methods which have been proposed, none are so convenient or easy of execution as that of precipitating the iodine in the form of protiodide of palladium. The separation is complete, and the chlorine in the filtrate may be precipitated by nitrate of silver. Should bromine likewise be present, it is precipitated with the chlorine in the form of bromide of silver; the mixed silver salts are analyzed by the method described in the last section, viz., by converting the bromide of silver into chloride by heat, in a current of dry chlorine gas.

Hydrocyanic Acid.

This acid, when in a free state, is best estimated by precipitating it in the form of cyanide of silver. It falls as a white curdy mass, which is insoluble in water, and in dilute nitric acid, but soluble in ammonia. Unlike the chloride, bromide and iodide of silver, it does not change colour when exposed to light, neither will it bear ignition without being decomposed. It may, however, be dried at 212°, without alteration. For its composition, see page 175. Soluble cyanides may also be precipitated by nitrate of silver; insoluble cyanides, which do not readily dissolve in dilute nitric acid, may be analyzed by determining the amount of carbon and nitrogen which they contain by the methods of organic elementary analysis; or the amount of cyanogen may be determined in the indirect manner, by igniting the compound, and weighing the residue. *Smith** proposes to decompose and estimate hydrocyanic acid by means of chloride of lime, a process which occupies but a few seconds; the products are nitrogen gas and carbonate of lime. In some cases he prefers the employment of chloride of soda to chloride of lime, on account of the solubility of the compounds that are formed. The same method is applicable to the analysis of the salt of cyanogen, and also to that of the ferrocyanides.

The usual method of analyzing the latter, when free from alkali, is to fuse them, in small portions at a time, at an intense heat, in a porcelain crucible, with nitre. The bases which remain are separated from each other by the ordinary processes, and the cyanogen is estimated in a fresh portion by the direct determination of the carbon and nitrogen. Alkaline ferrocyanides are decomposed by boiling sulphuric acid, nitric acid, or aqua regia, and the evaporated mass treated as usual for the bases. The reason why it is inadmissible to decompose them by fusion with nitre is, that an explosion would certainly result from the contact of the nitre with the fused salt. Those alkaline double cyanides, which resist decomposition by boiling concentrated acids, are kept for a long time ignited in the air, or in contact with oxide of copper; and, should the ferrocyanide under examination contain a volatile metal, the latter must be determined by dissolving a separate portion of the compound in caustic potassa, or in hydrochlorine acid, and precipitating the metal with sulphuretted hydrogen.

A method of analyzing compounds of cyanogen, founded on the action of *iodine*, has been proposed by *M. V. Gerdy**. It was found by this chemist, that, in many of the soluble combinations of cyanides, the cyanogen may be substituted, atom for atom, by iodine; so that, from the amount of solution of iodine employed and decolourized before its action on starch becomes evident, it is possible to calculate with the greatest ease, and in a few moments, the amount of the cyanogen contained in the liquid, and the quantity of metal with which it was combined. *Gerdy* has thus analyzed cyanide of potassium with great accuracy. He states, also, that the method is equally applicable to the analysis of cyanide of mercury; of the double compound of cyanide of potassium and cyanide of silver, which contains eight atoms of cyanogen to one of silver; of cyanide of silver, dissolved in ferrocyanide of potassium; of cyanide of potassium and copper; of cyanide of gold dissolved in cyanide of potassium, &c. The analysis of cyanide

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* In a paper read before the Royal Society, Jan. 29th, 1846.

* Comptes Rendus, Jan. 2, 1843.

of gold is, he says, not so easy of execution, according to this method, as is the case with the other compounds above mentioned, and requires some care. The reaction is here of a different description; for, while eight atoms of cyanogen are required to dissolve one atom of gold, viz., four atoms combined with the gold, and four with the potassium, four atoms of iodine alone suffice to effect the decomposition. This peculiarity he considers to be owing to the cyanide of gold not being acted on by the iodine, and being only precipitated entirely when the iodine has decomposed the whole of the cyanide of potassium.

Separation of Cyanogen from Chlorine, Bromine, and Iodine.

The best method is to precipitate all three of the electro-negative elements with nitrate of silver, and, having carefully collected, washed, and dried the precipitate in the water-bath, to determine the amount of carbon and nitrogen yielded by the mixture by the ordinary methods of organic analysis. From the numbers obtained, the amount of cyanide of silver is calculated, and the proportion of iodine, bromine, and chlorine is inferred from the difference.

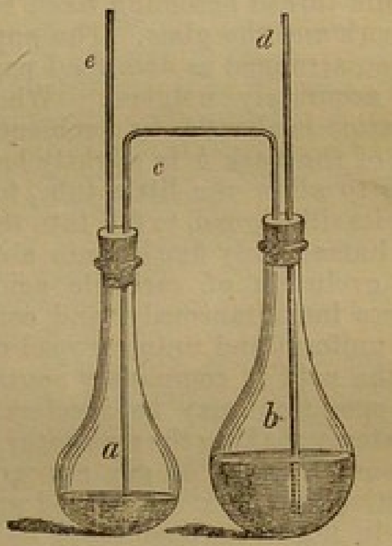
Fresenius gives the following method of determining the relative proportions of hydrocyanic and hydrochloric acids, when together present in a solution. It is founded on the circumstance, that percyanide of mercury is not decomposed by nitrate of silver. The solution is divided into two equal parts. One portion is precipitated with nitrate of silver, and the mixed precipitate of chloride and cyanide of silver weighed; the other portion is mixed with peroxide of mercury, and the mixture agitated until perfectly inodorous. The fluid is then filtered off, the filtrate subsequently precipitated with nitrate of silver, and the precipitate weighed. The difference between the respective weights of the two precipitates indicates the amount of cyanide of silver contained in the precipitate in the first portion.

Nitric Acid.

This acid is best estimated by the *indirect* method.

1. *Estimation of by Hydrate of Baryta.*—To the solutions containing the acid in a free state water of barytes is added, until it begins to acquire an alkaline reaction; the whole is then evaporated to dryness. The dry mass is redissolved in water, and the solution being filtered off from the carbonate of baryta, which may have formed during the evaporation, is precipitated by the addition of dilute sulphuric acid. The quantity of nitrate of baryta is calculated from the weight of the sulphate precipitated, and from this is deduced the weight of the nitric acid originally present in the solution.

2. *By the Process of Acidimetry.*—This method, which is based on the determination of the amount of carbonic acid expelled by a weighed quantity of the acid under examination, is best performed with the alkalimetrical apparatus of *Fresenius* and *Will*, see annexed figure. It being indispensable that the bicarbonate employed for this experiment should be entirely free from neutral or sesquicarbonate (though its perfect freedom from any admixture of sulphate and chloride is not of consequence). *Fresenius* and *Will* recommend to purify the bicarbonate of soda of commerce in the following manner*. Half a pound or a pound is reduced to a uniform powder, and a portion of it first tested with chloride of mercury; if the solution becomes merely turbid or milky at first, it is tolerably free from carbonates, the powder is then put into a glass jar and covered with the same amount of cold rain water; it is allowed to stand for 24 hours, with frequent stirring. The salt is then placed upon a funnel, the tube of which is stopped with loose



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* New Method of Alkalimetry and Acidimetry, p. 89. Edited by J. L. Bullock.

cotton, so as to allow the ley to drop off. The salt is then washed several times with small quantities of cold rain water, what remains is generally pure, and adapted for acidimetrical purposes. It is dried between some sheets of blotting paper, without the aid of heat, and kept for use in a well-closed glass jar. The operation is conducted as follows:—A portion of the fluid to be examined is carefully weighed into *b*; if the acid be concentrated, from four to eight times its amount of water should be added. A little glass tube is provided, capable of holding about 75 grains of bicarbonate of soda; it is filled nearly to the brim with the alkali, and, a silk thread being tied round its upper end, it is lowered down into *b*, so as to remain suspended perpendicularly when the flask is closed, the silk thread becoming fixed between the cork and the glass. The apparatus is then arranged as described page 145, and accurately weighed. When the operation is about to be commenced, the cork of the flask *b* is slightly loosened, so as to allow the little tube, together with its silk thread, to fall into the acid, and immediately fixed again air tight. The evolution of carbonic acid commences instantaneously, and continues in a uniform and uninterruped manner till the acid is completely neutralized. The operation may be accelerated by repeatedly shaking the apparatus. When no more bubbles of gas appear upon agitation, the flask *b* is placed up to its neck in hot water, and there left until the renewed evolution of gas has completely ceased; this is also promoted by agitating the apparatus. The wax stopper is then removed from *d*; the flask removed from the hot water, wiped dry, and suction applied to *e* until the carbonic acid is completely removed. The apparatus is allowed to cool, and again weighed; the amount of anhydrous acid in the sample examined is determined from the amount of carbonic acid evolved; every two equivalents of the latter indicate one equivalent of nitric acid. It is evident that this method applies to all acids capable of decomposing bicarbonate of soda, and, consequently, that it cannot be employed to determine nitric acid in the presence of any other free acid.

Analysis of Nitrates.—Those nitrates whose bases form with sulphuric acid compounds which are not decomposed by mere ignition, may be analyzed by heating them in a platinum crucible, with sulphuric acid, and, having expelled the excess of acid by feeble ignition, determining the quantity of nitric acid expelled by calculation from the weight of the sulphate obtained. Nitrates which contain no water of crystallization may also be analyzed by simple ignition, nothing but pure metallic oxide being in most cases left; the amount of nitric acid is inferred from the loss of weight. If the salt to be examined be mixed with two or three times its weight of perfectly anhydrous borax, the decomposition is effected at a lower temperature, and without danger of deflagration. Hydrated nitrates are analyzed by determining the base in one portion, and the water and nitric acid in another, by the method of organic elementary analysis. Nitrates, the bases of which are precipitable by sulphuretted hydrogen, may be analyzed by removing the base by that reagent, excess of which should be avoided, and determining the amount of nitric acid in the filtrate by hydrate of baryta, in the manner described at the beginning of this section.

The analysis of those nitrates which are insoluble in water may be effected also by sulphuretted hydrogen. They should be reduced to a state of minute division, and kept suspended in water while a stream of sulphuretted hydrogen is passed through the liquid.

From *baryta*, *strontia*, and *lime*, nitric acid may be separated by mixing the solution with slight excess of sulphuric acid; and, in the case of lime and strontia, adding also alcohol, to render the precipitation more complete. Water of baryta is added to the fluid filtered off from the precipitate, until it is slightly alkaline; it is then evaporated to dryness on the water-bath, redissolved in water, filtered, and the filtrate treated as above directed. Another method, which may be adopted for determining the amount of nitric acid in the nitrates, is to distil them in a retort, with sulphuric acid, and to collect the products in a receiver containing baryta water. The distillation is continued until fumes of sulphuric acid begin to make their appearance. Should the nitrate under examination contain an *iodide*, or *bromide*, or a *chloride*, the solution should be treated with sulphate of silver, previous to commencing the distillation, the precipitated iodide, bromide, or chloride of silver being removed by filtration, the solution should be mixed with a slight excess of carbonate of soda, and then the distillation with excess of sulphuric acid proceeded with.

New Methods of estimating Nitric Acid. 1*st. Method of Gossart*[*].—This is founded on the oxidizing action of nitre under the influence of sulphuric acid. The reagents employed in analyzing crude nitre are—1st, an acid solution of protosulphate of iron; and, 2nd, a very dilute solution of the ferricyanide of potassium. The analysis is performed as follows:—Into a flask with a long neck is poured a certain measured quantity of sulphuric acid, sp. gr. 1.704, and half that volume of a solution of saltpetre, containing about 150 grains per 30 cubic inches (10 grammes of refined saltpetre in a *demilitre*); a few drops of the solution of protosulphate of iron are then added from a graduated burette, and the mixture gently agitated; it becomes brown, suddenly clears again, and acquires a more or less deep straw colour, the normal solution of saltpetre is cautiously added drop by drop, waiting each time till the liquid brightens; when the changes of colour become less rapid, a gentle heat is applied, and, when they are no longer perceptible, it is examined whether on taking out a few drops with a pipette they yield a blue colour with the red prussiate of potash. When the blue colour appears and no longer disappears on boiling the liquids, the number of divisions of the burette which have been employed is noted. A second examination, in which a great number of the trials may be dispensed with, will give an accurate result.

Let N be the number of divisions of the normal solution requisite to saturate completely a certain measure of the standard solution of refined nitre, 10 grammes of the saltpetre to be examined are then dissolved in a demilitre of water, and it is ascertained how many divisions of the normal solution of iron are required to saturate an equal quantity of the sample precisely in the same manner as when testing the solution of refined saltpetre; let N^1 be the number of divisions required, then $\frac{N^1}{N}$ gives the strength of the saltpetre under examination with great accuracy.

This process, which is applicable to the estimation of nitric acid as well as to the nitrates in general, may also, according to the author, be employed for determining the quantity of nitric acid contained in gun cotton.

For this purpose he directs the whole of the cotton to be oxidized with a mixture of sulphuric acid and peroxide of manganese: the liquid is filtered and decolourized with a few drops of solution of protosulphate of iron, which decomposes the whole of the sesquioxide of manganese before acting upon the nitric acid. In this manner a solution is obtained containing the whole of the nitric acid which existed in the pyroxyline, and the amount of which may be readily estimated.

2nd. *Method of Pelouze*[*]. — This is founded on the peroxidation of a protosalt of iron by the oxygen of the nitric acid, a solution of permanganate of potash being employed, as in *Marguerite's* experiments (*see* page 170), to indicate the completion of the oxidation. It is particularly adapted to the analysis of nitre. The operation is as follows:—It is first accurately determined how much pure nitrate of potash is requisite to peroxidize a known weight of iron dissolved in excess of hydrochloric acid. *Pelouze* found that 2 grammes (30.88 grains) of pure iron (pianoforte wire) dissolved in a considerable excess of hydrochloric acid required from 1.212 to 1.220 gramme (from 18.7 to 18.8 grains); on an average therefore 1.216 gramme (18.77 grains) of pure nitrate of potash. He examined the nature of the gases given off in this reaction, and found them to consist of hydrochloric acid and deutoxide of nitrogen. Converting these numbers into equivalents, they correspond to 6 equivalents of iron and 1 equivalent of nitrate of potash: the acid of this last salt is decomposed, therefore, into deutoxide of nitrogen, which is disengaged, and into 3 equivalents of oxygen, which deprive the hydrochloric acid of 3 equivalents of hydrogen to form 3 equivalents of water and liberate 3 equivalents of chlorine, which produce with the 6 equivalents of protochloride of iron 3 equivalents of perchloride. These reactions will be better understood by putting them into an equation, thus:—

$$6\,FeCl + KO,NO_5 + 4\,HCl = \\ 4\,HO + KCl + NO_2 + 3\,(Fe_2Cl_3)$$

It will be observed, by the way, that this decomposition of nitrates by proto-

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[*] Comptes Rendus, Jan. 4th, 1847.

[*] Comptes Rendus, Feb. 15th, 1847.

salts of iron in the presence of an excess of hydrochloric acid furnishes a good mode of preparing deutoxide of nitrogen. This decomposition being established, it occurred to *Pelouze* that it might be made the basis of a ready and simple method of analyzing the nitrates. He found that the presence of sulphates and chlorides in no way interfered with the decomposition in whatever proportion they were present, and there only, therefore, remained to be found a safe and ready method of determining, in the assay of an impure nitrate, the quantity of iron not peroxidized. Such a method has been described by *Marguerite* (see page 170). Suppose, for instance, that, having operated upon 30.88 grains of iron, and 18.77 grains of impure nitre, the mineral chameleon indicates that 3.088 grains of iron have not been peroxidized: it may be concluded that 30.88 grains minus 3.088 grains or 27.79 grains have been peroxidized : now, if the nitre had been pure, the whole 30.88 grains would have been peroxidized : we, therefore, have the proportion—

As 30.88 : 18.77 : : 27.79 : 16.89 ;

the 18.77 grains of impure nitre consequently contain 16.89 grains of nitrate of potash, or 90 per cent.

The following example will illustrate the practical details of the method. The specimen may be supposed to be taken from a sample of the crude nitre of commerce as it is sent to the refiner.

30.88 grains of pianoforte wire are placed in a flask of the capacity of about 10 cubic inches, and on them are poured about 1500 grains of strong hydrochloric acid, the flask is closed with a cork furnished with a drawn out tube, and the iron dissolved at a gentle heat. When the whole is dissolved, 18.52 grains of the nitre under examination are introduced, the flask is immediately closed, and the liquid boiled ; it becomes of a brown colour ; dense vapours of hydrochloric acid, mixed with deutoxide of nitrogen, issue from the orifice of the drawn out tube, and prevent the access of air. As soon as the liquor loses the brown colour, it becomes yellow, and gradually brightens : after boiling for 5 or 6 minutes, and when the liquid has become perfectly transparent, the flask is removed from the fire, the liquid which it contains and the wash water are poured into a flask capable of holding about 60 cubic inches, which is then entirely filled with ordinary water : upon this a solution of permanganate of potash of known strength is gradually added from a graduated burette. The operation is then finished, and there remains only to calculate the result.

Let us suppose that the solution of mineral chameleon was of such a strength that 25 divisions of the burette were required to peroxidize 7.72 grains of iron, or 50 divisions for 15.44 grains of that metal ; and let us further suppose that to complete the preceding experiment 10 divisions of the same solution were required ; now, if 50 divisions of this permanganate suffice to peroxidize 20 of iron, how much ought 10 divisions to peroxidize ?

As 50 : 15.44 : : 10 : 3.088

3.088 therefore are subtracted from 30.88 grains of iron, and it may be concluded that the remaining 27.888 have been peroxidized by 18.52 grains of crude nitre : but it is known that 30.88 grains of iron represent 18.77 grains of pure nitrate of potash, the quantity of that salt therefore corresponding to 27.888 grains of iron is found by the following proportion :—

As 30.88 : 18.77 : : 27.888 : 16.95.

In the 18.52 grains of saltpetre submitted to analysis there were therefore 16.95 grains of pure nitre = 91.4 per cent. In performing the experiment the operator must be careful in guarding against access of air : otherwise this would be apt to act upon the deutoxide of nitrogen, and render it capable of peroxidizing a further quantity of iron, so that the amount of nitre would be exaggerated. However, the peroxidation of iron, when the metal is dissolved in a strongly acid liquid, is very slow, as *Marguerite* has shown, and in the manner of conducting the process, as described above, the inconvenience is avoided, for as soon as the iron has disappeared in the acid the flask is filled with hydrogen and hydrochloric acid gases : the nitrate which is introduced carries with it but a mere trace of air, and the liquid kept boiling disengages, by the drawn out tube, acid and aqueous vapours, the issuing forth of which being always visible and readily maintained, does not allow the admission of any air.

The nitrates may be employed either in the solid state or in solution in water

Pelouze prefers the former; though in the case of crude nitre, where great differences frequently occur in the same sample, and where the mean composition is the object sought, he recommends to dissolve 120 grammes (1852.8 grains) of the nitre to be examined in a vessel capable of holding two quarts, which is finally filled exactly with ordinary water; twenty cubic centimetres (1.318 cubic inches) of the solution, containing 1.20 gramme (18.52 grains) of the salt, are then poured into the solution of 30.88 grains (two grammes) of iron in about 1500 grains of concentrated hydrochloric acid, just as the metal has disappeared, and the experiment is proceeded with as before.

Pelouze states that he has confirmed the accuracy of his method by the analysis of several other nitrates, such as those of soda, ammonia, lead, &c., and he observes further that it will enable us to determine the amount of water in certain nitrates, the composition of which is at present doubtful; and that it will prove of great value in analyzing mixtures of nitric and sulphuric acid destined for the preparation of gun cotton, as the sulphuric acid in no way interferes with its accuracy: nitric acid diluted with water only, or mixed with sulphuric acid, may be estimated just as easily as a neutral nitrate. But it is principally in determining the value of crude saltpetre that he anticipates that his method will prove of the greatest utility. In most cases the saltpetre of commerce contains only one nitrate, that of potash, which is mixed with earthy matters, sulphates, and alkaline chlorides. Its analysis may therefore be made with the greatest accuracy and quickness by the above process, as far, that is, as regards the determination of the amount of nitric acid. It scarcely requires twenty minutes, and is accurate to within two or three thousandths.

Ordinary Methods of testing or "refracting" Saltpetre.—The methods in general use have no pretensions to scientific accuracy, neither is such necessary for practical purposes. In *Sweden* a very rough plan is adopted. It consists in casting the melted salt into the form of a cake, one inch in thickness, by means of a small tin box, and then examining its fracture; pure saltpetre has, in the melted state, a coarsely fibrous structure and is very translucent; if it contains $\frac{1}{40}$th of common salt, the nucleus is no longer fibrous, and, if it amount to $\frac{1}{30}$th, the fibrous texture is perceptible only at the edges of the cake.

In France saltpetre is tested by a process introduced by *Riffaut*[*]. A weighed quantity of the dried crude salt is gradually washed, at the temperature of the testing room, with a saturated solution of pure saltpetre in water. When as much of this solution has been used for washing as would be sufficient to dissolve four or five times as much chloride as can possibly be contained in the worst sample of crude saltpetre, it is then quite certain that nothing but pure saltpetre can remain. For a sample consisting of 12¾ ounces, 18½ ounces of a pure solution of saltpetre is used, which will dissolve 8½ ounces of common salt, or 66 per cent. of the sample, a quantity which is never actually present. Nothing now remains to be done but to weigh the saltpetre remaining upon the filter; there is, however, some difficulty attending this, as the solution which clings to it must be first removed. To effect this removal the filter is spread out upon blotting paper, placed upon a porous substance (a slab of gypsum, for instance), that, at the expiration of twenty-four hours, the saltpetre may be taken out and dried. From the weight found, which indicates the amount of saltpetre in the sample, two per cent. must always be deducted, as that quantity has been found by experiment to remain in the wash water, and which it is impossible wholly to remove. It is obvious that this process must be both tedious and inaccurate.

Gay Lussac's Method.—He uses his alkalimeter (see page 143); with which view he converts the saltpetre into carbonate of potash, by fusion with charcoal, when all the nitrogen is evolved. That the evolution of gas may not be too violent, and thus a portion of the test ejected, four parts of common salt, which in no way affect the test, are mixed with half of charcoal powder or soot by way of dilution, and the whole is brought into a state of fusion in an iron spoon. The fused saline mass gives a solution of carbonate of potash and chloride of sodium, which must be filtered and treated with test acid in

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[*] Knapp's Technology. Edited by Drs. Ronalds and Richardson.

the manner described in page 143. Every per cent. of potash indicated by the alkalimeter proves the presence of 2.14 per cent. of saltpetre; every per cent. of carbonate of potash, 1.46 of saltpetre in the sample tested. The only objection that can be raised against this method is, that it requires as much care and dexterity in its execution as any regular chemical analysis, which rather unfits it for practical use.

Husz's Method.—This is a *physical* analysis, and is founded on the fact that the temperature at which a cooling solution of saltpetre loses the property of dissolving more saltpetre, or, what is the same thing, the temperature at which it begins to deposit crystals is a fixed temperature, and depends solely upon the relative proportion of water to that of the saltpetre dissolved, whether chlorides are present or not. If, therefore, the quantity of water remains the same in different cases, the point of saturation will solely depend upon the quantity of saltpetre, and the temperature at which saturation occurs will be a means of ascertaining the amount of saltpetre in a given specimen. Experiments must have been made previously to determine the point of saturation of solutions containing different quantities of saltpetre in an equal amount of water. This method was introduced by the author into Austria, but we have not heard that it has been ever practised in this country.

No suitable means have as yet been discovered of ascertaining the amount of nitrate of soda, which frequently accompanies the first crop of crystals obtained in preparing saltpetre from cubic nitrate of potashes. The discovery of a ready method of determining this point is a great desideratum, since the absence of this salt in nitre employed for making gunpowder is indispensable, on account of the facility with which it absorbs moisture from the atmosphere, a property which would soon render gunpowder, into the composition of which it entered, perfectly useless.

Chloric Acid.

When this acid exists in a free state in aqueous solution, it is most simply estimated, according to *Fresenius*, by converting it into hydrochloric acid by means of sulphurous acid, in the following manner. The solution is mixed with a considerable excess of an aqueous solution of sulphurous acid, and well agitated; the flask is then stopped, and its contents digested for some time. The excess of sulphurous acid is then removed by bichromate of potash, and the liquid, being acidified with nitric acid, is precipitated with nitrate of silver, and the amount of chloric acid originally present calculated from the quantity of chloride of silver obtained.

Chlorates are analyzed either by measuring the volume of oxygen gas which they evolve by their decomposition, or by exposing a known weight to ignition and calculating the amount of chloric acid from the loss of weight thereby experienced; should the salt under examination contain water of crystallization, it must be ignited in a retort of hard glass, to which there is attached a previously weighed tube containing chloride of calcium.

When a *chloride* and a *chlorate* are contained in the same solution, and are each to be estimated, the amount of chlorine in the chloride is first determined in a weighed quantity of the solution by precipitating it as chloride of silver, another weighed portion of the solution is evaporated to dryness and ignited, by which the chlorate present is converted into chloride; it is then redissolved in water and precipitated by nitrate of silver; from the amount obtained we have merely to deduct that yielded by the first experiment to obtain the requisite data for calculating the quantity of chloric acid.

CHAPTER III.

On the Elementary Analysis of Organic Bodies.

Numerous and diversified as are the forms and properties of vegetable and animal substances, and complex as is in general their composition, they are nevertheless made up of a very few of the so-called elements of the material world. A vast number of organic substances consist but of three of these elements, viz., *carbon*, *hydrogen*, and *oxygen;* and very many contain only two, *carbon* and *hydrogen*. There is, again, a very large class of organic bodies, into the composition of which *nitrogen* enters in conjunction with *carbon*, *hydrogen*, and *oxygen*, and there are a few to which, together with these four principles, *sulphur* and *phosphorus iron*, *manganese* and a few other elements appear to be essential. Thus, of the 58 or 59 substances at present recognised by chemists as simple, not more than ten or a dozen are found in the organic world. It is true that organic compounds may contain other bodies; but such are of artificial production, and do not therefore militate against the fact we have just stated, viz., that by far the greater number of that almost bewildering variety of substances which we meet with as the products of animal and vegetable life, and of their reactions on each other, are constituted of three or four only of the at present recognised elements; and that about a dozen of them are the most that are ever found to enter into their composition.

The older chemists, being unacquainted with any methods of resolving organic substances into their ultimate constituents, or of re-arranging their elements into such forms of combination as might enable them to pronounce upon their constitution, were obliged to satisfy themselves with the examination of the results of their destructive distillation; they thus resolved them into a series of products which, being liable to infinite variation dependent upon the manner in which the distillation was effected and the degree of heat employed, could, it is obvious, throw but little light on the composition or properties of the substance under examination. A vast number of analyses were, however, made in this way by the earlier pneumatic chemists, of whom *Hales* and the celebrated *Priestley* studied attentively the gaseous products of the operation.

The first chemists who attempted to combat the difficulties which surrounded the original attempts to gain an insight into the composition of organic substances by the examination of the results of their combustion in oxygen, were *Gay Lussac* and *Thenard*. Their method was to mix a certain weight of the substance to be analyzed into one or more pellets with chlorate of potassa, and to drop them, by a suitable contrivance, into an ignited glass tube, receiving the products of the combustion into a jar filled with mercury and inverted in a mercurio-pneumatic apparatus. It was soon found, however, that a perfect combustion of the substance could not be effected with chlorate of potash, in consequence of the sudden manner in which this salt liberates its oxygen when exposed to heat. *Gay Lussac*, therefore, suggested the employment of oxide of copper, a substance which does not decompose when ignited alone, but which readily yields its oxygen when heated strongly with an organic substance. The idea of using this oxide was a very happy one, and there can be no doubt that we owe to its application in a great measure that vast addition which has of late years been made to our knowledge in this department of chemistry.

Dr. Prout employed an entirely different method; it was complicated, though exceedingly accurate, as is evident from the fact that the analyses performed by its distinguished inventor are still regarded as models of scientific research, and from the circumstance that *Dumas* has been induced to recur to it notwithstanding its complexity. *Dr. Prout's* object was to burn the substance effectually in oxygen gas; in which case, supposing it to contain three elements, hydrogen, carbon, and oxygen, one of three things must happen:—1st, the original bulk of the oxygen must remain the same, in which case the hydrogen and oxygen in the substance exist in it in the same proportion in which they exist in water; or, 2nd, the original bulk of the oxygen is increased, in which case that element must exist in the compound in a *greater* proportion than it exists in water; or, 3rd, the original bulk of the oxygen is *diminished*, in which case the *hydrogen* must predominate. In the first case, the composition of a substance may be known by determining the quantity of carbonic acid gas yielded by a known quantity of it; while in the other two the same can be readily ascertained by the same data, by noting the excess or diminution of the original bulk of oxygen. For full details respecting the manner of conducting the whole operation, the student is referred to *Dr. Prout's* original paper in the "Philosophical Transactions for 1827," or to an abstract of the same in *Brande's* "Manual of Chemistry," where he will also find wood-cut illustrations of the different parts of the apparatus. We must content ourselves here with a general statement of the advantages of this method of analyzing organic compounds as summed up by the inventor. In the first and chief place there is nothing to be apprehended from moisture. Whether the substance to be analyzed be naturally a hydrate, or in whatever state it may be with respect to water, the results will not be affected; and the great problem whether the hydrogen and oxygen exist in the substance in the proportions in which they form water, or whether the hydrogen or oxygen predominates, will be equally satisfactorily solved, and that (within certain limits) independently of the weight of the substance operated on. When, however, it is the object to ascertain the quantity of carbonic acid gas and water yielded by a substance, it is of course necessary to operate on a known weight; but, this being once determined, there is no fear, as in the common methods, of exposing the substance to the atmosphere as long as may be necessary. The hygrometric properties of the oxide of copper, as well as its property of condensing air, are also completely neutralized; for the whole, at the end of the experiment, being left precisely in the same state as it was at the commencement, the same condensation of course must take place, and any little differences that may exist are rendered quite unimportant from the bulk of oxygen gas operated on, which of course, in all cases, should be considerably greater than that of the carbonic acid gas formed. Another advantage of this method is, that *perfect combustion* is insured by it. There is, also, no trouble of collecting and estimating the quantity of water, a part of the common process atended with much trouble, and liable to innumerable accidental errors; here, on the contrary, the results are obtained in an obvious and permanent form, and, from the ease with which they are thus verified, comparatively very little subject to error.

We shall now proceed to describe, somewhat in detail, the more modern methods of analyzing organic substances, for the perfection of which the scientific world is indebted to *Baron Liebig*, the renowned chemist of Giessen. This method combines with great exactness such simplicity of execution, that it is frequently resorted to as the easiest method of testing the purity of a substance; and it is generally admitted that to its invention must be ascribed the rapid progress of organic chemistry within the last few years. The process consists in burning the organic substance together with oxide of copper or chromate of lead, by which its carbon is converted into carbonic acid and its hydrogen into water, both of which are collected and weighed; if the body contains nitrogen, it is either collected in a gaseous state or is determined by other methods, and the oxygen is calculated by deducting from the original weight of the substance analyzed the combined weights of the carbon, hydrogen, and nitrogen formed.

Preliminary testing of the Organic Substance.—Before commencing the ultimate analysis of an organic compound, the operator must assure himself of its purity. The presence or absence of inorganic non-volatile matter is easily ascertained by heating the substance on platinum foil over a spirit lamp, and, if necessary, urging the flame with the blowpipe; if it does not wholly disappear, the residue must be minutely examined; and if it has been determined to proceed with the ultimate analysis of the compound, notwithstanding the presence of inorganic matter, the amount of the latter must be accurately ascertained. We will suppose, however, that the substance has been proved to be free from inorganic non-volatile matter; it has next to be tested for nitrogen, sulphur, and phosphorus.

Testing for Nitrogen.—If the quantity of this element be large, it is easily detected by simply burning the body, which emits during ignition a smell of singed hair. In smaller quantities it may be detected by mixing the substance with soda lime, and heating it in a test tube; the water of the hydrate is thereby decomposed, its oxygen passing to the carbon and hydrogen of the organic substance, and its hydrogen to the nitrogen (if it contain any), giving rise to the formation of ammonia, which may be detected at the orifice of the tube by holding near it a feather, moistened with strong acetic acid. The following beautiful and delicate test for minute quantities of nitrogen in organic substances has also been recommended by *Lassaigne**. It is based on the facility with which cyanuret of potassium is formed, when an organic substance, containing even very little nitrogen, is calcined at a red heat and protected from the atmosphere, together with an excess of potassium.

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* Bibliothèque Univ., April, 1843.

A small piece of this metal is placed at the bottom of a tube, and the matter to be tested is then added. The end of the tube is heated to a dark red in the flame of a lamp; then left to cool, and the potash salt, formed by the calcination, dissolved with four or five drops of distilled water. The decanted liquor is tested with a drop of solution of ferroso-ferric oxide (magnetic oxide of iron); a dirty greenish precipitate is immediately formed, which, being brought into contact with a drop of hydrochloric acid, becomes of a beautiful dark blue, if the matter under examination contains a trace of nitrogen. In the contrary case the precipitate of the hydrate of oxide of iron is entirely redissolved, without any blue colouring. *Lassaigne* found that neither potash nor its carbonate could be substituted for potassium in this process, neither is it applicable when the organic substance is accidentally mixed with a nitrate, or with an ammoniacal salt. Of these two methods of testing for nitrogen the latter is in its indications the least liable to misconstruction.

Testing for, and Estimation of, Sulphur.—A variety of methods have been proposed for detecting and estimating the amount of this element in organic substances. The subject is invested with a high degree of interest, in consequence of the sharp discussion which has lately taken place between Professors *Liebig* and *Mulder*, respecting the existence or non-existence of this principle in the so-called *proteine* of the latter chemist. The following are the principal methods which have been published:—

1. *Rüling's Process*[*].—The finely pulverized substance is fused in a spacious silver dish, with about twelve times its weight of caustic potash, perfectly free from sulphuric acid; it is then mixed with pure nitre, in weight equal to about half the potash employed, and heated till the fused mass appears perfectly white. The whole is then supersaturated with hydrochloric acid, and a salt of baryta added: the formation of a white precipitate indicates sulphur. It consists of sulphate of baryta, and is collected, washed, dried, and ignited. Its weight furnishes the datum for calculating the amount of sulphur originally present in the substance.

2. *Kemp's Process*[†].—Fine quartz sand, which has been carefully tested for sulphuric acid, is mixed with chlorate of potash, in the proportion of two-thirds of the former to one-third of the latter. The substance to be examined is intimately mixed with the above, introduced into a large platinum crucible, and exposed to a high temperature over a spirit lamp. The process is completed in a few seconds. The contents of the crucible are treated with boiling distilled water, the insoluble portion separated by filtration, and washed till no traces of sulphuric acid remain: the sulphates and phosphates, if any exist, may by this plan be estimated simultaneously by means of a salt of baryta. The object of the sand is to prevent the too rapid oxidation of the organic body, and the risk of a portion being thrown out of the crucible.

3. *Weidenbusch's Process*[*].—The substance is mixed with an excess of nitrate of baryta, and stirred in a beaker glass, with the most concentrated fuming nitric acid to a thin paste; the beaker is covered and exposed to the temperature of the sand bath, replacing the evaporated nitric acid until the organic substance is entirely destroyed, which is perceptible from the circumstance that, on evaporating the nitric acid still present, the mass begins to thicken, but no longer ascends in large bubbles in the glass, and dries quietly without frothing. The decomposed mass is now carefully washed into a platinum dish, dried at 212°, and then heated gradually until the saline mass is perfectly liquid. If the organic substance had not been completely destroyed by the nitric acid, it frequently happens that the mass takes fire, and a portion is projected from the slight deflagration. This must be avoided, as it occasions a loss of substance; but, even though this were not the case, a smaller quantity of sulphate of baryta would probably be obtained, since it appears that the sulphur still contained in organic combination is not oxidized so readily by the deflagration of the mass as by the slow action of the nitric acid. The fused mass is carefully separated from the platinum dish, and treated in a beaker glass with dilute acetic acid, and heat applied as long as any evolution of gas is perceptible. The carbonate of baryta is decomposed, and the residue (if any) consists of pure sulphate, which is collected on a filter,

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[*] Chemical Gazette, vol. iv. p. 362.

[†] Ibid., vol. iv. p. 371.

[*] *Liebig's Annalen*, March 1847.

washed, dried, heated to redness, again digested with acetic acid after ignition, and again heated to redness. After the second ignition it is perfectly pure, and the amount of sulphur may be calculated from it.

4. *Heintz' Process**.—He converts the sulphur into sulphuric acid by burning the organic substance with oxygen and oxide of copper. For this purpose an ordinary combustion tube, open at both ends, is half filled with copper turnings, and a little vessel containing the dry and pulverized substance placed in the tube, which is then connected with a bulb apparatus, filled with solution of potash, perfectly free from sulphuric acid, and the combustion made in a current of oxygen. The contents of the bulb apparatus are now decanted into a spacious flask, containing a warm solution of chlorate of potash in dilute nitric acid, and closed with a glass stopper. The sulphurous acid absorbed by the potash, and which had formed from the decomposition of a portion of the sulphate of copper, is by this means perfectly oxidized. The mixture of oxide, sulphate, and metallic copper is treated in a beaker with the above mixture, and entirely dissolved at a gentle heat; the sulphuric acid is precipitated by chloride of barium, and estimated as usual. As, along with the sulphurous acid, sulphuric acid always passes over into the bulb apparatus, it is advisable, in order to avoid all loss of sulphuric acid, which might arise from condensation of the latter on the cork of the combustion tube, to employ a tube which is drawn out at one extremity at a very obtuse angle into a fine tube, which fits into the stronger arm of a bulb apparatus made for the purpose, and then connected with caoutchouc. The author examined *taurine* by this process, and found in three experiments, in the first, 25.68; in the second, 25.66; and in the third, 25.49 per cent. of sulphur. *Redtenbacher's* formula $C_4\,H_7\,NO_6\,S_2$ requires 25.60 per cent. The combustion must not be carried on too quickly, otherwise a slight loss might readily occur from vapour passing through the solution of potash without being absorbed thereby. In illustration of the importance of carefully examining organic substances for sulphur, and of the great mistakes which may be committed from neglecting to do so, it may be mentioned that the substance above alluded to, viz., *taurine*, which contains nearly 26 per cent. of sulphur, had originally assigned to it the formula $C_4H_7NO_{10}$, and was supposed to be altogether free from that element.

5. *By Acetate of Lead.*—A very convenient method of detecting minute quantities of sulphur in organic substances, which does not, however, enable us quantitatively to estimate it, is to boil the compound nearly to dryness with a concentrated solution of caustic potash. The residue is dissolved in water, and introduced into a flask provided with a tube funnel; a strip of paper, which has been thoroughly moistened with acetate of lead, and subsequently touched with a few drops of carbonate of ammonia, is suspended inside the flask between the cork and the neck; on pouring a little dilute hydrochloric acid slowly through the tube-funnel, sulphuretted hydrogen gas will be evolved should sulphur be present, and the lead-paper will turn brown.

Testing for, and Estimation of, Phosphorus.—The substance may be oxidized by the process of either *Rüling* or *Kemp*, or with fuming nitric acid, or with a mixture of nitric acid and chlorate of potash, and the solutions obtained may be examined for phosphoric acid by one of the methods described in the section on phosphoric acid.

1. *Analysis of non-volatile Solids, not containing Nitrogen.*—The first important point is to dry the substance thoroughly. This is done either in the water or air-bath, or in vacuo over sulphuric acid, or by any other of the methods described in the first chapter of this treatise, the means employed depending on the physical and chemical characters of the substance under examination. With the view of illustrating the details of the whole operation, we will take, as the simplest case that can be brought before the student, the analysis of the crystallizable sugar of manna, namely, *mannite*, giving the results as they occurred in an actual analysis.

The crystalline sugar, having been finely pulverized, is dried in a watch-glass in the water-bath until two weighings, made at the interval of half an hour from each other, furnish a constant result. The fine powder is now introduced into a small stoppered bottle, the exact size and shape of *fig.* 38. The weight of the bottle (which is kept in the water-bath along with the sub-

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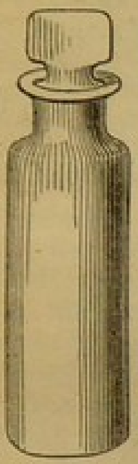
* *Poggendorff's Annalen*, 72, p. 145.

stance, to insure its being thoroughly dry) is, when empty, 76.66 grains, and, when filled with the mannite, 84.76 grains.

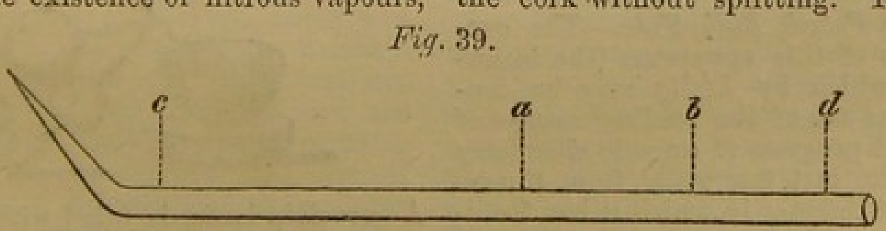
Fig. 38.



A Hessian crucible, of the capacity of about four ounces, is nearly filled with oxide of copper, carefully prepared in the following manner: — Some shreds of pure copper (clippings from electro-types) are dissolved in pure nitric acid; the solution is evaporated to dryness in a porcelain basin, and the residual basic salt heated to moderate redness in a Hessian crucible until fumes of nitrous vapour cease to be evolved. It is constantly stirred during the ignition with a copper rod, to promote the escape of the gas. The last traces of nitric acid adhere somewhat obstinately to the oxide of copper; the process should not, therefore, be hurried, but it is better to keep up a moderate heat for a considerable time than to attempt to quicken the operation by urging the fire, as in this case the lower portions of the oxide are apt to fuse, and, on cooling, the mass becomes so hard that it is difficult to remove it from the crucible, and, subsequently, to reduce it to powder. Before considering the process to be finished, a portion of the oxide should be tested; with which view a small quantity is introduced into a tube of combustion glass and strongly heated, the aperture of the tube being closed with the finger. On removing the latter, the smell will generally indicate the existence of nitrous vapours, and the tube itself should be carefully examined for the appearance of ruddy fumes. The decomposition being complete, the oxide is allowed to cool, then transferred to a mortar, in which it is reduced to a tolerably fine powder, after which it is fit for use, and may be preserved in a wide mouth stoppered bottle. The same oxide may be employed for several experiments: by merely pouring a little acid on it, the metal is oxidized afresh, and the oxide is restored to its former purity by calcination. The Hessian crucible above alluded to is nearly filled with oxide of copper thus prepared; its cover is put on, and it is placed among the coals of a coal or charcoal fire, taking the greatest care that no organic matter from the fire comes accidentally into contact with it. It is heated to low redness: meanwhile, the other materials required for the analysis are being prepared.

1. *The Combustion Tube.* — This is drawn out from a tube of hard German glass, with the aid of the blowpipe lamp. (*Fig* 22, Treat. I.) A tube free from flaws, and which has been previously tested as to its capability of bearing the requisite heat without blowing out, is selected, from thirty inches to three feet long; it is heated, first gradually, and then with the full power of the lamp, in the middle, until it becomes sufficiently soft to rend asunder; the two ends are then drawn from each other, and by a dexterous turn of the wrist two tubes are prepared, shaped as shown in *fig.* 39, each from fifteen to eighteen inches long. The fine points of the tubes are then sealed, and the open ends are fused at the edges, so as to enable them to bear the pressure of the cork without splitting. The tube, which is selected for the combustion, is thoroughly cleaned and dried; for this purpose a piece of clean filtering paper is twisted round the end of a long stout copper wire, and with this the tube is well wiped out; it may, perhaps, be necessary to wash it out with distilled water. In this case the greatest care must be taken to dry it thoroughly afterwards, which may be done either by folding loosely over the mouth a piece of filtering-paper and burying it in the sand of the sand-bath, or by heating it from end to end over a spirit-lamp, drawing a current of air through it the whole time by putting a long tube, open at both ends, to the bottom, and sucking with the mouth. If the tube has been washed out with water, a small drop of the liquid will often obstinately remain at the very point of the sealed end, which is expelled with a sort of explo-

Fig. 39.



sion on putting the point into the flame of a spirit-lamp. The tube being thus cleaned and dried is kept corked till about to be used, in order to prevent the entrance of any impurity.

2. *The Chloride of Calcium Tube*—This is shown in *fig.* 40. The chloride of calcium is prepared by dissolving chalk in hydrochloric acid, filtering the solution, and evaporating it to dryness: the dry mass is then fused in a Hessian crucible: it must be kept in a well-stopped bottle. In filling the tube, a little cotton wool is first introduced at the large end, which is then closed with the finger; vigorous suction is now applied at the small end (seen in the figure with its cork attached), the finger is then suddenly removed, and the cotton is forced up to the end of the bulb, where it acts as a plug in preventing any of the small fragments of the chloride from getting into and choking up the narrow neck of the tube. The bulb is next filled with coarse pieces of chloride of calcium, and the remainder of the tube, to within half an inch of the end, is then filled up with finer fragments; a second plug of cotton-wool is introduced, and, finally, the tube is closed with a good sound cork, well secured with sealing-wax, nicely smoothed round the edges; through the centre of this cork there proceeds a piece of stout quill tube about three inches long, through which connection is established between the chloride of calcium tube and the potash apparatus. A small hook is seen in the figure attached to the tube. This is made of platina wire, and is intended to offer a facility for hanging the apparatus to the scale of the balance, in which it is accurately weighed.

Fig. 40.

3. *The Potash Bulb Tube.*—The construction of this apparatus (the invention of which by *Liebig* may be considered as one of the leading causes of the rapid progress of organic chemistry within the last few years, from the remarkable manner in which it has facilitated the analysis of organic bodies) will be understood by reference to the annexed figure. It consists of a tube on which five bulbs are blown, three at the bottom, the middle of which is the largest, and one on each of the sides; the three bottom bulbs communicate with each other by pretty wide openings, but each outer bulb is separated from the other by about two inches of tube; one of the side bulbs, *d*, must be larger than either of the others. The object of this arrangement is to expose a large surface of caustic potash ley to the gases evolved during the combustion of the organic substance, so as to insure the complete absorption of the carbonic acid. The method of filling the bulbs with the alkaline ley is shown in *fig.* 41.

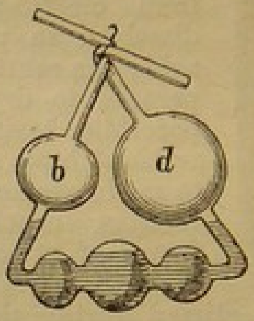
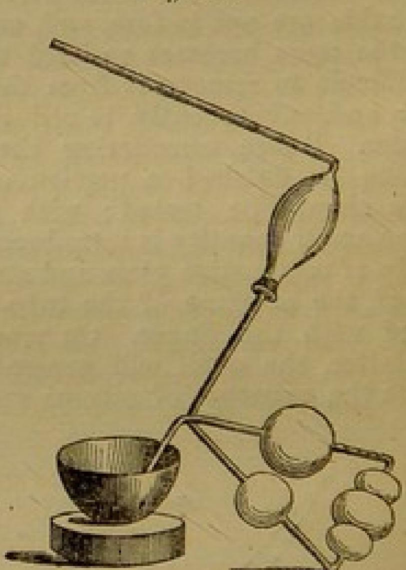


Fig. 41.



A porcelain basin is filled with a solution of caustic potash, specific gravity about 1.27. This is prepared in the usual manner, or more conveniently by the following receipt, given by Dr. Gregory*. Two parts of the subcarbonate of potash of the shops are dissolved in twenty or twenty-four of boiling water. One part of quicklime is slaked by

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* Instructions for the Chemical Analysis of Organic Bodies, by Jusius Liebig. Translated by *Dr. W. Gregory.*

being covered with hot water in any convenient vessel. In this way the whole of the lime is converted into a uniform cream, without the formation of any hard sandy particles which occur in the ordinary method of slaking. The cream of lime is added in small portions to the boiling solution of carbonate of potash, which is boiled a few minutes after each addition, water being occasionally added to supply the loss by evaporation. When the whole of the lime has been added, the mixture is boiled for a short time longer, and is then allowed to cool, the cover of the vessel being carefully closed. After twelve hours the whole of the ley may be decanted perfectly clear and quite caustic, if the vessel has been nearly full. The carbonate of lime is sandy, and occupies a very small bulk. The clear liquid is now to be boiled down rapidly in a clean iron vessel, till small crystals begin to separate. It is then allowed to cool in a stoppered bottle of green glass, when it deposits the whole of the sulphate of potash originally present in the subcarbonate, that salt being entirely insoluble in a strong solution of caustic potash. The specific gravity of this ley is from 1.25 to 1.27; it is nearly pure, containing no foreign matter except a little chloride of potassium, and it is perfectly adapted for organic analysis.

The basin being filled with the ley the end of the tube communicating with the largest of the side bulbs is dipped into the liquor, and to the extremity of the tube, communicating with the smaller bulb, a suction tube is attached by means of a perforated cork: suction is now applied with the lips, and the ley is thus drawn into the apparatus to the extent shown in the figure. The bulbs are then moved from their inclined position, the suction tube taken off, and the interior of the tube which had been immersed in the alkaline liquor is wiped dry with a twisted slip of filtering-paper; and, finally, the whole apparatus is wiped thoroughly dry with a clean cloth. It is now accurately weighed, being suspended from the pan of the balance in the manner shown in *fig*. 2.

3. *The Combustion Furnace*.—This is shown in *fig*. 42. It is made of sheet iron, from twenty-two to twenty-four inches long, and four inches high. The bottom is three inches wide, and is furnished with a series of small slips or apertures, which serve as a grate. The side walls are slightly inclined outwards, and are, at the top, about five inches apart. To support the combustion tube, a series of straight and upright pieces of strong sheet iron are riveted to the bottom of the furnace, between the apertures; they are of exactly equal heights, and their upper edges are slightly curved, so as to coincide exactly with the aperture at the end of the furnace. To confine the fire to particular portions of the tube, two screens are employed of the form represented in *fig*. 43, and seen also in their places in *fig*. 42. The openings in these screens must be sufficiently large to receive the analyzing tube without difficulty; a screen is placed at the anterior part of the furnace during the combustion, to protect the cork of the tube from the heat of the coals. The furnace is placed, during the combustion, either on a large tile resting on a block of wood, a wedge being thrust between the tile and the wood to give the air free access to all the holes of the grating, or it may be placed on an iron tripod stand as shown in *fig*. 46.

Fig. 42.

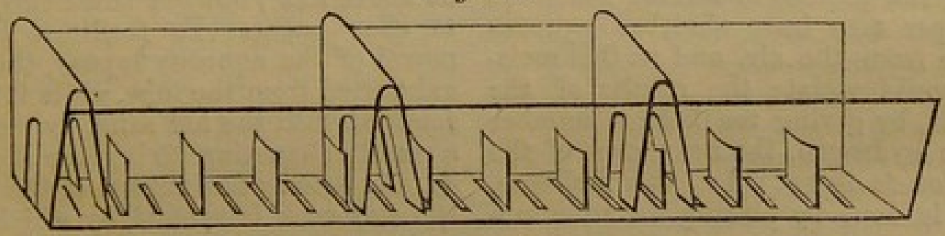
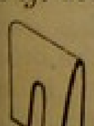


Fig. 43.



4. *Charging the Combustion Tube*.—A sheet of clean glazed paper being laid on the table, the cork is removed from the combustion tube, and warm oxide of copper introduced to about *a* (*fig* 39), this serves as a measure for the quantity required for the analysis; it is shaken from the tube into a clean warm porcelain mortar, which should have a rough or unglazed bottom, as rendering the mixture less liable to adhere to it; about an inch of oxide is left at the end of the tube. The substance to be analyzed is now shaken from the little stoppered bottle, in which it has been weighed, into the oxide in the mortar,

and the whole gently but well mixed together with the pestle. The incorporation being complete, the mixture is transferred from the mortar to the tube, which is best done by depressing the open extremity into the mixture, and turning the tube round; the portions which cannot in this way be got into the tube are poured on a smooth glazed card, and thus introduced. The mortar is now rinsed out with a fresh quantity of warm oxide, which is also transferred to the tube, and which will occupy the space from *a* up to about *b;* lastly, the tube is filled to within an inch of the end with pure oxide from the crucible. The distribution of the mixture in the tube is, therefore, as follows:—From the extremity to *c*, pure oxide; from *c* to *a*, the mixture of oxide and the organic substance; from *a* to *b*, rinsings of the mortar; and from *b* to *d*, pure oxide. The process of filling the tube should be completed before the oxide of copper has got cold. The cork is now put in its place, and the tube, being grasped between the fore-finger and thumb of each hand, is tapped smartly a few times on the table, so as to shake together the contents, to free the pointed extremity entirely from oxide, and to have a channel above the mixture from end to end to allow of the escape of the gaseous products of decomposition which would otherwise force the mixture from the tube. *Fig.* 44 shows the tube as it should appear with the mixture shaken into its place; now, as during the process of mixing the oxide of copper may have absorbed aqueous vapour from the air, and as this moisture would vitiate the results of the analysis, by giving too high a number for the hydrogen, the next step of the operation is to get rid of this moisture, which is done by placing the tube in a wooden trough and covering it with hot sand, the temperature of which should be above 212°, but not sufficiently high to char paper. To facilitate the removal of the aqueous vapour, the air is exhausted from the tube, while it is surrounded with the hot sand, by means of a small exhausting syringe, as shown in *fig*. 45; after a few strokes of the piston the stop-cock is opened, by which fresh air is admitted, which becomes completely dried by passing through a chloride of calcium tube. This process of alternate exhaustion and readmission of air is repeated ten or a dozen times, and the absence of all hygroscopic moisture is thereby ensured.

Fig. 44.

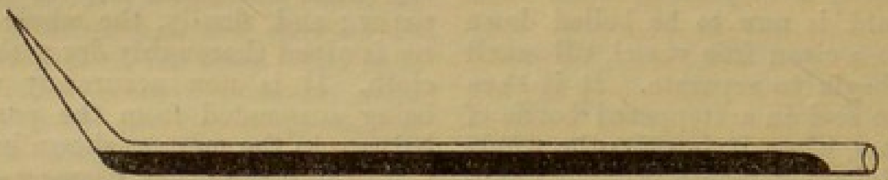
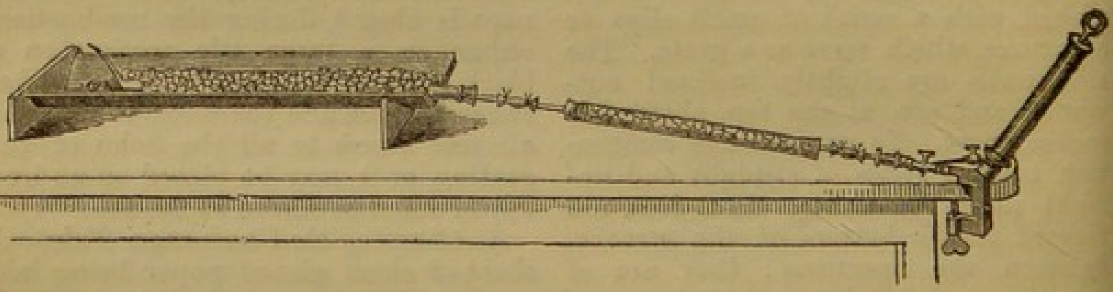
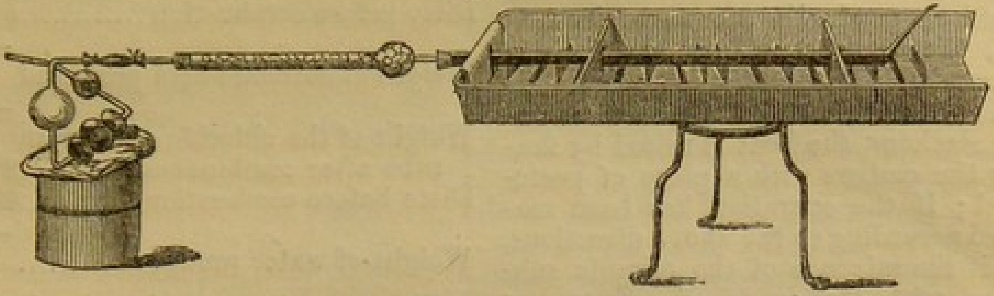


Fig. 45.



5. *Arrangement of the Apparatus for the Combustion.*—This will be perfectly understood from an inspection of *fig*. 46. The chloride of calcium tube is connected with the combustion tube by means of a perforated cork, which has been thoroughly dried in the water bath; the operator must be careful in the selection of this cork, as, if a deficiency of tightness is detected when the apparatus comes to be examined previous to commencing the analysis, it is here that the fault will generally be found to lie. The cork should be thoroughly sound, and should be cut smooth and tapering; the hole through which the chloride of calcium tube enters should be round and smooth. The chloride of calcium tube is con-

Fig. 46.



nected with the potash apparatus by a double caoutchouc tube secured by strong silk cord; the caoutchouc should be soft so as to yield to the pressure of the cord, which should be tied in a bow and not in a knot, in order that it may be readily removed at the end of the analysis. It will be noticed that it is the extremity of the potash apparatus, in connection with the *large* bulb, which is attached to the chloride of calcium tube. The combustion tube should project a full inch from the end of the furnace, the screen being placed over it to protect the cork, as shown in the figure. The bulbs of the potash tube rest on a folded towel or silk handkerchief placed on blocks of wood raised to the requisite height, and the apparatus is inclined slightly by placing a cork underneath one of the side bottom bulbs, as seen in the sketch. The whole arrangement should have a slight inclination forwards, from the sealed end of the combustion tube to the junction of the chloride of calcium tube with the potash-bulbs. The apparatus being thus far disposed, the next step is to see that the junctions are all perfectly air-tight; this is done in the following manner:—A red-hot coal is held near the large side bulb of the potash tube, the inclosed air becomes hereby expanded, the ley sinks, and, as the heat increases, a portion of the expanded air escapes in bubbles through the several bulbs, out at the open end of the tube; when about a dozen bubbles have in this way been expelled, the hot coal is removed, and the bulbs are set level on the cloth; as the bulb cools, the air remaining in it contracts, and the potash ley rushes back and fills it more or less. It is now left for a few minutes, during which time the operator may be employed in reweighing the little bottle which contained the substance about to be analyzed; if at the end of five minutes or so the potash ley should show no disposition to recede from the large side bulb, and once more take up a horizontal position, it may be concluded that the apparatus is perfectly tight: on the other hand, should the liquid not preserve the level which it had acquired after the cooling of the large bulb, then the junctions are not tight, and the fault will most likely be found in the cork. Supposing, however, the apparatus to have been proved to be air-tight; the potash apparatus is once more inclined, and the combustion commenced.

6. *Management of the Combustion.*—A good supply of red-hot charcoal being provided close at hand, that part of the tube included between the anterior part of the furnace and the first screen is quickly surrounded with small pieces of hot coal, so as to bring it speedily to a red heat; the potash in the large bulb will almost immediately be seen to recede, owing to the expansion of the heated air; the screen is then gradually shifted backwards about an inch at a time, exposing a fresh portion of the tube, which, as before, is surrounded with red-hot charcoal; as soon as the heat reaches the mixture of the organic substance and the metallic oxide, the decomposition of the former commences, carbonic acid and aqueous vapour begin to be evolved—the latter is seen lining the interior of the front part of the chloride of calcium tube in the form of dew, while the former passes into the potash apparatus, driving forward all the air present in the bulbs. At first, the bubbles appear to pass through the ley without being absorbed; but as the combustion proceeds the absorption is more and more complete, and, after a time, if the substance under analysis is free from nitrogen only a solitary bubble occasionally breaks through the liquid, nothing but pure carbonic acid passing through the chloride of calcium. The combustion should be so managed

that the bubbles of gas shall follow each other in a uniform, uninterrupted, and tolerably rapid stream; and the screen should be gradually moved backwards until the whole length of the tube is surrounded with red-hot charcoal. As soon as the evolution of gas in some degree slackens, the heat is raised by fanning the embers with a piece of pasteboard; if the operation has been managed according to the above directions, and if the mixture of the organic substance with the oxide of copper has been thoroughly made, the gas generally ceases suddenly. On this taking place the cork is removed from underneath the small side bulb of the potash apparatus, and the latter laid level on the cloth. The alkaline ley soon begins to recede, slowly at first, but, when it reaches the large bulb which is left at the end of the combustion full of carbonic acid, it rushes rapidly into it; there is no danger, however, of any of the liquid being carried into the chloride of calcium tube if the proper proportion between the bulbs has been observed in the construction of the potash apparatus. As soon as the operator sees the potash rushing back into the large side bulb, he clips off the extremity of the tube with a pair of nippers; this allows air to enter, and the alkaline liquor immediately recedes. The hot coals are now removed from the posterior part of the tube, a long tube open at both ends is held over the broken extremity, either by an assistant, or supported by some convenient rest, and the operator, having inclined the potash bulbs, places a suction tube on the end, and draws a current of air through the whole apparatus; by this means all the carbonic acid and aqueous vapour which remained in the apparatus are swept into the chloride of calcium tube and potash bulbs.

The analysis is now finished, and it only remains to take the apparatus apart, and, after the lapse of about half an hour, to weigh the potash bulbs and chloride of calcium tube, and calculate the results.

7. *Calculation of Results.*—The particulars of the analysis of mannite are as follows:—

	Grains.
Weight of the bottle and substance	83.76
Ditto of the bottle and residue ...	79.64
Weight of substance analyzed ...	4.12

	Grains.
Weight of the potash bulbs after combustion	586.64
Ditto before combustion	580.65
Weight of carbonic acid produced	5.99
Weight of the chloride of calcium tube after combustion............	276.06
Ditto before combustion............	273.20
Weight of water produced	2.86

These numbers furnish the data for calculating the per-centage composition of the substance. We have proved by the preliminary experiments that there is no nitrogen, sulphur, phosphorus, or inorganic matter present; it is evident, therefore, that, after deducting from the weight of the mannite submitted to analysis the amount of carbon and hydrogen obtained in the forms of carbonic acid and water, the remainder must be calculated as oxygen. Let us see what quantities of these several elements we obtain as the result of our experiment. In the chloride of calcium tube we obtain 2.86 grains of water; how much hydrogen, then, in 4.12 grains of mannite? Now, as every 9 grains of water contain 1 grain of hydrogen, we find the quantity contained in 1 grain by the proportion:—

$$\text{As } 9 : 1 :: 1 : x, \text{ or}$$

$$\frac{9}{1} = \frac{1}{x}, \text{ or } 9 = \frac{1}{x} \text{ or } x = \frac{1}{9}$$

that is, the amount of water obtained, divided by 9, gives the amount of hydrogen; consequently, $\frac{2.86}{9} = .31777 =$ the hydrogen in 4.12 grains of mannite; but it is far more convenient to express the amount in per-centage parts, thus:— $\frac{2.86 \times 100}{9 \times 4.12} = 7.71 =$ per-centage amount of hydrogen.

Again, in the potash bulbs we have condensed 5.99 grains of carbonic acid; what is the per-centage amount of carbon? 22 grains of carbonic acid contain 6 grains of carbon.

$$\text{As } 22 : 6 :: 11 : 3$$

$$\text{As } 11 : 3 :: 1 : x$$

$x = \frac{3}{11}$; consequently, the quantity of carbonic acid found, multiplied by 3 and divided by 11, gives the amount of carbon; and we get it in per-centage parts by multiplying by 300 and dividing by 11 times the quantity of substance analyzed, thus:—

$$\frac{5.99 \times 300}{11 \times 4.12} = 39.61 = \text{per-centage amount}$$

of carbon.

The composition of the mannite, according to the above analysis, is therefore

Carbon	39.61
Hydrogen	7.71
Oxygen	52.68
	100

Construction of a Formula from the per-centage Composition of a Substance.—Although we may not, as in the case of mannite, be able always to determine the atomic weight of a compound, it is an easy matter to ascertain the *relative* proportion of the equivalents of the elements of which it is composed, provided we have before us a correct statement of its per-centage composition; in other words, we can, from such data, deduce its *empirical* formula; for this purpose we have only to divide the per-centage number of each element by its atomic weight, and to reduce the figures obtained to the simplest expression possible: thus, in our experiment with mannite, we have

$$\frac{39.61}{6} = 6.601 = \text{equivalent of carbon.}$$

$$\frac{7.71}{1} = 7.710 = \text{equivalent of hydrogen.}$$

$$\frac{52.68}{8} = 6.585 = \text{equivalent of oxygen.}$$

Now here the numbers 6.601 and 6.585 are so nearly alike that it is at once evident that in mannite the number of atoms of carbon and of oxygen are the same; and, on considering the above figures, it is seen that the simple numbers with which they best correspond are 6, 7, and 6. Let us see, then, how nearly the numbers calculated in per-centage parts from the formula

$$C_6\,H_7\,O_6$$

agree with the experimental ones:—

		Theory.	Experiment.
C_6	36	39.57	39.61
H_7	7	7.69	7.71
O_6	48	52.74	52.68
	91	100	100

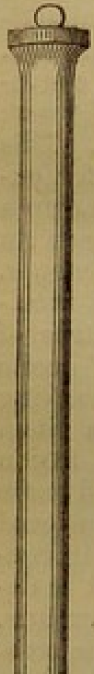
The coincidence is so close that there can be no doubt that the above formula is the correct one, though we have no way of confirming it by determining the atomic weight of this peculiar kind of sugar. We shall give presently a case in which the absolute as well as the relative proportion of the atoms of an organic substance can be determined, and a *rational* formula deduced for it.

Combustion with Chromate of Lead.—Some organic substances cannot be thoroughly oxidized by burning them with oxide of copper, partly, according to *Dumas*, in consequence of the formation of a small quantity of *carburet of copper*, together with the reduced metal, and partly owing to the deposition here and there of small particles of carbon. With such substances this source of error is sometimes obviated by introducing into the posterior end of the combustion tube some chlorate of potassa, mixed with oxide of copper: this salt, being heated at the end of the combustion, gives off pure oxygen, in which all the combustible matter must be thoroughly oxidized. The object is, however, more conveniently attained by employing *chromate of lead* instead of oxide of copper. This substance is admirably adapted for oxidizing purposes, from its yielding up a portion of its oxygen by heat alone; a property not possessed by oxide of copper. Chromate of lead is prepared by precipitating a clear solution of acetate of lead, containing slight excess of acetic acid, by bichromate of potassa, washing the precipitate thoroughly on a linen strainer, drying, and igniting to fusion in a Hessian crucible. The fused mass is pulverized, and kept in a stoppered bottle. By heat, either alone or in contact with an organic substance, it is decomposed into green oxide of chromium, and basic chromate of lead. The combustion of an organic body, with chromate of lead, is conducted precisely in the same manner as with oxide of copper. The chromate is finely pulverized, and mixed while warm with the substance; but, as it is not in the least degree hygroscopic, the process of exhausting the analyzing tube while buried in hot sand may be omitted; a narrower tube than that employed with oxide of copper may be used, and the chromate which has served for one experiment may be used again after refusion.

II. *Analysis of Volatile Solids and Liquids not containing Nitrogen.*—The analysis of waxy substances, and of volatile organic solids, is performed in tubes which are somewhat longer and wider than those generally employed. The analyzing tube is filled also in a different manner, as it would obviously be inadmissible to triturate volatile substances with hot oxide of copper, and the nature of oily and waxy bodies renders their admixture in the usual manner impracticable. Solid fusible fats, oils, &c., are weighed in a little tube, the size and shape of *fig.* 47. The chromate of lead or oxide of copper is introduced, while hot, into a wide thin glass tube, about twenty inches long, or into a copper tube which can be closed air-tight with a brass cap and lead washer, *fig.* 48; in this it is allowed to cool; if chromate of lead is the oxidizing agent employed, a layer of about two inches is first introduced into the combustion tube; but, if oxide of copper is to be used, the same quantity of a mixture of chlorate of potash and oxide is shaken in; the little tube, with its charge of substance, is then dropped into the analyzing tube, and heat applied so as to melt it, and cause it to spread over the lower side; the tube is then filled with the oxidizing agent by introducing its open end within the copper or wide glass tube, containing the oxide of copper or chromate of lead, and turning it round. The tube being filled, the substance to be analyzed is diffused through the oxide or chromate by placing it for a few minutes in hot sand; keeping it well corked during the time, the combustion is then proceeded with in the usual manner. If the substance is not of a waxy or fatty nature, it is mixed with the oxide or chromate by means of a copper wire, the end of which is formed like a corkscrew; but the operation requires to be conducted with skill and rapidity.

Fig. 47.

Fig. 48.



Volatile liquids, such as alcohol, ether, &c., are weighed in two or three small glass bulbs, the size and shape shown in *fig.* 49. These bulbs should be drawn out of a long piece of quill tubing, in order to prevent any moisture from getting into them while they are being expanded by the breath. They are filled by heating them slightly over a spirit-lamp, and immersing their pointed extremities in the fluid to be analyzed; on cooling, the liquid enters the bulb from the contraction of the heated air, the bulb is again gently heated, on which more air is expelled, and then, on once more dipping the open end into the liquid, an additional quantity enters. In this manner the bulb is about three parts filled with the liquid; upon which its extremity is sealed, and it is weighed, and, the weight of the empty bulb having been previously taken, that of the included liquid is found. The analyzing tube employed should be longer and wider in proportion as the liquid is more volatile. The oxidizing agent is allowed to cool in the closed copper or glass tube, *fig.* 48, and, a layer of two inches having been introduced into the combustion tube, the centre of the neck of one of the little bulbs is slightly scratched with a file, the point is quickly broken off, and both bulb and point are dropped into the tube and covered immediately with three or four inches of oxide of copper; another bulb is then introduced in a similar manner, covered with a layer of oxide, and so on with a third, should the substance to be analyzed be included in more than two bulbs. The tube is then tapped to open a channel for the escape of the gases.

Fig. 49.

The analysis of volatile liquids requires a great deal of care on the part of the operator. Thus, if a high heat were suddenly applied to one of the bulbs, a sudden gush of vapour would be produced, a portion of which might either be expelled from the tube without undergoing combustion, or, if it were resolved into carbonic acid and water, these products would be evolved with such impetuosity as to eject the potash from the bulbs. The greatest care is therefore necessary in conducting the operation. About six inches of the anterior portion of the tube are first heated to redness, and a screen placed behind to prevent the communication of heat to the locality of the bulbs; the fluid in the first bulb is then gently distilled out by holding a red-hot charcoal near it, and the vapour, thus gradually coming into contact with the oxidizing agent, is quietly burned. In this way, the contents of all the bulbs are brought into contact with the heated oxide, and it is advisable to keep a few pieces of hot charcoal against the closed end of the tube, to prevent any of the liquid from distilling back and condensing there.

III. *Analysis of Organic Substances containing Nitrogen.*—The determination of the nitrogen of an organic compound is always an operation distinct from that of the determination of the carbon and hydrogen. It is necessary, however, to modify in some degree the arrangements for the latter process, in the analysis of substances containing nitrogen, or the number for the carbon would always come out too high. The reason of this is, that, when an organic compound containing nitrogen is burnt with oxide of copper or chromate of lead, a portion of the nitrogen becomes converted into nitric oxide gas, which, on coming into contact with the potash in the bulb, is further oxidized into nitrous acid, and is retained by the alkali. It is necessary, therefore, to decompose these oxygen compounds of nitrogen before they can leave the combustion tube; which object is perfectly attained by introducing a layer of four or five inches of fine and pure copper turnings into the anterior part of the tube and keeping them intensely ignited during the whole analysis. The nitric oxide and nitrous acid are completely decomposed by copper at a high temperature, nitrogen being evolved in a gaseous form, which passes unabsorbed through the chloride of calcium tube and potash bulbs.

The copper turnings employed for this purpose must be free from impurities, to insure which it is advisable to tarnish them by heating them in a crucible, with free access of air, and then to reduce the film of oxide which has formed on their surface by heating them to redness in a glass tube, through which a current of hydrogen is passing.

There are three different ways of estimating the nitrogen of an organic substance, namely, 1st, by collecting the gas in a free state and measuring its volume; 2nd, by determining the relative proportion between the evolved carbonic acid and nitrogen gases; and 3rd, by converting the nitrogen into ammonia, and estimating it as such.

1. *Estimation of Nitrogen in a gaseous State.*—This is the method of *Dumas*, and is applicable to the analysis of all nitrogenous substances, in whatever form that element may exist in them. The substance is burned in the usual way with oxide of copper or chromate of lead, a layer of reduced copper turnings being placed in the anterior portion of the tube, which should be at least two feet long and not drawn out at the closed extremity, but merely sealed; and from five to eight inches of dry bicarbonate of soda at the posterior end, the object of which is to enable the operator to expel all the atmospheric air from the analyzing tube at the commencement of the operation, and all the nitrogen from it at the end by a current of carbonic acid. The mixture of the substance with the oxidizing agent is made in the manner already described, and the tube filled as shown in *fig.* 50; thus, from *a* to *b*, bicarbonate of soda: from *b* to *c*, pure oxide or chromate: from *c* to *d*, the intimate mixture of the substance with the oxidizing agent: from *d* to *e*, rinsings of the mortar: from *e* to *f*, pure oxide or chromate: and from *f* to *g*, copper turnings. The tube is arranged in the furnace, as shown in *fig.* 51, and, the first object being to expel the whole of the atmospheric air, a screen is placed about three inches from the end, and hot coals are applied round the tube behind it so as to heat intensely the bicarbonate of soda, and fill the whole tube with carbonic acid. The conducting tube *c d* fitted into the combustion tube *a b*, with

Fig. 50.

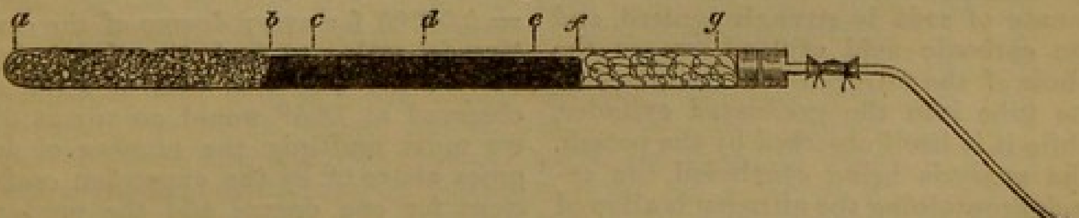
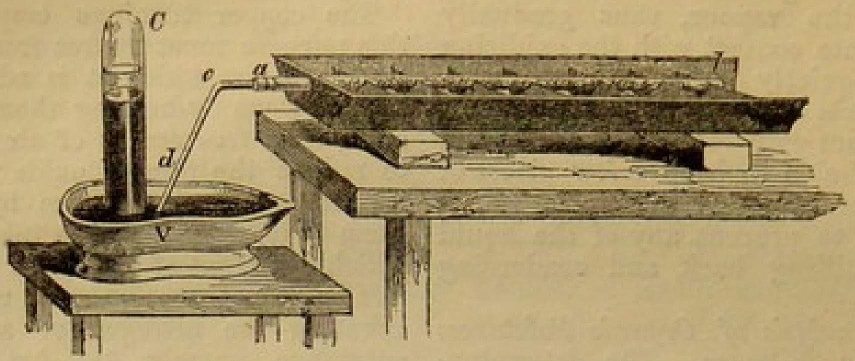


Fig. 51.



a good sound cork, passes under the surface of mercury contained in a small pneumatic trough v. The bubbles of gas, as they break through, are received from time to time into a test-tube filled with caustic potash; and, when they are completely absorbed, it may be concluded that the atmospheric air has been thoroughly expelled from the apparatus. As the success of the experiment depends in a great measure on thus perfectly driving off the air, the operator must not hurry this preliminary process, but continue to apply heat to the bicarbonate of soda till a dozen or so bubbles following are completely absorbed by the caustic ley. A stout glass cylinder *c*, very accurately graduated into *cubic centimetres* or hundredths of a cubic inch, and of the capacity of about 200 c. c. or 13 c. i. is now filled two-thirds with mercury and one-third with potash ley and inverted in the pneumatic trough immediately over the conducting-tube *a*[*]; the combustion is then proceeded with in the ordinary manner, the carbonic acid yielded by the decomposition of the substance is absorbed by the ley, while the nitrogen passes into the cylinder in its gaseous form. At the end of the operation, the remainder of the bicarbonate of soda is strongly ignited, and the carbonic acid evolved sweeps the whole of the nitrogen still contained in the tube into the graduated cylinder, while it is itself absorbed by the potash. The analysis being concluded, the cylinder containing the nitrogen is allowed to remain at rest for some time, to insure the complete absorption of the carbonic acid: it is then carefully transferred to a large deep glass vessel containing water, by placing underneath its edge the ground glass plate, on removing which under the water the mercury and the alkaline ley sink to the bottom of the vessel, their places being supplied by the water. The water within and without the cylinder is then brought to the same level, and the volume of gas read off, the state of the barometer and thermometer being at the same time noted. The analysis is now concluded, and it only remains to calculate the results. The method of doing this will be best understood by quoting the results of an actual experiment.

Weight of substance submitted to analysis .600 grains = 9.264 grains.

Volume of nitrogen gas collected 41.5 cubic centimetres = 2.531 cubic inches; thermometer, 18.5° cent. = 65.3 Fahr.; barom. 7573 millimetres = 29.9 inches.

Correction of the Gas for Temperature. —It is assumed that gases when heated from the freezing to the boiling point of water, that is, from 0° to 100° of *Celsius's* thermometer; expand 0.3665, or, in other words, that they expand $\frac{0.3665}{100}$ = 0,00365 for every degree of the centigrade scale: to find, therefore, what volume the 41.5 cub. cent. of nitrogen observed at 18.5° would occupy at 0°, we must multiply the number of degrees above 0° by the expansion coefficient for one degree, add the product to 1 and divide the observed volume by this sum thus:—

$$\frac{41.5}{1 + (18.5 \times 0.00365)} = 38.87 \text{ cub.}$$

cent., the volume the gas would occupy at 0° cent. This volume has now to be corrected for pressure; but before doing so it is necessary to take into considera-

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[*] As caustic potash acts on the cuticle, making the skin slippery, the best way of filling the cylinder is first to pour in the mercury, then the requisite quantity of potash ley, and lastly pure water; the jar is then inverted by laying on its edge (which should be ground perfectly smooth) a ground glass plate. If the fingers are allowed to become soiled with the alkali, there will be a danger of the tube slipping through them when the operator is in the act of inverting it in the pneumatic trough.

tion *the tension of the aqueous vapour* at the observed temperature: for since the gas was measured in its moist state it must have contained a quantity of vapour of water diffused through it proportional to the temperature, which would counterbalance part of the column of air pressing on the gas; this portion must, therefore, be subtracted from the observed height of the barometer, in order to arrive at the true pressure. We have already (page 129) given a Table from *Faraday's* Chemical Manipulation, founded on the experiments of *Dalton* and *Ure*, showing the proportion, by *volume*, of aqueous vapour existing in any gas standing over or in contact with water at the corresponding temperatures, and at a mean barometric pressure of 30°, and in the appendix will be found a similar Table extracted from *Fresenius's* "Quantitative Analysis," in which the force of the aqueous vapour at every degree of Celsius from 0° to 40° is expressed in *millimetres.* Referring to this latter Table, it will be found that at the temperature at which the experiment we are now considering was made, viz., 18.5 cent., the tension of the aqueous vapour amounts to 15.85 millimetres: this, therefore, being deducted from 757.3 millimetres, the observed height of the barometer, gives .741.45 millimetres as the true pressure from which to correct the volume of gas.

Correction of the Gas for Pressure.—The normal pressure is assumed to be 760 millimetres (29.9 in.): therefore—760 : 741.45 : : 38.87 : 37.92 cub. cent. = the volume of nitrogen corrected for temperature, pressure, and aqueous vapour. The next question is—

What is the weight of 37.92 cub. cent. of dry nitrogen gas at 0° cent. and 760. millimetres barom.?

The specific gravity of nitrogen is 0.9706, atmospheric air being unity; and it has been ascertained by careful experiments that 1 litre (1000 cubic centimetres, or 61.03 cubic inches) weighs at 0° cent. and 0.76 metre barom. 1.2609 grammes (19.46 grains): therefore—

As 1000 : 1.2609 : : 37.92 : .0478 grammes (.738 grs.) = the weight of the nitrogen yielded by .600 grammes of the substance at the standard temperature and pressure; and—

As .600 : .0478 : : 100. : 7.96 = the percentage amount of nitrogen in the substance analyzed.

Having thus detailed the general principles of the method of deducing the per-centage amount of nitrogen from the volume of gas obtained, we will give a formula, founded on the above considerations, by which the calculation may be made in a few minutes, and a good deal of trouble saved.

Let v be the observed volume of gas.
B the observed height of the barometer.
p the tension of aqueous vapour.
t the observed temperature.
m the weight of the substance analyzed.

Then—

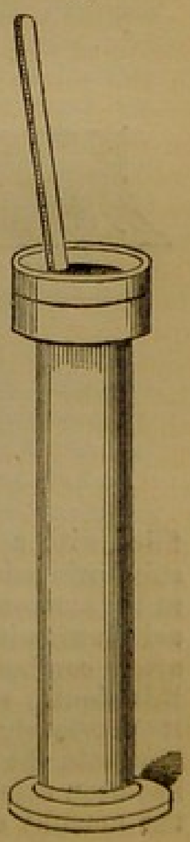
$$\frac{0.12609\, v\, (B - p)}{m\, 0.76\, (1 + 0.003665\, t)} \text{ or}$$

$$\frac{0.1659\, v\, (B - p)}{m\, (1 + 0.003665\, t)} =$$

the per-centage amount of nitrogen. If the analysis quoted above as an illustration be calculated according to this formula, the result will be found to be the same as that at which we arrived by the more circuitous method.

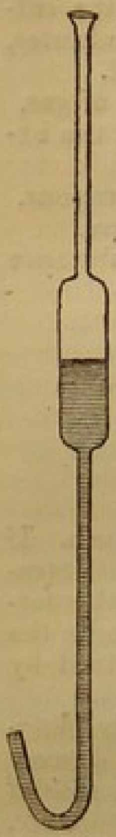
II. *Estimation of Nitrogen by determining the Relative Proportion between the Carbonic Acid and Nitrogen yielded by the Decomposition of the Substance. Liebig's Method.*—This method, which is applicable only to the analysis of substances rich in nitrogen, is performed by burning the substance in the usual way with oxide of copper in a long tube not drawn out at the closed end, and containing at least 5 inches of reduced copper turnings at its anterior end. After a considerable portion of the substance has been decomposed, and when it is concluded that all the atmospheric air has been expelled from the tube, the evolved gases are collected over mercury in a series of graduated tubes about a foot long and half an inch wide. These tubes are then transferred, one at a time, to a tall cylinder, *fig.* 52, containing mercury, where the united volumes of carbonic acid and nitrogen are accu-

Fig. 52.

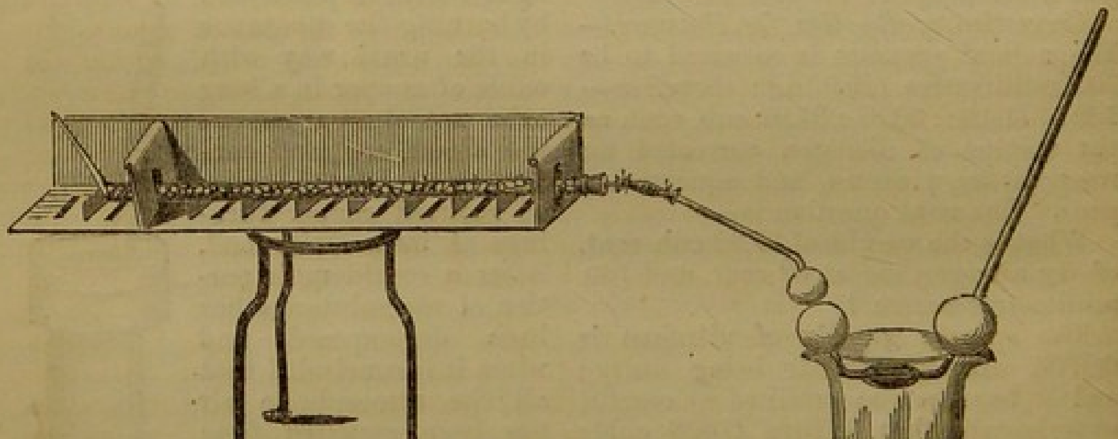


rately measured, the mercury within and without the tubes being brought to the same level: a small quantity of potash ley is then thrown up into the tubes from the siphon, *fig.* 53, by gently blowing, the bent extremity being introduced at the open end of the tubes; and after the absorption of the carbonic acid is complete the residual gas is again measured, the mean result of all the tubes is taken, and the relative proportion of the carbonic acid to the nitrogen gas expresses immediately, without any further calculation, the proportion of the equivalents of carbon to those of nitrogen, since one equivalent of carbon is consumed by two equivalents of oxygen, without the volume of the latter undergoing any alteration, yielding, therefore, two volumes of carbonic acid; and one equivalent of nitrogen yields also two volumes of nitrogen gas.

Fig. 53.



The amount of carbon must have been ascertained by a previous experiment; and, that being known, the weight of the nitrogen may be calculated from the atomic weights of carbonic acid and nitrogen: thus, suppose the proportion of carbonic acid to nitrogen to be as 10 to 4, then the compound analyzed contains 10 × 6 = 60 carbon to 4 × 14 = 56 nitrogen. This is the proportion in which these elements exist in uric acid, for the analysis of which this method answers very well; but in cases where the proportion of nitrogen is very small, or where it is evolved in a variable proportion at different stages of the analysis, it is inapplicable, and the method before described, or the one we shall next consider, must be adopted.



Estimation of Nitrogen by converting it into Ammonia.—This method, which was invented by *Drs. Will* and *Varrentrap*, and which is founded on the action of the hydrates of the alkalies on nitrogenous compounds at high temperatures has already been described (page 147). This process, though exceedingly accurate, is very tedious, on account of the necessity of evaporating the platinum salt on the water bath, and it is expensive, on account of the alcohol and ether which are required. An important modification of the method has, in consequence of these objections, been devised by *Peligot*[*]. The combustion is executed in the same manner as in *Will* and *Varrentrap's* method, and the ammonia condensed in a similar bulb apparatus (see annexed cut), but which, instead of containing hydrochloric acid, is partly filled with a fixed weight or volume of sulphuric acid of known strength. Now, as the ammonia which combines with the acid lowers its strength, by determining after combustion the composition of this liquid, and comparing it with that it previously possessed, it is easy to ascertain the quantity of ammonia that has been condensed; and, consequently, the amount of nitrogen yielded by the substance submitted to analysis. This operation is executed with as much rapidity as precision, by means of an alkaline solution, likewise of known strength. *Peligot* prefers a solution of lime in syrup. By triturating slaked lime with a solution of sugar, it dis-

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[*] Comptes Rendus, March 29th, 1847; and Chem. Gaz., May, 1847.

solves in far greater proportion than in pure water; and the compound formed possesses the same alkaline reaction as if the base which it contains were free. It is easily preserved, without alteration*, in bottles protected from contact with the carbonic acid of the atmosphere, as with this acid it forms carbonate of lime: nevertheless, as this insoluble salt renders the liquid turbid, it need only be filtered to serve again to determine the strength of the sulphuric acid. The operation is conducted as follows:—

A certain quantity of sulphuric acid of known strength is accurately measured into the condensing apparatus. The acid employed by *Peligot* contains 61.250 grammes of SO_3HO to 1 litre of water; consequently, 100 cubic centimetres correspond to 2.12 grammes of ammonia, or 1.75 gramme of nitrogen.

When the combustion is finished, the acid which has served to condense the ammonia is poured into a cylindrical glass, the apparatus carefully washed, and to this liquid, diluted with much water, a few drops of litmus are added, to give it a red colour. By means of the solution of lime in sugar, which is contained in a burette graduated in cubic centimetres and in tenths of a cubic centimetre, the acid liquid is accurately saturated, being guided by the blue colour which the liquor suddenly acquires when the point of saturation is attained. The quantity of alkaline liquor required to produce this effect is read off on the burette; and as the amount of the lime compound which saturates 10 cubic centimetres of the normal solution of sulphuric acid has been determined by a previous experiment, by subtracting from this quantity that found for the acid which has absorbed the ammonia from the nitrogenous substance, we find the volume of the acid solution which has been saturated by the ammonia, and, consequently, the weight of the nitrogen which the body contained.

Shortly after the publication of this method, some experiments to test its accuracy were undertaken by the author of this Treatise; as they were perfectly satisfactory, it may be worth while to quote them†.

The substance experimented upon was *Vitelline*, a nitrogenous principle extracted from the yolk of the egg. The standard sulphuric acid employed was of the specific gravity 1.0504; the quantity of dry acid which a small bottle of about one cubic inch capacity contained was very accurately determined by precipitation with chloride of barium to be 15.8 grains, which agrees exactly with the theoretical amount calculated from the specific gravity by *Ure's* Table. By a simple calculation it was ascertained that this quantity of dry acid is equivalent to 6.704 grains of ammonia, or 5.521 grains of nitrogen. The solution of lime in sugar was of such a strength that it required 54.25 divisions of the burette to neutralize exactly the bottle full of standard acid. The condensing apparatus employed is larger than it is usually made: it has three bulbs instead of two, and will hold about two-thirds of the contents of the bottle without being sufficiently full to excite any apprehension of the rushing back of the acid into the combustion tube at the close of the operation.

Example 1. 7.53 grains of vitelline were burned with soda, lime, and the ammonia condensed in the standard acid, which, after the combustion was finished, was transferred to a beaker, and the apparatus rinsed out repeatedly with distilled water; the remainder of the acid in the bottle was then added, and the whole diluted to about half a pint, and a few drops of litmus added; 45 burette measures of the sugar lime were required to saturate the acid, 9.25 measures (54.25 — 45) therefore represent the quantity of sugar lime equivalent to the ammonia given off by the substance; a simple calculation shows this to be equal to 0.941 grains of nitrogen, or 12.5 per cent.

In a second experiment, in which 10.17 grains were burned, 42 measures of the sugar lime were required to saturate the acid, which gives 12.25 as the representative of the sulphuric acid condensed by the ammonia, 1.246 grains as the amount of nitrogen =12.35 per cent.

In a third experiment a different standard acid was employed, and a fresh preparation of vitelline analyzed. The acid was equivalent to 4.004 grains of ammonia, or 3.297 grains of nitrogen; and it required for neutralization 32 divisions of sugar lime, which was also a fresh preparation.

7.24 grains were burned; after the

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* It has been objected that this solution does not keep of a uniform strength. I have found, however, in accordance with the statement in the text, that it may be kept for a great length of time perfectly clear, provided the bottle is carefully closed.

† Chemical Gazette, Oct. 15th, 1847.

combustion 23.25 measures of sugar lime were required to saturate the acid; $32 - 23.25 = 8.75$ represent, therefore, the sulphuric acid neutralized by the ammonia; this gives 0.9016 for the ammonia in the substance, or 12.45 per cent.

These three experiments agree, it will be observed, very closely with each other. Two experiments, in which the nitrogen was estimated as double chloride of platinum and ammonium, gave 13.02 and 12.6 per cent. of nitrogen, numbers which are rather higher than those obtained by the new method; indeed, from the very principles of *Peligot's* process, the results must always be a trifle below the truth, it being always necessary to add a slight excess of the alkaline solution, in order to see, by the change of the liquid from red to blue, when neutralization has taken place. It is true that, when we are experimenting with a perfectly colourless acid, the smallest addition of the lime solution above that required for the perfect neutralization of the acid immediately determines the blue colour; but, after the acid has served to condense the ammonia given off by the combustion of an animal substance with soda-lime, it is always more or less coloured; nor can a considerable tinge of yellow be prevented, although it may be much diminished by using a long combustion tube and a great excess of soda lime: this colour renders it somewhat difficult to hit the precise moment when neutralization takes place; if the sugar lime be added till the liquor becomes distinctly blue, a deficiency of nitrogen amounting nearly to *one* per cent. may easily occur, and it is only practice that will enable the operator to stop exactly at the proper time. The best practical rule is, to use a long combustion tube; to keep its anterior portion very hot, and to dilute the acid considerably with water previous to adding the alkaline solution. One great advantage which this new method of *Peligot's* possesses over all others is the great saving of time which it effects, as by it a nitrogen determination may be executed in less than half an hour, with as much accuracy as by the other methods which require at least 3 hours.

Peligot states that it is equally applicable to the analysis of substances containing but very little nitrogen, as wheat, vegetable soil, &c., provided a sufficient quantity of the substance be employed; and he expresses his belief that the process will prove very useful to chemists, especially to those engaged in investigations bearing upon animal and vegetable physiology, by enabling them to multiply, at a far less expense of time and money, determinations which are only of value in as far as they are comparative, and, consequently, very numerous.

Should the prelimenary examination of the organic compound have indicated the presence of *chlorine*, it must be burned with chromate of lead, since, if oxide of copper were employed, a portion of sub-chloride of that metal would form, and condense in the chloride of calcium tube; and, should *sulphur* be present, a tube of perfectly dry *peroxide of lead* must be included between the chloride of calcium tube and the potash bulbs, in order to convert into sulphuric acid and retain as sulphate of lead all the sulphurous acid which may have formed from the oxidation of the sulphur.

The amount of chlorine in chlorinated compounds is determined by igniting them with soda lime, or by transmitting their vapour through soda lime should they be of a volatile nature. The ignited mass is dissolved in dilute nitric acid, and the chlorine determined as chloride of silver. When the organic compound is of an acid nature, *Löwig* dissolves it in dilute potash ley, evaporates the solution to dryness, and ignites the residue, by which the chlorine present is converted into a metallic chloride.

Determination of the Rational Formula and Atomic Weight of an Organic Substance.

1. *An Organic Acid.*—The most satisfactory method is to convert it into a silver salt, and to determine accurately the amount of metal which it contains.

Example.—From 0.320 gramme of a certain crystalline substance having acid properties, there are obtained 0.825 gramme of carbonic acid, and 0.1715 gramme of water. Another portion of the acid is exactly neutralized with ammonia, and the solution mixed with nitrate of silver. A white curdy precipitate falls, which is washed on a filter with cold water and purified by two or three crystallizations out of boiling water; 0.334 gramme of this new substance, being ignited, yields 0.1485 gramme of pure silver.

These numbers calculated in per cents. give the following as the composition of the acid, and salt:—

Acid.

Carbon	70.31
Hydrogen	5.95
Oxygen	23.74
Hydrated acid ...	100

Salt.

Oxide of silver ...	47.73
Anhydrous acid ...	52.27
Silver salt	100

Now, the atomic weight of oxide of silver is 116; therefore,

$$47.73 : 52.27 :: 116 : x$$

$x = 127.03$, the atomic weight of the anhydrous acid, and $127.03 + 9 = 136.03$ the atomic weight of the hydrated acid; and, to deduce from this number the formula of the hydrated acid, we have, first, the proportions:—

As $100 : 70.31 :: 136.03 : x$; $x = 95.64$
As $100 : 5.95 :: 136.03 : x$; $x = 8.09$
As $100 : 23.74 :: 136.03 : x$; $x = 32.29$

Then, by dividing each of these numbers respectively by the atomic weights of carbon, hydrogen, and oxygen, we have

$$\frac{95.64}{6} = 15.94 \text{ for the carbon}$$
$$\frac{8.09}{1} = 8.09 \text{ for the hydrogen}$$
$$\frac{32.29}{8} = 4.036 \text{ for the oxygen}$$

numbers which evidently correspond closely with the formula $C_{16}H_8O_4$, which is, therefore, the rational formula of the acid in question; and which, when calculated in per-centage parts, agrees almost exactly with that determined by experiment. Thus,

Calculation.	Experiment.
C 70.58	70.31
H 5.88	5.95
O 23.54	23.74
100	100

2. *An Organic Base.*—The atomic weight and formula of this interesting class of bodies is best determined by analyzing with great accuracy the insoluble double salts which they form with *bichloride of platinum.*

Example.—*Hofmann* and *Muspratt* obtained by acting on *nitrotoluide* with sulphuretted hydrogen a crystalline body having basic properties, 0.1955 gramme of which, by combustion with oxide of copper, gave 0.5630 gramme of carbonic acid and 0.1515 gramme of water. A double salt of the hydrochlorate of this base and platinum was formed, 0.4337 gramme of which gave, by cautious ignition, 0.1372 gramme of platinum. Now there is every reason for supposing that this double salt is analogous in composition to the double chloride of platinum and ammonium

$$NH_4Cl + PtCl_2$$

if so, its atomic weight is found from the proportion—

As $0.1372 : 0.4337 :: 98.68$ (the atomic weight of platinum) $: x$

$x = 311.93$, and by deducting from this number the sum of the atomic weight of one equivalent of bichloride of platinum (169.68) and one equivalent of hydrochloric acid 36.5, we get the atomic weight of the new base, $311.93 - 206.18 = 105.75$.

The per-centage composition of the base, as found experimentally, is—

Carbon	78.53
Hydrogen	8.61
Nitrogen	12.86
	100

from which numbers its empirical formula may be deduced thus:

As $6 : 78.53 :: 1 : x$; $x = 13.09$
As $1 : 8.61 :: 1 : x$; $x = 8.61$
As $14 : 12.86 :: 1 : x$; $x = 0.918$

or $C_{14}H_9N$, which agrees best with the experimental numbers. Thus:

C_{14}	84	78.50
H_9	9	8.41
N	14	13.09
	107	100

The theoretical number 107 agrees so well with the experimental number 105.75, that there can be no doubt that $C_{14}H_9N$ is the correct formula for the new substance.

CHAPTER IV.

On the Quantitative Analysis of Mineral Waters.

The substances to be estimated may be, amongst bases, *potassa, soda, lithia, ammonia, lime, magnesia, strontia, alumina, protoxide of manganese* and *iron*, and, amongst electro-negative bodies, *sulphuric, phosphoric, silicic, nitric* and *carbonic acids; chlorine, bromine, iodine, fluorine* and *sulphuretted hydrogen; crenic* and *apocrenic acids.*

If the operator should have the opportunity of collecting the water himself at the source, he should pay attention to the following particulars:—1st, its temperature as compared with that of the air; 2nd, the geological formation of the locality whence the spring originates; 3rd, the yield of water; 4th, its physical appearance; 5th, whether or not it deposits any solid matter in the pipes or channels through which it makes its exit from the spring or well; 6th, its smell and taste: in short, he should make himself acquainted as accurately as possible with every particular he can obtain with respect to the general history of the water he is about to analyze.

The quantity of water required for a thorough examination is about twelve gallons; if, however, the analyst should have an opportunity of evaporating down a considerable quantity (say *ten gallons* to two or three pints) on the spot for the detection and estimation of those ingredients which only exist in minute quantities, such as *iodine, bromine, phosphoric acid, fluorine, manganese, alumina, strontia, lithia,* and the *organic acids:* or, if he should choose to dispense with a search for these bodies, then a few pints will suffice for a complete analysis of the water for the other ingredients. It is important, however, that a certain quantity of the water should be collected at the spring for the express determination of the total amount of carbonic acid; for this purpose, four or five stoppered bottles of about a pint capacity should be charged each with one ounce of a strong solution of chloride of calcium and an ounce and a half of ammonia, free from carbonic acid; they should then be filled with the water taken slowly from the spring, and poured quietly in, to prevent any loss of carbonic acid from splashing; all the carbonic acid contained in the water will thus be precipitated in the form of carbonate of lime. Thus

$$\mathrm{Ca\,Cl + NH_4O + CO_2 = Ca\,O, CO_2 + NH_4Cl.}$$

The precipitates in the different bottles, which should be nearly alike in quantity, are collected on a filter, dried at 212°, and weighed. They are then mixed together and analyzed by *Fresenius* and *Will's* method; the result shows the total amount of carbonic acid in the united volumes of the several bottles of water.

Should the water contain sulphuretted hydrogen, the bottles are charged with a small quantity of a solution of *arsenious acid* in hydrochloric acid; they are then filled carefully with the water as before, sulphuret of arsenic is precipitated. It is collected on a filter, washed with cold water, dried at 212° and weighed; for its composition, see page 195. From the weight obtained, the quantity of sulphuretted hydrogen in the volume of water from which it was precipitated is calculated.

Determination of the Specific Gravity of the Water.—This is effected in a very simple manner by the method described in page 125. As the specific gravity bottle has been adjusted with distilled water at 60° F., it is of course necessary that the mineral water should be brought to the same temperature previous to weighing it. The bottle contains exactly 1000 grains of distilled water; the specific gravity, therefore, of the mineral water is exactly as its weight, water being 1000.

Determination of the Total Amount of Solid Ingredients.—One thousand grains of the water are carefully evaporated to dryness on the water-bath in a platinum crucible, the residue is dried at various temperatures, and the weight taken when no further diminution is perceptible. If the water contain any considerable amount of earthy chlorides, and especially if it contain ammoniacal salts, a very exact result cannot, in this manner, be obtained regarding the amount of the solid contents, for the earthy chlorides require for their existence a small proportion of water, which they do not lose at 212°, while, at a higher temperature, some hydrochloric acid may be set free; chloride of ammonium is also partly volatilized at temperatures higher than 212°. If the water does not contain *ammonia, oxide of iron,* or *alumina, Schweitzer* * recommends, as an excellent control, to change the carbonates, chlorides, &c., into sulphates, the total amount of which must closely correspond with the amount of the various ingredients when com-

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* See his account of the analysis of the Bonnington Water, Mem. Chem. Soc., vol. ii. p. 201.

puted as sulphates; this method is indeed applicable when ammonia is present, as that substance being dissipated by heat must be deducted from the total amount of ingredients obtained by analysis. Another method, in cases where great accuracy is desirable, is to evaporate the water with a proportionate quantity of chemically pure anhydrous carbonate of soda sufficient to decompose the earthy chlorides and sulphates. This method of evaporating with carbonate of soda is advantageous, moreover, in preventing the formation of sulphate of lime, which is a troublesome ingredient, inasmuch as it adheres closely to the evaporating vessel, is not soluble in dilute hydrochloric acid, and very sparingly soluble in water. As the solid matters obtained by the evaporation of a mineral water are frequently very deliquescent, the crucible should be cooled underneath a receiver in close proximity to a vessel containing sulphuric acid, and weighed as quickly as possible.

The general character of the water having been ascertained by a qualitative examination, conducted in the manner directed in Part i. p. 95, the quantitative examination is proceeded with in the following manner.

Estimation of the Sulphuric Acid.—Ten thousand grains (more or less, according as the preliminary experiment has indicated a greater or less amount of sulphuric acid) are acidified with hydrochloric acid, and precipitated at a boiling temperature by chloride of barium; the precipitate is allowed to settle, then collected on a filter, washed, dried, ignited, weighed, and the amount of sulphuric acid calculated as directed, page 149[*].

Estimation of the Chlorine, Iodine, and Bromine (should the water contain the two latter), *conjointly.*—Two thousand or three thousand grains of the water according to the quantity of chlorine, &c., supposed to be present, are acidified with nitric acid, the chlorine precipitated with nitrate of silver, and estimated as directed, page 174.

Should the water contain organic matter, it should be freed from it before estimating the chlorine, or it would be partly precipitated, together with the silver salt, increasing its weight; with this view it should be evaporated with carbonate of soda, the liquid filtered from the earthy carbonate thereby precipitated evaporated to dryness, the residue fused, redissolved in water, nitric acid added, and then precipitated with nitrate of silver. As an illustration of the interference of organic matter with a correct determination of the chlorine, *Schweitzer* obtained from the Bonnington water, as a mean of several experiments, 10.053 grains of chloride of silver from 4 ounces of the *fresh* water, and 9.694 grains after evaporating it with carbonate of soda, as above described.

Estimation of the total Amount of Lime and Magnesia, Silicic Acid, and Oxide of Iron.—About 1200 grains of the water are acidified with nitric acid, and evaporated to dryness at a heat below ebullition. The perfectly dry residue is digested with dilute hydrochloric acid, the silicic acid remains undissolved, having, by the evaporation, been reduced to its insoluble condition. It is separated by filtration, and estimated as directed, page 220. The filtrate which contains the oxide of iron, lime, and magnesia in the form of chlorides, is supersaturated with ammonia, by which oxide of iron is precipitated, and is collected and determined as directed at page 166. The lime is precipitated from the filtrate from the oxide of iron with oxalate of ammonia, and estimated as carbonate, in the manner described at page 150, and the magnesia, from the filtrate from the oxalate of lime (concentrated, if necessary, by evaporation), with phosphate of soda, and estimated as pyrophosphate, as directed, page 151.

Schweitzer proceeds in a different manner. He commences with evaporating a large quantity of the water down to a few ounces, together with a proportionate quantity of anhydrous carbonate of soda; he throws the residue on a filter, and lixiviates the solid matter with boiling distilled water till the filtered liquor gives no indications of sulphates and chlorides; he then makes analyses of the soluble and insoluble ingredients separately. The soluble portion contains the alkalies and magnesia in the form of sulphates, chlorides, nitrates, bromides, or iodides; and the insoluble portion of the earths in the form of carbonates, silica, oxide of iron, oxide of manganese, &c.

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[*] It is better to determine the various ingredients of a mineral water from *weighed* than from *measured* quantities of the water; if the operator has not the advantage of the large balance, *fig.* 3, he can employ the specific gravity bottle, the contents of which, when quite full and the stopper in its place, are known accurately.

Estimation of the Lime, Magnesia, and Oxide of Iron dissolved in the water by free Carbonic Acid. — Ten or twelve thousand grains of the water are boiled for some time in a flask, the free carbonic acid is hereby expelled, and the substances which it held in solution are precipitated. The operator must be careful not to allow the volume of the water to be much diminished by the ebullition, or a portion of *sulphate* of lime may be precipitated, together with the earthy carbonates; boiling distilled water should be added from time to time to the flask. The precipitate is collected on a filter, dissolved in hydrochloric acid, a few drops of nitric acid added, and the oxide of iron, lime, and magnesia separated from each other in the usual manner.

Schweitzer dissolves the insoluble matter obtained by his process in nitric acid, evaporates the solution to dryness, and leaves the residue for several hours in contact with nitric acid; he then boils with hydrochloric acid, and, having separated the silicic acid, he precipitates the iron by succinate of ammonia. To the filtrate from the persuccinate of iron he adds hydrosulphuret of ammonia, which throws down the manganese; he boils the sulphuret of manganese with hydrochloric acid, precipitates it with carbonate of soda, washes and ignites the precipitate which he estimates as *red oxide of manganese.* Having removed the excess of hydrosulphuret of ammonia from the fluid filtered from the sulphuret of manganese, by boiling it with hydrochloric acid, *Schweitzer* mixes it in a vessel that can be closed with ammonia; the precipitate which hereupon forms he filters quickly, protecting it as much as possible from the air, and, having washed and ignited it, he redissolves it in hydrochloric acid. He mixes the solution with bicarbonate of potash, and, having dissolved the precipitate (should any form) in hydrochloric acid, he boils the solution with caustic soda; if a precipitate should hereby be produced, it is oxide of iron, and must be redissolved in hydrochloric acid and precipitated by ammonia: the caustic ley may contain alumina; to obtain which, it is supersaturated with hydrochloric acid, and precipitated by ammonia. All the magnesia present is retained in solution by the bicarbonate of potash; to obtain it, *Schweitzer* neutralizes the fluid with hydrochloric acid, evaporates it quickly with carbonate of potash, and, when nearly dry, mixes it with boiling water and filters; he then washes, ignites, and estimates the residue as magnesia. The ammoniacal solution from which the magnesia had been precipitated contains the *lime,* which is precipitated with oxalate of ammonia.

Estimation of the Lime and Magnesia in the Filtrate from the Precipitate produced by Ebullition. — They are determined in the usual manner, the lime being first precipitated by oxalate of ammonia, and the magnesia by phosphate of soda. The joint amount of the oxide of iron, lime, and magnesia obtained in the precipitate by boiling, and, in the filtrate, ought to correspond with the total quantity of those ingredients found by the previous experiment.

Estimation of the Alkalies. — About 10,000 grains of the water are evaporated to about one-half, then mixed with excess of bryta water, filtered, carbonate of ammonia added, again filtered, the filtrate evaporated to dryness, ignited, and the alkalies separated from each other, and determined as directed, page 141. If, however, the water contains a fixed alkaline carbonate, a different plan is adopted. The water is concentrated by evaporation, filtered, and divided into two parts; in one, the amount of chlorine is at once determined by nitrate of silver; the other is evaporated to dryness with slight excess of hydrochloric acid, the residue ignited, redissolved in water, and precipitated in its turn by nitrate of silver. The amount of chlorine obtained from this second portion above that obtained from the first is the equivalent of the quantity of carbonated alkali originally present in the water. Having thus ascertained the amount of carbonated alkali, the total quantity of the alkalies present is found by boiling the water with chloride of barium for some time, and then adding baryta water and filtering; the filtrate is precipitated with carbonate of ammonia, again filtered and evaporated to dryness; the residue consists of the alkalies in the form of chlorides. *Fresenius* says, that a mineral water which contains an alkaline carbonate cannot contain *soluble* lime and magnesia salts, and that, therefore, all the lime and magnesia which is found must be considered as carbonates kept in solution by the agency of carbonic acid. It may be doubted whether this proposition is altogether correct; it is certain that a soluble double carbonate of soda and magnesia exists, and there are grounds for believing that a similar double salt of lime and soda may be formed under the same circumstances in a mineral water; it is better, at all events, to determine the lime and magnesia in the residue left by evaporation than in the precipitate formed by boiling.

Estimation of the Iodine.—The filtrate from the precipitate produced by evaporating ten or twelve gallons of the water down to two or three pints, is evaporated to dryness together with carbonate of soda, the residue is digested repeatedly with alcohol, the alcoholic extract evaporated to dryness, and the residue gently ignited in a platinum crucible to destroy the organic matter; it is then dissolved in water and filtered, the clear liquor is carefully neutralized with dilute hydrochloric acid, and then precipitated with protochloride of palladium; the protiodide of palladium, after standing at rest twelve hours, is collected on a filter, washed with warm water, dried at a temperature below 212°, and weighed. For its composition, see page 235.

Estimation of the Bromine.—The fluid filtered from the protiodide of palladium is saturated with sulphuretted hydrogen gas, in order to remove the excess of the palladium salt; it is then filtered, boiled with nitric acid, filtered again if necessary, and then precipitated with nitrate of silver; the precipitate which contains all the bromine, together with the chlorine in the form of bromide and chloride of silver, is analyzed according to the directions given, page 234. *Schweitzer*, having separated the excess of the palladium salt, evaporates to dryness, redissolves in water, concentrates, and then adds to the solution a few drops of an ammoniacal solution of chloride of silver, prepared by mixing one part of a saturated solution of chloride of silver in ammonia, with one part of ammonia and one of water; this solution, though it produces no turbidity in a saturated solution of chloride of sodium, he finds to indicate a very minute quantity of bromine, which it precipitates as bromide of silver*.

Estimation of the Nitric Acid.—About a gallon of the water, more or less, according to the amount of solid ingredients, is concentrated to a few ounces, filtered from the insoluble matter, and the filtrate macerated with a sufficient quantity of sulphate of silver to change the chlorides, iodides, and bromides into sulphates. The fluid separated from the silver precipitate is made alkaline by carbonate of soda, concentrated in the water bath, and then mixed in a tubulated retort, with an adequate quantity of chemically pure sulphuric acid (previously boiled), more than sufficient to convert all the ingredients present into bisulphates. The mixture is heated on the sand bath, and the vapours conducted into a glass receiver containing a solution of hydrate of barytes, the distillation being stopped as soon as fumes of sulphuric acid begin to make their appearance. The fluid thus obtained in the receiver is evaporated in the water bath nearly to dryness, and the residue left for twelve hours exposed to the air, in order to change the excess of hydrate of baryta into a carbonate. It is advisable to evaporate the fluid twice nearly to dryness, and filter each time, and to use for lixiviation as little water as possible, so as to prevent any of the carbonate of baryta from being dissolved. The carbonate of baryta being separated, the fluid is precipitated with dilute sulphuric acid, and from the amount of sulphate of baryta obtained the quantity of nitrate is calculated, and from this the proportion of nitric acid. This method was adopted by *Schweitzer* in his analysis of the *Bonnington* water.

Estimation of the Ammonia.—A considerable measured quantity of the water is concentrated by evaporation, having previously acidified it slightly with hydrochloric acid. The concentrated fluid is mixed in a tubulated glass retort with considerable excess of caustic soda, and boiled for a long time, the evolved vapours being condensed in a receiver containing dilute hydrochloric acid, and kept cool by being surrounded with ice or cold water. The boiling having been continued till only two or three ounces of fluid remain in the retort, the distilled fluid is mixed with bichloride of platinum, and evaporated in a porcelain vessel. The dry residue is lixiviated by a mixture of two volumes of alcohol and one of ether, in which the ammonio-chloride of platinum is perfectly insoluble; it is then dried at 212° and weighed: for its composition, see page 147. To control the correctness of the weight, the double salt may be ignited, and the weight of the platinum obtained compared with theory.

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* See his analysis of Bonnington water, also of the sea water in the English Channel, near Brighton. L. and E. Phil. Mag., vol. xv. p. 51.

Schweitzer states, that the addition of bichloride of platinum to the distillate, previous to evaporating it even at a temperature below 212°, is quite essential to obtaining correct results; inasmuch as the chloride of ammonium rises with the aqueous vapours,—a fact easily ascertained by covering the vessel during evaporation with filtering paper, which, when lixiviated, will clearly evince the presence of chloride of ammonium, as has been noticed by *Berzelius.*

Estimation of Lithia.—Should there be reasons for suspecting the presence of this alkali, it must be looked for in the filtrate, produced by evaporating 10 or 12 gallons of the water, about a pound of which should be retained for the purpose. It is boiled to dryness with excess of carbonate of soda; the residue redissolved in water, filtered, and again evaporated to dryness with phosphate of soda; an insoluble double phosphate of soda and lithia is hereby formed: for the properties and composition of which see page 148.

Estimation of the Protoxide of Manganese.—This is to be looked for in the precipitate produced by boiling down a large quantity of the water; a portion of it is dissolved in hydrochloric acid, supersaturated with ammonia, and precipitated by hydrosulphuret of ammonia; the precipitate, which may contain *iron, alumina, manganese,* and possibly *strontia,* is redissolved in hydrochloric acid; and, nitric acid having been added to peroxidize the iron, the alumina is separated by caustic potassa, and the iron from the manganese by succinate or benzoate of ammonia; the *strontia,* should it be present, is precipitated from the filtrate with solution of sulphate of lime.

Estimation of the Phosphoric Acid.—This is also to be looked for in the precipitate by boiling down several gallons of the water, a portion of which is dissolved in hydrochloric acid, and the phosphoric acid tested for and precipitated by sesquichloride of iron and acetate of soda, in the manner directed, page 215; another portion of the precipitate may be tested for *fluorine* by dissolving it in hydrochloric acid, precipitating by ammonia, and heating the washed and dried precipitate in a platinum crucible with sulphuric acid, and observing whether the evolved fumes have any action on a clean glass plate held over the crucible.

Estimation of the Organic Acids (Crenic and Apocrenic).—According to the observations of *Mulder,* which will be referred to again in the section on the analysis of soils, there exist in the soil at least seven different organic substances, viz., *crenic acid, apocrenic acid, gēic acid, humic acid, ulmic acid, humin,* and *ulmin;* he divides these substances into two groups—the *humic,* including *gēic acid, humic acid, ulmic acid, humin* and *ulmin,* and the *crenic,* including *crenic* and *apocrenic* acids; of these bodies *humin* and *ulmin* are insoluble in water and in alkalies, the others are more or less soluble in both; the humic group are precipitated from their alkaline solution by an acid, while *apocrenic* and *crenic* acids are retained in solution; none of these acids contain nitrogen as a constituent element, though they all stand in the closest relation to ammonia, with which they form salts in the soil, and the same is probably the case when the two latter exist in mineral waters.

The *crenic* and *apocrenic* acids are not precipitated from their alkaline solutions by an acid as above stated. To detect and estimate them in water, therefore, a weighed portion of the precipitate, produced by boiling down some gallons, is boiled for some time with potassa ley, then passed through a filter, acidified with acetic acid, and acetate of copper added, the formation of a brownish precipitate indicates apocrenate of copper, in which, according to *Mulder,* about 50 per cent. of apocrenic acid is contained. The fluid filtered from this precipitate is mixed with excess of carbonate of ammonia, and then boiled; if crenic acid be present, a blueish green precipitate is formed, which, when dried at 284° Fahrenheit, contains, according to *Mulder,* 74.12 per cent. of oxide of copper.

Besides these organic acids most mineral waters contain certain other organic matters, which may be determined in the filtrate from the precipitate produced by boiling down a considerable quantity of the water, by evaporating it to dryness with carbonate of soda: the residue is dried at about 284° Fahrenheit, weighed, ignited, and then again weighed: the loss indicates the amount of extracted matter.

Arrangement of the Results of Analysis.—The usual method, and the one which seems the most rational (though it must be observed that there is a diversity of opinion on the subject amongst chemists), is to arrange the electro-negative and electro-positive ingredients, as established by direct experiment, into binary combinations, in the ratio of their mutual affinities, the strongest acid being combined with the strongest base, paying attention, however, to the fact, long since pointed out by *Berthollet*, viz., that the force of affinity is considerably modified by the degree of solubility of the salts. It is impossible to lay down any but very general rules for the classification of the results of the analysis of a mineral water, so much depending on the nature of those results, and on various circumstances connected with the history of the water; but, however the results are arranged, the total amount of the fixed constituents must correspond to the joint amount of the several ingredients; the amounts of the chlorine and sulphuric acid obtained must agree with the joint amounts of the chlorides and sulphates, and the quantity of lime obtained from an evaporated quantity of the water should agree with that obtained jointly from the precipitate produced by boiling a corresponding weight of the water, and from the boiled water filtered from that precipitate.

Of the several analyses of waters which have lately been published, we select that of the *Thames* water, conducted by *Mr. G. F. Clark**, under the superintendence of *Dr. Hofmann*, as an illustration of the method of arranging the results of analysis according to the views of *Fresenius*.

The water was collected on the 16th of December, 1847, from the middle of the river, two hours after high tide, in the neighbourhood of *Twickenham*, which is fourteen miles from London Bridge.

The temperature of the water was 9° 5 cent., or 49° 1 Fahr., that of the air being 13° cent., or 55° 4 Fahr.

The specific gravity was 1.0003, distilled water being 1. A careful qualitative analysis pointed out the presence of *potassa*, *soda*, *lime*, *magnesia*, *iron*, *alumina*, *chlorine*, *sulphuric acid*, *silicic acid*, and *organic matter*. A trace of *phosphoric acid* was also observed; neither *bromine* nor *iodine* could be detected in the water, even after considerable concentration. The quantitative analysis gave the following results:—

A. *Determination of the total Amount of fixed Constituents.*

Amount of water employed. Grammes.	Amount obtained. Gramme.	Per-centage.
I. 1182.582	.378	.0319639
II. 1000.208	.323	.0322932
	Mean ...	.03212855

B. *Determination of Sulphuric Acid.*

Amount of water employed. Grammes.	Amount of sulphate of baryta obtained. Gramme.	Per-centage of sulphuric acid.
I. 610.293	.350	.0024265
II. 581.275	.330	.0024294
	Mean ...	.0024279

C. *Determination of Chlorine.*

Amount of water employed. Grammes.	Amount of chloride of silver obtained. Gramme.	Per-centage of chlorine.
I. 610.65	.039	.0015794
II. 580.35	.038	.0016192
		.0015993

D. *Determination of Silicic Acid.*

Amount of water employed. Grammes.	Amount of silicic acid obtained. Gramme.	Per-centage of silicic acid.
I. 1182.582	.0045	.0003805
II. 1000.208	.0040	.0003999
		.0003902

E. *Determination of Lime and Magnesia.*

	Amount of water employed. Grammes.	Amount of carbonate of lime obtained. Gramme.	Per-centage of lime.
a	I. 1000.598	.2096	.0117305
	II. 906.002	.1899	.0117377
		Mean ...	.0117341

Determination of the Magnesia in the Filtrate from the Oxalate of Lime.

	Amount of water employed. Grammes.	Amount of pyrophosphate of magnesia obtained. Gramme.	Per-centage of magnesia.
b	I. 1000.598	.0195	.0007140
	II. 906.002	.0175	.0007077
			.0007108

F. *Determination of the Alkalies.*

	Amount of water employed. Grammes.	Amount of mixed chlorides obtained. Gramme.
a	I. 1000.000	.0305
	II. 1184.304	.0390

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* Quarterly Journ. of the Chem. Soc., in which periodical several other analyses of mineral waters will be found, and may be profitably consulted by the student. *Schweitzer's* elaborate analysis of the Bonnington water, to which allusion has repeatedly been made in the text, will amply repay a careful perusal.

Determination of Potassa.

	Amount of water employed. Grammes.	Amount of chloride of platinum and potassium obtained. Gramme.	Per-centage of potassa.
I.	1000.000	.0265	.0005105
II.	1184.304	.0320	.0005205
		Mean ...	.0005155

Determination of Soda.

	Amount of water employed. Grammes.	Amount of chloride of sodium obtained. Gramme.	Per-centage of soda.
I.	1000.000	.0022407	.0011867
II.	1184.304	.0024679	.0013071
		Mean ...	.0012469

3193.6 grammes of the water were evaporated down to 574.475 grammes. The precipitate, which was formed and separated, weighed 5.558 grammes.

Determination of Organic Matter in the Filtrate.

	Amount of filtrate employed. Grammes.	Amount of organic matter burnt off. Gramme.	Per-centage upon the whole amount of water.
I.	81.520	.148	.0032629
II.	129.839	.236	.0032668
		Mean ...	.00326485

Determination of Organic Matter in the Precipitate.

	Amount of precipitate employed. Gramme.	Amount of organic matter burnt off. Gramme.	Per-centage upon the whole amount of water.
I.	.0925	.0090	.0016918
II.	.1565	.0155	.0017221
		Mean ...	.00170695

Determination of Carbonic Acid.—At the time of collecting the water, a siphon capable of containing 557 cubic centimetres (about 34 cubic inches) of distilled water was filled three times, and discharged into a bottle containing chloride of calcium and ammonia; the precipitate which was formed weighed, when dry, 0.937 gramme.

	Amount of precipitate employed. Gramme.	Amount of carbonic acid evolved. Gramme.	Amount calculated on the whole precipitate. Gramme.
I.	.4175	.156	.3052263
II.	.4585	.155	.3167611
		Mean ...	.3109937

per-centage in the water .01860565.

Arrangement of the results according to the principles laid down by *Fresenius**.

The potassa and soda are assumed to be in combination with sulphuric acid: we have, therefore, .0005155 potassa combined with .0004387 sulphuric acid, forming .0009542 sulphate of potash, and .0012469 soda combined with .0016104 sulphuric acid, forming .0028573 sulphate of soda.

Total per-centage amount of sulphuric acid 0024279
Of which there is combined with the alkalies 0020491
Leaving 0003788

which is assumed to be in combination with .0002651 lime, forming .0006439 sulphate of lime.

Total per-centage amount of lime 0117341
Of which there is combined with sulphuric acid 0002651
Leaving 0114690
Total per-centage amount of chlorine 0015993

which is assumed to be combined with .0009010 calcium, forming .0025003 chloride of calcium, leaving .010276 lime, which must be in combination with .0080202 carbonic acid, forming .0182278 carbonate of lime.

Total per-centage amount of magnesia 0007108
Which is assumed to be combined with 0007565

carbonic acid, forming .0014673 carbonate of magnesia.

The following are, therefore, the proportions in which the ingredients of the water exist.

	In 100 litres. Grammes.	In a gall. Grains.
Sulphate of potassa...	.9542...	.66794
—— of soda......	2.8573...	2.00011
—— of lime......	.6439...	.45073
Chloride of calcium...	2.5003...	1.75021
Carbonate of lime ...	18.2278...	12.75946
—— of magnesia	1.4673...	1.02711
Silicic acid	.3902...	.27314
Phosphoric acid	traces ...	traces
Alumina	traces ...	traces
Carbonate of oxide of iron	traces ...	traces
Soluble organic matter....................	3.2648...	2.28536
Insoluble ditto.........	1.7069...	1.19483
	32.0127	22.40889
Direct determination of fixed constituent	32.1285	22.48995

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* Quantitative Analysis.

Having deducted from the per-centage of carbonic acid that portion in combination with lime and magnesia, the per-centage of free carbonic acid is found to be .0098289, corresponding to 513.44 cubic centimetres in 100 litres, or 1.4233 cubic inches in an imperial gallon.

The iron and alumina were not separated, but both determined in the state of sesquioxides; the mean of two experiments gave .00001335 per cent.

CHAPTER V.

On the Analysis of Soils.

The following directions are from a paper issued from the "Museum of Economic Geology."*

In selecting specimens, care must be taken to obtain a fair average sample, and to insure the true subsoil or subjacent hard rock, clay, sand, &c. Specimens of the latter should be obtained as near as possible beneath the spot whence the soil may have been selected, for it sometimes happens that the soil of a field varies in places from resting on different kinds of subsoil.

The quantity of soil taken as a specimen should weigh about a pound, which should be tied up in a canvas bag and labelled.

With respect to specimens of subsoils, if of marl, sand, or clay, portions weighing about a pound should be tied up in a canvas bag, labelled to correspond with the respective soils above them. If the subjacent rocks be hard, a piece also weighing about a pound, and fresh broken from the body of the rock, as nearly as possible beneath the surface whence any specimen of soil may have been selected should suffice, and should be wrapped in strong brown paper, labelled to correspond with the soil above it.

I. Dry the specimen at 212° Fahr., powder, sift through a lawn sieve, rub in a mortar, again dry at 212°, and put into a stoppered bottle.

II. Spread 500 grains on a sheet of writing paper, and expose to the air for twelve hours; note the increase of weight—from seven to ten grains is a favourable indication.

III. Determine the amount of carbonic acid in 100 grains, by treating it in a counterpoised bottle with hydrochloric acid with the usual precautions.

IV. Determine the amount of organic matter in 200 grains, by heating to redness in a platinum crucible, with occasional stirring: weigh the residue, and divide it into two equal parts: introduce one into a counterpoised bottle containing hydrochloric acid, and estimate the disengaged carbonic acid; if this be less than that obtained before calcination, the difference must be added to the weight of the calcined product under operation, and this deducted from the weight before calcination will indicate the amount of organic matter.

V. The other half of the residue left after calcination is now to be boiled in a flask with about an ounce of hydrochloric acid. By this means all the ingredients except the silica and part of the alumina will be dissolved, some of them being decomposed. The insoluble part is to be separated by filtration, washed until no longer acid, and dried. The solution, together with the washings of the insoluble powder, is to be marked A, and put aside for further examination. The powder is to be finely pulverized and mixed with four times its weight of dried carbonate of soda; the mixture is then to be heated in a platinum crucible until it fuses into a glass. The crucible and its contents being placed, while warm, in a Wedgewood dish containing distilled water, about an ounce of hydrochloric acid is to be added and heat applied. More acid and water may be added if necessary, until nothing more is dissolved. This being done, the solution and insoluble part are to be evaporated to dryness, in order to aggregate the silica held in suspension; and care must be taken, during this operation, that no hard lumps are left in the solution, as the silica sometimes forms a coating over such particles through which the acid will not act. The residue, after the evaporation, is to be heated with water mixed with about half an ounce of hydrochloric acid, the solution is to be filtered, and the insoluble part washed. The latter is the silica, which must be carefully heated to redness, and weighed while warm*. To the so-

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* Pharm. Journ., vol. iv.

* Or rather the crucible should be allowed to cool underneath a receiver close to a vessel containing sulphuric acid, and weighed with the cover on.

lution from which the silica has been separated ammonia is to be added; the *alumina* is hereby precipitated, which is washed, ignited, and weighed with the same precautions as the silica.

VI. The solution A is now to be examined. For this purpose add ammonia in excess, and afterwards strong acetic acid in considerable excess, and boil the mixture; *phosphate of peroxide of iron* and *phosphate of alumina* (if present) will be precipitated. Collect and wash the precipitate, and label the solution C. Treat the precipitate with solution of caustic potassa, which will redissolve the *phosphate of alumina*, and leave the *phosphate of iron:* separate, wash, dry, and weigh the latter; add ammonia to the potash solution to throw down the phosphate of alumina, which is, in like manner, to be collected and weighed.

It must not be inferred that the phosphates of iron and alumina obtained in this manner existed as such in the soil; the phosphoric acid may have been, at least in part, in combination with lime or magnesia, while the iron may have been in the state of peroxide, and the alumina uncombined; but, on dissolving these ingredients in the hydrochloric acid, the phosphate of lime or magnesia would be decomposed, and phosphate of iron and alumina formed. As this decomposition would always take place under the circumstances indicated, it next becomes a question whether the equivalent proportions of peroxide of iron, or alumina, or of phosphoric acid existed in excess. To determine this point, divide the solution C into two parts; to one add a few drops of solution of perchloride of iron, which, if any earthy phosphates still remain undecomposed, will occasion a precipitate of phosphate of iron, in which case it may be concluded that the whole of the iron originally in the solution has been obtained in the state of phosphate of iron. Continue the addition of perchloride of iron as long as a precipitate is formed, and treat this precipitate the same as that first obtained from solution A. If, on the other hand, no precipitate be formed from the perchloride of iron, it will be necessary to try whether there be more iron or alumina in the solution. In this case, add to the other half of the solution C liquid ammonia, so as to render it slightly alkaline; then add hydrosulphuret of ammonia, which will throw down peroxide of iron, oxide of manganese and alumina, if present; collect and wash this precipitate, and label the solution D. Dissolve the precipitate in hydrochloric acid and boil the solution, add caustic potassa in excess, which will throw down peroxide of iron and oxide of manganese, but will retain alumina in solution; the two former being thus separated, add hydrochloric acid to the filtered solution in slight excess, and finally precipitate the alumina by ammonia.

VII. The quantity of manganese contained in soils is usually so small as to render its separation from the iron unnecessary. Its presence may be indicated by the black colour which the iron precipitate assumes on being exposed to the air, or by the smell of chlorine, which is afforded on adding a few drops of hydrochloric acid to the precipitate. If thought desirable to separate the two oxides, dissolve them in hydrochloric acid and add *precipitated carbonate of lime*, which will throw down the oxide of iron. Separate the precipitate, and add to the filtrate ammonia and oxalate of ammonia, by which the lime is removed; then add *caustic soda.* Collect, dry, and weigh the precipitate, which may be estimated as oxide of manganese.

VIII. The solution D may still contain lime, magnesia, and salts of potassa and soda. Boil, to drive off any sulphuretted hydrogen which it may contain, then add oxalate of ammonia as long as a precipitate of oxalate of lime is formed. Collect, dry, and weigh this precipitate, and label the solution E; if the precipitate be dried at 212°, it will contain one atom of water.

IX. Add hydrochloric acid to the solution E; evaporate to dryness, and heat to dull redness. Redissolve in water, and add *red oxide of mercury;* treat the residue with water, pure magnesia (if present) will remain, which is to be collected and weighed.

X. The *chlorides of potassium and sodium*, as well as the sulphate of lime, have yet to be determined. Boil 200 grains of the dried specimen in ten ounces of distilled water; filter the solution and wash the insoluble part: divide the solution into two equal parts; to one add nitric acid, and then *chloride of barium* as long as any precipitate occurs. Collect, wash, and dry this precipitate, which is sulphate of baryta, obtained from the decomposition of sulphate of lime. To the other half of the solution add nitric acid, and then *nitrate of silver* as long as any precipitate occurs, which treat as in the former case. This will be chloride of silver, obtained from the decomposition of the *chlorides of potassium* and *sodium*.

The above process, though it has no pretensions perhaps to great accuracy, is sufficiently exact for most practical purposes. When a complete analysis is to be made, *Dr. Ure* adopts the following method *. A known weight (about 100 grains) of the soil is introduced into a large glass flask with a thin concave bottom, capable of holding at least a quart of water, and over it is poured a sufficient quantity of dilute hydrochloric acid. The flask is placed on the ring of a retort-stand and exposed to a gentle heat, while the beak of a large glass funnel, having its mouth covered with a porcelain basin filled with distilled water, is inserted into its neck. By this arrangement, a continuous ebullition may be maintained in the mixture of soil and acid, without loss of acid or nuisance from its fumes, because the vapours are condensed whenever they reach the cold basin above the funnel; and in this way a boiling heat may be kept up till every constituent of the soil, except the silica, becomes dissolved. The funnel and porcelain basin should be properly supported on the rings of the retort-stand. *Dr. Ure* maintains the action for *six* or *eight hours*, at the end of which time he throws the contents of the mattrass on a filter, and supersaturates the filtered liquor with ammonia. The silica, which remains on the filter having been washed, is dried and weighed.

The *alumina*, *oxide of iron*, and *phosphate of lime* thrown down by the ammonia being washed on the filter, and dried to a cheesy consistence, are removed with a bone spatula into a silver basin, and digested with heat in a solution of pure potassa, whereby the alumina is dissolved; the alkaline solution is passed through a filter and saturated with hydrochloric acid; ammonia is then added, pure white *alumina* falls, which is collected on a filter, washed, ignited, and weighed.

The *iron* and *phosphate of lime* on the filter may be dried, gently ignited and weighed, or otherwise directly separated from each other without that step, by the action of dilute alcohol, acidulated with sulphuric acid at a gentle heat. Thus the oxide of iron will be dissolved, and its solution may be passed through a filter, while the *sulphate of lime* will remain undissolved, and may be dried, ignited, and weighed; *five* parts of it correspond with *four* of phosphate. The *iron* is obtained in the state of sesquioxide by precipitation with ammonia.

The first filtered liquor, with excess of ammonia, contains the *carbonate of lime* and the *magnesia*. The former is separated by solution of oxalate of ammonia, and digestion, at a gentle heat, for a few hours; it is then filtered, washed, dried, and gently ignited, by which it is converted into carbonate, in which form it is weighed. The *magnesia* in the filtrate is precipitated with phosphate of soda.

For some refractory soils, in which the alumina exists as a double or triple silicate, it becomes necessary to fuse about fifty grains of the sample in fine powder, mixed with four times its weight of dry carbonate of soda, the mixture being put into a platinum crucible, and into a cavity in the centre fifty grains of hydrate of potassa being laid. The crucible is slowly raised to a red white heat, when its contents fuse into a homogeneous liquid, of a gray or brown colour, according to the metals present in it. *Manganese* gives a purple tint: and *iron* a red brown. The fused matter should be poured out into a shallow platinum basin, and, as soon as it is cold, it should be pulverized, dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the dry mass again digested with hot water acidulated with hydrochloric acid, and the whole thrown down upon a filter. Pure *silica* remains, which is washed, dried, ignited, and weighed. The filtered liquor, which contains the remaining constituents of the soil, is treated as already described.

Besides these systematic investigations, *Dr. Ure* directs researches to be made for certain peculiar substances, and especially for the so-called *neutro-saline* constituents, in the following manner. One hundred grains of the soil are triturated with twenty times their weight of distilled water, placed in a beaker till the clayey matter subsides, and the clear liquor is then decanted into a filter. A little of the filtered solution should be tested with nitrate of baryta, and also with oxalate of ammonia. If precipitates are afforded, the presence of *sulphate of lime*

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* Pharm. Journ., June, 1845.

is indicated, and the following steps must be taken to eliminate it entirely:—Two hundred grains of the soil are triturated with a quart of distilled water, holding in solution fifty grains of sal ammoniac. The mixture should be allowed to clarify itself by subsidence, when the supernatant clear liquor should be evaporated down to two ounce measures, and then mixed with an equal bulk of *strong whisky* (11 per cent. over proof). The whole of the sulphate of lime will then be separated from the fluid, and, after being drained on a filter, may be dried, ignited, and weighed.

For determining the *alkaline salts*, the water filtered from the one hundred grains of soil should be evaporated down to one-fifth of its bulk, and then treated, 1st, with nitrate of baryta for the *sulphates;* 2nd, with nitrate of silver for the *chlorides;* 3rd, with oxalate of ammonia for the *nitrate of lime*, or *chloride of calcium*, provided no sulphate of lime is indicated by the first test; 4th, with litmus paper for the *alkaline* or *acid* reaction; 5th, with soda chloride of platinum for *potassa*, salts which are very valuable for the vigorous growth of many plants. The portions of the soil tested for potassa salts should, before being digested in water, be gently calcined, to insure the expulsion of every particle of ammoniacal salt; otherwise the precipitate afforded by soda chloride of platinum would be fallacious.

Another peculiar research to which *Dr. Ure* directs especial attention is that which determines the amount of ammonia in a soil, which may exist either ready formed, or in its elements, capable of affording a portion of that azotic food so indispensable to vigorous vegetation. The actual ammonia is easily obtained, by distilling the soil along with *milk of lime;* the distillate will contain all the volatile alkali, which may be estimated by a standard solution of sulphuric acid, according to *Peligot's* method, described, page 259. What *Dr. Ure* calls the *potential* ammonia, *slumbering*, so to speak, in its embryo elements, may be estimated by igniting 200 grains of the soil with its own weight of a mixture of hydrate of soda and quicklime.

Dr. Ure gives also the following simple method of testing for phosphoric acid in a soil:—Digest it for an hour or so, at a moderate heat, with dilute *nitric* acid (free from hydrochloric acid). Throw the mixture on a filter; to the filtered liquor add *potassa water* cautiously, till the instant that a precipitate begins to appear; then drop into it a weak solution of nitrate of silver. If any phosphoric salts be present, a yellowish precipitate will immediately fall, which is resoluble in an excess of nitric acid. Whatever is not thus dissolved is chloride of silver, and ought to be separated by filtration. On adding then weak potassa water cautiously to the filtered liquor, pure *phosphate of silver* will be obtained, without any alumina or iron, provided the liquor be still acidulous in a slight degree. The portion of soil should be fresh, not calcined, because the phosphates, when ignited, afford a white precipitate with nitrate of silver. The stronger the solution of the phosphoric compound is, the more characteristic is the yellow precipitate with silver; and then ammonia may be used to effect the partial separation of the excess of acid.

A solution of *sulphate of magnesia*, containing a little sal ammoniac, is probably the best test liquor for detecting phosphates in faintly acidulous, but still better in neutral, solutions.

The determination of phosphoric acid in soils is best effected by the following process, proposed originally by *Schulze*, and modified by *Liebig*. It is founded on the insolubility of phosphate of peroxide of iron and phosphate of alumina in *acetic* acid:—The hydrochloric solution of the soil is evaporated to dryness, nitric acid being added during the evaporation; the dry mass is treated with dilute hydrochloric acid, and the solution filtered off from the insoluble silica. To the acid solution ammonia is added, and then acetic acid; the mixture is boiled, filtered while hot, and the precipitate, which contains the whole of the phosphoric acid, in combination with iron and alumina, is collected on a filter, washed, dried, weighed, and digested with caustic potassa, which dissolves the latter. This is the process as originally proposed by *Schulze*. According to *Liebig's* modification [*], ammonia is added to the hydrochloric solution of the soil, till a precipitate begins to form; acetic acid is then added, and, finally, acetate of soda in excess; the mixture is boiled and filtered. The precipitate, having been washed with hot water, is dissolved in

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[*] *Fresenius*—Quantitative Analysis, p. 516.

hydrochloric acid, ammonia added to alkaline reaction, and then hydrosulphuret of ammonia. The fluid is filtered off from the precipitated sulphuret of iron, and the latter is washed with water mixed with hydrosulphuret of ammonia. The filtrate is concentrated by evaporation, *sulphate of magnesia* added, and the mixture stirred; the formation of a crystalline precipitate indicates phosphoric acid; this precipitate consists of basic phosphate of magnesia and ammonia. It is collected on a filter, washed with water containing a little ammonia, dried, and ignited; the phosphoric acid is estimated as pyrophosphate of magnesia.

According to *Mr. Nesbit** this process is inapplicable where phosphate of alumina is contained in the solution, the phosphoric acid being kept back in the precipitate formed by ammonia and hydrosulphuret of ammonia, and cannot be obtained in the filtrate.

Although the quantity of soluble saline matter extracted from a moderate quantity of any of our soils is rarely so great as to admit of a rigorous quantitative examination, it is, nevertheless, very desirable that a qualitative analysis of the aqueous extract should be made, in order to furnish information as to the ingredients which are supplied directly to the plant with the water which they imbibe from the soil. In some soils, those, for instance, of Egypt and India, and of other warm countries, soluble saline matter in the form of chlorides, sulphates, and nitrates, to the amount of 14 per cent., has been found*. The qualitative examination will always inform the operator whether or not a quantitative analysis is required. The most convenient plan, therefore, is to digest a large quantity (from two to three pounds) of the soil with distilled water, and, having thrown it on a moist filter and thoroughly washed the insoluble matter, to divide the filtrate into two parts, using one part for the qualitative, and setting aside the other for the quantitative examination, should such be found necessary.

As the analysis of soils is a subject which is likely early to occupy the attention of the student in analytical chemistry, we have, with the view of assisting him in his labours, collected in a tabular form the different steps of the treatment of the hydrochloric solution. The substance of this Table is taken from the article on the analysis of soils, in *Johnstone's* Agricultural Chemistry, a work which we take the liberty of strongly recommending to the attention of the agricultural student.

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* Quarterly Journ. of the Chemical Society, No. 1, p. 45.

* See Johnstone's Lectures on Agricultural Chemistry and Geology, p. 43, Appendix.

<table>
<tr><td colspan="9">To the hydrochloric solution
Add ammonia in excess.</td></tr>
<tr><td colspan="5">The solution contains
Lime, magnesia, oxide of manganese, potassa, and *soda.*
Add oxalate of ammonia, and cover from the air.</td><td colspan="4">The precipitate contains
Oxide of iron, alumina, and the *phosphates of iron* and *alumina.*
Digest in acetic acid.</td></tr>
<tr><td colspan="4">The solution contains
Oxide of manganese, magnesia, potassa, and *soda.*
Add hydrosulphuret of ammonia.</td><td rowspan="4">The precipitate is *Oxalate of lime.* Wash, heat to redness to convert into carbonate, and weigh.</td><td colspan="2">The solution contains *Alumina* and *oxide of iron.* Add ammonia, and digest the precipitate in a solution of caustic potassa.</td><td colspan="2">The precipitate contains *alumina* and *oxide of iron* in the state of *phosphates.* It may be treated according to Liebig's plan; or, where great accuracy is not particularly desired, it may be fused in a platinum crucible with three times its weight of carbonate of soda: the fused mass is extracted with water.</td></tr>
<tr><td colspan="3">The solution contains
Magnesia, potassa, and *soda.*
Acidify with hydrochloric acid, boil, filter, evaporate to dryness, and heat to incipient redness to drive off the ammoniacal salt. Redissolve in water, mix with a little pure red oxide of mercury: evaporate again to dryness, heat to redness, and treat with water.</td><td rowspan="3">The precipitate is *Sulphuret of manganese.* Dissolve in hydrochloric acid, precipitate by carbonate of soda. Wash, heat to redness in the air, and weigh. Every 100 grains may be considered to indicate the presence of 93.84 grains of protoxide of manganese.</td><td rowspan="3">The solution contains *Alumina.* Add hydrochloric acid till the solution is sour, and then excess of ammonia; alumina is precipitated, which collect, wash, dry, ignite, and weigh.</td><td rowspan="3">The precipitate is *Oxide of iron,* which wash, dry, ignite, and weigh.</td><td rowspan="3">The solution contains *Alkaline phosphate.* Neutralize with nitric acid, and add nitrate of silver, when phosphate of silver will fall; or with hydrochloric acid, and add chloride of calcium and ammonia, when bone earth will fall: every 100 grains of phosphate of silver are equal to 23.51 of phosphoric acid or 48.50 of bone earth, and every 100 grains of bone earth contain 48.45 of phosphoric acid.</td><td rowspan="3">The insoluble residue consists of *alumina* and *oxide of iron.* Dissolve in hydrochloric acid, and add the solution to that containing the rest of the iron and alumina.</td></tr>
<tr><td colspan="2">The solution contains the chlorides of potassium and sodium. Evaporate to dryness, weigh, redissolve in water, and add bichloride of platinum.</td><td rowspan="2">The residue is caustic magnesia. Wash, ignite, and weigh.</td></tr>
<tr><td>The solution contains chloride of sodium, the weight of which is found by deducting from the weight of the mixed chlorides that of the chloride of potassium.</td><td>The precipitate is the double chloride of platinum and potassium. Wash with dilute alcohol, dry at a gentle heat, and weigh.</td></tr>
</table>

In reference to the detection of minute quantities of phosphoric acid in soils, rocks, &c., we may allude to the method adopted by *Mr. Fownes*, by which he succeeded in obtaining evidence of the existence of this important acid in several rocks of igneous origin, such as white porcelain clay from *Dartmoor*, green basalt from *Derbyshire*, and various *lavas*, &c., &c. The minerals were finely powdered in a porphyry mortar, and boiled with dilute hydrochloric acid: the solutions contained large quantities of alumina and oxide of iron. The liquids were separated from the insoluble part by decantation, evaporated nearly to dryness, water added, and then an excess of ammonia. The copious bulky precipitate obtained was washed and digested in dilute acetic acid. The undissolved residue was dried, ignited, and fused with *silica* and carbonate of soda; when cold, the melted mass was acted on with boiling water, and the soluble and highly alkaline portion was separated by filtration from the insoluble silicate of alumina. The solution was mixed with excess of nitric acid, evaporated to dryness, water added, and the product filtered. The liquid thus obtained was divided into two portions: one of these was carefully neutralized with a little ammonia, and then mixed with a few drops of nitrate of silver, a *distinct yellow precipitate* appeared, which was freely soluble in dilute nitric and acetic acids. The other portion was mixed with excess of ammonia, sal ammoniac added, and then a few drops of solution of sulphate of magnesia; after a short time a distinct crystalline precipitate appeared, which increased on agitation. It was found necessary to add *silica* to the undissolved residue previous to fusion with carbonate of soda, in order to retain the whole of the alumina in an insoluble condition.

Determination of the Specific Gravity of a Soil.—A portion is dried in the water bath until it ceases to lose weight; a small bottle is filled up to a mark made in its neck with distilled or rain water, and the weight accurately taken. Part of the water is then poured out of the bottle, and 1000 grains of the dry soil introduced in its stead, the bottle is well shaken to expel all the air from the pores of the soil, filled up to the mark in the neck with water, and again weighed. The weight of the soil divided by the difference between the weight of the bottle with soil and water, and the sum of the weights of the bottle of water and soil together gives the specific gravity.

Example.—Suppose the bottle with the water to weigh 2000 grains, and with water and soil 2600, then—

	Grains.
Weight of bottle with water alone	2000
Do. with dry soil	1000
Sum, being the weight which the bottle and the soil *would have had* could the soil have been introduced without displacing any of the water.	3000
Actual weight of bottle and water	2600
Difference, being the weight of water taken out to admit 1000 grains of dry soil.	400

Therefore 1000 grains of soil must have the same bulk as 400 grains of water, or the soil must be $2\frac{1}{2}$ times heavier than water, since $\frac{1000}{400} = 2.5 =$ its specific gravity.

Determination of the Relative Proportions of Gravel, Sand, and Clay.—A certain quantity (say four or five hundred grains) of the soil is well agitated with hot water in a large flask, the whole is then poured into a *Phillips's* precipitating jar, and allowed to stand for a couple of minutes; the water, together with the fine floating matter, is then poured off into another vessel, and the process is repeated several times, till nothing but sand and gravel remains; these are now dried and weighed, and then sifted through a gauze sieve more or less fine, when the gravel and coarse sand are separated and may be weighed, and their respective proportions estimated. These separated portions of gravel and sand should now be moistened with water and examined carefully with the aid of a microscope, with the view of ascertaining if they are wholly silicious, or if they contain also fragments of the different kinds of rock, *sandstones*, *slates*, *granites*, *traps*, *limestones*, or *iron-stones*. A few drops of strong hydrochloric acid should also be added, when the presence of limestone is shown more distinctly by an effervescence, which can be readily perceived by the aid of a glass—of peroxide of iron, by the brown colour which the acid speedily assumes; and of black oxide of manganese, by the distinct smell of chlorine, which is easily recognised.

Determination of the absorbing Power of the Soil; its Power of holding Water; and the Rapidity with which it Dries.—*Johnston* gives the following directions for determining these several points. A thousand grains of the perfectly dry soil are spread over a sheet of paper, and exposed to the air for twelve or twenty-four hours, and then weighed. The increase of weight shows its power of absorbing moisture from the air. If it amounts to 15 or 20 grains, it is so far an indication of great agricultural capabilities. This same portion of soil may now be put into a funnel on a double filter, and cold water poured upon it drop by drop, till the whole is wet, and the water begins to trickle down the neck of the filter. It may now be covered with a piece of glass, and allowed to stand for a few hours, occasionally adding a few drops of water, until there remains no doubt of the whole soil being perfectly soaked. The two filters and the soil are then to be removed from the funnel, the filters opened and spread for a few minutes upon a linen cloth, to remove the drops of water which adhere to the paper. The wet soil and inner filter being now put into one scale and the outer filter into the other, and the whole carefully balanced, the true weight of the wet soil is obtained. Suppose the original wet soil now to weigh 1400, then the soil is capable of holding 40 per cent. of water; for—

As 1000 : 400 : : 100 : 40

The wet soil, with its filter, may now be spread out upon a plate and exposed to the air, in what may be considered ordinary circumstances of temperature and moisture for 4, 12, or 24 hours, and the loss of weight then ascertained. This will indicate the comparative rapidity with which such a soil would dry, and the consequent urgent demand for draining, or the contrary. As great a proportion of the water is said to evaporate from a given weight of sand saturated with water, in 4 hours, as from an equal part of pure clay in 11, and of peat in 17 hours, when placed in the same circumstances-

The Organic Constituents of the Soil.—We have already in the last chapter alluded to the observations of *Mulder*[*] on this subject, and have stated that he reduces the number of organic substances as at present known to exist in the soil to *seven.* The varieties would indeed be incalculable but for the existence of a general cause which reduces them to a small number. This cause is the transformation and decomposition which vegetables undergo at their death, by which they are converted chiefly into a substance called *humus.* This change is remarkably uniform, since from the innumerable organic combinations which exist in plants and animals the same few constituents of the black layer of soil are derived; and if we exclude those substances which are mixed accidentally with the black soil, as well as those substances which have not yet undergone sufficient decomposition, its constituents are limited to a small number of organic substances—substances existing in it everywhere, and on the decomposition of which the growth of plants depends. These substances have the following properties:—Some of them are soluble in water, others in alkalies; others again are insoluble in both, while some dissolve more or less readily in alcohol and ether. The latter are of a resinous nature, and do not appear to have any share whatever in vegetation.

If a soil be exhausted by means of water, a great many salts may be extracted from it, among which may be mentioned the alkalies, lime, magnesia, and ammonia, in combination with *formic, acetic, carbonic, crenic, apocrenic,* and *humic* acids. From the soils thus treated with water, alkaline solutions extract substances which may be precipitated by acids. In different kinds of soils the substances thus extracted are sometimes different. They all consist, however, of one or more of the following:—

Geïc acid	$C_{40} H_{12} O_{14}$
Humic acid	$C_{40} H_{12} O_{12}$
Ulmic acid	$C_{40} H_{14} O_{12}$

The latter is that which, in neutral vegetable substances undergoing decay, is formed first. From it, by absorption of oxygen from the air, *humic acid* is produced, and finally, by a further absorption, *geïc acid.* The substances which are insoluble in alkalies, *ulmin* and *humin,* can be rendered soluble, and so converted into *ulmic* and *humic* acids respectively, by the decomposition which is always going on in the constituents of the soil.

The base by which *Mulder* supposes

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[*] Chemistry of Vegetable and Animal Physiology. Translated, with Notes, by *Johnston,* pp. 143 *et seq.*

these acids to be rendered soluble in water, is *ammonia*. He does not adopt the idea of *Liebig*, that this ammonia is carried down to the soil from the atmosphere, by means of rain water, but he accounts for its presence in the following manner:—Nitrogen in the state of pure gas, and also atmospheric air are possessed of one common property, namely, that when in contact within an inclosed space with putrefying substances, from which hydrogen is in consequence given off, *the nitrogen combines with the hydrogen, and forms ammonia.* This property of nitrogen is well known. It is the principle on which *saltpetre* is formed, the production of that substance being always preceded by that of ammonia. Now, air is contained in the soil, and is in continual contact with moist and decomposing substances. This air could produce saltpetre, if there were only a sufficient abundance of bases, and that even without the presence of putrefying organic substances.

There are in *Ceylon* 22 natural saltpetre grottos, where there are no organic substances from which nitrogen might be supplied. Nitrogen is derived from the air contained in these caverns, and in favourable circumstances even the water is decomposed, and ammonia at the same time produced, which afterwards is oxidized into nitric acid by the oxygen of the air, in places where it has more easy access; this acid then combines again with the bases from the walls of the grottos, and forms nitrates. All this would happen in the soil if organic substances were not present to absorb the oxygen, and thus to prevent the oxidation of the nitrogen in the ammonia, and the formation of saltpetre. In a porous soil in which moist air is contained, nitrogen is combined with the hydrogen of the organic bodies only into ammonia, the oxygen of the water, and from the air, being consumed in the higher oxidation of the organic substances themselves. In this way the first product of the decomposition of organic substances, namely *ulmic* acid, ($C_{40}H_{14}O_{12}$) is converted into *humic* acid ($C_{40}H_{12}O_{12}$), and this again into *geïc* acid ($C_{40}H_{12}O_{14}$), which in its turn is further oxidized into *apocrenic* acid ($C_{48}H_{24}O_{32}$), and, finally, into *crenic* acid ($C_{24}H_{12}O_{16}$).

It is to this formation of ammonia from the constituents of atmospheric air and water that we must look, according to the Dutch chemist, for the cause of one of the most important peculiarities in the growth of plants. It is owing to this slow formation of ammonia, that the organic substances of the soil insoluble in water are rendered soluble, and can be offered to plants as organic food, even without a supply of ammoniacal manure to the soil. In other words, it is owing to this cause that the five acids already mentioned can be converted into soluble ammoniacal salts. It is particularly worthy of remark, and a fact of great interest, that these humic substances, which can be extracted from the soil by alkalies, and precipitated by acids, have a great uniformity, from whatever kind of soil they may have been prepared; and they are remarkably similar to those substances which by the action of several chemical agents may be obtained from the materials which are generally diffused through the animal and vegetable kingdoms. The manner in which *sugar* is changed into ulmin, humin, and geïc acid, by a simple transposition of its elements, is thus suggested by *Mulder*:—

	C.	H.	O.
$\frac{1}{2}$ of 7 equiv. of sugar + O_2	42	35	37
2 equiv. of carbonic acid .	2		4
19 ditto water		19	19
1 ditto *ulmin*	40	16	14
	42	35	37
$\frac{1}{2}$ of 7 equiv. of sugar + O_4	42	35	39
2 equiv. of carbonic acid .	2		4
23 ditto water		23	23
1 ditto *humin*	40	12	12
	42	35	39
$\frac{1}{2}$ of 7 equiv. of sugar + O_6	42	35	41
2 equiv. of carbonic acid .	2		4
23 ditto water		23	23
1 ditto geïc acid . . .	40	12	14
	42	35	41

In the same manner the conversion of *cellulose*, *starch*, *gum*, *pectin*, and other analogous substances, which are so very much diffused through plants into the humic substances, may be represented; and the way in which his *protein* even may be converted into humic acid, by the influence of hydrochloric acid and oxygen, is shown in a very ingenious manner by *Mulder*[*].

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[*] Chemistry of Vegetable and Animal Physiology, p. 159.

The *crenic* and *apocrenic* acids, like the humic acids, exist in the soil in the state of salts of ammonia, potassa, and soda, combined with lime, magnesia, and oxide of iron; they never exist in the soil uncombined. They unite intimately with ammonia, which, however, can be completely separated from them by caustic potassa. *Apocrenic* acid, when artificially prepared, is a *five-basic* acid. It is produced in the form of apocrenate of ammonia when humic acid in whatever way prepared, or wood charcoal, is exposed to the action of nitric acid. Its value in the soil is very highly estimated by *Mulder*, as in consequence of its *five-basic* character it may supply plants either with several bases at once, or these bases may be alternately exchanged according as the proportion of a more powerful base in the soil is less, and that of a more feeble one temporarily greater; in consequence of these properties he assigns to it a much higher rank than the humic class of acids.

The formation of *apocrenate* of ammonia, by the oxidation of humate of ammonia, is continually going on in the soil during the warmth of summer (except on the very surface which is directly exposed to the air). Each minute portion produced can be taken up by the roots of plants, in the form of double apocrenates of ammonia and various fixed bases, provided there be a sufficient supply of water at hand; and, while in this way the soil loses its apocrenates, a new portion of apocrenate of ammonia is formed from the *humic acid* or *humin*, which is present in large excess. We may thus call the production of apocrenic acid in one respect an organic nitrification.

The series of organic acids present in the soil is, according to the views of *Mulder*, concluded by a fifth important substance, a final product of the oxidation of organic substances before they are entirely changed into carbonic acid and water, namely, *crenic* acid, the composition of which is $C_{24}\ H_{12}\ O_{16}$. *It* also is combined with ammonia in the soil, and forms double salts, which are soluble in water. These exist, along with the apocrenates, in all kinds of water* which have been in contact with organic substances in the soil. They were first found by *Berzelius* in spring water; they exist also in the waters of ditches, marshes, and bogs. *Crenic* acid is four-basic. By the continual tendency to nitrification in the soil, apocrenic acid must always be converted into crenic acid, the series of *ulmic*, *humic*, *geic*, and *apocrenic* acids thus terminating with *crenic* acid. In the upper layer of the soil, however, where the air is not inclosed, and consequently no tendency to nitrification exists, crenic acid must conversely be changed into apocrenic acid.

Johnston thinks* that to the five acids, mentioned by *Mulder*, several others may be added, as occurring in certain circumstances in the soil. Thus, from a sample of compressed peat, he extracted by ammonia a substance, from which hydrochloric acid threw down a dark brown acid, having the composition $C_{24}\ H_{12}\ O_{12}$; the same peat, when digested with solutions of caustic potassa, or of carbonate of potassa, or carbonate of soda, and precipitated by an acid, gave a substance, having the formula $C_{24}\ H_{14}\ O_{9}$; agreeing, therefore, with the ulmic acids of *Mulder*, in containing an excess of hydrogen, but not reducible to his ulmic group, the excess of hydrogen being very much greater than in ulmic acid, and the equivalent containing only twenty-four instead of forty equivalents of carbon. These acids agree with those of *Mulder* in their tendency to unite with several bases at once, and to combine with oxygen and nitrogen from the air, producing ammonia and acids containing more oxygen than the humic and ulmic acids. Again, from a substance called *Pigotite*, found on certain parts of the rocky coasts of Cornwall, where caves occur, *Johnston* extracted an acid, represented by the formula $C_{12}\ H_{5}\ O_{8}$. This acid was obviously formed from the decaying vegetable matter of the soil, and was combined with alumina. It approaches very closely in composition to the *crenic* acid of *Mulder*, and is called by its discoverer *Mudeseous* acid; on treating its compound with alumina, with nitric acid, *Johnston* obtained still another acid, the formula of which is $C_{12}\ H_{5}\ O_{10}$.

The above is a very brief and imperfect outline of the present state of our knowledge regarding the nature of the organic constituents of the soil. It will be seen that the subject is still quite in its infancy, and that no attempt can as yet be made to point out a method of

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* See last Chapter.

* See his translation of Mulder's work, p. 184.

analyzing a soil with a view of isolating any particular acid. The following mode of examination must, therefore, for the present suffice.

Determination of the total Amount of Organic Matter.—From 100 to 200 grains of the soil thoroughly dried, at a temperature not higher than between 250° and 300° Fahrenheit, are burned in a platinum crucible till all blackness disappears. The earth is then moistened with carbonate of ammonia, dried, and again gently ignited. The difference in weight furnishes a close approximation to the amount of organic matter present. It is not absolutely exact, because it is impossible thoroughly to expel the whole of the water from some soils, without partially decomposing the organic matter.

Determination of the Acids of the Humic Group.—About 500 grains of the soil are digested for several hours at about 200° Fahrenheit, with a solution of carbonate of soda; the fluid is then filtered off, an operation which, with soils containing much alumina, frequently takes a considerable time*; the filtrate is mixed with slight excess of hydrochloric acid, whereupon the humic acid separates in the form of light brown flakes; these are collected on a tared filter, washed, dried, and weighed; the dry mass is then burned, and the weight of the ashes subtracted from that of the dry flakes: the remainder is the amount of humic acid.

Determination of the Humus.—About 500 grains of the soil are digested for some hours with caustic potassa in a porcelain basin; the alkaline ley is diluted with water, filtered, the undissolved matter washed, and the filtrate precipitated by hydrochloric acid. The whole of the *humus* is by this treatment converted into humic acid; and the difference in weight between the precipitate thus obtained and that in the former experiment, when carbonate of soda was employed as the solvent, represents the quantity of organic matter existing in the soil in the form of *humus;* and the two weights added together, and deducted from the amount which the soil lost by ignition, shows the quantity of the other organic ingredients not belonging to the humic group.

Should the operator wish to determine the amount of resinous and waxy matters in the soil, he may extract them by digesting about 2000 grains with strong alcohol, precipitating them from the alcoholic solution by water; and, should he desire to know the quantity of nitrogen which the soil contains, he may burn a known quantity with soda lime in the manner described in detail at page 147.

CHAPTER VI.

On the Analysis of Ashes of Plants.

The method recommended by *Drs. Will* and *Fresenius* is the following*:—

First preparation.—Plants in a normal and healthy condition should be selected, unless the design be to study diseases and their causes. All foreign matter, such as dirt, dust, &c., should be carefully removed; but the plants should not be washed, or certain soluble salts might be extracted. Plants which have been exposed to moist weather should, for the same reason, be rejected.

The design of analyzing the ashes of plants may be—1st, simply to ascertain the amount and nature of their inorganic constituents; or, 2ndly, the operator may have in view the discovery of the presence or absence of certain substances in the soil, such as *alkalies, alkaline earths,* and *phosphates.* For the latter purpose an examination of the ashes of all the varieties of plants growing upon the soil must be undertaken; and when a knowledge is hereby obtained of the composition of the inorganic constituents of both weeds and of cultivated plants, and when to this is added an acquaintance with the nature of the soluble constituents of the soil itself, the analyst is in a position to determine for what crops the soil in question is best adapted. *Woods, herbs,* and *roots,* after being perfectly dried, may be burned upon a clean iron plate; *leaves, fruit,* and *seeds* will be best burned in a Hessian crucible, by means of charcoal or coke: the crucible should be placed somewhat obliquely in the fire, in order to favour the access of air. Sometimes the ashes

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* Should the first filtrate be still muddy, it should be concentrated by evaporation, and again passed through the filter, when it will, in most cases, be obtained quite clear.

* Memoirs of the Chemical Society, vol. ii. p. 179, *et seq.*

are left perfectly white, but some seeds require a higher temperature than others to rid the ashes entirely of charcoal: care must, however, be taken not to allow the heat to rise sufficiently high to fuse the alkaline salts, or it will be found afterwards almost impossible thoroughly to burn away the charcoal. During the operation of burning, and especially towards the end of the process, the ashes should be allowed to lie as lightly in the crucible as possible, in order that air might circulate freely through them; they should not, therefore, be stirred together: by attending to this, a much whiter ash is procured than would otherwise be the case. After the ashes have been well burnt in the crucible, it is advisable to transfer them to a platinum dish, and to heat them to low redness over a gas or spirit lamp, with constant stirring; they should then be rubbed to a fine powder, and transferred while warm to a well-stoppered bottle. *Rose* objects to this mode of preparing the ash for analysis; his important observations on this subject will be referred to at length further on.

The ash being prepared, the first step is to determine, by means of a qualitative examination, to which class the ashes belong:—whether to the *silicious*, or to the *phosphoric*, or to the *carbonic* class. A small portion is treated with concentrated hydrochloric acid, which generally dissolves it completely, unless the ash abounds in silica; if a strong effervescence accompany the solution in hydrochloric acid, carbonates of the alkalies or alkaline earths predominate, and the whole of the phosphoric acid present is probably combined with peroxide of iron; if no (or only moderate) effervescence attend the solution, phosphates predominate; and, if complete solution in hydrochloric acid cannot be obtained, the ash belongs to the silicious class.

To the clear hydrochloric solution acetate of ammonia is either at once added, or it is first neutralized by means of caustic ammonia, and free acetic acid afterwards added. In most cases a yellowish white gelatinous precipitate is formed, consisting of *phosphate of peroxide of iron*. This precipitate is collected on a filter, and ammonia added in excess to the clear filtrate, by which means a fresh precipitate may be obtained: if it be red, it is peroxide of iron. The solution is well protected from the air, and allowed to stand for some time; if no further precipitation take place, then it is known that the ash contains no other phosphate than that previously precipitated; but, should a white deposit gradually form, it consists of *phosphates of lime and magnesia*, and shows that the ash under examination contains more phosphoric acid than is combined with the peroxide of iron. It is not necessary to proceed further with the qualitative examination, unless the operator should wish to test for *fluorine, oxide of manganese, iodine, bromine*, or any other peculiar substance, the presence of which may be suspected, and in such cases separate portions of the ash must be used for each experiment, as also for determining quantitatively the amounts of carbonic acid in the ashes abounding in that principle, and of the alkalies in the ashes belonging to the *silicious* class.

I. *Determination of the Quantity of Ashes yielded by a given weight of the Plant.*—This is a problem, the solution of which is of considerable importance: a quantity of solid matter is annually removed from the soil in the crop taken from it, which loss should be repaired as nearly as possible by the judicious addition of manure. It is the nature of the manure to be furnished which the farmer seeks from the analytical chemist; but the farmer must take his share in the inquiry by informing the analyst as to the weight of the crop which a given surface of soil should yield, and this he can in most cases do with sufficient accuracy. The vegetable substance under examination should be dried in the water bath, or still better in a current of dry air produced by the efflux of water in the apparatus, depicted in *fig.* 22, page 137, till it ceases to lose weight. The quantity of substance employed in this experiment depends on the proportion of its inorganic constituents. Of *herbs* and *seeds*, which are in general rich in these matters, from 30 to 50 grains will be sufficient, whilst of *woods* ten times that amount must be taken. The combustion succeeds best in a platinum crucible, which should at first be covered, and a gentle heat only applied, but a stronger heat must afterwards be employed, the lid of the crucible being removed to ensure the perfect combustion of the charcoal. Those ashes which do not effervesce with acids, as the ashes of seeds, may be treated with nitric acid, and again ignited, by which treatment they will speedily be rendered quite white. If a very strong heat has been employed, the carbonic acid in those ashes which effervesce with hydrochloric acid will be expelled, but it may be restored by moistening the ashes with solution of carbonate of ammonia, and afterwards again exposing them to gentle ignition: so also, at a high temperature in contact with charcoal, the sulphates (if any be present) may be converted into sulphurets, but the reconversion of those compounds into the original salts may be effected by heating the ashes intensely, and for a considerable time, together with pure peroxide of mercury. Although the above method of estimating the amount of ashes yielded by a plant is not altogether free from objection, it is, nevertheless, a sufficiently close approximation to truth to answer every practical purpose; indeed, it is doubtful whether more accurate methods would really be more valuable, since it is found that the amount of ashes yielded by the same plant is not constant.

II. *Analysis of Ashes, rich in Carbonates and Sulphates.—Determination of the Silica, Charcoal, and Sand.*—About 60 grains of the ashes, which have been found to be soluble in hydrochloric acid, are treated with concentrated acid in a matrass, held obliquely so as to avoid any loss of the liquid during the evolution of the carbonic acid; a gentle heat is then applied, until it is evident that everything is dissolved excepting the carbonaceous and sandy particles. The whole is now carefully removed into a porcelain basin, evaporated to dryness over a water bath, and then heated somewhat more strongly, as is usual in separating silica (see page 220). The mass when cold is moistened with strong hydrochloric acid, digested for half an hour with a sufficient quantity of water, and boiled; after which the acid liquor is poured upon a stout filter, which has previously been dried at 212°, and weighed. The silica remains on the filter; and, if the ashes were not perfectly white and pure, some sand and charcoal also. The filter is washed and dried, and the substance carefully removed from it into a platinum or silver crucible without injury to the paper. This is effected without difficulty if the matters be perfectly dry, the paper in most cases only retaining so much as to be slightly coloured by the charcoal. The powder is now boiled for half an hour with pure potash ley (free from silica), by which the whole of the silica, natural to the ash, will be gradually dissolved, leaving the sand and charcoal unacted upon. The insoluble matter is again collected on the same filter, and after being well washed it is dried at 212°, till it no longer loses weight. The increase upon the weight of the dried filter is to be estimated as charcoal and sand. The silica in the alkaline solution is determined by adding hydrochloric acid in excess, whereby it is precipitated; the whole is evaporated to dryness, and the further treatment conducted in the manner directed at page 220.

The acid solution originally filtered from the *silica, sand,* and *charcoal,* after being well mixed, is divided into *three,* or more conveniently into *four* equal portions, one portion being reserved in case of an accident happening with either of the other quantities. The division is best effected by means of an accurately graduated tube or cylinder; the whole of the fluid is collected into the tube or cylinder, the measure of which thus represents the weight of ash experimented upon. The solution is now divided into three or four equal or known portions, the volume of each is noted, and they are labelled respectively with the letters *a, b, c,* and *d.*

In *a* the *peroxide of iron* (oxide of manganese) and the alkaline earths are estimated.

In *b* the alkalies.

In *c* the *phosphoric* and *sulphuric* acids.

a. Estimation of the peroxide of iron, oxide of manganese, and *alkaline earths.*—To the solution ammonia is added until the precipitate thereby produced no longer entirely redissolves; acetate of ammonia is next added, and sufficient acetic acid to render the solution strongly acid. From the form and appearance of the precipitate, it can easily be judged whether it still contains *phosphate of lime;* if this be the case, more acetic acid must be added. The yellowish white precipitate which remains consists of *phosphate of peroxide of iron* $2Fe_2O_3 + 3PO5$; its separation from the fluid is assisted by gently heating: it is then well washed on the filter with hot water, ignited, and weighed. To the filtered solution neutral oxalate of ammonia is added as long as a precipitate continues to be formed, and the amount of lime is determined in the usual manner (see page 150). When it has been shown by the qualitative analysis that, besides phosphate of iron, the ash contains peroxide of iron or oxide of manganese (in which case the presence of the earthy phosphates is very rarely detected), the solution, previous to the separation of the lime, should be supersaturated with ammonia, and precipitated by means of sulphuret of ammonium, the two oxides being afterwards separated according to one of the methods given at page 168. If the ashes under examination contained earthy phosphates, the solution filtered from the oxalate of lime will contain free acetic acid; if otherwise, there will be free ammonia; it is next somewhat concentrated, rendered ammoniacal, treated with a solution of phosphate of soda, and the precipitate formed collected and estimated as pyrophosphate of magnesia. (See page 151.)

b. Estimation of the Alkalies.—The solution is treated with baryta water until it gives an alkaline reaction; it is then gently heated and filtered. By this means we get rid of all the *sulphuric* and *phosphoric acids*, the *peroxide of iron*, the *magnesia*, and part of the lime. The precipitate is washed on a filter as long as the washings render turbid a solution of nitrate of silver. It is next warmed, treated with caustic and carbonate of ammonia, and allowed to stand until the precipitate becomes heavy and granular. The whole is now filtered, and the solid matter washed, after which the solution is evaporated to dryness, and the residue heated to redness in a platina capsule to expel the ammoniacal salts. What remains consists of the chlorides of potassium or sodium, or more generally of a mixture of the two. The weight being noted, a little water is added, which generally leaves undissolved a trace of magnesia; this is collected on a filter, its quantity subtracted from that of the supposed alkaline chlorides, and added to that of the magnesia, as previously ascertained. The quantity of potash is determined by means of chloride of platinum in the usual way (see page 140), and that of the soda is calculated from that of the chloride of sodium indicated by deducting the weight of the chloride of potassium from that of the mixed alkaline chlorides; or the amount of the two alkalies may be determined by the *indirect* method as directed in page 142.

c. Estimation of the Sulphuric and Phosphoric Acids.—From the acidulous solution the sulphuric acid is first separated by chloride of barium; the filtered liquor is nearly neutralized by ammonia; acetate of ammonia is added, and then a solution of perchloride of iron until the liquor begins to turn red in consequence of the formation of acetate of iron. Care must here be taken that sufficient acetate of ammonia be added to convert the whole of the chlorine of the perchloride into salammoniac. The solution is now boiled until it becomes colourless, all the iron being then precipitated. The precipitate, after being washed with hot water, consists of phosphate of iron and a quantity of basic acetate of iron. It is dried, ignited in a platinum crucible, treated with a few drops of nitric acid, re-ignited and weighed. It is next digested with concentrated hydrochloric acid, by which it is speedily dissolved. The solution is diluted with hot water mixed with tartaric acid, and ammonia added until the yellowish white precipitate, which is at first formed, disappears. A clear solution of a dingy green colour is thus obtained, from which the iron is precipitated by hydrosulphuret of ammonia. The precipitate and supernatant fluid are digested together in the water-bath until the latter loses its green tinge, and is of a clear yellow colour, resembling that of hydrosulphuret of ammonia with excess of sulphur. It is now rapidly filtered, access of air being prevented, and the precipitate is washed with hot water containing a little hydrosulphuret of ammonia, until a drop of the filtered liquid, dried upon a platinum spatula and ignited, no longer gives any acid reaction. The sulphuret of iron is dissolved from the filter by means of hot and dilute hydrochloric acid; the solution is boiled, treated with a few drops of nitric acid to peroxidize the iron, and ammonia is then added in excess. The precipitate is pure peroxide of iron, the weight of which, deducted from that of the basic phosphate, gives the quantity of phosphoric acid. (See page 215.) The perchloride of iron used in this experiment must be quite free from sulphuric acid.

Estimation of the Chlorine.—A fresh portion (about 15 grains) of the ashes is weighed out and exhausted with hot water, slightly acidulated with nitric acid; the solution is precipitated with nitrate of silver, following the directions given at page 137. If the ashes should contain appreciable quantities of *iodine* and *bromine*, these bodies will be found in the precipitated silver salt; for their quantitative estimation, however, a larger quantity of the ashes must be employed.

Estimation of the Carbonic Acid.—The amount of this acid is determined with the apparatus of Drs. *Fresenius* and *Will*, described at page 144.

III. *Analysis of Ashes abounding in Silica.*—Ashes of this kind are in general only partially soluble in acids. Their alkalies must, therefore, be determined in a separate portion of the ash. The chlorine and carbonic acid are determined in the same manner as when the ash is entirely soluble in acids. The quantity of chlorine found in ashes of this class is, however, probably always somewhat less than it should be, since the alkaline chlorides, when ignited with silica and carbon, undergo a partial decomposition.

Estimation of the Silica.—Pure potassa or soda ley is poured upon about sixty grains of the ashes, and evaporated to dryness in a platinum or silver dish. The silicic acid compounds are, by this treatment, dissolved, leaving the sand unaffected. The heat should not be so great as to fuse the mass, or some of the charcoal might be oxidated at the expense of the water of the hydrated alkali. Diluted hydrochloric acid is poured upon the mass, the whole evaporated, and the silica, charcoal, &c. determined in the manner already described. The acidulous solution filtered from the insoluble matter is divided into two parts; one is employed for the determination of the sulphuric and phosphoric acids, and the other for that of the peroxide of iron and the alkaline earths by the methods detailed above.

Estimation of the Alkalies.—A second portion of the ash (about fifty grains) is ignited in a platinum crucible with four times its weight of *hydrated baryta*. The acid solution which remains after separating the silica, &c. is precipitated successively with baryta water and carbonate of ammonia, the alkalies being then obtained in the state of chlorides. The further treatment has already been described.

Arrangement of the results.—Since the analysis of the ashes of a plant can convey no precise information as to the manner in which the several acids and bases found are actually combined in the living vegetable, the method recommended by *Fresenius* and *Will*[*], namely, that of enumerating the per-centage weights of the acids and bases found is probably the best which the present state of our knowledge admits of; but, whether this or any other method be adopted, it is highly desirable that there should be uniformity on the subject, for it is only thus that the results of different analyses can be compared together, and so applied to the solution of certain interesting questions in physiology and in agriculture. The chlorine found in the analysis is always calculated as chloride of sodium, and the manganese as *manganoso-manganic oxide* (Mn_3O_4). As an illustration of this method, we may quote *Messrs. Rowney* and *How's* analysis of the ashes of the orange-tree[†].

Amount of ash left by—

100 parts of the root	4.48
100 parts of the stem	2.74
100 parts of the leaves	13.73
100 parts of the fruit	3.94
100 parts of the seeds	3.30

Per-Centage Composition of the Ashes of the Root.

Potassa	15.43
Soda	4.52
Lime	49.89
Magnesia	6.91
Sesquioxide of Iron	1.02
Chloride of Sodium	1.18
Phosphoric acid	13.47
Sulphuric acid	5.78
Silicic acid	1.75
	100

Per-Centage Composition of the Ashes of the Stem.

Potassa	11.69
Soda	3.07
Lime	55.13
Magnesia	6.34
Sesquioxide of iron	0.57
Chloride of Sodium	0.25
Phosphoric acid	17.09
Sulphuric acid	4.64
Silicic acid	1.22
	100

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[*] *Fresenius'* Quantitative Analysis, p. 507.

[†] Mém. Chem. Soc., vol. iii. p. 370.

Per-Centage Composition of the Ashes of the Leaves.

Potassa	16.51
Soda	1.68
Lime	56.38
Magnesia	5.72
Sesquioxide of iron	0.52
Chloride of sodium	6.66
Phosphoric acid	3.27
Sulphuric acid	4.43
Silicic acid	4.83
	100

Per-Centage-Composition of the Ashes of the Fruit.

Potassa	36.42
Soda	11.42
Lime	24.52
Magnesia	8.06
Sesquioxide of iron	0.46
Chloride of sodium	3.87
Phosphoric acid	11.07
Sulphuric acid	3.74
Silicic acid	0.44
	100

Per-Centage Composition of the Ashes of the Seed.

Potassa	40.28
Soda	0.92
Lime	18.97
Magnesia	8.74
Sesquioxide of iron	0.80
Chloride of sodium	0.82
Phosphoric acid	23.24
Sulphuric acid	5.10
Silicic acid	1.13
	100

In the above calculations the unessential constituents, viz. *carbonic acid*, *sand*, and *charcoal*, are deducted[*].

Rose's Method of examining the Ashes of Organic Bodies.—It has been mentioned above, that the method of preparing the ashes of plants for analysis, by igniting the vegetable in Hessian crucibles, and continuing the heat until all the organic matter is destroyed, has been objected to by *Rose*, who observes[*] that, if the fixed constituents of plants are examined according to the process which he adopted in examining the ashes of *ox-blood*, results differing entirely from those yielded by the ash analyses hitherto published may be obtained.

The process adopted by the Berlin chemist in his analyses of the ashes of blood was this. The blood was exposed in a covered platinum crucible to a very faint red heat, then extracted with cold water, and the colourless liquid evaporated to dryness. It was found to consist of alkaline chlorides and carbonates, with very minute quantities of alkaline sulphates and phosphates. The charred mass, extracted with water, was now treated with hydrochloric acid: the filtered solution did not yield, with ammonia, a very considerable precipitate, which, though it looked almost like pure hydrated oxide of iron, contained some phosphoric acid as well as lime and magnesia. In the filtered solution a pretty considerable quantity of oxalate of lime was obtained with oxalate of ammonia, proving the presence of carbonate of lime in the charred blood; and in the liquid separated there was also a small quantity of magnesia. The cinder, after treatment with water and hydrochloric acid, yielded a very considerable quantity of a red-coloured ash, on being burnt in an atmosphere of oxygen. It was in a semifused state, and contained peroxide of iron (which formed the chief part) and earthy and alkaline phosphates. These results differ considerably from those of *M. Enderlin*, whose method was[†] to evaporate fresh blood to dryness, and then to powder and incinerate the residue. The ash thus obtained dissolved in hydrochloric acid *without* effervescence, whence he concluded that the alkalinity of blood cannot be caused by an alkaline carbonate, and that there cannot exist in the blood any alkaline salts with organic acids. The salts found by *M. Enderlin* in the ashes of blood he states to be *tribasic phosphate of soda* ($3\,NaO, PO_5$), *chlorides of sodium and potassium*, *sulphate of soda*, *phosphate of lime*, *phosphate of magnesia*, and *oxide*, with some *phosphate of iron*, the alkalinity of the blood being produced by phosphate of soda

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[*] The reader is referred to a paper by *Mr. Watts* on the "Analysis of the Ash of the Hop," published in the third volume of the "Memoirs of the Chemical Society," p. 392, *et seq.* In this analysis an entirely different system from that above detailed was pursued; separate examinations of the aqueous and the hydrochloric solutions were made, and the acids and bases are arranged as they were supposed to exist in the plant. The analysis itself is remarkable as pointing out the unusual presence of *phosphate of alumina*.

[*] In a paper read before the Royal Academy of Berlin; Chem. Gaz., vol. v. p. 158, *seq.*

[†] See *Liebig's* Annalen, and Chem. Gaz., vol. iii. p. 229.

($3NaO, PO_5$). If the phosphate of soda in the blood were the ordinary phosphate ($2NaO, HO, PO_5$), it would, according to *M. Enderlin*, be converted by a red heat into the *pyrophosphate* ($2NaO, PO_5$), the third atom of base (HO) escaping; but, according to *Rose*, the ordinary phosphate of soda ($2NaO, HO, PO_5$) would, at a high temperature, decompose *carbonate of soda* and be converted into tribasic phosphate ($3NaO, PO_5$); and that, in consequence, the conclusions of *M. Enderlin* are erroneous. It has been shown, also, by *Marchand*[*], that the circumstance of no carbonates being found in the ash does not in the least prove that they are not contained in the blood, and that we are as little justified in admitting unconditionally the presence of tribasic phosphate of soda ($3NaO, PO_5$) because that salt is found in the ash. Indeed *Marchand* declares that the admission of the presence of $3NaO, PO_5$ in the blood *absolutely requires* the admission of that of carbonate of soda, since it has been proved that $3NaO, PO_5$ is converted, on exposure to a moist atmosphere containing carbonic acid, into $2NaO, HO, PO_5$, and NaO, CO_2.

The same objections which have been urged against the conclusions drawn by *Enderlin* with regard to the salts existing in the blood, from the analysis of the ashes prepared at high temperatures, have been also applied by *Rose* to the conclusions drawn from the results of the analyses of the ashes of plants prepared in the usual manner. It had previously been remarked by *Erdmann*[†] that the mode of preparation of the ashes for analysis has great influence on their apparent composition. His method was to burn the plant or seeds in a muffle furnace, in which, in the course of three or four hours, upwards of 200 grains of the most beautiful ash of corn may be obtained. The ashes so prepared, especially in those seeds that are difficult to reduce to ash, generally contain the phosphoric acid in a lower state of saturation than those prepared in a crucible. Thus the ash of rye, which usually contains an alkaline phosphate, yielding, with oxide of silver, a white precipitate, gives a yellow one when it has been prepared by long-continued ignition in a covered crucible; and biphosphate of potassa, when ignited for a long time with carbonized sugar, is converted into a bibasic, and finally even into a tribasic salt. It is evident, therefore, that a reduction of the phosphoric acid has taken place, and the same is the case with the sulphuric acid. These facts induced *Rose* to undertake an examination of the fixed constituents of certain plants by the same method which he had adopted in the analysis of ox-blood, a method which, although it may be objected to in that it takes more time, furnishes (he says) far more correct results, and gives satisfactory answers to several questions as to how, or in what combinations, the constituents found in the ash were contained in the organic substance.

His method is as follows[*]. The organic substance is charred at a very faint red heat, so that the water with which it is extracted is not coloured yellowish or brownish. At this temperature, which, owing to the volatilization of so many substances, is much lower than would appear, no alkaline chlorides are volatilized, nor can chlorine be expelled from them, in the form of hydrochloric acid, by acid phosphates. The alkaline and earthy phosphates are not able to expel the carbonic acid from the alkaline carbonates, either contained in the organic substance or formed by charring; nor can phosphoric acid be eliminated, from its combinations, from silica, reduced by carbon, and volatilized in the form of phosphorus. The charring is effected either in a spacious covered platinum crucible, over a spirit lamp; or, with larger quantities of the organic substances, in a spacious covered Hessian crucible, especially if they do not fuse. When there is no longer much empyreumatic odour perceptible, the heating is discontinued, the cold mass left for some time in contact with water, and the solution of the salts furthered by heating. The edulcoration requires considerable time and much hot water; but, if the highest degree of accuracy is not desired, the edulcoration may be discontinued when several drops of the wash-water leave a scarcely perceptible residue on evaporation upon a slip of

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[*] Journ. für Prakt. Chem., April 6th, 1846; and Chem. Gaz., vol. iv. p. 210.

[†] See *Liebig's* Annalen, liv. p. 341—356, 360—363; lvi. p. 122; lvii. pp. 67, 68; and Chem. Gaz., vol. iv. p. 230, *et seq.*

[*] For the report of *Prof. Rose's* important paper on the "Examination of the Ashes of Organic Bodies," given in the text, the author is indebted to the "Chemical Gazette;" he has preferred transcribing the paper almost in full to giving any abstract of it, to avoid the possibility of any misconception in any of the details of the operation.

platinum foil: this point is very soon attained.

The aqueous extract contains the alkaline salts. The alkaline chlorides were contained as such in the organic substance previous to the charring, as well as at least a part of the alkaline sulphates and phosphates. If, as in most cases, carbonated alkali is found in the aqueous extract of the charred mass, it either pre-existed in the organic substance, or the alkali in it was combined with an organic acid, or some other organic body which acted the part of an acid towards the alkali. If the organic substance contain sulphate of lime, this, when carbonated alkalies are present in sufficient quantity in the charred mass, is converted, on treating the latter with water, into carbonate of lime and alkaline sulphate. In the same way, when phosphate of lime is present, a certain quantity of alkaline phosphates is formed from it, in the aqueous extract, by the alkaline carbonates. Carbonated alkali and phosphate of lime are not perfectly decomposed even by fusion at very high temperatures.

The decomposition in presence of much water is likewise imperfect; and, the more alkaline phosphate is obtained in the aqueous extract, the more concentrated the solution, the more carbonated alkali it contains, and the longer the charred mass has been digested at an elevated temperature. Alkaline sulphates and phosphates will, however, be found in far smaller quantities in the aqueous extract of the charred mass than was to be expected from the ash analyses that have hitherto been published. Frequently the two, and especially the latter, are present only when too high a temperature has been employed in the charring. From this, however, it is evident that the nature of the salts in the aqueous extract may vary somewhat, according to the temperature employed and the longer or shorter digestion of the mass with water. When the charring is effected at too high a temperature, the greater portion of the carbonated alkalies are decomposed by the earthy phosphates.

The accurate examination of the salts in the aqueous extract is not accompanied with any great difficulties. One circumstance, however, renders it somewhat less easy. Carbonate and phosphate of lime and magnesia frequently dissolve to a considerable extent in neutral solutions of alkaline salts, particularly of alkaline carbonates and phosphates; in the course of time they are deposited from the solutions, especially after the application of heat. When, therefore, the aqueous extract is evaporated, it frequently becomes somewhat turbid, and deposits small quantities of earthy salts. It should consequently be evaporated nearly to dryness, diluted with water, and the solution set aside for some time; when the earthy salts have subsided, it is filtered, the filtered solution evaporated to dryness, and its weight determined. When there is no alkaline sulphate or phosphate present, the examination is very easy. The quantity of carbonic acid is determined in a suitable apparatus, by decomposition with nitric acid; and, upon this, that of the chlorine by a solution of silver: upon which, after removing the excess of silver by hydrochloric acid and concentrating the liquid, the potash may be separated from the soda by chloride of platinum. With the presence of alkaline sulphate or phosphate, it is advisable to divide the quantity of the alkaline salts, and in the one-half to determine the quantity of the chlorine and the alkalies, and in the other that of the carbonic acid by decomposition with hydrochloric acid; that of the sulphuric acid by a salt of barytes; and, after removing the baryta by means of sulphuric acid, and supersaturating with ammonia, to ascertain the quantity of phosphoric acid by means of a solution of a salt of magnesia, to which chloride of ammonium has been added.

The charred mass, exhausted with water, is now digested with hot hydrochloric acid for some length of time, and then washed with water. This operation requires considerably more time and water than in the treatment of the charred mass with water; and, if the washing were to be continued until some drops of the filtered liquid no longer produced any opalescence in a solution of silver, an enormous length of time, several months, would be required especially in operating upon large quantities. The edulcoration, therefore, is only continued until a considerable quantity of the wash-water does not exhibit a trace of a precipitate when treated with ammonia; it will then also be seen that a large quantity of the wash-water, when evaporated upon platinum, no longer leaves any perceptible residue; this does not require much time, especially when hot water is used.

The acid solution contains the earthy phosphates which existed as such in the organic substance, and the peroxide of iron. It is precipitated by ammonia, and, after having determined the weight of the precipitate, the bases are separated from the phosphoric acid. On separating the earthy phosphates by means of ammonia, a small quantity remains dissolved in the filtered liquid, owing to the presence of chloride of ammonium; consequently, upon adding oxalate of ammonia, a precipitate of oxalate of lime is obtained, but its quantity is usually larger than corresponds to the phosphate of lime dissolved by the chloride of ammonium; consequently, a portion of the lime existed as carbonate of lime in the charred mass, or was formed by the decomposition of the sulphate or phosphate of lime by the alkaline carbonates. The liquid filtered from the oxalate of lime indicates, on the addition of a solution of phosphate of soda, the presence of some magnesia. The insoluble earthy salts, which separated from the aqueous extract, may be examined conjointly with those in the acid extract.

With respect to the charred mass which has been exhausted with water and hydrochloric acid, it might be imagined that it could contain only silica or silicates, undecomposable by dilute hydrochloric acid; but it yields a very large amount of ash on complete combustion, even when the organic substance contains no silica or mere traces. *Rose* effects the complete combustion of the charred mass in a thin porcelain crucible, provided with a platinum cover, which is perforated in the centre, and into which there passes a curved silver tube about eight inches long, through which dry oxygen gas is conveyed into the crucible. The crucible is half filled with the substance and heated over a spirit-lamp, and, with proper care, not a particle of the ash is carried away, and the combustion proceeds with great rapidity: a further quantity of the substance is conveyed from time to time into the crucible. The ash thus obtained may be weighed with great accuracy. Its weight added to that of the evaporated aqueous extract of the charred mass, and to that of the insoluble earthy salts dissolved by the hydrochloric acid, gives the correct quantity of fixed constituents in the organic substance employed.

The ash obtained, especially when derived from vegetable substances, consists of the same constituents as were found in the aqueous and acid extracts; if alkalies were present in them, we likewise find them in the ash of the exhausted charred substance; otherwise, it consists principally of earthy phosphates. When the subject of the analysis is *the blood*, nearly the whole of the *iron* is met with in this ash. Only about a tenth part of it is found in the acid extract of the charred mass, and indeed the less the more carefully the charring was effected with exclusion of the air. When the organic substance contains no silica, various views may be entertained respecting the origin of the ash from the charred mass which has been exhausted with water and acid. The most probable is, perhaps, to derive it from an imperfect exhaustion of the two solvents. When an organic substance is destroyed by heat, the charcoal formed may contain such cavities that the inorganic salts surrounded by them are protected from the action of the solvents. The globules of the blood, those of yeast, and the cells of plants, form, perhaps, after charring, extremely minute vesicles, with such small apertures that no liquid can penetrate into them. That the vessels of wood are capable of forming extremely thin filaments with minute apertures by charring is known from the investigations of *Degen*. The charred mass of an organic substance (yeast), after it has been most carefully exhausted by water and hydrochloric acid, was ground to the finest powder upon a plate of agate; the two solvents now extracted only imperceptible traces of fixed constituents, and, after burning the exhausted charred mass, *Rose* obtained the same large amount of ash as from the non-pulverized charcoal. It may, nevertheless, be supposed that the extremely minute vesicles were not destroyed and torn by the friction upon the agate plate. The microscope threw no light upon the subject.

It is known that charcoal is capable, by a weak kind of affinity, of removing certain salts from their solutions. *Rose* found it almost impossible, also, to remove entirely by washing the whole of the hydrochloric acid from the charred mass which had been digested in hot acid; but the quantity of ash is too considerable for us to ascribe this origin to it, since it is known that the salts which the charcoal has combined with may be entirely separated by long treatment with water at different temperatures. If *sulphate of potash* and *phosphate of lime* are mixed with *sugar* and the whole charred, water, and after this hydrochloric acid, will extract the two salts completely, so that, on subsequently burning the charred mass in an atmosphere of oxygen, not a trace of ash is obtained. *Rose* then discusses the several views which might be advanced to account for the ashes obtained from the charred mass. The following is remarkable from the curious considerations it involves with respect to the combinations of the organic with the inorganic materials in the living vegetable. The salts found in the ashes may, perhaps, not have pre-existed as such in the organic substances, but were first formed by oxidation after the burning of the coal. It has long been known that the protein compounds, of both animal and vegetable origin, contain *sulphur* and *phosphorus* in an unoxidized state; but the supposition has never been advanced, that the radicals of the earths and alkalies may likewise be contained in organic substances, in an unoxidized state, perhaps combined with those elements. These would certainly constitute a very peculiar class of combinations, such as at present we are not acquainted with. If they are really combined with organic substances in the living body, they cannot have been essentially altered on destroying the organic body by charring, or they have entered into combination with carbon and nitrogen, which are insoluble both in water and in hydrochloric acid.

The salts found in the ashes of the charred mass exhausted with water and acid, especially when derived from vegetable substances, are similar to those which occur in the aqueous and acid extract. If this be really true, then those salts found in the ash after the destruction of the living plants are probably contained in them only in part as such, and in part in a deoxidized state. The inorganic salts, therefore, which are taken up from the soil by the living plant are partially deoxidized by it, and in this state form combinations with organic substances contained in the plant.

This view (observes *Rose*) is far more probable with respect to several animal substances, especially the blood, than in reference to plants. It has long been suspected that the iron in the blood was contained in it in an unoxidized state: and, according to the recent investigations of *Mulder*, the iron is actually extracted by acids from *hæmatine* with evolution of hydrogen gas. On the other hand, it is very remarkable that iron cannot be extracted from the charred blood by hydrochloric acid. This subject deserves investigation. With respect to plants, the view above advanced can evidently only be confirmed or refuted by following the method of analysis above described, and thus it is that *Rose* has pronounced it by far the most rational mode of investigation.

It has been shown by *Rose* that frequently very considerable quantities of alkaline carbonates are extracted by water from several organic substances by charring, in the ashes of which no carbonic acid was found by former investigators. But all organic substances do not yield alkaline carbonates when treated in this manner, even though considerable quantities of alkali are contained in their ash. Highly remarkable in this respect is *yeast*, the ashes of which, according to *Mitscherlich*, contain no carbonic acid and no metallic chlorides; and *Rose's* experiments show that they are likewise not to be found in the aqueous extract of the charred yeast. Yeast diffuses, on being charred, an odour similar to that of the protein compounds: the aqueous extract did not turn litmus paper blue—became turbid on evaporation, and deposited a large quantity of earthy phosphates. The mass evaporated to dryness yielded, on filtration, a clear solution which faintly reddened litmus-paper, and contained, therefore, not a trace of alkaline carbonates; the only substances that could be found in it were alkaline phosphates, with very minute traces of alkaline sulphates and chlorides. The charred mass gave, on treatment with hydrochloric acid, a solution from which ammonia threw down a considerable precipitate of earthy phosphates. The cinder, exhausted with water and acid, furnished on combustion a very large quantity of ash, which contained the same constituents which had been extracted from the charred mass.

CHAPTER VII.

On the Analysis of Urine and Urinary Calculi.

From the following analysis of this important secretion by *Berzelius*, it will be seen that its composition is very complicated ; indeed the Chemistry of Urine is as yet very imperfect, for in no complete analysis which has hitherto been published has any account been taken of the *hippuric acid*, or the *kreatine*, or *kreatinine*, which *Liebig* has announced to be constant constituents, while, according to the same chemist, normal urine contains no lactic acid ; so that in the subjoined analysis the 17.14 parts which are set down to this acid and its salts are, in reality, something else, the nature of which has yet to be discovered.

Analysis of Urine by Berzelius.

Water	933.00
Urea	30.10
Uric acid	1.00
Lactic acid, lactates, and animal matter	17.14
Mucus of the bladder	0.32
Sulphate of potash	3.71
Sulphate of soda	3.16
Phosphate of soda	2.94
Phosphate of ammonia	1.65
Chloride of sodium	4.45
Hydrochlorate of ammonia	1.50
Earthy matters, with a trace of fluoride of calcium	1.00
Silicious earth	0.03
	1000

Urine may be acid, neutral, or alkaline, even in a healthy condition of the body, its reaction to test paper as well as the nature of the salts which it contains depending in a great measure on the nature of the food, so that the physician has the saline condition of this secretion greatly under his control, a fact of great value in the treatment of calculous diseases. When the food contains salts of potassa and soda with organic acids, the urine becomes alkaline ; these acids becoming oxidized in the circulation yield carbonic acid, which combines with the alkalies, and the alkaline carbonates appear in the urine. When the food contains but very little of such salts of organic acids, the urine may be neutral, and when it contains none at all it becomes acid from the solution of uric or hippuric acid, or both, in phosphate of soda[*].

The specific gravity of healthy urine may vary from 1.012 to 1.030, and contain about 7 or 8 per cent. of solid matter, the remainder being water. In certain diseases, however, the density of the secretion may be considerably greater, as well as its proportion of solid ingredients. The following table, showing the quantity of solid matter in diabetic urine of different specific gravities between 1.020 and 1.050, was drawn up by *Dr. Henry*, and, assuming its correctness, *Dr. Frampton*[†] has given the following simple method of determining, without having recourse to actual experiment, the amount of solid matter voided in a given time in urine of any specific gravity. If *Dr. Henry's* table be examined, it will be found that there is an increase of solid matter in each wine pint of urine, corresponding to the increase of one degree of specific gravity of exactly 12.2 grains, or of 1.2 grains of solid matter in each ounce for every one degree of specific gravity. Hence, to determine the amount of solid contents in urine, say specific gravity 1.025, we have only to multiply the constant quantity, 1.2 grains, by 25, making 30 grains, to give us the solid contents of one ounce, whose specific gravity is 1025, and this again by the number of ounces voided in a given time, say 40 ounces (making 1200 grains), to give us the whole contents of solid matter dissolved in the urine passed in that time. This rule will be found, on trial, to give results so nearly coinciding with those of the table (the error is constantly just 1.6 grains in excess in the wine pint), it is so easy both to recollect and to apply, and so much more convenient than a table not always at hand, that it is well worthy of the notice of medical men.

In the experiments, which furnished the following table, the urine was evaporated at a steam heat till it ceased to lose weight, and till it left an extract which, on cooling, became quite solid. In reference to such tables, *Dr. Bence Jones*[‡] observes, that though they may be true for the total quantity of water

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[*] Turner's Chemistry, by *Liebig* and *Gregory*. Eighth Edition.

[†] Medical Gazette.

[‡] Phil. Trans., Part iv., for 1846.

passed in twenty-four hours, they are not so for the urine made at any one period of the day. The water made before and after dinner, for instance, may have the same specific gravity, but the total quantity of solid residue in each case may be entirely different.

Dr. Henry's Table of Solid Matter in Urine of different Densities.

Spec. grav. of the urine, water being 1000.	Quantity of solid extract in a wine pint in grs.	Quantity of solid extract in a wine pint in oz.	dr.	scr.	grs.
1020	382.4	0	6	1	2
1021	401.6	0	6	2	1
1022	420.8	0	7	0	0
1023	440.0	0	7	1	0
1024	459.2	0	7	1	19
1025	478.4	0	7	2	18
1026	497.6	1	0	0	17
1027	516.8	1	0	1	16
1028	536.0	1	0	2	16
1029	555.2	1	1	0	15
1030	574.4	1	1	1	14
1031	593.6	1	1	2	13
1032	612.8	1	2	0	12
1033	632.0	1	2	1	12
1034	651.2	1	2	2	11
1035	670.4	1	3	0	10
1036	689.6	1	3	1	9
1037	708.8	1	3	2	8
1038	728.0	1	4	0	8
1039	747.2	1	4	1	7
1040	766.4	1	4	2	6
1041					
1042	804.8	1	5	1	4
1043					
1044	843.2	1	6	0	3
1045					
1046	881.6	1	6	2	1
1047					
1048	920.0	1	7	1	0
1049					
1050	958.4	1	7	2	15

It is no part of our plan, neither would it be at all suited to the design of the present work, to give any detailed account of the numerous and important investigations which have been made within the last few years on the urine, both in health and in disease. To the physiologist and pathologist it cannot be doubted that the subject must be one of the highest interest; but it is not to a general treatise on chemical analysis that the cultivator of medical science would refer for such information as he might require in this department of his studies. We have, nevertheless, thought that it might add to the usefulness of our work to bring together some of the later methods, which have been adopted by chemists for the detection and quantitative estimation of certain of the ingredients of this complicated secretion.

Quantitative Estimation of Urea.—Two methods have long been in use, viz., separating it as *nitrate*, and calculating its proportion; or as *oxalate*, this being subsequently decomposed by carbonate of lime, and the urea weighed in its pure state. Both these methods are fallacious, on account of the solubility of both the salts; the following have therefore been proposed as substitutes.

1. *Rabsky's Method*[*].—Concentrated sulphuric acid, in the quantity of half that of the urine used, is added to the latter, and the mixture kept in a moderate state of ebullition; much water is thus vaporized, and the fluid becomes black. The temperature continues to rise, until at about 392° (it should not very much exceed this temperature) carbonic acid is evolved in small bubbles; the cessation of this disengagement of gas indicates that the urea is completely decomposed. The black residue is then thoroughly exhausted with water, and the solution filtered: the clear yellow filtrate is then evaporated in the water bath, and the generated sulphate of ammonia treated with alcohol and chloride of platinum. Since urine contains salts of potassa and ammonia, which will likewise be precipitated upon the addition of chloride of platinum, their exact proportion must be determined from a separate weighed portion by precipitation with chloride of platinum, and the corresponding amount must be subtracted from the first quantity. The author found this method to give accurate results, which were not interfered with by mixing the urea with sugar previous to analysis: in applying it, however, it is necessary to remove all those substances which might introduce error, such as *uric acid*, *hippuric acid*, *albumen*, &c. In many instances it may be advisable to separate the urea previously by oxalic acid, and to decompose the oxalate subsequently with sulphuric acid. In calculating the amount of urea, one part of ammonia–chloride of platinum corresponds to 0.134498 of urea.

The conversion of urea into carbonate of ammonia, which also takes place when the urine is left to itself, will be understood from the following equation, in

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[*] Lancet, Dec. 6, 1845.

which it is seen that by the addition of the elements of water all its carbon is converted into carbonic acid, and all its nitrogen into ammonia.

$$\left.\begin{array}{lll} 1 \text{ equivalent urea} & C_2N_2H_4O_2 \\ 2 \quad \text{do.} \quad \text{water} & H_2O_2 \\ \hline & C_2N_2H_6O_4 \end{array}\right\} = \left\{\begin{array}{lll} 2 \text{ equivalents carbonic acid} & C_2 \quad O_2 \\ 2 \quad \text{do} \quad \text{ammonia} & N_2H_6 \\ \hline & C_2N_2H_6O_2 \end{array}\right.$$

The carbonate of ammonia thus formed is of course instantly decomposed in the above experiment by the sulphuric acid, sulphate of ammonia being generated, and carbonic acid set free.

2. *Heintz's Method**.—*Estimation of the Potassa and Ammonia.*—A weighed quantity (from 100 to 120 grains) of the urine is treated with about 30 drops of hydrochloric acid, and set aside in a cool place for 24 hours; it is then filtered through a very small filter into a large platinum or porcelain crucible; the filter and glass are washed with a small quantity of water; the filtrate is treated with about 100 grains of sulphuric acid, and the liquid evaporated over a small spirit lamp, taking care that it does not boil, until the evolution of carbonic acid commences. The crucible is then covered with a watch glass, and heated until the evolution of carbonic acid ceases, the temperature not being allowed to exceed 180°. The contents of the crucible are then filtered into a porcelain dish, the crucible and the watch glass are well washed, and the filtrate is evaporated until almost all the water has passed off. About 20 drops of hydrochloric acid are then added to the residue, and afterwards a sufficient quantity of chloride of platinum and alcohol mixed with æther. If the liquid from which the precipitate has subsided is of a very pale colour, more chloride of platinum must be added. After 8 or 10 hours the precipitate is separated by filtration, washed, dried, and heated to redness in a crucible, which is at first covered, but subsequently open. The residue is treated with boiling dilute hydrochloric acid, the solution filtered, and this is repeated until the liquid which drops from the filter leaves no residue when evaporated upon platinum foil; the crucible and filter are dried at a gentle heat: the latter is burnt in the former, and weighed. Thus the amount of platinum, which corresponds to that of the *potassa*, *ammonia*, and *urea*, is obtained.

Another weighed quantity of the fresh urine is treated at once with chloride of platinum, 3 volumes of alcohol and 1 of ether: at the end of 10 or 12 hours the mixture is filtered, and the precipitate heated to redness in a well-covered and weighed platinum crucible. The residue is treated as above with dilute hydrochloric acid, and the filter is burned and weighed. We thus obtain the weight of platinum which corresponds to the potash and ammonia contained in the urine; its per-centage is calculated, and then deducted from that obtained in the first experiment: the difference gives the amount of platinum which corresponds to the urea.

In estimating the urea, if perfect accuracy be not required, the separation of the lithic acid may be avoided, the error hereby introduced amounts to about 0.7 part per 1000, placing the average amount of lithic acid in the urine at 1.0 per 1000. The filtration of the residue after the action of the sulphuric acid may be avoided, and it may be mixed at once with the chloride of platinum, alcohol, and ether.

The estimation of the amount of *potash* and *ammonia* in the urine should not be neglected, as it is liable to considerable variation: the author found it 1.0 to 11.6 parts per 1000. These two alkalies are precipitated together by treating fresh urine with chloride of platinum, alcohol, and ether. To separate them, the yellow precipitate is heated to redness, and the residue repeatedly extracted with boiling dilute hydrochloric acid: the solution is filtered, and the filter burnt. The platinum remaining corresponds to the quantity of ammonia and potash in the urine. On evaporating the filtered liquid with chloride of platinum and alcohol, a precipitate of *platino-chloride of potassium* is obtained, which is treated as above to estimate the potash it contains.

Separation of Albumen.—To estimate the urea in *albuminous* urine, a carefully weighed portion is treated with *bichloride of mercury* and boiled in a capacious dish. The liquid is then filtered, the precipitate slightly broken up and washed with water. When this

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* *Poggendorff's* Annalen, No. 9, 1845; and Chem. Gaz., vol. iv. p. 17.

is perfectly effected, a slow current of sulphuretted hydrogen is passed through the filtrate, and the liquid is filtered from the sulphuret of mercury formed.

The separation of the mercury may also be omitted, if care be taken to guard against the vapours of mercury which escape on heating it with sulphuric acid. The filtrate is evaporated with the addition of sulphuric acid until the urea is completely decomposed. The fluid thus obtained is treated as above described. Another weighed portion of the urine is also precipitated with bichloride of mercury, the precipitate washed with alcohol, and the filtrate treated with bichloride of platinum and ether. The platinum obtained enables us to calculate the amount of potash and ammonia present.

The author found that *albumen* is not perfectly precipitated by boiling even from acid urine, neither indeed is it admissible to use nitric acid when the urine is subsequently to be treated for the estimation of urea, since, by the action of sulphuric acid, nitrous acid would be formed, which decomposes the urea so as to liberate part of the nitrogen in the gaseous state. He also found that with *alcohol* a considerable amount of albumen may, in many cases, remain unprecipitated; and that, moreover, the albumen precipitated by alcohol is very difficult to wash. The above process has been shown by *Heintz* to be applicable to the estimation of the urea in urine containing *blood*, *milk*, and *bile*. In the latter case, should the urea amount to *one-ninth* of that of the urine (which could hardly occur), the error would not exceed 0.16 per 1000.

Bunsen's method of estimating Urea[*]. —It is founded on the fact, that aqueous solutions of urea are readily decomposed into carbonate of ammonia when heated above 212° in hermetically closed vessels. The metamorphosis begins even below 248°, but proceeds so slowly at this temperature that it is not completed in three or four hours; while, if the temperature is kept between 428° and 464°, three or four hours suffice for perfect decomposition. To apply this reaction to the determination of the amount of urea in liquids, it suffices to heat them, in strong glass tubes, with an ammoniacal solution of chloride of barium up to 428°—464°, a precipitate of carbonate of baryta equivalent to the amount of urea is obtained.

The author found that none of the different nitrogenous substances present in the urine interfered with the accuracy of this method, and he proved, by direct experiment, that it possesses sufficient accuracy even in the presence of substances the most widely diffused in the animal body. In order to avoid the influence which the so-called extractive substances of the urine may exert, *Bunsen* determines the urea from two separate portions of the urine, one of which has been previously deprived of its extractive substances by basic acetate of lead, and he gives a formula for facilitating the calculation from the results of the analysis[*].

Estimation of the Uric Acid.—A weighed quantity of the fresh urine is precipitated by strong acetic acid; the precipitate is collected on a weighed filter, and washed with water acidified with acetic acid. According to *Liebig*, the uric acid in the urine is held in solution by phosphate of soda; it has been proved, however, by *Heintz*, that this in nowise interferes with the accuracy of the method. The uric acid, during its precipitation, carries with it a certain quantity of the colouring substances of the urine; but, according to *Heintz*, the increase of weight from this cause is about compensated for by the loss which the uric acid sustains by washing. Lastly, the same chemist has proved, by direct experiment, that neither *sugar*, *albumen*, nor *blood*, have any essential influence upon the quantitative estimation of uric acid, provided acetic acid be employed as the precipitant.

Estimation of the Hippuric Acid[†].—A weighed or measured quantity of fresh urine is evaporated over the water-bath to the consistence of a thin syrup, and, on cooling, one-twentieth part of strong hydrochloric acid added to it, then shaken with ether, this dissolves the hippuric acid which has separated. It frequently happens that the ethers, as in an emulsion, separate with difficulty from the resin; but this is instantly effected by the addition of a few drops of alcohol. In this case the

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[*] *Liebig's* Annalen, March, 1848; and Chem. Gaz., vol. vi. p. 222.

[*] For this formula, and for the reasoning on which it is founded, the reader is referred to the original paper, which is too lengthy for our limited space.

[†] *Liebig*, in Archiv. der Pharm. for March, 1844.

etherial solution of the hippuric acid should be shaken previous to evaporation, with some water, in order to remove the urea taken up by the etherial solution through the intermediation of the alcohol. When this is done, crystals of pure hippuric acid are obtained on evaporation of the etherial solution. In stale urine the hippuric acid gives place to benzoic acid, and, when concentrated and distilled, a large quantity of acetic acid is also obtained. Another method of separating the hippuric acid from normal urine, is to evaporate until the salts are deposited, and then to add strong alcohol and apply heat; uric acid remains undissolved. The clear solution is evaporated nearly to dryness, the residue redissolved in hot water, and the urea decomposed by passing a current of *chlorine* through the solution; a small quantity of a mineral acid is then added, and the solution concentrated, when the hippuric acid is obtained in a crystalline state.

Detection of Bile in Urine.—A spirituous extract of the secretion is evaporated nearly to dryness on the water-bath; the residue, when cold, is transferred to a test tube. When quite cold, *sulphuric acid* and a very small quantity of a solution of one part of *cane-sugar* to four or five of water is added, the temperature of the solution being kept as low as possible. In the course of a few minutes, if the most minute trace of bile be present, a *violet red colour*, of more or less distinctness, is produced. Concentrated hydrochloric acid, heated with bile and sugar, likewise produces a red colour, but it is much lighter and less beautiful than that with sulphuric acid. The following precautions, in the application of this test, are prescribed by its author* (*M. Pettenkofer*).

1st. The temperature must not exceed 144° Fahr., otherwise the colour may be destroyed; 2nd, the quantity of sugar must not be too large, or sulphurous acid may be formed, whereby the colour may be concealed; 3rd, the sulphuric acid must be free from sulphurous acid; 4th, if the fluid should contain albumen, it should be previously coagulated; 5th, great excess of chlorides convert the colour to a brownish red; they should, therefore, be separated. To detect the constituents of the bile in urine, *M. Schwertfeger*† recommends precipitating with basic acetate of lead. When bile is present, a yellow precipitate is formed, from which a green solution is obtained with alcohol containing some sulphuric acid, and from which pure alcohol extracts, with the assistance of heat, bilate of lead. It is impossible to conclude from the colour of the urine as to the presence of bile, since similar colours may likewise originate from other causes.

Detection and Separation of Kreatine.—*Pettenkofer* and *Heintz* give the following as the most advantageous method*. To the alcoholic extract of the urine an alcoholic solution of chloride of zinc is added; in a short time a deposit is formed, which contains the *kreatine* in combination with chloride of zinc, together with a small quantity of phosphate of zinc. These two substances are separated by boiling water, which dissolves the first, but which is without action upon the latter. The pure *kreatine* is obtained from the aqueous solution of its combination with chloride of zinc, by precipitating the zinc with hydrosulphuret of ammonia; after having evaporated the filtered liquor as far as possible without a precipitate being formed from the boiling solution, absolute alcohol is added to it, when the *kreatine* is immediately deposited in the form of small crystals resembling those obtained in operating upon the alcoholic solution of the aqueous extract of *meat*. The composition of these crystals, according to *Heintz*, leads to the formula $C_8H_9N_3O_4 + 2HO$, which is the same as that advanced by *Liebig*.

Detection of Oxalate of Lime.—The following process is recommended by *Dr. Golding Bird*†. Allow a portion of the urine passed a few hours after a meal to repose in a glass vessel; if this be done in winter, or during the prevalence of frequent and rapid alterations of temperature, a more or less dense deposit of *urate of ammonia* will generally make its appearance, arising either from the sudden cooling of the urine, or from interference with the functions of the skin prior to excretion. In warm weather, however, or when the functions of the skin are tolerably perfect, the urine, albeit it may be loaded with oxalate of lime, may still appear limpid, or, at furthest, its lower layers only be rendered opaque by the deposi-

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* Ann. der Chem. und Pharm., Oct. 1844.

† Jahrb. für Prakt. Pharm., ix. p. 375.

* Comptes Rendus, March 22, 1847.

† Lond. Med. Gaz., 1841-2, p. 638.

tion of a cloud of vesical mucus. Decant the upper $\frac{6}{7}$ths of the urine; pour a portion of the remainder into a watch glass, and gently warm it over a lamp; in a few seconds the heat will have rendered the fluid specifically lighter, and induced the deposition of crystals of *oxalate*, if any were present; this may be hastened by gently moving the glass to and fro, so as to give the fluid a rotatory motion, which will collect the oxalate to the bottom of the capsule. The application of warmth serves also to remove the obscurity arising from the presence of urate of ammonia, which, as is well known, is readily dissolved by exposing the urine containing it to a gentle heat.

Having allowed the urine to repose for a minute or two, remove the greater portion of the fluid with a pipette, and replace it by distilled water. A white powder, often of a glittering appearance, will now become visible, and this, under a low magnifying power, as by placing the capsule under a microscope furnished with a half-inch object-glass will be found to consist of splendid crystals of oxalate of lime, in beautifully formed *octohedra*, with sharply defined edges and angles. It sometimes occurs that the oxalate is present in the form of exceedingly minute crystals: it then resembles a series of minute cubes, often adhering together like blood-discs; these, however, are readily and rapidly resolved into octohedra under a high magnifying power.

Determination of the Alkaline and Earthy Phosphates.—Dr. Bence Jones[*], in his investigations relative to the amount of phosphates in the urine of a healthy man, adopted the following method:—The specific gravity of the urine was first taken, and if ever it was not strongly acid, a drop or two of hydrochloric acid was added. Then, from a weighed quantity, usually about 1000 grains, the earthy phosphates were precipitated by means of pure ammonia, filtered, washed with ammoniacal water, and then heated to redness; a drop or two of nitric acid being added at last. The alkaline phosphates were estimated by taking usually about 500 grains of the urine, adding an excess of chloride of calcium and then pure ammonia; by this means all the phosphoric acid was precipitated as phosphate of lime; this was filtered, well washed, and heated to redness with nitric acid; by deducting the previously determined earthy phosphates, the difference was considered as alkaline phosphates. The results, though they answered well for purposes of comparison, are somewhat too high, in consequence of the formation of a small quantity of carbonate of ammonia and the precipitation of some sulphate of lime, which even long washing cannot entirely remove.

Detection of Sugar in Urine.

1. *Hünefeld's Test*[*]. — Place four ounces of the suspected urine in a glass exposed to the sun's rays, and add about six drops of a tolerably strong solution of chromic acid. In a few minutes the mixture, previously orange red, becomes brownish, and soon after assumes a bistre-brown colour, if sugar be present. These changes take place much more quickly if the mixture of urine and chromic acid be gently warmed before exposure to light. This test depends for its action upon the deoxidizing power of the sugar, by which the chromic acid is reduced to oxide of chromium; for, after warming the mixture, the addition of a few drops of *liquor potassæ* produces a copious deposit of green oxide. There is an important objection to this test, which renders all its indications liable to serious fallacy, depending upon the fact, that all urine containing a normal proportion of colouring matter deoxidizes chromic acid; and consequently urine, whether saccharine or not, will partially convert this acid into oxide. This change certainly does not occur so readily in non-saccharine urine as in a diabetic state of that fluid, but still it is sufficiently marked to prevent *Hünefeld's* test being regarded in any other light than a fallacious one.

2. *Runge's Test*[†].—Allow a thin layer of the suspected urine to evaporate on a white surface, as the bottom of a white plate; and, whilst warm, drop upon the surface a few drops of sulphuric acid, previously diluted with six parts of water. With healthy urine the part touched with the acid becomes merely of a pale yellow colour, from the action of the latter on the colouring matter of the urine; whilst if sugar be present the spot becomes deep brown, and soon

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[*] Contributions to the Chemistry of the Urine, Phil. Trans., Part 2, 1845.

[*] Journ. für Practische Chemie, vii. 42.

[†] *Poggendorff's* Annalen, Band 33, s. 431.

black from the decomposition of sugar by the acid, and consequent evolution of carbon. This test is stated to be so delicate that 1 part of sugar dissolved in 1000 of urine can be readily detected; and even when mixed with 2000 parts the indications are tolerably distinct. According to *Dr. Golding Bird*[*], the presence of *albumen* introduces a fallacy into the application of this test, the acid assuming a tint nearly resembling that produced by sugar.

3. *Trommer's Test*[†].—This is a very trustworthy test, and much superior to either of the preceding. Add to the suspected urine contained in a large test-tube a few drops of a solution of sulphate of copper. A very inconsiderable troubling generally results, probably from the deposition of a little phosphate of copper. Sufficient *liquor potassæ* should then be added to render the whole strongly alkaline; a greyish green precipitate of hydrated oxide of copper falls, which, if sugar be present, wholly or partly redissolves in an excess of the solution of potassa, forming a blue liquid not very unlike the blue ammoniuret of copper. On gently heating the mixture nearly to ebullition, the copper falls in the state of sub-oxide, forming a red and copious precipitate. If sugar be not present, the copper is deposited in the form of black oxide. This test is founded on a fact long known, but not previously applied to the detection of sugar, of the power possessed by some organic matter of reducing oxide of copper, as well as some other oxides, to a lower state of oxidation. It is important that no more of the solution of sulphate of copper be used than is sufficient to afford a decided precipitate on the addition of the *liquor potassæ*. If this precaution be not attended to, a part only of the black oxide will be reduced to red oxide, unless a very large quantity of sugar be present, and thus the indications of the test will be rendered indistinct.

4. *Test of Fermentation.*—The development of the vinous fermentation, on the addition of a little ferment or yeast to a fluid, has long been applied to the detection of sugar. When a little yeast is added to healthy urine, and exposed to a temperature of about 80°, no other change occurs for some time, except the development of a portion of carbonic acid mechanically entangled in the yeast. When sugar is present in the urine thus treated, it soon becomes troubled, a tolerably free disengagement of bubbles of carbonic acid takes place, and a frothy scum forms on the surface of the fluid, which evolves a vinous odour. These changes take place with great rapidity, even when the quantity of sugar present is very small. If the evolved carbonic acid be collected, the quantity of sugar in the urine may be determined by measuring it, as a cubic inch of the gas very nearly corresponds to a grain of sugar.

In the great majority of specimens of diabetic urine it is not necessary to add yeast to excite fermentation, provided a sufficient temperature be employed.

5. *Test afforded by the Growth of Torulæ.*—If the smallest proportion of sugar exists in urine, exposed for a few hours to a temperature above 70°, and a drop of the fluid (taken from the surface) be examined under the microscope, numerous very minute ovoid particles will be discovered. In the course of a few hours more these become enlarged, and appear as distinct oval or egg-shaped vesicles, which soon become developed into a confervoid or fungoid vegetation, identical with that which appears in ordinary saccharine fluids when undergoing the vinous fermentation. The advantages of this test are the facility with which its indications are observed by the microscope with an object glass of one-seventh or one-eighth inch focus, and the certainty of any possible fallacy being corrected by the subsequent development of fermentation. It is, however, less convenient than *Trommer's*, in consequence of the time required before its indications can be observed.

6. *Löwig's Method.*—Evaporate the urine to the consistence of a syrup, then exhaust the residue with alcohol. The alcoholic urinary solution is then mixed with an alcoholic solution of potash, when, if sugar be present, a white precipitate, a compound of sugar and potash, is formed, which, when washed with alcohol, and then dissolved in water, yields a saccharine solution, which is fit for any further examination, and from which the amount of sugar may be ascertained quantitatively, if necessary.

Urinary Calculi.

Uric Acid.—These, which are the most abundant, are known by their solubility

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[*] London Medical Gazette.
[†] Phil. Mag., March, 1842.

in caustic potassa, and their precipitation from the alkaline solution by acids. In nitric acid, with the aid of heat, they are soluble, and the solution, when evaporated to dryness, leaves a residue, which, on the addition of ammonia, assumes a purple red colour (murexide). Before the blowpipe the uric acid calculus is consumed, leaving a small quantity of a white ash, which has an alkaline reaction.

Urate of Ammonia.—This calculus is distinguished from the last by its solubility in *carbonate of potassa*, and by its evolving ammonia when digested with caustic potassa.

Bone Earth.—This also is a common calculus. It is insoluble in caustic alkalies, and does not burn when heated. In a strong heat it fuses. It is insoluble in *acetic acid*, but is soluble in the mineral acids even when diluted.

Ammonia-Magnesian Phosphate.—This calculus *is* soluble in *acetic acid*, and again precipitated by ammonia. It evolves ammonia when digested with caustic potassa, and also when heated alone. It has frequently a crystalline appearance.

Fusible Calculus.—This is a mixture of the two preceding. It is partly soluble in acetic, and wholly in hydrochloric acid. It melts easily before the blowpipe into a pearly bead.

Oxalate of Lime.—Insoluble in acetic acid: converted by heat into carbonate of lime, which dissolves in acids with effervescence. It is also decomposed by boiling with carbonate of potassa. It is very hard, and has a dark-coloured rough surface.

Xanthic Oxide.—This calculus is rare. It is soluble in potash, but is reprecipitated by carbonic acid. It dissolves in nitric acid without effervescence. It is distinguished from uric acid in not furnishing *murexide* when ammonia is added to the residue on evaporating the nitric solution.

The above are the most frequently occurring calculi. It is not uncommon, however, to meet with calculi in which layers of uric acid alternate with layers of phosphate of lime, ammonio-magnesian phosphate, and fusible calculus.

TABLE I.

For the Conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
— 50°	— 58.0°	5°	41.0°	60°	140.0°	115°	239.0°	170°	338.0°
— 49	— 56.2	6	42.8	61	141.8	116	240.8	171	339.8
— 48	— 54.4	7	44.6	62	143.6	117	242.6	172	341.6
— 47	— 52.6	8	46.4	63	145.4	118	244.4	173	343.4
— 46	— 50.8	9	48.2	64	147.2	119	246.2	174	345.2
— 45	— 49.0	10	50.0	65	149.0	120	248.0	175	347.0
— 44	— 47.2	11	51.8	66	150.8	121	249.8	176	348.8
— 43	— 45.4	12	53.6	67	152.6	122	251.6	177	350.6
— 42	— 43.6	13	55.4	68	154.4	123	253.4	178	352.4
— 41	— 41.8	14	57.2	69	156.2	124	255.2	179	354.2
— 40	— 40.0	15	59.0	70	158.0	125	257.0	180	356.0
— 39	— 38.2	16	60.8	71	159.8	126	258.8	181	357.8
— 38	— 36.4	17	62.6	72	161.6	127	260.6	182	359.6
— 37	— 34.6	18	64.4	73	163.4	128	262.4	183	361.4
— 36	— 32.8	19	66.2	74	165.2	129	264.2	184	363.2
— 35	— 30.0	20	68.0	75	167.0	130	266.0	185	365.0
— 34	— 29.2	21	69.8	76	168.8	131	267.8	186	366.8
— 33	— 27.4	22	71.6	77	170.6	132	269.6	187	368.6
— 32	— 25.6	23	73.4	78	172.4	133	271.4	188	370.4
— 31	— 23.8	24	75.2	79	174.2	134	273.2	189	372.2
— 30	— 22.0	25	77.0	80	176.0	135	275.0	190	374.0
— 29	— 20.2	26	78.8	81	177.8	136	276.8	191	375.8
— 28	— 18.4	27	80.6	82	179.6	137	278.6	192	377.6
— 27	— 16.6	28	82.4	83	181.4	138	280.4	193	379.4
— 26	— 14.8	29	84.2	84	183.2	139	282.2	194	381.2
— 25	— 13.0	30	86.0	85	185.0	140	284.0	195	383.0
— 24	— 11.2	31	87.8	86	186.8	141	285.8	196	384.8
— 23	— 9.4	32	89.6	87	188.6	142	287.6	197	386.6
— 22	— 7.6	33	91.4	88	190.4	143	289.4	198	388.4
— 21	— 5.8	34	93.2	89	192.2	144	291.2	199	390.2
— 20	— 4.0	35	95.0	90	194.0	145	293.0	200	392.0
— 19	— 2.2	36	95.8	91	195.8	146	294.8	201	393.8
— 18	— 0.4	37	98.6	92	197.6	147	296.6	202	395.6
— 17	+ 1.4	38	100.4	93	199.4	148	298.4	203	397.4
— 16	3.2	39	102.2	94	201.2	149	300.2	204	399.2
— 15	5.0	40	104.0	95	203.0	150	302.0	205	401.0
— 14	6.8	41	105.8	96	204.8	151	303.8	206	402.8
— 13	8.6	42	107.6	97	206.6	152	305.6	207	404.6
— 12	10.4	43	109.4	98	208.4	153	307.4	208	406.4
— 11	12.2	44	111.2	99	210.2	154	309.2	209	408.2
— 10	14.0	45	113.0	100	212.0	155	311.0	210	410.0
— 9	15.8	46	114.8	101	213.8	156	312.8	211	411.8
— 8	17.6	47	116.6	102	215.6	157	314.6	212	413.6
— 7	19.4	48	118.4	103	217.4	158	316.4	213	415.4
— 6	21.2	49	120.2	104	219.2	159	318.2	214	417.2
— 5	23.0	50	122.0	105	221.0	160	320.0	215	419.0
— 4	24.8	51	123.8	106	222.8	161	321.8	216	420.8
— 3	26.6	52	125.6	107	224.6	162	323.6	217	422.6
— 2	28.4	53	127.4	108	226.4	163	325.4	218	424.4
— 1	30.2	54	129.2	109	228.2	164	327.2	219	426.2
0	32.0	55	131.0	110	230.0	165	329.0	220	428.0
+ 1	33.8	56	132.8	111	231.8	166	330.8	221	429.8
2	35.6	57	134.6	112	233.6	167	332.6	222	431.6
3	37.4	58	136.4	113	235.4	168	334.4	223	433.4
4	39.2	59	138.2	114	237.2	169	336.2	224	435.2

TABLE I.—CONTINUED.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
225°	437.0°	245°	473.0°	265°	509.0°	285°	545.0°	305°	581.0°
226	438.8	246	474.8	266	510.8	286	546.8	306	582.8
227	440.6	247	476.6	267	512.6	287	548.6	307	584.6
228	442.4	248	478.4	268	514.4	288	550.4	308	586.4
229	444.2	249	480.2	269	516.2	289	552.2	309	588.2
230	446.0	250	482.0	270	518.0	290	554.0	310	590.0
231	447.8	251	483.8	271	519.8	291	555.8	311	591.8
232	449.6	252	485.6	272	521.6	292	557.6	312	593.6
233	451.4	253	487.4	273	523.4	293	559.4	313	595.4
234	453.2	254	489.2	274	525.2	294	561.2	314	597.2
235	455.0	255	491.0	275	527.0	295	563.0	315	599.0
236	456.8	256	492.8	276	528.8	296	564.8	316	600.8
237	458.6	257	494.6	277	530.6	297	566.6	317	602.6
238	460.4	258	496.4	278	532.4	298	568.4	318	604.4
239	462.2	259	498.2	279	534.2	299	570.2	319	606.2
240	464.0	260	500.0	280	536.0	300	572.0	320	608.0
241	465.8	261	501.8	281	537.8	301	573.8		
242	467.6	262	503.6	282	539.6	302	575.6		
243	469.4	263	505.4	283	541.4	303	577.4		
244	471.2	264	507.2	284	543.2	304	579.2		

TABLE II.

Showing the respective Degrees of Tension of Aqueous Vapour for different Temperatures.

(FROM FRESENIUS'S "INSTRUCTION IN CHEMICAL ANALYSIS.")

Temperature in Degrees (Celsius).	Force of the Aqueous Vapour expressed in Millimetres.	Temperature in Degrees (Celsius).	Force of the Aqueous Vapour expressed in Millimetres.
0	4.525	21	18.505
1	4.867	22	19.675
2	5.231	23	20.909
3	5.619	24	22.211
4	6.032	25	23.582
5	6.471	26	25.026
6	6.939	27	26.547
7	7.436	28	28.148
8	7.964	29	29.832
9	8.525	30	31.602
10	9.126	31	33.464
11	9.751	32	35.419
12	10.421	33	37.473
13	11.130	34	39.630
14	11.882	35	41.893
15	12.677	36	44.268
16	13.519	37	46.758
17	14.409	38	49.368
18	15.351	39	52.103
19	16.345	40	54.969
20	17.396		

TABLE III.

Showing the Quantity of Oil of Vitriol of Specific Gravity 1.8485, *and of Anhydrous Acid in* 100 *Parts of dilute Sulphuric Acid, of different Densities, according to Dr. Ure.*

Liquid.	Specific Gravity.	Dry.	Liquid.	Specific Gravity.	Dry.
100	1.8485	81.54	50	1.3884	40.77
99	1.8475	80.72	49	1.3788	39.95
98	1.8460	79.90	48	1.3697	39.14
97	1.8439	79.09	47	1.3612	38.32
96	1.8410	78.28	46	1.3530	37.51
95	1.8376	77.46	45	1.3440	36.69
94	1.8336	76.65	44	1.3345	35.88
93	1.8290	75.83	43	1.3255	35.06
92	1.8233	75.02	42	1.3165	34.25
91	1.8179	74.20	41	1.3080	33.43
90	1.8115	73.39	40	1.2999	32.61
89	1.8043	72.57	39	1.2913	31.80
88	1.7962	71.75	38	1.2826	30.98
87	1.7870	70.94	37	1.2740	30.17
86	1.7774	70.12	36	1.2654	29.35
85	1.7673	69.31	35	1.2572	28.54
84	1.7570	68.49	34	1.2490	27.72
83	1.7465	67.68	33	1.2409	26.91
82	1.7360	66.86	32	1.2334	26.09
81	1.7245	66.05	31	1.2260	25.28
80	1.7120	65.23	30	1.2184	24.46
79	1.6993	64.42	29	1.2108	23.65
78	1.6870	63.60	28	1.2032	22.83
77	1.6750	62.78	27	1.1956	22.01
76	1.6630	61.97	26	1.1876	21.20
75	1.6520	61.15	25	1.1792	20.38
74	1.6415	60.34	24	1.1706	19.57
73	1.6321	59.52	23	1.1626	18.75
72	1.6204	58.71	22	1.1549	17.94
71	1.6090	57.89	21	1.1480	17.12
70	1.5975	57.08	20	1.1410	16.31
69	1.5868	56.26	19	1.1330	15.49
68	1.5760	55.45	18	1.1246	14.68
67	1.5648	54.63	17	1.1165	13.86
66	1.5503	53.82	16	1.1090	13.05
65	1.5390	53.00	15	1.1019	12.23
64	1.5280	52.18	14	1.0953	11.41
63	1.5170	51.37	13	1.0887	10.60
62	1.5066	50.55	12	1.0809	9.78
61	1.4960	49.74	11	1.0743	8.97
60	1.4860	48.92	10	1.0682	8.15
59	1.4760	48.11	9	1.0614	7.34
58	1.4660	47.29	8	1.0544	6.52
57	1.4560	46.48	7	1.0477	5.71
56	1.4460	45.66	6	1.0405	4.89
55	1.4360	44.85	5	1.0336	4.08
54	1.4265	44.03	4	1.0268	3.26
53	1.4170	43.22	3	1.0206	2.446
52	1.4073	42.40	2	1.0140	1.63
51	1.3977	41.58	1	1.0074	0.8154

TABLE IV.

Showing the Quantity of Real or Anhydrous Nitric Acid in 100 *Parts of Liquid Acid, at different Densities, according to Dr. Ure.*

Specific Gravity.	Real Acid in 100 Parts of the Liquid.	Specific Gravity.	Real Acid in 100 Parts of the Liquid.
1.5000	79.700	1.2947	39.850
1.4980	78.903	1.2887	39.053
1.4960	78.106	1.2826	38.256
1.4940	77.309	1.2765	37.459
1.4910	76.512	1.2705	36.662
1.4880	75.715	1.2644	35.865
1.4850	74.918	1.2583	35.068
1.4820	74.121	1.2523	34.271
1.4790	73.324	1.2462	33.474
1.4760	72.527	1.2402	32.677
1.4730	71.730	1.2341	31.880
1.4700	70.933	1.2277	31.083
1.4670	70.136	1.2212	30.286
1.4640	69.339	1.2148	29.489
1.4600	68.542	1.2084	28.692
1.4570	67.745	1.2019	27.895
1.4530	66.948	1.1958	27.098
1.4500	66.155	1.1895	26.301
1.4460	65.354	1.1833	25.504
1.4424	64.557	1.1770	24.707
1.4385	63.760	1.1709	23.910
1.4346	62.963	1.1648	23.113
1.4306	62.166	1.1587	22.316
1.4269	61.369	1.1526	21.519
1.4228	60.572	1.1465	20.722
1.4189	59.775	1.1403	19.925
1.4147	58.978	1.1345	19.128
1.4107	58.181	1.1286	18.331
1.4065	57.384	1.1227	17.534
1.4023	56.587	1.1168	16.737
1.3978	55.790	1.1109	15.940
1.3945	54.993	1.1051	15.143
1.3882	54.196	1.0993	14.346
1.3833	53.399	1.0935	13.549
1.3783	52.602	1.0878	12.752
1.3732	51.805	1.0821	11.955
1.3681	51.068	1.0764	11.158
1.3630	50.211	1.0708	10.361
1.3579	49.414	1.0651	9.564
1.3529	48.617	1.0595	8.767
1.3477	47.820	1.0540	7.970
1.3427	47.023	1.0485	7.173
1.3376	46.226	1.0430	6.376
1.3323	45.429	1.0375	5.579
1.3270	44.632	1.0320	4.782
1.3216	43.835	1.0267	3.985
1.3113	43.038	1.0212	3.188
1.3110	42.241	1.0159	2.391
1.3056	41.444	1.0106	1.594
1.3001	40.647	1.0053	0.797

TABLE V.

Showing the Quantity of Absolute Alcohol in Spirits of different Specific Gravities, according to Lowitz.

100 Parts.		Specific Gravity.	
Alcohol.	Water.	At 68°.	At 60°.
100	0	0.791	0.796
99	1	0.794	0.798
98	2	0.797	0.801
97	3	0.800	0.804
96	4	0.803	0.807
95	5	0.805	0.809
94	6	0.808	0.812
93	7	0.811	0.815
92	8	0.813	0.817
91	9	0.816	0.820
90	10	0.818	0.822
89	11	0.821	0.825
88	12	0.823	0.827
87	13	0.826	0.830
86	14	0.828	0.832
85	15	0.831	0.835
84	16	0.834	0.838
83	17	0.836	0.840
82	18	0.839	0.843
81	19	0.842	0.846
80	20	0.844	0.848
79	21	0.847	0.851
78	22	0.849	0.853
77	23	0.851	0.855
76	24	0.853	0.857
75	25	0.856	0.860
74	26	0.859	0.863
73	27	0.861	0.865
72	28	0.863	0.867
71	29	0.866	0.870
70	30	0.868	0.872
69	31	0.870	0.874
68	32	0.872	0.875
67	33	0.875	0.879
66	34	0.877	0.881
65	35	0.880	0.883
64	36	0.882	0.886
63	37	0.885	0.889
62	38	0.887	0.891
61	39	0.889	0.893
60	40	0.892	0.896
59	41	0.894	0.898
58	42	0.896	0.900
57	43	0.899	0.902
56	44	0.901	0.904
55	45	0.903	0.906
54	46	0.905	0.908
53	47	0.907	0.910
52	48	0.909	0.912
51	49	0.912	0.915
50	50	0.914	0.917
49	51	0.917	0.920
48	52	0.919	0.922
47	53	0.921	0.924
46	54	0.923	0.926
45	55	0.925	0.928
44	56	0.927	0.930
43	57	0.930	0.933
42	58	0.932	0.935
41	59	0.934	0.937
40	60	0.936	0.939
39	61	0.938	0.941
38	62	0.940	0.943
37	63	0.942	0.945
36	64	0.944	0.947
35	65	0.946	0.949
34	66	0.948	0.951
33	67	0.950	0.953
32	68	0.952	0.955
31	69	0.954	0.957
30	70	0.956	0.958
29	71	0.957	0.960
28	72	0.959	0.962
27	73	0.961	0.963
26	74	0.963	0.965
25	75	0.965	0.967
24	76	0.966	0.968
23	77	0.968	0.970
22	78	0.970	0.972
21	79	0.971	0.973
20	80	0.973	0.974
19	81	0.974	0.975
18	82	0.976	0.977
17	83	0.977	0.978
16	84	0.978	0.979
15	85	0.980	0.981
14	86	0.981	0.982
13	87	0.983	0.984
12	88	0.985	0.986
11	89	0.986	0.987
10	90	0.987	0.988
9	91	0.988	0.989
8	92	0.989	0.990
7	93	0.991	0.991
6	94	0.992	0.992
5	95	0.994	
4	96	0.995	
3	97	0.997	
2	98	0.998	
1	99	0.999	
0	100	1.000	

TABLE VI.

*Showing the Quantity of Absolute Alcohol by Weight in Mixtures of Alcohol and Water of different Specific Gravities, according to Mr. Drinkwater***.*

Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.
1.0000	0.00	.9959	2.22	.9918	4.64	.9877	7.30
.9999	0.05	.9958	2.28	.9917	4.70	.9876	7.37
.9998	0.11	.9957	2.34	.9916	4.76	.9875	7.43
.9997	0.16	.9956	2.37	.9915	4.82	.9874	7.50
.9996	0.21	.9955	2.45	.9914	4.88	.9873	7.57
.9995	0.26	.9954	2.51	.9913	4.94	.9872	7.64
.9994	0.32	.9953	2.57	.9912	5.01	.9871	7.71
.9993	0.37	.9952	2.62	.9911	5.07	.9870	7.68
.9992	0.42	.9951	2.68	.9910	5.13	.9869	7.85
.9991	0.47	.9950	2.74	.9909	5.20	.9868	7.92
.9990	0.53	.9949	2.79	.9908	5.26	.9867	7.99
.9989	0.58	.9948	2.85	.9907	5.32	.9866	8.06
.9988	0.64	.9947	2.91	.9906	5.39	.9865	8.13
.9987	0.69	.9946	2.97	.9905	5.45	.9864	8.20
.9986	0.74	.9945	3.02	.9904	5.51	.9863	8.27
.9985	0.80	.9944	3.08	.9903	5.58	.9862	8.34
.9984	0.85	.9943	3.14	.9902	5.64	.9861	8.41
.9983	0.91	.9942	3.20	.9901	5.70	.9860	8.48
.9982	0.96	.9941	3.26	.9900	5.77	.9859	8.55
.9981	1.02	.9940	3.32	.9899	5.83	.9858	8.62
.9980	1.07	.9939	3.37	.9898	5.89	.9857	8.70
.9979	1.12	.9938	3.43	.9897	5.96	.9856	8.77
.9978	1.18	.9937	3.49	.9896	6.02	.9855	8.84
.9977	1.23	.9936	3.55	.9895	6.09	.9854	8.91
.9976	1.29	.9935	3.61	.9894	6.15	.9853	8.98
.9975	1.34	.9934	3.67	.9893	6.22	.9852	9.05
.9974	1.40	.9933	3.73	.9892	6.29	.9851	9.12
.9973	1.45	.9932	3.78	.9891	6.35	.9850	9.20
.9972	1.51	.9931	3.84	.9890	6.42	.9849	9.27
.9971	1.56	.0930	3.90	.9889	6.49	.9848	9.34
.9970	1.61	.9929	3.96	.9888	6.55	.9847	9.41
.9969	1.67	.9928	4.02	.9887	6.62	.9846	9.49
.9968	1.73	.9927	4.08	.9886	6.69	.9845	9.56
.9967	1.78	.9926	4.14	.9885	6.75	.9844	9.63
.9966	1.83	.9925	4.20	.9884	6.82	.9843	9.70
.9965	1.89	.9924	4.27	.9883	6.89	.9842	9.78
.9964	1.94	.9923	4.33	.9882	6.95	.9841	9.85
.9963	1.99	.9922	4.39	.9881	7.02	.9840	9.92
.9962	2.05	.9921	4.45	.9880	7.09	.9839	9.99
.9961	2.11	.9920	4.51	.9879	7.16	.9838	10.07
.9960	2.17	.9919	4.57	.9878	7.23		

The absolute alcohol, with which the experiments which furnished the data for the above Table were made, was prepared as follows:—Carbonate of potassa was exposed to a red heat to deprive it of water; and, when sufficiently cool, was pulverized and added to ordinary alcohol of specific gravity .850 at 60° Fahr. till it ceased to dissolve any more: the whole was then allowed to digest 24 hours, being frequently agitated, when the alcohol was carefully poured off. As much fresh-burned quicklime as was considered sufficient, when powdered, to absorb the whole of the alcohol, was introduced into a retort, and the alcohol added to it; after digesting 48 hours, it was slowly distilled in a water-bath, at a temperature of about 180° Fahr. The alcohol thus obtained was carefully redistilled, and its specific gravity at 60° Fahr. was found in two experiments to be .7946 and .7947. It was subsequently digested a second and a third time for several days with recently ignited quicklime, and redistilled at 172° Fahr. The mean of several determinations gave the number .79381, which the author thinks may be regarded as expressing the true specific gravity of absolute alcohol at 60° Fahr.

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* Memoirs of the Chemical Society, vol. iii. page 454.

TABLE VII.

In the following Table the figures are all calculated on the equivalent numbers assigned to the elementary substances in the Table inserted at page 139, and which is from the latest authorities; few of the numbers differ very considerably from those given in similar Tables in other works on Chemical Analysis; but, with the accuracy which is now introduced into the science, it was thought that the advantages of having a series of numbers in accordance with the atomic weights, as at present received, were sufficiently great to justify the time consumed in the recalculation.

The application of these Tables, and their great convenience in quantitative analysis, may be illustrated by the following example:—

1. Suppose, as the result of an experiment to determine the amount of sulphuric acid in a certain substance, 37.45 grains of sulphate of baryta are obtained: on turning to the Table we find under the head of "required" *sulphuric acid*, "found" *sulphate of baryta*, a series of figures arranged in nine columns, those in the first column representing the quantity of sulphuric acid in a *unit* of sulphate of baryta, and those in the other columns the multiples of that number by 2, 3, 4, 5, 6, 7, 8, and 9. In the case we are considering we require to learn the amount of sulphuric acid in 37.45 grains of sulphate of baryta; we turn to column 3, where we find the number 1.02872; we put down this number therefore, shifting the decimal point one figure further to the right; we next turn to column 7, where we find the number 2.40058; we place this number under the former, preserving the decimal point unaltered; we have thus filled up the *tens*' and the *units*' place; the next number is 4, under which column we find the number 1.37176; but as this in our experiment is the first place of decimals, in writing down the number we shift the decimal point one figure further to the left; in like manner, the last number being 5, and in the second place of decimals, we shift the decimal point of the number found under column 5, viz., 1.71470 two places further to the left: the whole will consequently stand thus:—

$$
\begin{array}{r}
10.2872000 \\
2.4005800 \\
.1371760 \\
.0171470 \\
\hline
12.8421030 \\
\hline
\end{array}
$$

37.49 grains of sulphate of baryta contain, therefore, 12.842 grains of sulphuric acid.

TABLE VII.

Required.	Found.	1	2	3	4	5	6	7	8	9
Aluminum Al_2	Alumina Al_2O_3	0.53289	1.06578	1.59867	2.13156	2.66445	3.19734	3.73023	4.26312	4.79601
Ammonia NH_3	Chloride of Ammonium NH_4Cl	0.31776	0.63552	0.95328	1.27104	1.58880	1.90656	2.22432	2.54208	2.85984
Ammonia NH_3	Ammonio-chloride of Platinum $NH_4ClPtCl_2$	0.07611	0.15222	0.22833	0.30444	0.38055	0.45666	0.53277	0.60888	0.68499
Antimony Sb	Oxide of Antimony SbO_3	0.84317	1.68634	2.52951	3.37268	4.21585	5.05902	5.90219	6.74536	7.58853
Oxide of Antimony SbO_3	Antimony Sb	1.18600	2.37200	3.55800	4.74400	5.93000	7.11600	8.30200	9.48800	10.67400
Oxide of Antimony SbO_3	Sulphuret of Antimony SbS_3	0.86443	1.72886	2.59329	3.45772	4.32215	5.18659	6.05101	6.91545	7.77988
Oxide of Antimony SbO_3	Antimonious Acid SbO_4	0.95032	1.90064	2.85096	3.80128	4.75160	5.70192	6.65224	7.60256	8.55288
Arsenic As	Arsenious Acid AsO_3	0.75757	1.51514	2.27271	3.03028	3.78785	4.54542	5.30299	6.06056	6.81813
Arsenic As	Arsenic Acid AsO_5	0.65217	1.30434	1.95651	2.60868	3.26085	3.91302	4.56519	5.21736	5.86953
Arsenious Acid AsO_3	Arsenic Acid AsO_5	0.86087	1.72174	2.58261	3.44348	4.30435	5.16522	6.02609	6.88696	7.74783
Arsenious Acid AsO_3	Sulpharsenious Acid AsS_3	0.80488	1.60976	2.41464	3.21952	4.02440	4.82928	5.63416	6.43904	7.24392

TABLE VII. CONTINUED.

Required.	Found.	1	2	3	4	5	6	7	8	9
Baryta BaO	Sulphate of Baryta $BaO\,SO_3$	0.65706	1.31412	1.97118	2.62824	3.28530	3.94236	4.59942	5.28648	5.91354
Baryta BaO	Carbonate of Baryta $BaO\,CO_2$	0.77696	1.55392	2.33088	3.10784	3.88480	4.66176	5.43872	6.21568	6.99264
Baryta BaO	Silico-fluoride of Barium $BaFl, SiFl_2$	0.52460	1.04720	1.57380	2.09440	2.64300	3.14760	3.67220	4.18880	4.72140
Bismuth Bi	Oxide of Bismuth BiO	0.89867	1.79734	2.69601	3.59468	4.49335	5.39202	6.29069	7.18936	8.08803
Boron B	Boracic Acid BO_3	0.31241	0.62483	0.93724	1.24966	1.56207	1.87449	2.18690	2.49932	2.81173
Bromine Br	Bromide of Silver $AgBr$	0.42016	0.84032	1.26043	1.68064	2.10080	2.52096	2.94112	3.36128	3.78144
Cadmium Cd	Oxide of Cadmium CdO	0.87449	1.74899	2.62348	3.49797	4.37246	5.24696	6.12145	6.99594	7.87044
Calcium Ca	Lime CaO	0.71429	1.42857	2.14286	2.85714	3.57143	4.28571	5.00000	5.71429	6.42857
Lime CaO	Sulphate of Lime $CaO\,SO_3$	0.41176	0.82353	1.23529	1.64706	2.05882	2.47059	2.88235	3.29412	3.70588
Lime CaO	Carbonate of Lime $CaO\,CO_2$	0.56000	1.12000	1.68000	2.24000	2.80000	3.36000	3.92000	4.48000	5.04000
Carbon C	Carbonic Acid CO_2	0.27273	0.54545	0.81818	1.09091	1.36364	1.63636	1.90909	2.18181	2.45455

TABLE VII. CONTINUED.

Required.	Found.	1	2	3	4	5	6	7	8	9
Carbonic Acid CO_2	Carbonate of Lime $Ca O C O_2$	0.44000	0.88000	1.32000	1.76000	2.20000	2.64000	3.08000	3.52000	3.96000
Chlorine Cl	Chloride of Silver $AgCl$	0.24729	0.49458	0.74188	0.98917	1.23646	1.48375	1.73104	1.97834	2.22563
Hydrochloric Acid $H Cl$	Chloride of Silver $AgCl$	0.25427	0.50853	0.76280	1.01707	1.27133	1.52560	1.77987	2.03414	2.28840
Chromium Cr	Oxide of Chromium Cr_2O_3	0.70112	1.40224	2.10336	2.80448	3.50560	4.20672	4.90784	5.60896	6.31008
Chromic Acid $2 CrO_3$	Oxide of Chromium Cr_2O_3	1.29888	2.59776	3.89664	5.19552	6.49440	7.79328	9.07216	10.39104	11.68992
Chromic Acid CrO_3	Chromate of Lead $Pb O Cr O_3$	0.31855	0.63710	0.95565	1.27420	1.59275	1.91130	2.22985	2.54840	2.86695
Protoxide of Cobalt $Co O$	Cobalt Co	1.27141	2.54283	3.81424	5.98566	6.35707	7.62849	8.89990	10.17130	11.44273
Copper Cu	Oxide of Copper $Cu O$	0.79839	1.59677	2.39516	3.19355	3.99193	4.77032	5.58871	6.38710	7.18548
Fluorine Fl	Fluoride of Calcium $Ca Fl$	0.48320	0.96640	1.44960	1.93280	2.41600	2.89920	3.38240	3.86560	4.34880
Fluorine $3 Fl$	Fluoride of Silicon $Si Fl_3$	0.72434	1.44868	2.17302	2.89736	3.62170	4.34604	5.07038	5.79472	6.51906
Hydrogen H	Water $H O$	0.11111	0.22222	0.33333	0.44444	0.55555	0.66667	0.77778	0.88889	1.00000

TABLE VII. CONTINUED.

Required.	Found.	1	2	3	4	5	6	7	8	9
Iodine I	Iodide of Silver AgI	0.53917	1.07834	1.61751	2.15668	2.69585	3.23502	3.77419	4.31336	4.85253
Iron Fe_2	Oxide of Iron Fe_2O_3	0.70000	1.40000	2.10000	2.80000	3.50000	4.20000	4.90000	5.60000	6.30000
Protoxide of Iron 2FeO	Oxide of Iron Fe_2O_3	0.90000	1.80000	2.70000	3.60000	4.50000	5.40000	6.30000	7.20000	8.10000
Lead Pb	Oxide of Lead PbO	0.92829	1.85658	2.78487	3.71316	4.64145	5.56974	6.49803	7.42932	8.35464
Oxide of Lead PbO	Sulphate of Lead $PbOSO_3$	0.73608	1.47216	2.20823	2.94431	3.68039	4.41647	5.15255	5.88862	6.62470
Oxide of Lead PbO	Chloride of Lead PbCl	0.80250	1.60500	2.40749	3.20999	4.01249	4.81499	5.61749	6.41998	7.22248
Lead Pb	Chloride of Lead PbCl	0.74495	1.48990	2.23485	2.97980	3.72475	4.46970	5.21465	5.95960	6.70455
Oxide of Lead PbO	Sulphuret of Lead PbS	0.93309	1.86618	2.79926	3.73235	4.66544	5.59853	6.53162	7.46470	8.39779
Magnesium Mg	Magnesia MgO	0.61204	1.22407	1.83611	2.44815	3.06018	3.67222	4.28426	4.89630	5.50833
Magnesia MgO	Sulphate of Magnesia $MgOSO_3$	0.34015	0.68030	1.02046	1.36061	1.70076	2.04091	2.38106	2.72122	3.06137
Magnesia 2MgO	Pyrophosphate of Magnesia $2MgO, PO_5$	0.36468	0.72936	1.09404	1.45872	1.82340	2.18808	2.55276	2.91744	3.28212

TABLE VII. CONTINUED.

Required.	Found.	1	2	3	4	5	6	7	8	9
Manganese Mn	Protoxide of Manganese MnO	0.77571	1.55142	2.32713	3.10284	3.89855	4.65426	5.42997	6.20568	6.98139
Manganese Mn_3	Manganoso-manganic Oxide $MnO + Mn_2O_3$	0.72176	1.44352	2.16528	2.88704	3.60880	4.33056	5.05232	5.77408	6.49584
Protoxide of Manganese MnO	Protosulphate of Manganese MnO, SO_3	0.47138	0.94276	1.41414	1.88552	2.35690	2.82828	3.29966	3.77104	4.24242
Protoxide of Mercury Hg_2O	Mercury Hg_2	1.03997	2.07994	3.11991	4.15988	5.19985	6.23983	7.27980	8.31977	9.35974
Binoxide of Mercury HgO	Mercury Hg	1.07994	2.15988	3.23983	4.31977	5.39971	6.47965	7.55959	8.63954	9.71948
Mercury Hg_2	Protochloride of Mercury Hg_2Cl	0.84951	1.69902	2.54852	3.39803	4.24754	5.09705	5.94656	6.79606	7.64557
Mercury Hg	Sulphide of Mercury HgS	0.86215	1.72431	2.58646	3.44862	4.31077	5.17293	6.03508	6.89724	7.75939
Nickel Ni	Protoxide of Nickel NiO	0.78684	1.57369	2.36053	3.14738	3.93422	4.72106	5.50791	6.29475	7.08160
Nitrogen N	Ammonio-chloride of Platinum $NH_4Cl, PtCl_2$	0.06285	0.12570	0.18855	0.25140	0.31425	0.37711	0.43996	0.50281	0.56566
Nitrogen N	Platinum Pt	0.14207	0.28415	0.42622	0.56830	0.71037	0.85245	0.99452	1.13660	1.27867
Nitric acid NO_5	Sulphate of Baryta BaO, SO_3	0.46295	0.92590	1.33335	1.35180	2.31475	2.77770	3.24065	3.70360	4.16655

TABLE VII. CONTINUED.

Required.	Found.	1	2	3	4	5	6	7	8	9
Sodium Na	Chloride of Sodium Na Cl	0.39318	0.78637	1.17955	1.57274	1.96592	2.35910	2.75229	3.14547	3.53866
Soda Na O	Carbonate of Soda Na O, C O_2	0.58470	1.16940	1.75410	2.33880	2.92349	3.50819	4.09289	4.67759	5.26229
Strontium Sr	Strontia Sr O	0.84567	1.69134	2.53701	3.38268	4.22835	5.07402	5.91969	6.76536	7.61103
Strontia Sr O	Sulphate of Strontia Sr O, S O_3	0.56446	1.12892	1.79338	2.25784	2.82230	3.58676	3.95122	4.51568	5.38014
Strontia Sr O	Carbonate of Strontia Sr O, C O_2	0.70205	1.40410	2.10615	2.80420	3.51025	4.21230	4.91435	5.60840	6.31845
Sulphur S	Sulphate of Baryta Ba O, S O_3	0.13717	0.27434	0.41151	0.54868	0.68585	0.82302	0.96019	1.09736	1.23353
Sulphur S_3	Sulphuret of Arsenic As S_3	0.39024	0.78048	1.17072	1.56096	1.95130	2.34144	2.73168	3.12192	3.51216
Sulphuric Acid S O_3	Sulphate of Baryta Ba O, S O_3	0.34294	0.68588	1.02872	1.37176	1.71470	2.05764	2.40058	2.74352	3.08646
Tin Sn	Oxide of Tin Sn O_2	0.78616	1.57233	2.35849	3.14466	3.93082	4.71698	5.50315	6.28931	7.07547
Protoxide of Tin Sn O	Oxide of Tin Sn O_2	0.89308	1.78616	2.67924	3.57232	4.46543	5.35848	6.25156	7.14464	8.03772
Zinc Zn	Oxide of Zinc Zn O	0.80260	1.60520	2.40781	3.21041	4.01301	4.81561	5.61821	6.42082	7.22342

ANALYTICAL TABLES.

TABLE I.

COURSE OF ANALYSIS FOR THE DETECTION OF A SINGLE BASE BELONGING TO GROUPS I. OR II., THE SALT BEING SOLUBLE IN WATER.

Evaporate a few drops of the solution to dryness on Platinum foil, and ignite *gently; if no fixed residue remain,* heat a little of the solution in a test-tube, with *Caustic Potash* or *Hydrate of Lime,* and test for Ammonia (p. 33, col. 2). *If a fixed residue remain,* proceed as under :—

To a portion of the original solution
add Carbonate of Soda and heat.

<table>
<tr>
<td colspan="4">A precipitate is formed. It may contain
<i>Baryta, Strontia, Lime,</i> or <i>Magnesia.</i>
To another portion of the original solution
<i>add Chloride of Ammonium and Carbonate of Ammonia.</i></td>
<td colspan="2">No precipitate is formed. The solution may contain
<i>Potash</i> or <i>Soda.</i>
Concentrate (if necessary) a portion of the original solution;
<i>add excess of Tartaric Acid, and well agitate.</i></td>
</tr>
<tr>
<td colspan="3">A precipitate is formed. It may contain
<i>Baryta, Strontia,</i> or <i>Lime.</i>
To another portion of the original solution
<i>add Solution of Sulphate of Lime and heat.</i></td>
<td>No precipitate is formed.
<i>Add Phosphate of Soda.</i></td>
<td rowspan="2">A granular precipitate is formed.
POTASH.
Confirm by Bichloride of Platinum, and the Blowpipe.
(P. 32, col. 2.)</td>
<td rowspan="2">No precipitate is formed.
SODA.
Confirm by Antimoniate of Potash.
(P. 33. col. 1.)</td>
</tr>
<tr>
<td>I.
A precipitate is <i>immediately</i> formed.
BARYTA.
Confirm in original solution by Hydrofluosilicic Acid.
(P. 33, col. 2.)</td>
<td>II.
A precipitate is formed <i>after some time.</i>
STRONTIA.
Confirm in original solution by Alcohol flame.
(P. 34, col. 1.)</td>
<td>III.
No precipitate is formed.
LIME.
Confirm in original solution by Oxalate of Ammonia.
(P. 34, col. 2.)</td>
<td>A white precipitate is formed.
MAGNESIA.</td>
</tr>
</table>

TABLE II.

COURSE OF ANALYSIS FOR THE DETECTION OF A SINGLE BASE BELONGING TO GROUPS III. AND IV., THE SALT BEING SOLUBLE IN WATER.

To a portion of the solution rendered alkaline by Ammonia
add Hydrosulphuret of Ammonia.

The precipitate is black. It may contain *Iron, Cobalt,* or *Nickel.*			The precipitate is not black. It may contain *Manganese, Zinc, Chromium,* or *Aluminum.*			
To a portion of the original solution *add Caustic Potash.*			It is *flesh-coloured.*	It is *bluish green.*	It is *white.* It may consist of *Hydrate of Alumina,* or of *Sulphide of Zinc.* To a portion of the original solution add *Caustic Potash,* till the precipitate first formed is redissolved. Divide into two portions:	
The precipitate is *dingy green,* turning *reddish brown* by exposure to the air.	The precipitate is *bright green.*	The precipitate is *blue,* becoming *dingy red* when boiled.	Sulphide of Manganese.	Oxide of Chromium.	I. *Add Sulphuretted Hydrogen Water.*	II. *Add Chloride of Ammonium.*
Protoxide of Iron.	Oxide of Nickel.	Oxide of Cobalt.	Confirm in original solution with *Potash* or the *blowpipe.* (P. 40. col. 2.)	Confirm in original solution with *Potash* or the *blowpipe.* (P. 37, col. 2.)	A white precipitate is formed.	A white precipitate is formed.
Confirm in original solution with *Ferricyanide of Potassium.* (P. 41, col. 2.)	Confirm in original solution with *Ammonia.* (P. 39, col. 2.)	Confirm by *blowpipe.* (P. 40, col. 1.)			Sulphide of Zinc.	Alumina.
					Confirm by *Protonitrate of Cobalt* and *blowpipe.* (P. 39, col. 2.)	Confirm by *Protonitrate of Cobalt* and *blowpipe.* (P. 35, col. 2.)

TABLE III.

COURSE OF ANALYSIS FOR THE DETECTION OF A SINGLE BASE BELONGING TO GROUPS V. AND VI., THE SALT BEING SOLUBLE IN WATER.

To a portion of the solution *add Hydrochloric Acid.*

The formation of a white precipitate indicates *Chloride of Silver, Chloride of Lead,* or *Subchloride of Mercury.*

To the turbid liquid *add Ammonia in excess.*

I.	II.	III.
The precipitate is redissolved.	The precipitate becomes black.	The precipitate is unaltered.
CHLORIDE OF SILVER.	SUBCHLORIDE OF MERCURY.	CHLORIDE OF LEAD.
Confirm in original solution with *Chromate of Potash.* (P. 44, col. 2.)	Confirm in original solution with *Protochloride of Tin.* (P. 45, col. 1.)	Confirm in original solution with *Sulphuric Acid.* (P. 44, col. 1.)

No precipitate is formed on the addition of Hydrochloric Acid ;
add Sulphuretted Hydrogen water, till the solution smells strongly of it, and gently heat.

<table>
<tr><td colspan="4">The precipitate is <i>yellow</i>, or <i>yellowish white.</i></td><td rowspan="4">The precipitate is <i>orange colour.</i>
ANTIMONY.
Confirm by blowpipe. (P. 49, col. 1.)</td><td colspan="7">The precipitate is <i>brown</i> or <i>black.</i>
It may contain <i>Protoxide of Tin, Lead, Copper, Bismuth, Gold, Platinum,</i> or <i>Mercury.</i></td></tr>
<tr><td rowspan="3">It is <i>yellowish white.</i>
It consists of sulphur, and indicates
PEROXIDE OF IRON.
(P. 42, col. 1.)
Confirm in original solution with <i>Ferrocyanide of Potassium.</i> (P. 42, col. 1.)</td><td colspan="3">It is <i>yellow.</i>
It may contain <i>Cadmium, Tin</i> (peroxide), or <i>Arsenic.</i>
Suspend the precipitate in water and <i>add Ammonia.</i></td><td rowspan="3">I.
<i>It is brown.</i>
To a portion of the original solution <i>add Chloride of Gold.</i>
A <i>purple</i> precipitate is produced.
PROTOXIDE OF TIN.
(P. 54, col. 2.)</td><td rowspan="3">II.
To a portion of the original solution <i>add dilute Sulphuric Acid.</i>
A <i>white</i> precipitate is formed.
LEAD.
Confirm by <i>blowpipe</i> and <i>Potash.</i> (P. 44, col. 1.)</td><td rowspan="3">III.
To a portion of the original solution <i>add Ammonia in excess.</i>
A <i>blue</i> precipitate is formed.
COPPER.
Confirm by <i>Ferrocyanide of Potassium.</i> (P. 47, col. 1.)</td><td rowspan="3">IV.
To a portion of the original solution <i>add Potash.</i>
A <i>yellow</i> precipitate is formed.
PEROXIDE OF MERCURY.
Confirm by <i>Iodide of Potassium.</i> (P. 45, col. 2.)</td><td rowspan="3">V.
Evaporate a portion of the original solution nearly to dryness, and <i>add water.</i>
It becomes <i>milky.</i>
BISMUTH.
Confirm by <i>blowpipe.</i> (P. 46, col. 1.)</td><td rowspan="3">VI.
To a portion of the original solution <i>add Protosulphate of Iron.</i>
A <i>black</i> precipitate is formed.
GOLD.
Confirm by <i>Protochloride of Tin.</i> (P. 56, col. 1.)</td><td rowspan="3">VII.
To a portion of the original solution <i>add Chloride of Ammonium.</i>
A <i>yellow</i> precipitate is formed.
PLATINUM.
Confirm by <i>ignition.</i> (P. 55, col. 1.)</td></tr>
<tr><td rowspan="2">It does not dissolve.
CADMIUM.
Confirm in original solution by blowpipe. (P. 46, col. 2.)</td><td colspan="2">It dissolves.
<i>Arsenic</i> or <i>Tin.</i>
To a portion of the original solution <i>add Ammonia.</i></td></tr>
<tr><td>A white precipitate is formed.
PEROXIDE OF TIN.
Confirm by blowpipe. (P. 55, col. 1.)</td><td>No precipitate is formed.
ARSENIC.
Confirm in original solution by reduction with Hydrogen. (P. 51, col. 1.)</td></tr>
</table>

TABLE IV.

COURSE OF ANALYSIS FOR THE DETECTION OF AN INORGANIC ACID.

To a portion of the original solution *add Hydrochloric Acid.*

Effervescence takes place, indicating *Carbonic* or *Hydrosulphuric* Acid. The former is confirmed by conducting it into *lime water* (p. 61, col. 2); the latter by its *odour*, and by paper moistened with solution of lead (p. 71, col. 2).	Effervescence does not take place, proceed as under.

To a portion of the original solution made feebly alkaline by Ammonia, and filtered (if necessary), *add Chloride of Barium.* The precipitate may contain *Sulphuric, Phosphoric, Boracic,* or *Oxalic Acid; add Hydrochloric Acid.*

The precipitate does not dissolve. Sulphuric Acid.	The precipitate dissolves. To another portion of the original solution *add Chloride of Ammonium* * and *Sulphate of Lime.* The precipitate may contain *Phosphoric* or *Oxalic Acid; add Acetic Acid in excess.*

The precipitate dissolves. Phosphoric Acid. Confirm in original solution with Chloride of Ammonium, Ammonia, and Sulphate of Magnesia (p. 63, col. 2).	The precipitate does not dissolve. Oxalic Acid. Confirm in original solution with concentrated Sulphuric Acid (p. 73, col. 2).

To a fresh portion of the original solution acidified with Nitric Acid *add Solution of Nitrate of Silver.* The precipitate may contain *Chlorine, Iodine,* or *Cyanogen; add Ammonia in excess.*

The precipitate does not dissolve. Iodine. Confirm in original solution with *Starch* (p. 68, col. 2).	The precipitate dissolves readily. Chlorine. Confirm in original solution with *Nitrate of Suboxide of Mercury* (p. 67, col. 1).	The precipitate dissolves with difficulty. Cyanogen. Confirm in original solution with *Potash, Hydrochloric Acid,* and *Magnetic Oxide of Iron* (p. 70, col. 2).

The original solution is tested for Boracic Acid by evaporating a portion to dryness and treating the residue with *Sulphuric Acid* and *Alcohol* (p. 64, col. 2); for Nitric Acid, by *Sulphuric Acid* and *Solution of Indigo;* for Silicic Acid, by converting it into its insoluble modification by evaporation (p. 65, col. 2); for Chloric Acid, by heating a fragment of the solid salt in a test tube, and introducing an ignited splinter of wood (p. 73, col. 1); for Hydrofluoric Acid, by heating with Sulphuric Acid and observing whether the fumes act upon glass (p. 66, col. 1); and for Bromine, by *Chromate of Potassa* and *Sulphuric Acid* (p. 68, col. 1).

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* To keep Borate of Lime in solution (p. 64, col. 2).

TABLE V. (*a*)

COURSE OF ANALYSIS FOR THE DETECTION OF ALL THE COMMONLY OCCURRING BASES IN AN ACID OR NEUTRAL SOLUTION.

To a portion add Hydrochloric Acid in excess, and agitate.

The precipitate may contain *Silver, Mercury,* and *Lead;* filter and wash, reserving the filtrate to be treated as under. Pour boiling water repeatedly on the precipitate while on the filter.

<table>
<tr><td rowspan="2">The filtrate may contain
Chloride of Lead.
Test with Sulphuric Acid (p. 44, col. 1).</td><td colspan="2">The insoluble portion may contain Silver and Mercury;
wash with Ammonia.</td></tr>
<tr><td>The insoluble portion becomes black.
Subchloride of Mercury.</td><td>The filtrate may contain Chloride of Silver; add Nitric Acid.
A white curdy precipitate is formed.
Chloride of Silver.</td></tr>
</table>

To a small portion of the filtrate from the precipitate by Hydrochloric Acid, or to a small portion of the original solution if no precipitate was produced by Hydrochloric Acid, *add excess of sulphuretted Hydrogen Water;* if no precipitate, or only a *white* one (which is Sulphur, and indicates *Peroxide of Iron*), is thereby formed, pass on to Table V. (*b*); if a coloured precipitate is formed, *pass sulphuretted Hydrogen through a larger portion of the acid liquor previously diluted with water, till it smells strongly of it; gently warm, and well agitate.*

Treatment of the Precipitate (A).

It is allowed to subside, the clear fluid is poured off to be treated according to Table V. (*b*); it is well washed, and a *portion* digested for some time with *yellow Hydrosulphuret of Ammonia,* or *with solution of Sulphuret of Potassium,* should the presence of *Copper* have been detected in the original solution by metallic iron (p. 47, col. 1).

It is completely dissolved.	It is not completely dissolved.
Neither *Bismuth, Copper, Cadmium, Lead,* or *Mercury* can be present. *Digest the entire precipitate with Hydrosulphuret of Ammonia,* or *with Sulphuret of Potassium, and proceed as under.*	Some of the metals named on the other side are present; *filter,* and *to the filtrate add Hydrochloric Acid in excess;* if a milkiness only is produced, neither *Gold, Platinum, Arsenic, Tin,* or *Antimony* can be present; if a coloured precipitate is formed, *digest the whole of the first precipitate* TWICE *with Hydrosulphuret of Ammonia,* or *with Sulphuret of Potassium; allow the insoluble portion to subside, decant the soluble portion, and proceed with it as under.*

Treatment of the Portion of the Precipitate by Sulphuretted Hydrogen (A) soluble in Hydrosulphuret of Ammonia (B).

Add Hydrochloric Acid in excess.

If the precipitate has a brownish-black colour, test a portion of the solution for *Gold* (p. 56, col. 1) and for *Platinum* (p. 55, col. 2); it may also contain *Antimony, Arsenic,* and *Tin.* If the precipitate is *orange yellow,* it can contain no gold or platinum, but *may* contain antimony, arsenic, and tin. If the precipitate is *pure yellow,* without a shade of orange, *antimony* is probably absent; and if a portion, when heated on the lid of a porcelain crucible, completely volatilizes, *Tin* is absent.

Tin, Antimony, and Arsenic are supposed to be present.

Agitate the well-washed precipitate for a few seconds with a dilute solution of Bicarbonate of Ammonia; filter rapidly, and to the filtrate add excess of Hydrochloric Acid; should a yellow precipitate be thereby formed, ARSENIC is probably present, and a fresh portion of the original solution should be specially examined for this metal by the method described (p. 51, col. 1), the metallic mirror obtained being converted first into Sulphuret and then into Chloride (according to p. 52, col. 1).

TREATMENT OF THE PORTION OF THE PRECIPITATE INSOLUBLE IN BICARBONATE OF AMMONIA.

Digest with Hydrochloric Acid, filter, transfer the clear solution to a *Marsh's Apparatus* (fig. 54, p. 51), add some metallic zinc, and, having inflamed the hydrogen gas evolved, hold over it a porcelain plate; if a *black stain, insoluble in Hypochlorite of Soda,* is formed, ANTIMONY is present. Boil the metallic powder precipitated by the zinc with strong Hydrochloric Acid; filter, dilute with water, and add Sulphuretted Hydrogen Water in excess. The formation of a *brownish-black* indicates TIN.

TREATMENT OF THE PORTION OF THE PRECIPITATE BY SULPHURETTED HYDROGEN INSOLUBLE IN HYDROSULPHURET OF AMMONIA OR IN SULPHURET OF POTASSIUM (C).

Wash and boil in Nitric Acid, with constant stirring.

A heavy black substance remains undissolved. SULPHURET OF MERCURY. Filter off, wash, dissolve in *aqua-regia, nearly* neutralize with ammonia, and test for mercury with clean *metallic copper* (p. 45, col. 2).	The solution may contain *Cadmium, Copper, Lead,* and *Bismuth.* Evaporate the greater part of the excess of Nitric Acid from a small portion, and *add solution of Sulphuretted Hydrogen.* If a precipitate is formed, proceed as under.

Expel the greater part of the free Nitric Acid from the remainder of the solution, add dilute Sulphuric Acid, and warm.

<table>
<tr><td rowspan="3">The precipitate is
SULPHATE OF LEAD.</td><td colspan="3">The solution may contain <i>Bismuth, Cadmium,</i> and <i>Copper; add Ammonia in excess, and warm.</i></td></tr>
<tr><td rowspan="2">The precipitate is
OXIDE OF BISMUTH.</td><td colspan="2">The solution may contain <i>Copper</i> and <i>Cadmium.</i>
<i>Evaporate nearly to dryness, add Hydrochloric Acid, and divide into two portions.</i></td></tr>
<tr><td>I.
<i>Add Ferrocyanide of Potassium.</i>
The formation of a <i>brown</i> precipitate indicates
COPPER.
If this metal was present in any but minute quantity, the ammoniacal solution will be <i>blue</i> (p. 47, col. 1).</td><td>II.
<i>Add Carbonate of Ammonia in excess, and warm.</i>
The formation of a <i>white</i> precipitate indicates
CADMIUM (p. 46, col. 2).
Confirm by redissolving in Hydrochloric Acid, and adding Sulphuretted Hydrogen Water (p. 46, col. 2).</td></tr>
</table>

TABLE V. (*b*)

TREATMENT OF THE FILTRATE FROM THE PRECIPITATE OCCASIONED BY SULPHURETTED HYDROGEN (A), OR OF THE ORIGINAL SOLUTION, IF THAT REAGENT HAS FAILED TO CAUSE A PRECIPITATE.

To a portion add Chloride of Ammonium, Ammonia, and Hydrosulphuret of Ammonia; if a precipitate is formed, treat the whole filtrate in the same manner, and digest.

The precipitate (D) may contain	The solution (E) may contain
Alumina and *Oxide of Chromium;* also *Cobalt, Nickel, Iron, Manganese,* and *Zinc,* as *Sulphurets;* it may also contain the Alkaline Earths in the forms of *Oxalates, Phosphates,* and *Hydrofluates,* but these are, for simplicity, disregarded in the present scheme (see p. 91, cols. 1, 2).	The *Alkaline Earths* and *Alkalies;* it is treated as below.

TREATMENT OF THE PRECIPITATE (D).

Filter, reserving the filtrate to be treated according to (E); *wash with water, to which a few drops of Hydrosulphuret of Ammonia have been added, and digest with dilute Hydrochloric Acid.*

<table>
<tr>
<td colspan="2">A black residue indicates <i>Cobalt,</i> or <i>Nickel,</i> or both.
<i>Wash, and divide into two parts.</i></td>
<td colspan="5">The solution may contain <i>Alumina</i> and the Oxides of <i>Iron, Chromium, Manganese,</i> and <i>Zinc.</i>
<i>Boil till all smell of Sulphuretted Hydrogen has disappeared, neutralize with Carbonate of Soda, and then boil with Caustic Soda or Potash (free from Alumina).</i></td>
</tr>
<tr>
<td rowspan="4">I.
<i>Mix with Borax and fuse on the ring of the platinum wire before the blowpipe.</i>
The formation of a blue bead indicates
COBALT.
(P. 40, col. 1.)</td>
<td rowspan="4">II.
<i>Dissolve in Aqua-regia, evaporate nearly to dryness, and examine for Nickel with Cyanide of Potassium</i> (according to p. 39, col. 2).</td>
<td colspan="2">The solution may contain <i>Alumina</i> and <i>Zinc.</i>
<i>Divide into two parts.</i></td>
<td colspan="3">The insoluble portion may contain <i>Iron, Chromium,</i> and <i>Manganese.</i>
<i>Mix with one part of Soda and three of Nitre, fuse in a porcelain crucible, and boil with water.</i></td>
</tr>
<tr>
<td rowspan="3">I.
<i>Add solution of Sulphuretted Hydrogen.</i>
The formation of a <i>white</i> precipitate indicates
ZINC.
(P. 39, col. 1.)</td>
<td rowspan="3">II.
<i>Acidify with Hydrochloric Acid, boil with a little Chlorate of Potash, and add Ammonia in excess.</i>
The formation of a bulky white precipitate indicates
ALUMINA.</td>
<td rowspan="3">A yellow solution indicates
CHROMIUM.
Confirm with Acetate of Lead.
(P. 44, col. 1.)</td>
<td colspan="2">Divide the insoluble portion into two parts.</td>
</tr>
<tr>
<td>I.
<i>Fuse on platinum foil with a mixture of Nitre and Carbonate of Soda;</i> the production of a fine green colour indicates
MANGANESE.
(P. 41, col. 1.)</td>
<td>II.
<i>Dissolve in Hydrochloric Acid, add a drop of Nitric Acid, and test the solution for</i> IRON <i>by Ferrocyanide of Potassium.</i>
(P. 42, col. 1.)</td>
</tr>
<tr>
<td colspan="2">N.B. If the original solution was colourless, the fusion with Nitre and Soda for the detection of <i>Chromium</i> may be omitted.</td>
</tr>
</table>

TREATMENT OF THE FILTRATE FROM THE PRECIPITATE BY HYDROSULPHURET OF AMMONIA (E), OR OF THE SOLUTION IN WHICH THAT REAGENT HAS FAILED TO CAUSE A PRECIPITATE.

To a portion add Phosphate of Soda and well agitate; if a precipitate is formed, boil the remainder with Hydrochloric Acid till all smell of Sulphuretted Hydrogen has disappeared; filter, add Chloride of Ammonium, and Carbonate of Ammonia mixed with a little Caustic Ammonia, and heat gently.

The formation of a precipitate indicates

Baryta, Strontia, Lime.

Dissolve in a small quantity of Hydrochloric Acid, and divide into three parts.

I.	II.	III.
Add solution of **Sulphate of Lime.** An immediate precipitate indicates **Baryta.**	Evaporate nearly to dryness, and *boil with strong Alcohol* in a porcelain dish; ignite and stir well. *A carmine-red flame* indicates **Strontia.**	*Add dilute Sulphuric Acid*, and let stand for half an hour; filter, and to the filtrate *add Ammonia* and *Oxalate of Ammonia.* The formation of a white precipitate indicates **Lime.**

Ammonia is detected in a portion of the original solution by heating it with *Hydrate of Lime* or with *Caustic Potash.*

The solution may contain *Magnesia* and the *Alkalies.*

Add a little more Carbonate of Ammonia, and warm to insure the complete separation of Lime, Baryta, and Strontia; filter (if necessary), and, to a portion of the filtrate, *add Phosphate of Soda.*

A white crystalline precipitate is formed—

Magnesia.

I.	II.
Magnesia **has** *been found.* Evaporate the remainder of the filtrate to dryness and ignite. Redissolve in water, and to the solution *add Baryta Water* as long as a precipitate continues to form and boil. Filter from the precipitate, and to the filtrate *add excess of Carbonate of Ammonia,* heat gently for some time, and then filter; evaporate the filtrate to dryness, and ignite to remove the ammoniacal salts. Redissolve in water, filter (if necessary), and test for *Potash* and *Soda,* as on the other side.	*Magnesia has* **not** *been found.* Evaporate the remainder of the filtrate to dryness, and ignite. Redissolve in a small quantity of water, *add Alcohol, heat to boiling, and inflame.*

I.	II.
The flame is *Yellow.* Presence of **Soda**, redissolve the residue in distilled water, and *add Bichloride of Platinum.* The formation of a yellow precipitate indicates **Potash.**	The flame is *Violet.* Absence of *Soda* and presence of **Potash.**

TABLE VI.

COURSE OF ANALYSIS FOR THE DETECTION OF THE BASES AND ACIDS IN A COMPOUND INSOLUBLE IN WATER AND ACIDS, WHICH MAY CONTAIN THE SULPHATES OF BARYTA, STRONTIA, LIME, AND LEAD, CHLORIDE OF LEAD, CHLORIDE OF SILVER, SUBCHLORIDE OF MERCURY, AND SILICA.

Test a small portion with Hydrosulphuret of Ammonia.

If it becomes *black*, some one or more of the *heavy metals* are present; *mix a portion of the substance with Carbonate of Soda, and heat on charcoal in the reducing flame of the blowpipe.*

A metallic bead is produced, which gradually sublimes in the oxydating flame, leaving a yellow incrustation on the charcoal, indicating Lead (p. 44, col. 1).

(A) Lead is found.

Fuse a portion of the substance in a porcelain crucible with three times its quantity of a mixture of dry Carbonate of Soda and Cyanide of Potassium, keep the mass in fusion for some time, then boil with distilled water, filter, and well wash the insoluble portion.

<table>
<tr><td colspan="3">The filtrate may contain <i>Sulphuric</i>, <i>Silicic</i>, and <i>Hydrochloric Acids.</i>
Divide into <i>three</i> parts.</td><td colspan="3">The insoluble portion may contain <i>Lead</i>, <i>Silver</i>, and the <i>Alkaline Earths.</i>
<i>Digest with Acetic Acid.</i></td></tr>
<tr><td rowspan="3">I.
Supersaturate with <i>Hydrochloric Acid</i>, filter (if necessary), and
<i>add Chloride of Barium.</i>
The formation of a white precipitate indicates
Sulphuric Acid.</td><td rowspan="3">II.
Supersaturate with <i>Hydrochloric Acid</i>, and evaporate to dryness. Treat the perfectly dry residue with boiling water. An insoluble residue indicates
Silicic Acid.
Confirm by blowpipe.
(P. 65, col. 2.)</td><td rowspan="3">III.
Supersaturate with <i>Nitric Acid</i>, filter (if necessary), and
<i>add Nitrate of Silver.</i>
The formation of a white curdy precipitate indicates
Chlorine.</td><td rowspan="3">The solution may contain <i>Lead</i> and the <i>Alkaline Earths.</i>
Precipitate the Lead from the acetic solution with Sulphuretted Hydrogen, filter, concentrate the filtrate by evaporation, and examine it for <i>Baryta</i>, <i>Strontia</i>, and <i>Lime</i>, according to (E), Table V.</td><td colspan="2">The residue may contain <i>Lead</i> and <i>Silver.</i>
<i>Digest with Nitric Acid, and divide into two parts.</i></td></tr>
<tr><td>I.
Drive off the excess of Nitric Acid by heat, and
<i>add Sulphuric Acid.</i>
The formation of a white precipitate indicates
Lead.</td><td>II.
Dilute with distilled water, and
<i>add Hydrochloric Acid.</i>
The formation of a white curdy precipitate indicates
Silver.</td></tr>
<tr><td colspan="2">The original substance is tested for Mercury by heating a portion in a glass tube with Carbonate of Soda (p. 45, col. 1).</td></tr>
</table>

(B) LEAD IS NOT FOUND.

Digest for some time with Hydrosulphuret of Ammonia, filter, and wash.

<table>
<tr>
<td rowspan="5">The solution may contain <i>Chlorine</i>.
Supersaturate with <i>Nitric Acid</i>, boil, filter, and to the filtrate, diluted with water,
<i>add Nitrate of Silver.</i>
The formation of a white curdy precipitate indicates
CHLORINE.</td>
<td colspan="5">The undissolved portion may contain <i>Silver</i> and <i>Mercury</i>, also <i>Silicic Acid</i> and the <i>Sulphates of the Alkaline Earths.</i>
<i>Boil with Nitric Acid.</i></td>
</tr>
<tr>
<td rowspan="4">The solution may contain <i>Silver</i>.
Filter from the insoluble residue, and to the clear filtrate
<i>add Hydrochloric Acid.</i>
A white curdy precipitate indicates
SILVER.</td>
<td colspan="4">The insoluble portion may contain <i>Mercury</i>, <i>Silicic Acid</i>, and the <i>Sulphates of the Alkaline Earths.</i>
It is <i>black</i>.
<i>Mercury</i> is present, digest with <i>Aqua-regia.</i></td>
</tr>
<tr>
<td rowspan="3">The solution contains
MERCURY.
Confirm with <i>Metallic Copper</i> and Protochloride of Tin.
(P. 44, col. 1.)</td>
<td colspan="3">The insoluble portion may contain <i>Silica</i> and the <i>Sulphates of the Alkaline Earths.</i>
<i>Fuse with a mixture of Carbonate of Potassa and Soda. Treat the fused mass with boiling water, and filter.</i></td>
</tr>
<tr>
<td colspan="2">The solution may contain <i>Sulphuric Acid</i> and <i>Silicic Acid.</i>
<i>Supersaturate with Hydrochloric Acid, and divide into two portions.</i></td>
<td rowspan="2">The insoluble residue may contain the Alkaline Earths.
Wash repeatedly with boiling water, and <i>treat with hydrochloric acid</i>, and filter. Examine the filtered solution for <i>Baryta</i>, <i>Strontia</i>, and <i>Lime</i>, according to (E), Table V.</td>
</tr>
<tr>
<td>I.
<i>Add Chloride of Barium.</i>
The formation of a white precipitate indicates
SULPHURIC ACID.</td>
<td>II.
Evaporate to perfect dryness, <i>and treat the residue with water;</i> if anything remains undissolved it is
SILICIC ACID.</td>
</tr>
</table>

TABLE VII.

COURSE OF ANALYSIS FOR THE DETECTION IN A SOLUTION OF THE INORGANIC ACIDS.

To a portion of the solution, neutralized (if necessary) with Ammonia, and filtered, *add Chloride of Barium.*

The precipitate may contain *Sulphuric, Phosphoric, Boracic, Silicic,* and *Oxalic* Acids.

Add Hydrochloric Acid, and heat.

An insoluble residue indicates SULPHURIC ACID.

To another portion of the solution *exactly* neutralized (if acid) with *Ammonia,* and (if alkaline) with *Nitric Acid, add Nitrate of Silver.*

The precipitate may contain *Chlorine, Iodine, Cyanogen, Phosphoric, Silicic, Oxalic,* and *Boracic* Acids.

Filter, wash, and digest with Nitric Acid.

The insoluble residue may contain *Chlorine, Iodine,* and *Cyanogen.*

Digest with Ammonia.

<table>
<tr>
<td rowspan="2">A yellowish residue remains.
IODIDE OF SILVER.
Test the original solution for Iodine with <i>Starch.</i>
(P. 68, col. 2.)</td>
<td colspan="2">The solution may contain <i>Chlorine</i> and <i>Cyanogen.</i> Test the original solution for Cyanogen with <i>Hydrochloric Acid</i> and <i>Magnetic Oxide of Iron</i> (p. 70, col. 2).</td>
</tr>
<tr>
<td><i>Cyanogen</i> is <i>not</i> found.
The ammoniacal solution can only contain
<i>Chloride of Silver.</i>
<i>Add Nitric Acid.</i>
A white curdy precipitate is formed.
CHLORIDE OF SILVER.</td>
<td><i>Cyanogen is</i> found.
To the ammoniacal solution <i>add Nitric Acid.</i> The precipitate may contain <i>Cyanogen</i> and <i>Chlorine.</i>
<i>Wash, transfer to a porcelain crucible, and ignite.</i>
Place a fragment of zinc on the ignited mass when cold, and pour over it <i>dilute Sulphuric Acid;</i> when the effervescence has ceased, filter, dilute with water, and
<i>add Nitrate of Silver.</i>
The formation of a white curdy precipitate indicates
CHLORIDE OF SILVER.</td>
</tr>
</table>

If both *Chloride of Barium* and *Nitrate of Silver* have produced a precipitate, and especially if that formed with Nitrate of Silver is *yellow,* PHOSPHORIC ACID is sought for in the original solution, by the addition of *Chloride of Ammonium, Ammonia,* and *Sulphate of Magnesia* (p. 63, col. 2).

If the precipitate produced by *Nitrate of Silver* is *purple,* the original solution becoming *red* or *yellowish red* on the addition of Hydrochloric Acid, CHROMIC ACID is present, but this acid, as well as ARSENIOUS and ARSENIC Acids, is always found in the examination for bases.

BORACIC, SILICIC, NITRIC, CHLORIC, and HYDROFLUORIC ACIDS and BROMINE are severally tested for, as directed in Table IV.

CARBONIC and HYDROSULPHURIC ACIDS are discovered in the search for bases.

TABLE VIII.

COURSE OF ANALYSIS FOR THE DETECTION OF BASE AND ACID IN THE FOLLOWING SUBSTANCES, INSOLUBLE, OR ONLY SPARINGLY SOLUBLE, IN WATER AND ACIDS.

Sulphates of Baryta, Strontia, Lime, and Lead ; Silica, Chloride of Lead, Chloride of Silver, and Subchloride of Mercury.

Treat a small portion with Hydrosulphuret of Ammonia.

It becomes black.

Mix a portion of the substances with excess of Carbonate of Soda, and heat in a glass tube, *metallic globules* sublime (p. 45, col. 2) **SUBCHLORIDE OF MERCURY.**

Mercury is not present. Digest another portion with Hydrosulphuret of Ammonia for some time, filter, and wash.

The filtrate may contain *Sulphuric* or *Hydrochloric Acid.* *Divide into two portions.*		The undissolved portion may contain *Silver* or *Lead.* *Well wash, dissolve in Nitric Acid, and divide into two portions.*	
I. Acidify with Hydrochloric Acid, boil and filter. To the filtrate *add Chloride of Barium,* A white precipitate is formed. SULPHURIC ACID.	II. Acidify with Nitric Acid, Boil and filter. To the filtrate *add Nitrate of Silver.* A white curdy precipitate is formed. HYDROCHLORIC ACID.	I. *Add Sulphuric Acid,* A white precipitate is formed. LEAD.	II. *Add Hydrochloric Acid.* A white curdy precipitate soluble in Ammonia is formed. SILVER.

It does NOT *become black on the addition of Hydrosulphuret of Ammonia.*

Mix a portion of the substance with four times its quantity of Carbonate of Potash and Soda, fuse in a platinum crucible, and boil the fused mass with water.

It is completely dissolved.	It is not completely dissolved.			
SILICA. Confirm by supersaturating the solution with Hydrochloric Acid, evaporating to dryness, and examining the residue by the blowpipe. (P. 65, col. 2.)	The solution contains SULPHURIC ACID. Confirm by acidifying with Hydrochloric Acid, and precipitating with Chloride of Barium.	The undissolved residue may contain *Baryta, Strontia,* or *Lime.* Wash well, dissolve in a small quantity of Hydrochloric Acid, filter, divide into three parts, and to each *add solution of Sulphate of Lime.*		
		I. A precipitate is immediately formed. BARYTA.	II. A precipitate is formed after a time. STRONTIA.	III. No precipitate is formed. LIME.

APPENDIX TO PART II.

QUANTITATIVE ESTIMATION OF SUBSTANCES,

AND THEIR SEPARATION FROM EACH OTHER.

POTASH; SODA.

Meta-antimoniate of Potash as a Test for Soda.—The following process for preparing this salt is recommended by *Fremy.* One part of antimony is acted upon with four parts of nitre in a red-hot earthern crucible; insoluble anhydrous antimoniate of potash is formed, which is washed with cold water to remove the nitrite and nitrate of potash. It is then boiled for two or three hours in water, in order to convert it into the gummy soluble antimoniate, water being added to supply the loss by evaporation. During ebullition the greater part of the antimoniate dissolves, there remaining but a small quantity of bi-antimoniate, which is separated by filtration. The solution is evaporated, several fragments of caustic potash being added, so as to render it very caustic. A few drops of the solution are tried from time to time, to see whether on cooling they become crystalline; and when this takes place the evaporation is to be discontinued; the meta-antimoniate of potash then crystallizing abundantly, the alkaline solution is to be poured off, and the salt dried on porcelain plates. It always contains excess of alkali, and should therefore be washed two or three times before it is used as a reagent. As the meta-antimoniate of potash decomposes in solution in water, it should be kept in a dry state and dissolved when wanted. According to *Fremy*, the delicacy of this reagent is so great, that he can detect ½ per cent. of carbonate of soda in commercial potash.—*Ann. de Ch. et de Phys., Août*, 1840.

Quantitative determination of Potash and Soda by Fluosilicic Acid.—According to *Rose* (*Pogg. Ann.*, No. 6, 1850), the fluosilicates of potash and soda are quite insoluble in strong spirits, and both of these alkalies may be quantitatively estimated by mixing their respective solutions with an equal volume of alcohol and adding to them fluosilicic acid. The precipitates must be dried at 212°, on a weighed filter. *Rose* draws attention to the fact that fluosilicic acid is by no means without action on glass, and that a very dilute acid even becomes contaminated with alkali, lime, and sometimes with iron, when kept for a long time in glass vessels. It is necessary, therefore, to prepare fresh acid for each quantitative analysis, though acid that has been kept for a long time in glass vessels is still good for many quantitative examinations.

AMMONIA.

Estimation of Ammonia.—For determining the amount of this base when accompanied with nitrogenous substances, *Schlœsing* places a known weight of the substance dissolved in water in a shallow vessel, over which is supported, on a glass tripod, a shallow saucer containing sulphuric acid of a known strength. He then mixes with the ammoniacal solution some caustic potash or milk of lime, and covers the whole with a bell glass, the edges of which rest on mercury contained in a large shallow dish. After a period varying from 24 to 28 hours, according to the bulk of the ammoniacal solution, the whole of the ammonia is disengaged from the solution and is absorbed by the sulphuric acid, the strength of which is then again determined by means of saccharate of lime, according to *Peligot's* method (p. 259, col. 2). This process does not answer so well with insoluble salts of ammonia, which the author directs to be dissolved in nitric acid; the operation then goes on very slowly, requiring sometimes as many as 72 hours for the complete absorption.—*Ann. de Chim., Feb.* 1851.

MAGNESIA.

Separation of Magnesia from the Alkalies by Carbonate of Silver—Sonneschein's Method.—The compounds to be separated are converted in the usual manner into chlorides, which are evaporated to dryness and then heated to faint redness, when any ammoniacal salt contained in the solution, as well as a portion of the muriatic acid combined with the magnesia, escapes. When the dry mass is cool, water is poured over it; it is then boiled with carbonate of silver until the liquid has a strong alkaline reaction. The boiling is continued for about ten minutes, stirring the whole time, when the decomposition is complete. The solution is then filtered as hot as possible, and the precipitate washed with hot water. The filtered liquid now contains only the alkalies and a trace of the silver salt, which is removed with muriatic acid, and the alkalies are then determined in the usual manner. The residue left upon the filter is digested with muriatic acid, and, after removing the chloride of silver, the magnesia is precipitated in the usual manner with phosphate of soda and ammonia. The carbonate of silver is best prepared by carefully precipitating nitrate of silver with carbonate of ammonia; after subsidence, the precipitate is easily freed from the ammoniacal salt by the frequent addition of water, and decantation. It is not necessary to filter it, or to dry it, as the moist precipitate is more easily decomposed.—*Poggendorff's Annalen*, 74, p. 313.

Heintz's Method.—The solution containing the three bases is supersaturated with ammonia, and if it contain no chlorides a few drops of sal-ammoniac are added. Should a troubled appearance arise in the liquid, it is treated with sal-ammoniac until this vanishes. The magnesia is then precipitated by phosphate of ammonia, the precipitate washed with ammoniacal water, dried, heated to redness, and weighed. The free ammonia in the filtrate having been partly removed by boiling, the phosphoric acid is precipitated at the boiling temperature by nitrate or acetate of lead. When an excess of the lead salt has been used, a solution of carbonate of ammonia, containing free ammonia, is added to the hot liquid, which is then allowed to stand for a few minutes; it is subsequently filtered, and the amount of potash and soda contained in the filtrate is ascertained by the usual methods. It is essential that some chloride should be present in the solution, in order that a compound of chloride and phosphate of lead may be produced, from which ammonia cannot extract any phosphoric acid.—*Poggendorff's Annalen*, 73, p. 119.

Estimation of Magnesia by Phosphate of Soda, and that of Phosphoric Acid by Magnesia.—It has been shown by *Weber* (*Pogg. Ann.*, 73, p. 137) that phosphoric acid in the bibasic modification, cannot be accurately determined by magnesia. The phosphate of magnesia and ammonia, and the pyrophosphate of magnesia, are not precipitated entirely by ammonia from solution in hydrochloric acid; neither is pyrophosphoric acid completely precipitated by the solution of a magnesian salt, even in the presence of ammonia or an ammoniacal salt, only after standing for several weeks in the presence of ammonia, is the bibasic acid converted into the tribasic modification, and rendered capable of forming an entirely insoluble compound with magnesia. If, therefore, the phosphoric acid in any substance is to be estimated by magnesia, it must first be ascertained by means of nitrate of silver, whether the acid exist in it in the tribasic or bibasic modification. If the latter is the case, the substance must be fused with from four to six parts of a mixture of equivalent quantities of carbonate of soda and potash, or treated for a length of time with concentrated sulphuric acid, by which means the bibasic acid and its compounds are converted into tribasic salts. The pyrophosphates of lime and other alkaline earths are, however, not entirely converted into tribasic phosphates by fusion with carbonated alkali; but by subsequent treatment with sulphuric acid and alcohol, the whole of the phosphoric acid may be obtained in the alcoholic solution. This must then be saturated with carbonate of soda, evaporated to dryness and fused, in order to determine with accuracy the amount of phosphoric acid present.

Separation of Magnesia from the Alkalies—Watts's Method.—It consists in precipitating the magnesia by a known weight of carbonate of soda, using considerable excess, then boiling and filtering; treating the filtrate with a slight excess of acid; evaporating to dryness, and igniting the residue to render it neutral; weighing the neutral salt thus obtained, and making the proper correction for the quantity of soda salt introduced. To ensure accuracy, the solution, after the addition of the carbonate of soda, must be well boiled for at least half an hour, in order to decompose a difficultly soluble double carbonate of soda and magnesia, which is formed on the first addition of the alkaline carbonate. The carbonate of soda must likewise be added in considerable excess; otherwise, the precipitation will not be complete. The precipitate of carbonate of magnesia must be washed with boiling water, and the washing not too long continued; the carbonate not being completely insoluble. The washing should be discontinued as soon as the wash-water ceases to give a distinct alkaline reaction; when this takes place, the water begins to dissolve the carbonate of magnesia.—*Quar. Journ. Chem. Soc.*, July 1, 1849.

Separation of Magnesia from the Alkalies, and Analysis of Alkaliferous Minerals—Ebelmen's Method.—In the analysis of alkaliferous minerals, which are not decomposable by hydrochloric acid, either the method of *Berzelius* and *Brunner* by hydrofluoric acid, or that of *Abich*, by fusion with hydrate or carbonate of baryta (p. 221, col. 2), is employed. In both cases the bases are obtained as sulphates, as in the first case the hydrofluoric acid has to be expelled by sulphuric acid, and in the second the baryta has to be removed also by sulphuric acid. The liquid is then successively precipitated by ammonia, hydrosulphuret, and oxalate of ammonia, then evaporated, and the residue strongly calcined to expel the ammoniacal salts; a mixture of sulphate of magnesia and sulphates of the alkalies is left. *Ebelmen* effects the separation of the magnesia from the alkalies by adding to the solution of the mixed sulphates recently-prepared carbonate of baryta, and then passing a stream of carbonic acid through the liquid till it contains a portion of the baryta in solution in the form of bicarbonate, which period is known by filtering a few drops of the liquid, and adding one drop of exceedingly dilute sulphuric acid: if a cloudiness is produced, the liquid can contain no sulphate in solution. It is then filtered, and the filtrate evaporated to dryness at a pretty high temperature; in order to reduce the whole to the state of neutral carbonates, the residue is treated with a small quantity of boiling water, which dissolves only the alkaline carbonates. When alumina and peroxide of iron are present, they are precipitated, together with a portion of manganese and magnesia, by ammonia, or the carbonate; the filtered liquid is then boiled with an excess of carbonate of baryta, which completely decomposes the sulphate of ammonia, and when the addition of a fresh quantity no longer causes the disengagement of carbonate of ammonia, the liquid is treated with carbonic acid. *M. Ebelmen* states that he has employed this method in the analysis of several rocks used in the manufacture of porcelain in China with very satisfactory results.—*Ann. de Chim. et de Phys.*, Nov. 1850.

LITHIA; STRONTIA; BARYTA.

Method of distinguishing Lithia from Strontia by the Blow-pipe.—Both of these substances communicate a crimson tinge to the blow-pipe flame, but it has been pointed out by *Chapman* (Ch. Gz. vol. vi. p. 188) that the addition of a small quantity of chloride of barium to the assay serves to distinguish between them, the red colour in the case of strontia being thereby destroyed, while that of lithia is not affected. Chloride of barium alone imparts an apple-green tint to the flame; but this, on the addition of strontia, is converted into an impure yellow colour, somewhat resembling that produced by soda.

Separation of Baryta from Strontia.—Fluosilicic acid was employed by *Berzelius* (p. 149, col. 2) for this purpose; but according to *Rose* (*Pogg. Ann.*, Nov. 6, 1850) the fluosilicate of baryta is not entirely insoluble in water: perfectly accurate results are only obtained when the precipitation is effected from a spirituous solution. A small quantity only of alcohol need be added to render the precipitation complete.

ALUMINA; IRON.

Separation of Alumina from Peroxide of Iron—Rivot's Method.—The following method has been proposed by *Rivot*, as being more correct and less tedious than that usually employed (p. 169, col. 1). The two oxides are precipitated together by ammonia; the precipitate is dried, separated from the filter, the filter burnt, and the ash united to the two hydrates; the whole is then calcined at a red heat in a platinum crucible. The mixture of the two oxides is reduced to powder, and accurately weighed, then placed in a counterpoised porcelain tray, in a porcelain tube, arranged horizontally in a furnace; a drawn-out tube is adapted to one of its extremities, whilst by the other a slow current of hydrogen gas, dried over chloride of calcium and sulphuric acid, is introduced. When the air of the apparatus has been completely expelled, the porcelain tube is gradually raised to a red heat, and this temperature maintained as long as water is seen to be deposited on the sides of the glass tube at the end of the apparatus; about one hour is required to complete the reduction. The tube is then allowed to cool, continuing the current of hydrogen; when perfectly cool, the tray is taken out and weighed; the loss indicates the oxygen of the peroxide of iron from which the proportion of the latter in the mixture can be calculated. When the proportion of alumina is large, it is advisable to digest the mixture of metallic iron and alumina for about 24 hours in the cold, with one part of ordinary pure nitric acid, and 30 parts of water. The iron becomes completely dissolved without the alumina being attacked. The solution of the iron is known to be complete when the alumina has acquired a nearly white colour. The alumina is separated by filtration; the nitric solution heated to peroxidize the iron, which is then precipitated by ammonia. In this manner the two oxides may be weighed separately.—*Ann. de Chim.*, Oct., 1850.

Separation of Alumina from Peroxide of Iron—Fresenius's Method.—Some experiments have been made by *Fresenius*, which show the inaccuracy of the usual method of separating peroxide of iron from alumina by caustic potash, or soda, a portion of the iron being dissolved with the alumina, and a portion of alumina being carried down with the hydrated peroxide of iron. He found, moreover, that a certain quantity of alumina escapes precipitation by ammonia, in consequence of a portion of the organic matter of the filtering paper becoming dissolved by filtering the caustic alkali through it. This source of error he proposes to avoid by boiling the hydrochloric solution with a little chlorate of potash, by which the organic matter is destroyed. The other sources of inaccuracy he avoids in the following manner:—The acid solution containing the alumina and peroxide of iron is heated to ebullition in a flask, removed from the fire, and a solution of sulphite of soda added till the colour has become pale green. The liquid is then boiled for some time, a coil of platinum wire being introduced into the flask to prevent succussion; it is then neutralized with carbonate of soda, an excess of caustic soda added, and, after being well shaken, boiled until the liquid has become black and granular. It is now removed from the fire and allowed to subside, the clear liquid passed through a close filter, and the precipitate washed with hot water, at first by decantation, and then upon the filter; the filtered solution, treated with muriatic acid and chlorate of potash, furnishes by precipitation with ammonia and several hours' standing, the *whole* of the alumina in a perfectly pure state. *Knopp's* method, with hydrosulphuret of ammonia (p. 169, col. 1), besides being inconvenient, is inaccurate; a portion of iron almost always passing through in the washing, whether pure water or water containing hydrosulphuret of ammonia is employed.—*Journ. für Prakt. Chem.*, Nov. 1, 1848.

Analysis of Chrome Iron Ore—Hunt's Method.—The mineral is first very finely levigated in an agate mortar; it is then to be mixed with ten or twelve times its weight of fused bisulphate of potash, and the mixture heated to fusion in a platinum crucible, and preserved at a gentle red heat for about thirty minutes. The crucible and its contents, when cold, are placed in water, which, with the aid of heat, soon dissolves the saline mass. The greater part of the chromium is left as a green basic sulphate, insoluble in water or hydrochloric acid, and apparently identical with that obtained when any salts of chromium are heated with an excess of strong sulphuric acid. The best mode of treating this mixture of soluble and insoluble salts is to boil the whole for a few minutes with an excess of carbonate of potash or soda, which precipitates the alumina, iron, and chromium that may be in solution, and decomposes the insoluble sulphate; it is not easy in this way, however, to remove all the sulphuric acid, and thus render the residue quite soluble in hydrochloric acid; but this is of no importance. The dried precipitate is fused with five times its weight of a mixture of equal parts of nitre and carbonate of soda. The operation is performed in a platinum or silver crucible over a spirit lamp, and the mixture kept in fusion ten or fifteen minutes, to ensure the perfect solution of the chromium. The chromate of potash is then dissolved out from the mixture of oxide of iron, alumina, and magnesia, which may be separated in the ordinary manner: if the precautions above-mentioned have been observed, no trace of undecomposed ore will be left after treating the mixture with hydrochloric acid. A small portion of magnesia remains dissolved in the filtrate from the precipitate by carbonate of soda, and may be obtained by evaporating to dryness. Any silica which the mineral contained is also dissolved, and may be separated in the usual manner. The presence of a small portion of sulphates prevents the determination of the chromic acid by a salt of lead; the solution is accordingly supersaturated with hydrochloric acid, and boiled with alcohol to convert it into chloride of chromium, from which the oxide is precipitated by adding ammonia in excess, and boiling for a few minutes.—*Silliman's Journal*, May, 1848.

Analysis of Chrome Iron Ore—Rivot's Method.—The finely-powdered mineral is placed in a porcelain tray, in a porcelain tube laid horizontally in a reverberatory furnace, and submitted for four hours to a current of dry hydrogen at a bright red heat; the loss in weight is the oxygen combined with the iron. The substance treated by hydrogen is digested for twenty-four hours with weak nitric acid, at a gentle heat; the acid dissolves the metallic iron and a trace of lime, but is without action on the oxide of chrome, silica, and alumina. The iron is precipitated from its nitric solution by ammonia; the undissolved portion is fused in a silver crucible with a mixture of 1 part of nitre, 3 parts of carbonate of soda, and 3 parts of caustic potash, and the mixture is kept for one hour well fused at an incipient red heat. After cooling it is dissolved in hot water; the liquid has a yellow colour. It is rendered acid with hydrochloric acid, and evaporated to dryness with alcohol, redissolved by hydrochloric acid, when the silica remains undissolved. The acid liquid contains the chloride of chromium, aluminum, and calcium. After filtration, to separate the silica, it is precipitated by ammonia: the precipitate contains alumina, sesquioxide of chromium, and a little lime; it is brought upon a filter, dried, and calcined with the ordinary precautions, but taking care to raise the temperature to a bright red heat towards the end of the operation. To separate the lime the strongly-calcined precipitate is treated with very weak cold acetic acid; the acetic solution is then united to the ammoniacal solution, the lime precipitated by oxalate of ammonia, and the liquid tested for magnesia. The oxides of chrome and alumina are weighed, then calcined, and the mixture treated with hydrochloric acid, which dissolves only the alumina; the undissolved oxide of chrome is weighed, and the alumina precipitated by ammonia. In case the alumina should be accompanied by a trace of oxide of chrome, dissolved by the hydrochloric acid, it will be necessary to separate it by means of potash.—*Ann. de Chim.*, Oct., 1850.

CHROMIUM.

Estimation of Chromium—Schwartz's Method.—The whole of the chromium is converted into chromic acid, and when oxide of chromium is present this is oxidized by fusion with hydrate and chlorate of potash; the chromic acid is then reduced to sesquioxide of chromium by a known quantity of protoxide of iron; the quantity which remains unoxidized after the operation being determined, according to *Marguerite's* method (p. 170, col. 1), by a standard solution of permanganate of potash; the difference between the protoxide of iron left and that consumed gives the amount of protoxide oxidized by the chromic acid, thus:

$$6\,FeO + 2\,CrO_3 = 3\,Fe_2O_3 + Cr_2O_3.$$

and from this formula the quantities of chromium, sesquioxide of chromium, and chromic acid, may be determined: 1·000 iron corresponds to 0·3143 chromium, 0·4571 sesquioxide of chromium, and 0·6000 chromic acid.—*Liebig's Annalen*, Feb., 1849.

NICKEL; ZINC; COBALT.

Separation of Nickel and Zinc—Brunner's Method.—It is founded on the fact that dilute hydrochloric acid has no action on the sulphuret of nickel prepared in the dry way, whilst it readily dissolves the sulphuret of zinc. The two metals are simultaneously precipitated by carbonate of soda, the precipitate collected on a filter, dried, and feebly calcined, then mixed with 1½ time its weight of sulphur, and three-fourths its weight of carbonate of soda, and this mixture heated for about half an hour in a small glass matrass, at as high a temperature as the glass will bear. The substance is then treated with hydrochloric acid diluted with 10 times its weight of water several times, until it no longer dissolves any zinc, which is ascertained by testing the liquid after each treatment with carbonate of soda. The residue of sulphuret of nickel is then dissolved in *aqua regia*, and the two metals precipitated from their separate solutions by carbonate of soda. When the alloy contains iron, if it has not been previously separated by ammonia from the nickel and zinc, it redissolves completely with the latter in the process just described.—*Bibliothèque Universelle*, April, 1851.

Extraction of Cobalt and Nickel from the Ore.—The following process is followed in a manufactory at Birmingham, the ore employed consisting principally of metallic sulpho-arseniurets, and containing generally about 6 per cent. of nickel and 3 per cent. of cobalt. The ore is mixed with a small quantity of carbonate of lime and fluorspar, and the whole is heated to a white red heat in a reverberatory furnace: the mass fuses at this high temperature, and a slag is obtained floating on the surface of a fluid mass of metallic appearance; the latter is let out of the furnace by a particular aperture, and watered in order that it may be broken into fragments with greater facility. It has been ascertained from experience that when the slag is of a dull colour, iron is present, but if its surface is black and brilliant, it is free from that metal. The metallic mass is then reduced to a very fine powder, which is calcined at a bright red heat in a furnace, graduating the temperature so as to avoid fusion, and constantly raking it: a considerable quantity of arsenious acid is driven off. The air has free access to the mass, which becomes oxidized and diminished in weight. The calcination, which lasts for about twelve hours, is continued until no more white fumes are given off, and the residue is treated with hydrochloric acid, which dissolves nearly the whole of it: the liquid is diluted with water, and milk of lime and chloride of lime added to precipitate the iron and the arsenic; the precipitate, after being well washed, is thrown away. A current of washed sulphuretted hydrogen, generated from sulphuret of iron and dilute sulphuric acid, is passed into the liquor until it is saturated: it is discontinued, when some ammonia, added to a sample of the filtered liquor, gives a black precipitate; if there was not an excess of sulphuretted hydrogen, the precipitate produced by ammonia would be green: the precipitate is washed and then thrown away, a current of sulphuretted hydrogen being passed into the wash waters. The cobalt is then thrown down with a solution of hydrochlorite of lime. The precipitate, washed, dried, and then heated to redness, is considered to be oxide of cobalt, and part is sent in this state into the market. Another portion is heated to a white red; by this treatment the oxide loses in weight, but increases in density; it is sold as protoxide of cobalt. The liquid from which the cobalt has been precipitated, is treated with milk of lime, which precipitates the nickel in the state of hydrate: this precipitate is washed, dried, and heated to redness; it is then mixed with charcoal, and, by means of a strong heat, reduced to the state of a spongy nickel, which is employed in the manufacture of German silver. The oxide of cobalt thus prepared is remarkably pure.

Preparation of Nickel and Cobalt—Liebig's Method.—The mixture of the two oxides is dissolved in pure cyanide of potassium, and is then heated to boiling to expel the free prussic acid, when the protocyanide of cobalt compound is converted with evolution of hydrogen, into cobalticyanide of potassium, and the nickel is contained in solution as nickelocyanide of potassium. Pure powdered peroxide of mercury is added to the hot solution, when the whole of the nickel is precipitated partly as oxide and partly as protocyanide, and the mercury takes the place of the nickel. If the liquid was neutral, previous to the addition of the peroxide of mercury, it becomes alkaline after boiling with the oxide. The precipitate which is formed is at first greenish; with an excess of peroxide of mercury it assumes a dirty grayish yellow colour. It contains the whole of the nickel, and moreover the excess of the peroxide of mercury. After washing and ignition, pure oxide of nickel, perfectly free from cobalt, remains.

The liquid, which has been treated with the peroxide of mercury, contains the whole of the cobalt in the form of cobalticyanide of potassium; to determine the amount of cobalt, the liquid is supersaturated with acetic acid, and precipitated with a solution of sulphate of copper. This is effected while boiling, and the precipitate retained for some time in the liquid in ebullition: otherwise it contains potash, and continues mucilaginous, which prevents its being washed. The precipitate is cobalticyanide of copper, and contains 2 equivalents of cobalt to 3 equivalents of copper. On treating it with potash, oxide of copper is precipitated, while cobalticyanide of potassium remains in solution; and from the amount of oxide of copper the quantity of cobalt may be *indirectly* determined.

If it is desired to determine the cobalt *directly*, the precipitate is heated to redness, and, after the destruction of the cyanogen, dissolved in muriatic acid, with the addition of a few drops of nitric acid. A current of sulphuretted hydrogen is passed through the solution to remove the copper; and now, after boiling it for a few minutes to expel the sulphuretted hydrogen, the cobalt is thrown down by a boiling solution of potash. The precipitate of the protoxide of cobalt must be well washed to remove the potash: after drying, it is heated to redness and weighed, and from a portion of the ignited oxide the cobalt is determined by reduction with hydrogen, and calculated for the entire amount. All these operations can be effected with the greatest ease and without any loss. The cobalt reduced from the oxide by hydrogen, after cooling in the current of hydrogen, cannot be exposed to the air without taking fire; but a trace of nickel deprives it of this property.—*Liebig's Annalen*, February, 1848.

Köhler states that protonitrate of mercury may be used for precipitating the cobalt and determining its weight *directly* after the precipitation of the nickel by the peroxide of mercury in the above process. With this view he directs that the liquid from which the nickel has been removed, and which contains the cobalt in the state of cobalticyanide of potassium, be carefully neutralized with nitric acid, and as neutral a solution as possible of protonitrate of mercury added. The whole of the cobalt is precipitated as cobalticyanide of mercury in the form of a heavy white precipitate, which is readily filtered and washed. It then merely requires to be heated with access of air to convert it into black oxide of cobalt.—*Liebig's Annalen*, lxx., p. 256.

MANGANESE.

Separation of Manganese from Cobalt, Nickel, and Zinc—Ebelmen's Method.

1. *From Cobalt.*—The weighed mixture of the two oxides is placed in a platinum or porcelain tray, and heated in a current of sulphuretted hydrogen. The action begins at the ordinary temperature. The mixture gives off considerable heat in the gas. The tube is then raised to a dark red heat: the sulphuret is allowed to cool in a current of the gas, the tray drawn out of the tube, and digested in cold water containing a little hydrochloric acid. The sulphuret of manganese alone is dissolved. After some hours' digestion it is filtered, the liquid boiled—precipitated with potash, and the oxide of manganese determined. The black residue of the sulphuret of cobalt is redissolved in nitric acid, and this solution also precipitated by potash.

2. *From Nickel.*—This is effected in the same manner, and the results are equally accurate.

3. *From Zinc.*—The dry sulphurets are treated with acetic acid, the action of which is assisted by heat, only manganese is dissolved, but the sulphuret of zinc always retains a certain portion of manganese which cannot be separated by this method.

Analysis of Kupfernickel—Ebelmen.—The purified mineral is treated with aqua regia. The sulphuric acid is precipitated by chloride of barium, and the excess of barium being removed by sulphuric acid, the arsenic acid is converted into arsenious acid by ebullition with sulphurous acid, and then precipitated by sulphuretted hydrogen. The sulphuret of arsenic obtained is, after drying and weighing, analyzed by aqua regia, to obtain the sulphur. The liquor freed from sulphuret of arsenic is concentrated with the addition of nitric acid, and precipitated by excess of ammonia; an abundant precipitate of peroxide of iron is formed, which generally retains a little nickel. It is redissolved on the filter by hydrochloric acid, and the liquor treated cold with carbonate of baryta. The peroxide of iron alone is precipitated; the carbonate of baryta with which it was mixed is readily separated. The liquor containing the nickel is treated with sulphuric acid, and after filtration is added to the ammoniacal solution of the rest of the nickel: this is precipitated by excess of potash, and, after drying and calcining, is weighed; its quantity indicates that of the metallic nickel. The ammoniacal liquor, afterwards treated with hydrosulphate of ammonia, sometimes yields a black precipitate, which, collected, calcined, and weighed, gives, with borax, the reaction of cobalt.—*Annales des Mines*, tome xi., p. 56.

IRON.

Analysis of Cast Iron—Wrightson's Method.—The specimen broken to small pieces in a steel mortar is digested for a few hours with hydrochloric acid, the black flakes which remain undissolved are collected on a tared filter, dried at 212°, and weighed; they are then fused with a mixture of nitre and carbonate of soda, and the iron, lime, and silica being separated in the usual manner, the loss indicates the amount of carbon, which may be verified by direct determination in a combustion tube (p. 171, col. 1). The filtered liquid and washings, evaporated to dryness, and again treated with acid and water, usually leaves a minute portion of silica, which is separated, weighed, and added to the former quantity. The iron is peroxidized by nitric acid and *nearly* precipitated by ammonia, the last portions being separated by benzoate of ammonia. The precipitated peroxide of iron being washed, dried, ignited, and weighed, is examined for manganese by fusion with nitrate and carbonate of potash; if care has been taken not to add too much ammonia, no manganese will be found with the iron. The solution from which the iron has been precipitated is evaporated to dryness, and ignited to expel the ammoniacal salts; the residue is redissolved in dilute hydrochloric acid, and ammonia and hydrosulphuret of ammonia added: it is gently warmed and allowed to stand for several hours. The sulphuret of manganese which separates is converted into sulphate, from which the percentage of manganese is calculated. The solution filtered from the sulphuret of manganese contains the lime and alkalies, which are determined in the usual manner.

Determination of Sulphur and Phosphorus.—From 20 to 30 grains of the specimen reduced to fragments are treated with fuming nitric acid and gently warmed: the solution is evaporated to dryness, and the dry mass treated with hydrochloric acid and water; a portion is tested with chloride of barium, and if a precipitate or cloudiness is thereby produced, the whole is treated in the same manner. The sulphate of baryta having been separated and weighed, the excess of chloride of barium is removed by a few drops of sulphuric acid: supertartrate of ammonia is then added in sufficient quantity to prevent the iron from being precipitated by the subsequent addition of ammonia; that alkali is added in considerable excess, and a current of sulphuretted hydrogen passed through the solution for several hours. The solution is allowed to stand in a warm place until it has become of a clear light yellow colour; it is then quickly filtered, and the sulphuret of iron washed with water containing a little hydrosulphuret of ammonia. The solution is evaporated to dryness, and ignited to expel the ammoniacal salts; and the residue, consisting of phosphoric acid with minute portions of lime, alumina, and alkalies, is fused with a little carbonate of potash or soda, and the phosphoric acid is determined in the usual manner as ammonia magnesian phosphate.

Quantitative Determination of Iron in Ironstones—Penny's Method. It is based on the reciprocal action of chromic acid and protoxide of iron, whereby a transference of oxygen takes place, the protoxide of iron becoming converted into the sesquioxide, and the chromic acid into sesquioxide of chromium, thus:

$$2\,CrO_3 + 6\,FeO = Cr_2O_3 + 3\,Fe_2O_3.$$

The iron in *clay-band* and *black-band* ironstone being chiefly in the state of carbonate of the protoxide, when the ore is boiled in hydrochloric acid, the metal is converted into protochloride, and on adding bichromate or neutral chromate of potash to the solution, the chromic acid will be deoxidized, and the protochloride of iron will become sesquichloride, thus:

$$KO,\,2\,CrO_3 + 6\,FeCl + 7\,HCl = 3\,(Fe_2Cl_3) + Cr_2Cl_3 + KCl + 7\,HO.$$

The process is conducted as follows:—A convenient quantity of the specimen is reduced to coarse powder, and one-half at least of this still further pulverized, until it is no longer gritty between the fingers. The test solution of bichromate of potash, is next prepared: 44·4 grains of the salt in fine powder are weighed out, and put into an alkalimeter (graduated into 100 equal parts), and warm distilled water afterwards poured in until the instrument is filled to 0. The palm of the hand is then securely placed on the top, and the contents agitated by repeatedly inverting the instrument until the salt is dissolved and the solution rendered of uniform density throughout. Each division of the solution thus prepared contains 0·444 grains of bichromate, which Dr. Penny ascertained to correspond to half a grain of metallic iron. The bichromate must be pure, and should be thoroughly dried by being heated to incipient fusion. 100 grains of the pulverized ironstone are now introduced into a Florence flask with 1½ oz. by measure of strong hydrochloric acid and ½ oz. of distilled water. Heat is cautiously applied, and the mixture occasionally agitated, until the effervescence caused by the escape of carbonic acid ceases; the heat is then increased, and the mixture made to boil and kept at moderate ebullition for ten minutes or a quarter of an hour. About 6 oz. of water are next added and mixed with the contents of the flask, and the whole filtered into an evaporating basin. The flask is rinsed several times with water, to remove all adhering solution, and the residue on the filter is well washed. Several small portions of a weak solution of pure *red* prussiate of potash (containing 1 part of salt to 40 water) are now dropped upon a white porcelain slab, which is conveniently placed for testing the solution in the basin during the next operation. The prepared solution of bichromate of potash in the alkalimeter is then added very cautiously to the solution of iron, which must be repeatedly stirred, and as soon as it assumes a dark greenish shade, it should be occasionally tested with the red prussiate of potash. This may be easily done by taking out a small quantity on the end of a glass rod, and mixing it with a drop of the solution on the porcelain slab; when it is noticed that the last drop communicates a distinct blue tinge, the operation is terminated. The alkalimeter is allowed to drain for a few minutes, and the number of divisions of the test liquor consumed read off. This number multiplied by 2 gives the amount of iron per cent. The necessary calculation for ascertaining the corresponding quantity of protoxide is obvious. If the specimen should contain peroxide of iron, as is the case with most of the common ironstones of this country, the hydrochloric solution must be boiled with sulphite of soda previous to the addition of the bichromate; the peroxide becomes thus reduced to protoxide, and a few minutes' ebullition suffices to decompose the excess of sulphite of soda, and to expel effectually every trace of sulphurous acid. The presence of peroxide of iron in an ore is easily detected by dissolving 30 or 40 grains in hydrochloric acid, diluting with water, and testing a portion of the solution with *sulphocyanide of potassium;* if a decided blood-red colour is produced, peroxide of iron is present. In reference to *Marguerite's* method (p. 170, col. 2), *Dr. Penny* makes a remark, which I believe will be assented to by every chemist who has employed it, viz., that, though elegant and exact, it is objectionable on account of the decomposition of the permanganate of potash by keeping, even in well-stoppered bottles, so that it becomes necessary to test its strength anew previous to every series of experiments.—*Proc. of Brit. Assoc., Edinburgh*, 1850.

URANIUM.

Test for ascertaining the Value of Uranium Ores—Patna.—A weighed quantity of the ore is dissolved in pure nitric acid, the liquid filtered from the insoluble silica, and mixed with an excess of carbonate of potash. There is thus obtained in solution a neutral uranate of potash, probably contaminated with arsenic and sulphuric acids. All the other metals present in the ore are precipitated as carbonates, and are removed by filtration. The neutral uranate of potash is evaporated to dryness in a gilt silver dish, and heated to redness when bi-uranate of potash is formed, which is insoluble in water, is very easily washed, and from which the amount of uranium may be calculated.

Lead; Bismuth.

Detection of Lead in the Presence of Bismuth in Blowpipe Experiments—Chapman's Method.—The only metals, which when heated before the blowpipe deposit a yellow oxide on the support, are *cadmium*, *lead*, and *bismuth.* The former, from its volatility, is never obtained in the metallic state; the production, therefore, of a metallic globule with a yellow incrustation indicates lead or bismuth, or both. The detection of bismuth is not difficult. The assay is treated with microcosmic salt in the reducing flame with the addition of a minute particle of tin, when the glass, which is colourless and quite transparent while hot, becomes on cooling grayish black and opaque, if bismuth be present. A similar reaction is produced with antimony, but that metal is entirely got rid off by fusing the assay with vitrified boracic acid in the oxidating flame, and the lead and bismuth, if present, are retained as oxides, and may be again brought to the metallic state by fusion in the reducing flame with carbonate of soda. The detection of a small quantity of lead, when mixed with a large quantity of bismuth, is effected by Mr. Chapman thus:—A small crystal of nitrate of bismuth is placed in a small porcelain crucible, and moistened with a few drops of water, the greater part of which is afterwards poured off, and the metallic button as obtained by the blowpipe, having been slightly flattened on the anvil until it begins to crack at the sides, is then placed in the midst of the subsalt of bismuth formed by the action of the water, when, in the course of a minute or less, minute arborescent crystals of metallic bismuth form and collect round the assay, provided the assay contained any lead. Mr. Chapman states that he has found this method to succeed perfectly with brittle alloys containing upwards of 85 per cent. of bismuth.

Silver.

Separation of Silver from Cupreous Solutions—Bolley's Method.—The solution is boiled with cane sugar and potash, or ammonia, and any precipitated oxide or protoxide of copper extracted with acetic acid. The silver is obtained as a mirror, and sometimes in the form of a powder.—*Jahrb. für Prakt. Chem.*, xviii. 384.

Removal of Silver Stains from the Skin.—*Brieger* recommends to brush the spot over with a solution of iodine in alcohol, and to wash immediately afterwards with a moderately-dilute solution of caustic potash.—*Jahrb. für Prakt. Chem.*, xx. p. 90.

Copper.

Estimation of Copper—Brunner's Method.—Instead of dissolving the precipitated sulphuret of copper in aqua regia, and precipitating the oxide by caustic potash (p. 185, col. 1), *Brunner* describes as a more ready and sure method to heat the sulphuret in a glass tube, while a current of hydrogen is passed over it; it is then reduced to the state of subsulphuret, the weight of which is precisely equal to that of the oxide of copper corresponding to the same quantity of metal.—*Bibliothèque Universelle, April,* 1851.

Antimony; Arsenic; Tin.

Separation of Antimony from Arsenic—Meyer's Method.—This is founded on the insolubility of antimoniate of soda. The mixture of the two metals is deflagrated with three times its weight of nitrate and carbonate of soda, the fused mass is washed with cold water, the whole of the arsenic passes through in solution, and may be precipitated with sulphuretted hydrogen, and determined in the usual manner.—*Leibig's Annalen, May*, 1848.

Qualitative Determination of Tin, Antimony, and Arsenic—Fleitmann.—With regard to the discrimination of tin and antimony, this is founded on the solubility of metallic tin in strong muriatic acid, and the insolubility of antimonial stains obtained according to Marsh's method (p. 52, col. 2) in hypochlorite of soda. When the muriatic solution of the two metals is treated with some metallic zinc, they are both precipitated, the antimony with disengagement of antimoniuretted hydrogen. When the precipitation is made in a small apparatus for the disengagement of hydrogen, the antimony is readily detected by the black stains insoluble in hypochlorite of soda, which it produces on a piece of porcelain, when subsequently the precipitated metallic powder of tin and antimony is boiled with strong muriatic acid, only tin dissolves forming protochloride, which, after subsequent dilution with water, is recognised by the brownish black precipitate produced by sulphuretted hydrogen. Neither of these reactions are modified by the presence of arsenic. The detection of arsenic when antimony is present, is founded upon a remarkable difference which these two metals exhibit towards nascent hydrogen when the latter is disengaged from an alkaline liquid. When a strongly alkaline solution of antimony is heated with metallic zinc, antimony is precipitated simultaneously with a lively disengagement of pure hydrogen, which does not show the slightest reaction of antimoniuretted hydrogen. If, on the contrary, a substance containing arsenic acid is mixed with an excess of potash, and some finely-divided zinc, the hydrogen given off on the application of heat is abundantly charged with arseniuretted hydrogen. The presence of this latter is ascertained most simply by holding a strip of paper dipped in nitrate of silver over the arseniferous mixture of potash and zinc; with the slightest trace of arsenic the paper is coloured distinctly black.—*Liebig's Annalen, Jan.*, 1851.

The distinguishing Reactions of the Arsenical and Antimonial Spots (p. 52, col. 1).—*Dr. Douglas Maclagan* (*Edinburgh Monthly Journal*, Nov., 1848) thinks that the two metals may be easily and readily discriminated, even in very minute quantities, without the employment of any chemical reagent whatever, by the difference of temperature at which they respectively undergo sublimation. According to his own observations, the temperature at which arsenious acid begins to sublime in a glass tube is about 380°; but he has not been able to observe metallic arsenic to sublime below 500° unless it became oxidated. In a medico-legal point of view, however, the question to be considered is, whether we can by a simple means obtain a regulated heat at which metallic arsenic will sublime and become oxidated, whilst antimony will undergo no such change. This can be easily accomplished by means of a bath of olive oil, which may be urged even to its boiling point without at all affecting an antimonial stain, while the heat so employed will entirely sublime an arsenical crust into a crystalline sublimate of arsenious acid; stains which are so faint as not to appear distinctly metallic till the tube is held over a sheet of white paper may be distinguished in this way. If, in addition to the disappearance of the stain from the portion of the tube immersed in the oil (in which a thermometer should be plunged, that the extreme temperature employed may be stated in evidence if asked for), we can observe the formation of a crystalline sublimate in the upper portion of the tube, the proof may be said to be absolute. Dr. Maclagan states that he has operated upon stains produced from a Marsh's apparatus, which contained less than a thousandth of a grain of arsenic, and has been able to see distinctly the crystalline character of the sublimate.

The following chemical reactions have been described by *Mr. Slater* (*Chem. Gaz.*, Feb. 1, 1851):—If a drop of bromine is placed on a saucer, and a capsule containing arsenical spots inverted over it, the spots take a very bright *yellow* tinge in a short time. Antimonial spots, under the same circumstances, are acted upon much more rapidly (in about five seconds at 52° Fahr.), and assume an *orange* shade. Both become colourless if exposed to the air, and are again restored if treated with a strong solution of sulphuretted hydrogen. The secondary yellow of the arsenical spots, as observed by *Lassaigne*, disappears on the addition of ammonia, whilst that of antimonial spots remains untouched. A concentrated solution of iodate of potash turns arsenical spots of a *cinnamon-red*, and dissolves them almost immediately. On antimonial spots it has no visible action within three or four hours. Solutions of hypochlorites (chlorides) of soda and lime, or chlorine water, dissolve arsenical spots instantaneously, leaving those of antimony. A concentrated solution of chlorate of potash gradually acts upon arsenical spots, but not upon those of antimony. Nitroprusside of potassium, on the other hand, slowly dissolves antimony, producing no sensible effect upon arsenic. Of these reactions the most decisive are those of iodate of potash, hypochlorites of soda and lime, and fresh chlorine water.

Quantitative Determination of Antimony—Rosé.—Dilute solutions of antimony, in which the amount of metal is to be determined, must not be concentrated by evaporation when they contain hydrochloric acid, as is almost always the case, because perchloride of antimony escapes with the vapours of acid. The volatilization of the metal cannot be prevented by the addition of sulphuric acid, but it may be pretty nearly by nitric acid. The estimation of sulphur in precipitated sulphuret of antimony may be made by treating a weighed quantity of it with hydrochloric acid, perchloride of antimony ($Sb\ Cl_3$) corresponding in composition to antimonious acid, is formed, and the equivalent quantity of sulphur escapes in the form of sulphuretted hydrogen. The remainder of the sulphur separates in the solid form, and after boiling with hydrochloric acid, it may be collected on a filter, washed, first with water containing some muriatic and tartaric acids, and lastly with pure water; its weight indicates the amount of the sulphuret of antimony.

Separation of Antimony from Tin and Arsenic.—The mixture of stannate and antimoniate of soda obtained by acting on the alloy with nitric acid, and subsequently fusing with hydrate of soda (p. 199, col. 2), is first washed thoroughly out of the crucible with water, and the insoluble antimoniate of soda allowed to separate. The solution which contains all the stannate of soda is now mixed with so much alcohol (specific gravity, 0·83), that its volume relatively to that of the water is as 1 to 3. In this spirituous solution the stannate of soda is completely soluble, while the last portions of antimoniate of soda are completely separated. The clear liquid having been filtered off, the antimoniate of soda is washed with stronger alcohol till some of the filtered liquid, rendered acid with a little dilute sulphuric acid, gives no longer a precipitate with sulphuretted hydrogen. The solution is heated to expel the alcohol, diluted with water, supersaturated with sulphuric acid, precipitated with sulphuretted hydrogen, and the sulphuret of tin converted into oxide. The antimoniate of soda is dissolved in a mixture of muriatic and tartaric acids, from which solution the antimony is precipitated by sulphuretted hydrogen. When arsenic is present in the alloy it is found in the solution containing the stannate of soda; this solution is supersaturated at once with hydrochloric acid without previously driving off the alcohol, and sulphuretted hydrogen passed through it without previously separating the precipitated arseniate of tin. The whole is set aside till it scarcely smells of sulphuretted hydrogen, and the precipitate collected on a weighed filter. The filtered liquid is heated for some time, by which any portion of sulphuretted hydrogen still present, and the greater portion of the alcohol, are expelled. It is then mixed with a solution of sulphurous acid, and again treated with sulphuretted hydrogen, when generally a further small quantity of sulphuret of arsenic is precipitated. This treatment with sulphurous acid is not, however, necessary, if sulphuretted hydrogen is again passed immediately through the liquid separated from the sulphurets. The small amount of sulphuret of arsenic which is precipitated in this case is always free from every trace of sulphuret of tin, and is kept separate, and only added to the sulphuret of arsenic obtained in the separation of the arsenic and tin. These two metals contained in the precipitate by sulphuretted hydrogen are separated by being heated in a current of sulphuretted hydrogen, when the sulphuret of arsenic is volatilized. The residual sulphuret of tin is converted into oxide, and the sublimed sulphuret of arsenic into arsenic acid. This method proved on examination to be absolutely accurate.—*Poggendorff's Annalen*, lxxvii. p. 110.

According to *Ullgren* (*Liebig's Annalen*, March, 1849), when antimony and arsenic are contained in a muriatic solution, the arsenic acid is converted by chlorine or an alkaline hypochlorite into arsenic acid, the solution mixed with a large excess of tartaric acid, then with a soluble salt of magnesia, and lastly supersaturated with ammonia. The basic arseniate of ammonia and magnesia falls, while not a trace of antimony is precipitated. The precipitate is washed with dilute ammonia. Both substances are now separated, and their amount can be readily determined according to the usual processes. *Rosé* also (*Berlin Berichte*, 1849) gives the preference to this method of determining arsenic, which was first proposed by *Levol*. The best way of converting arsenious into arsenic acid is by means of chlorate of potash and hydrochloric acid, avoiding a strong or long-continued heat. The precipitated arseniate of ammonia and magnesia should be dried at 212° till it ceases to lose weight; its composition is then $2\ MgO,\ NH_4O,\ AsO^5 + HO$.

Extraction of Arsenic from Organic Matters.—The precipitated sulphuret of arsenic obtained by passing sulphuretted hydrogen into a liquid prepared from an organic mixture by muriatic acid and chlorate of potash as directed (p. 53, col. 1), always contains some organic sulphurous matters which it is necessary to destroy before subjecting it to Marsh's test. This is best effected, according to *Wöhler* (*Liebig's Annalen*, March, 1849), in the following manner:—The filter with the precipitate is placed in a sufficiently capacious porcelain crucible, concentrated and *perfectly pure* nitric acid in sufficient quantity poured over it, and then digested until the whole is dissolved, and forms a homogeneous mass. The free nitric acid contained in it is saturated by the gradual addition of pure carbonate of soda, and the mass cautiously evaporated to dryness. The crucible is now heated over an Argand lamp gradually, until the nitrate of soda fuses. At first the mass turns brown, then black, and melts quietly, without any deflagration to a perfectly colourless transparent liquid. Every trace of organic matter is now perfectly destroyed, and the whole of the arsenic converted into arseniate of soda. Concentrated pure sulphuric acid is now gradually dropped upon the cold hard saline mass in the crucible, and finally warmed with it, until, after the addition of excess of acid, the whole of the nitric and nitrous acids have been completely expelled, and the mass is converted into bisulphate of soda. The acid saline mass is now dissolved in the crucible in the smallest possible amount of hot water, and this solution then gradually poured by means of a funnelled tube in the usual way into Marsh's apparatus, which has been previously exhausted of air and filled with hydrogen gas.

Nothing, observes *Wöhler*, is more easy than the detection of arsenic in an organic substance, even when this contains a mere imponderable trace; the great difficulty, and that which occasions anxiety and danger in such disagreeable tasks, is in the employment of reagents and apparatus to avoid the introduction of arsenic into the examination, and finding the poison where in reality it did not originally exist.

Analysis of Tin Ores—Rivot's Method.—The mineral reduced to a fine powder, is gradually heated to redness in a current of dry hydrogen, by which the oxides of iron and tin are completely reduced. The time requisite for reduction is about an hour and a half for 15 to 20 grains of the ore. It is allowed to cool in the hydrogen, then weighed, when the loss in weight gives the oxygen combined with the iron and the tin. By treating the substance with aqua regia, the iron and tin are dissolved; the gangue remains unattacked, and may be analyzed in the usual way. Ammonia is added to the solution of tin and iron to saturate the acids, and a sufficiently large excess of sulphuret of ammonium to dissolve the sulphuret of tin; it is then allowed to digest for about twelve hours, and filtered; the sulphuret of iron, after being well washed with water charged with hydrosulphate of ammonia, is converted into peroxide of iron; the sulphuret of tin in solution in the hydrosulphate of ammonia is precipitated by acetic acid, and converted, by roasting, into oxide of tin. The weight of the peroxide of iron, and of the binoxide of tin, indicates the weight of the iron and of the metallic tin, while the loss of weight of the mineral in hydrogen shows the amount of oxygen combined with the two metals, and enables us to determine their state of oxidation.

SULPHUR.

Determination of Sulphur in Nitrogenous Organic Compounds—Fleitmann.—Sulphur exists in nitrogenous organic substances, such as caseine, albumen, and fibrine, in two different forms; one portion is removed by heating the substance in a concentrated solution of caustic potash; the other portion remains combined with the organic substance. *Fleitmann* determines the amount of this combined sulphur, by first dissolving the compound in caustic potash, and then digesting the solution for some hours, with frequent agitation, with a sufficient quantity of recently-precipitated hydrated oxide of bismuth; when cold, the liquid is supersaturated and digested for some time with excess of acetic acid; it is then filtered, and the washed sulphuret of bismuth is oxidized with the filter in a silver crucible, by fusion with potash and nitre, and the sulphur thus converted into sulphuric acid is determined in the usual way as sulphate of baryta.

Nitroprusside of Sodium as a Test for Sulphur.—Any substance containing sulphur, when heated with carbonate of soda, either with or without the addition of carbonaceous matter, according as a deoxidizing action is or is not required, will yield an alkaline sulphuret. On adding the fused mass to a drop of the solution of nitroprusside of sodium, a magnificent purple colour is produced. This test is so delicate that, according to *Bailey* (*Silliman's Journal*, May, 1851), the presence of sulphur may be detected in the smallest particles of coagulated albumen, horn, nails, feathers, mustard seed, &c., which can be conveniently supported on a platinum wire for blowpipe experiments. *Dana* (*Silliman's Journal*, Nov., 1851) gives the following more minute directions for the use of this elegant test:—Heat, by the blowpipe, any sulphuret or sulphate (or anything containing sulphur) upon charcoal, with carbonate of soda; put the fused mass into a watch glass, with a drop of water, and a particle not larger than a pin's head of the nitroprusside of sodium; there will be a magnificent purple at once. When this test is tried on parings of nails, hair, albumen, &c., *Dana* advises that the carbonate of soda be mixed with a little starch, which appears to prevent the loss of any sulphur by oxidation. If a piece of hair four inches long be coiled round one point of a platinum support, moistened, dipped into a mixture of carbonate of soda with starch, and then heated by the blowpipe, the fused mass will give with the nitroprusside an unmistakable action indicative of sulphur.

Estimation of Sulphur in Volatile Organic Compounds—Debus—Liebig's Annalen, Oct., 1850.—One equivalent of bichromate of potash which has been purified by recrystallization, is dissolved with two equivalents of carbonate of potash, or soda, in water, and the liquid evaporated to dryness; in this way, a lemon-coloured mass, consisting of one equivalent of neutral chromate of potash and half an equivalent of carbonate of potash or soda, is obtained. It is powdered, and, in order to remove the last portions of water, exposed to a good red heat in a Hessian crucible, and then filled while hot, into a glass tube sealed at one end and drawn out somewhat at the other, so that when wanted, the chromate of potash can be conveniently poured into the combustion tube without loss. This precaution is necessary with the use of carbonate of potash, as it absorbs water from the air, and, on being subsequently heated in the combustion-tube, again parts with it, and cracks the tube. After the chromate of potash has cooled in the above-mentioned corked glass tube, a layer of it of about three to four inches in length is poured into a combustion-tube, such as is used in organic analysis; the substance then added, and then again a few inches of the mixture of chromate and carbonate of potash. When the substance to be analyzed is a solid, it is intimately mixed with the chromate of potash in the combustion-tube, by means of a wire, twisted at one end like a corkscrew. When this is done, the empty portion of the combustion-tube is filled with a mixture of chromate and carbonate of potash, placed in a furnace, and heated as for an organic analysis. When the whole is incandescent, oxygen is disengaged from a small retort, and passed in a slow current over the red-hot mixture for about half an hour or an hour. When cold, the tube is cleansed of adherent ash, cut into several pieces over a sheet of paper, these placed in a beaker, and so much water poured over them as may be necessary to dissolve the calcined mass. The liquid thus obtained is strongly acidified with hydrochloric acid, the chromic acid reduced with alcohol, and boiled till it becomes green. It is now filtered from the insoluble oxide of chromium, which is washed, first with water acidified with hydrochloric acid, afterwards with alcohol, and then dried. The filtered green liquid, which contains nearly the whole amount of sulphuric acid, is placed aside for a time, and the oxide of chrome collected on the filter, which always most tenaciously retains a small quantity, frequently one to two per cent., of sulphuric acid, in the form of a basic salt, is dried. The oxide of chrome is then emptied into a platinum crucible, and the filter burnt. It is mixed with one part of chlorate and two of carbonate of potash, and heated to redness until the whole of the oxide of chrome is converted into chromate of potash. The fused mass is dissolved in dilute muriatic acid, the chromic acid reduced by alcohol, and the liquid added to that previously obtained. The united solutions are now heated to boiling, the sulphuric acid precipitated with chloride of barium, and the amount of sulphur calculated from the sulphate of baryta.

PHOSPHORIC ACID.

Separation of Peroxide of Iron from Phosphoric Acid in the Presence of Alkaline Earths—Fresenius.—The solution is heated to boiling, removed from the lamp, and a solution of sulphite of soda added, until the colour has become pale green, and carbonate of soda produces a white precipitate; it is then boiled until the smell of sulphurous acid has disappeared, any excess of free acid neutralized with carbonate of soda, a few drops of chlorine water added, and, lastly, an excess of acetate of soda. The smallest quantity of phosphoric acid is immediately detected by the production of a white flocculent precipitate of perphosphate of iron. Chlorine water is now added gradually until the liquor appears reddish; it is then always turbid. It is boiled until it has become clear, which soon results, filtered hot, and the precipitate washed with hot water. This precipitate contains the whole of the phosphoric acid, as perphosphate of iron mixed with a minute quantity of basic peracetate of iron; the solution contains nearly the whole of the iron and the lime and magnesia, which are easily separated by sulphuret of ammonium, oxalate of ammonia, and phosphate of soda. The phosphoric acid is separated from the iron in the precipitate by dissolving it in muriatic acid, reducing it with sulphite of soda as above, and then boiling with caustic potash or soda (free from alumina), till it becomes black and granular; it is dissolved in muriatic acid, and united to the other solution of iron. The filtered solution contains the phosphoric acid which is precipitated in the usual manner, as ammonio-phosphate of magnesia.

Of the many methods that have been proposed for separating phosphoric acid from iron in the presence of alkaline earths, this is, perhaps, the best and least troublesome, but it is not perfectly accurate. I have lately employed it in the analysis of the mineral constituents of the blood, and previous to employing it for this purpose I tried it on prepared mixtures, containing known quantities of peroxide of iron, lime, magnesia, and phosphoric acid; the alkaline earths were very exactly separated, but the phosphoric acid could not be subsequently entirely separated from the peroxide of iron, either by sulphite of soda and caustic potash, or by ammonia and sulphuret of ammonium. I found, however, in accordance with the statement of Fresenius, that the separation of the phosphoric acid is much more accurately effected by this method than by fusing the compound with carbonated alkali and exhausting with boiling water. In analyzing the insoluble portion of the ash of blood, the whole of the iron is carried down with the perphosphate, not a trace passing through in solution with the lime and magnesia.

The analysis of a compound containing a large amount of peroxide of iron, protoxide of manganese, alumina, lime, magnesia, phosphoric acid, sulphuric acid, arsenic acid, silicic acid, and sand (iron ores), is thus effected. A weighed quantity (which should not be too small) of the finely-pulverized mineral is digested with moderately dilute muriatic acid in a flask, at a temperature near to the boiling point, until all that is soluble has passed into solution. The liquid is diluted, passed into a filter of known weight of ash, and the residue washed. With brown iron ore the quantity is in general very small. It is dried with the filter, carefully separated from it, calcined, and weighed. It is then transferred into a boiling solution of carbonate of soda, allowed to boil for some time, filtered through the filter first employed, washed, dried, calcined, and weighed. The difference between this weight (sand and alumina) and the one first obtained gives the amount of insoluble residue, or silicic acid.

The ferruginous muriatic solution is filtered from the residue, carefully evaporated to perfect dryness, and kept for some time at a temperature slightly above that of boiling water. After it has been moistened with muriatic acid, and kept for some time with it at a gentle heat, water is added, and any silica separated by filtration. Its weight, added to that above obtained, gives the total amount of silicic acid in combination.

The ferruginous solution is heated to boiling in a flask, and reduced as above with sulphite of soda. When the whole of the sulphurous acid has been expelled by boiling, sulphuretted hydrogen is passed into the liquid until it is saturated with it. The precipitate produced is the protosulphuret of arsenic. The amount of arsenic contained in it is ascertained, after deducting the sulphur in it, which has been previously determined as sulphate of baryta, from its weight determined at 212°. If the precipitate does not appear yellow, but brown or black, there is reason to suspect some other metallic oxides, and it must be further examined in the ordinary manner. The liquid filtered from the protosulphuret of arsenic is boiled to expel the whole of the sulphuretted hydrogen, then precipitated with carbonate of soda, and boiled with excess of soda until the precipitate appears black and granular. It is allowed to subside, the clear liquid poured off, the precipitate washed by decantation with hot water, and finally brought upon a filter of close texture and washed with hot water.

Treatment of the Precipitate.—It is digested, filter and all, in hydrochloric acid, filtered, and washed. The solution is reduced with sulphite of soda, exactly as above described, nearly neutralized with carbonate of soda, heated to boiling, mixed with a few drops of chlorine water, then with an excess of acetate of soda, and, when the liquid or the precipitate has not a reddish tint, chlorine water is added until this is the case. The whole is boiled until the precipitate has separated, filtered hot, and the precipitate, consisting of phosphate and some basic acetate of peroxide of iron, washed.

α. The filtered solution is precipitated, after the addition of ammonia and while hot, with sulphuret of ammonium, filtered quickly, and the precipitate, consisting of protosulphuret of iron and manganese, washed uninterruptedly with hot water. The lime in the solution is determined by oxalate of ammonia and the magnesia by phosphate of soda, the precipitated sulphurets are dissolved in muriatic acid, oxidized with chlorate of potash or nitric acid, boiled until all the chlorine is expelled, allowed to cool to about 140° nearly neutralized with carbonate of soda, the peroxide of iron precipitated with carbonate of baryta, and the other oxides estimated in the usual manner.

β. The precipitate containing the perphosphate of iron is dissolved in muriatic acid, reduced with sulphite of soda, boiled for some time with an excess of caustic soda, and filtered. The solution containing the phosphoric acid is supersaturated with muriatic acid and set aside. The precipitate of protoperoxide of iron is also dissolved in muriatic acid, oxidized with nitric acid, the solution added to the principal solution of the iron, separated from the manganese and baryta, and the whole precipitated with ammonia.

Treatment of the Filtered Alkaline Solution.—It is rendered acid, boiled with some chlorate of potash, precipitated with ammonia (avoiding a large excess), and chloride of barium added as long as a precipitate appears. After digesting for some time it is filtered. The precipitate which contains the whole of the alumina and phosphoric acid (the latter combined partly with alumina and partly with baryta) is collected upon a filter, washed with a little water, and dissolved in as little muriatic acid as possible. The solution is saturated with carbonate of baryta with the assistance of heat, an excess of caustic soda added, and heat applied. Any baryta contained in the solution is precipitated by carbonate of soda, and filtered. The whole of the alumina is now in solution, and the whole of the phosphoric acid in the precipitate. The solution is rendered acid with muriatic acid, boiled with chlorate of potash, precipitated with ammonia, allowed to stand for some time in a warm spot, and the alumina filtered, washed, calcined, and weighed. The precipitate is dissolved in muriatic acid, and the baryta is precipitated with dilute sulphuric acid. The solution containing the phosphoric acid is united with the above-mentioned liquid containing the other portion of phosphoric acid, supersaturated with ammonia, and precipitated with sulphate of magnesia, with the addition of chloride of ammonium if necessary.

The sulphuric acid in the mineral is determined in a separate portion by dissolving it in muriatic acid and precipitating with chloride of barium.

It is of importance, before commencing the quantitative analysis, to ascertain the presence or absence of alumina, manganese, and alkaline earths; for when no alumina is present the first precipitation with carbonate of soda and the boiling with caustic soda may be omitted: the whole of the phosphoric acid is contained in the alkaline liquid holding the alumina in solution, when no alkaline earths are present; and the residue which had remained undissolved by the potash may be at once treated for the separation of iron from manganese; or, when no manganese is present, precipitated at once with ammonia from the muriatic solution after previous oxidation, calcined, and calculated as peroxide of iron.—*Journ. für Prakt. Chem.*, Nov. 1, 1848.

The different methods proposed for the separation of phosphoric acid from bases have been submitted to a critical examination by *Prof. Rosé* (*Poggendorff's Annalen*, March, 1849). With regard to its estimation as ammonio-magnesian phosphate, it had been shown by *Weber* (p. 213, col. 1) that correct results are only obtained when the acid is in its tribasic modification, and, in this case, certain precautions must be observed; for example, the solution, after the addition of the sulphate of magnesia, ammonia, and chloride of ammonium, must not be boiled, but only warmed, and filtered after some hours. It will not do to neutralize with carbonate of ammonia instead of with pure ammonia, for then *ammonio-carbonate* of magnesia is slowly deposited, frequently coating the glass in stellate groups of crystals. Peroxide of iron cannot be entirely separated from phosphoric acid by digesting with hydrosulphuret of ammonia; the phosphate of magnesia obtained always contains iron. *Weber* was not more successful in effecting the separation in the dry way, viz., by fusing the phosphatic compound with three times its weight of carbonate of soda and sulphur in a porcelain crucible. *Berthier's* method, by adding to the solution of the alkaline phosphate a known quantity of solution of pure iron, and then precipitating by ammonia (p. 214, col. 1), does not give accurate results, especially when the solution contains pyrophosphoric acid; but with the following modification proposed by *Von Kobell* very satisfactory results are obtained, and it is moreover applicable to the separation of phosphoric acid from magnesia, and from all those metallic oxides which belong to the strong bases and are not precipitated in the cold by carbonate of baryta.

Von Kobell's Method.—The phosphatic compound being dissolved in hydrochloric acid, the solution is mixed with a solution of a known quantity of peroxide of iron, and then in the cold with an excess of carbonate of baryta instead of with ammonia; the whole of the phosphoric acid combined with peroxide of iron is precipitated by the carbonated earth, whilst the metallic oxide is held in solution combined with hydrochloric acid.

When the amount of peroxide of iron added is known, it is merely requisite to dissolve the washed and gently-calcined precipitate, and to precipitate the baryta from the solution by sulphuric acid, in order to calculate from the weight of the sulphate of baryta the amount of carbonate of baryta, which will then furnish the amount of phosphoric acid. The baryta dissolved in the liquid separated from the precipitate is removed by sulphuric acid, and the amount of base which has been combined with phosphoric acid determined. As the precipitate produced by carbonate of baryta is very bulky, *Von Kobell* proposes, when the object is mere separation, to treat the phosphate (if the base is insoluble in a solution of hydrate of potash,) previously, with this reagent, in order to remove the greater portion of the phosphoric acid; only a small quantity of solution of iron need then be added to the compound treated with potash, and the precipitate is less bulky. *Rosé* also obtained good results by employing carbonate of baryta alone, without any addition of solution of iron. Phosphates of *baryta*, *strontia*, and *lime*, particularly the last, are not completely decomposed by fusion with carbonated alkali; phosphate of *magnesia is* completely decomposed when a mixture of carbonate of potash and carbonate of soda in equivalent proportions is used. The phosphates of *zinc*, *manganese*, and *iron*, are completely decomposed by a similar treatment, and *Rosé* considers the method of decomposing the phosphate of iron by fusion with carbonate of soda far preferable to treating the solution in acids with sulphuret of ammonium.

From *oxide of uranium* and from *chromic acid* phosphoric acid may be separated by fusing the compound with three times its weight of carbonate of soda and as much cyanide of potassium, digesting the fused mass with water, filtering, supersaturating the filtrate with hydrochloric acid, and precipitating the phosphoric acid as ammonio-magnesian phosphate. After discussing various other methods, and showing their general inaccuracy, *Rosé* describes the following method for separating phosphoric acid from all bases by a single operation as being both accurate and quick.

Separation of Phosphoric Acid from Bases by means of Nitric Acid and Metallic Mercury.—The phosphatic compound is dissolved in a sufficient quantity of nitric acid, the solution is conveyed to a porcelain dish, and so much metallic mercury added that a small portion is left undissolved by the free acid. It is then evaporated to dryness on the water bath; the dry mass again moistened with water, and again evaporated, this operation being repeated until the dry mass no longer smells of nitric acid while warm. It is next mixed well with water, filtered through a small filter, and washed till a few drops of the wash water leave a residue, which disappears entirely on ignition. The filtrate contains all the bases combined with nitric acid together with protonitrate of mercury, which is separated by hydrochloric acid, the solution is again filtered and quickly washed, some chloride of ammonium having been previously added. If no iron or alumina are present, the alkalies, lime, magnesia, and other metallic oxides existing as nitrates in the filtered liquid, are separated from each other in the usual manner; or the protonitrate of mercury may be removed from the solution of the nitrates by evaporating the solution in a porcelain dish, and exposing the residue to a red heat in a platinum crucible. It should, however, be observed that, when alkaline nitrates are present, the dry residue on ignition must be mixed with a small quantity of dry carbonate of ammonia in order to convert into carbonates the free alkalies produced by the decomposition of the nitrates. If this precaution is neglected, the platinum crucible is very much acted upon. The calcined residue is dissolved in dilute hydrochloric acid, and the bases separated in the usual manner.

The phosphoric acid remains on the filter in combination with the mercury. There are likewise present protonitrate and metallic mercury. The whole is well dried, removed from the filter, and mixed in a platinum crucible with an excess of carbonate of soda, the filter is rolled up and thrust into the mixture, which is then covered with a layer of carbonate of soda, and exposed for half an hour under a chimney to a moderate, but not red, heat, that the contents may not fuse. At this temperature the whole of the metallic mercury and the mercurial salts, with the exception of the protophosphate, are expelled. The mass is now fused, and the fused mass treated with hot water, in which it dissolves entirely if the operation has been conducted with care, and no iron was present. It is supersaturated with hydrochloric acid, and the phosphoric acid estimated as ammonio-magnesian phosphate. When *peroxide of iron* is present, the greater portion is left on treating the dry residue with water with the protophosphate of mercury, and only a small portion dissolves with the nitrates; it is filtered and washed in the usual way, the peroxide of iron in the solution determined with the other bases, and the insoluble portion fused with carbonate of soda. On treating the fused mass with water, the peroxide of iron is obtained perfectly free from phosphoric acid, whilst the entire amount of phosphoric acid in combination with soda is dissolved. When *alumina* is present this method becomes inapplicable; but *Rosé* has since (*Bericht der Berliner Academie*, 1849, p. 220) given another, which he has found most advantageous for analyzing quantitatively complex phosphatic compounds containing alumina, such as rocks, soils, &c. The substance is dissolved in hydrochloric acid, and after dilution with water, a sufficient quantity of carbonate of baryta added. After it has stood for a couple of days in the cold, having been frequently agitated, it is filtered, and the insoluble residue washed with cold water. The filtered solution contains the bases which were combined with the phosphoric acid, except *alumina*, *peroxide of iron*, and other weak bases. These, as well as the whole amount of phosphoric acid, are thus completely precipitated. The dissolved baryta is removed from the solution by sulphuric acid. This is somewhat difficult when much lime is present. In the filtered solution the bases are determined according to the usual methods. The insoluble residue contains the whole amount of phosphoric acid which was present in the compound, as well as the alumina and the peroxide of iron. It is dissolved in dilute hydrochloric acid, and the baryta removed by sulphuric acid. The filtered solution is saturated with carbonate of soda and evaporated to dryness. The dry mass is mixed with silica and carbonate of soda, and heated to redness. The calcined mass is digested in water, and carbonate of ammonia added to it, when a considerable amount of silica is precipitated; it is filtered; the filtered liquor which contains the whole of the phosphoric acid is precipitated as ammonio-phosphate of magnesia. The insoluble residue is digested with muriatic acid, and the whole evaporated to dryness. The dry mass is moistened with hydrochloric acid, and the silica separated in the usual manner, after which the alumina and peroxide of iron are determined.

Molybdate of Ammonia as a Test for Phosphoric Acid.—The solution to be tested is mixed with molybdate of ammonia, and an excess of nitric acid added; if phosphoric acid be present, the solution assumes a yellow colour, and there appears, either immediately, or after some time, a yellow precipitate of molybdic acid, containing phosphoric acid. As the native sulphuret of molybdenum frequently contains phosphoric acid, it is always necessary to ascertain whether the molybdate of ammonia prepared from it does not give by itself a yellow precipitate upon addition of an excess of acid.

This reaction is only applicable to the detection of ordinary phosphoric acid. If the phosphate is insoluble in water, the test is best applied to the nitric acid solution.

Quantitative Determination of Phosphoric Acid—Ullgren.—The author gives two methods for separating phosphoric acid in the analysis of iron and iron ores, both of which he states to give satisfactory results. According to the first method, the nitric solution is evaporated to the thickness of a syrup after the addition of a little hydrochloric acid. This solution, somewhat diluted, is poured, with constant stirring, into a solution of sulphuret of potassium and silicate of potash, the former of which must be present in larger quantity than is sufficient to precipitate the iron; for every 15 grains of iron, 75 grains of sulphuret of potassium (prepared by igniting 1 part of soot with 3½ parts of sulphate of potash), and 15 grains of silica glass (prepared by melting 1 part of powdered quartz with 4 parts of carbonate of soda). The precipitate contains the whole of the electro-positive metals in the form of sulphurets, and the lime, magnesia, and alumina as silicates; while the solution contains phosphate of potash, and the sulphur salts of the electro-negative metals. Upon filtering, a clear liquid passes at the commencement, afterwards becoming greenish and cloudy; this may, however, be prevented by a previous addition of fresh precipitated hydrated oxide of lead in sufficient quantity. By this means the electro-negative sulphurets are removed by the decomposition of the sulphuret of potassium by the oxide of lead. The precipitate on the filter is then washed with water containing one-tenth of its volume of a tolerably-concentrated solution of carbonate of ammonia and some caustic ammonia. The liquid is evaporated almost to dryness, the residual mass moistened with hydrochloric acid, diluted with water, heated for an hour, and then filtered to separate the silicic acid; the filtrate contains the phosphoric acid; it is mixed with tartaric acid, and the phosphoric acid separated in the usual manner by sulphate of magnesia.

The second method is based upon the property of the ammonia-phosphate of magnesia to remain dissolved in small quantities in ammoniacal solutions of tartrate of iron, but not in ferricyanide of potassium. In the first place, two concentrated solutions are prepared, the one of 120 grains of tartaric acid, the other of 210 grains of cyanide of potassium; 15 grains of the iron are then dissolved in nitric acid, with the addition of a little hydrochloric acid. The tartaric acid solution is then added to that of the iron; a sufficient quantity of sulphate of magnesia is next added, then a large excess of ammonia, and finally the solution of cyanide of potassium. To this deep red liquid, a concentrated solution of sulphuret of potassium is carefully added, until the colour, which at first changes to bright yellow, again becomes dark. After the lapse of a few hours, a precipitate forms in the glass, which contains the whole of the phosphoric acid, combined with ammonia and magnesia, mixed with a little sulphur. It is washed with ammoniacal water, dried, heated till the sulphur ignites, and then melted with a carbonate of potash and soda in a platinum crucible. The melted mass is boiled with water, the solution filtered and strongly acidified with hydrochloric acid and evaporated, in which operation the pyrophosphoric acid is converted into ordinary phosphoric acid. After the addition of tartaric acid and excess of ammonia, the phosphoric acid is precipitated by magnesian salts. When lime is present, instead of using a solution of a magnesian salt, chloride of calcium is to be employed, in order that the whole of the phosphoric acid may be combined with lime. The phosphate of lime is then decomposed by sulphuric acid, the sulphate of lime separated by means of alcohol, the filtrate saturated with ammonia, tartaric acid added, and finally a solution of magnesian salt.—*Journ. für Prakt. Chem.*, vol. iii. pp. 33-37.

CYANOGEN.

Quantitative Estimation of Cyanogen—Heisch.—The substance to be analyzed is put into a small flask with some pieces of pure zinc, and a little water. A cork is fitted to the flask, perforated with two holes, through one of which a tube funnel passes to the bottom of the flask, and in the other is fixed a tube bent twice at right angles: the other end of this tube is dipped into a solution of nitrate of silver. Sufficient sulphuric acid is now added to cause a brisk evolution of hydrogen, when the whole of the cyanogen is converted into hydrocyanic acid, and is carried over into the nitrate of silver. The heat produced by the action is usually enough to drive over all the hydrocyanic acid formed; but should this not be the case, the flask may be heated till no more cyanide of silver precipitates. This method is stated to give very accurate results.—*Quar. Journ. Chem. Soc.*, Oct., 1849.

Determination of the Amount of Prussic Acid in the Medicinal Prussic Acid, Bitter Almond, and Cherry Laurel Waters—Liebig.—This process is founded on the fact that oxide and chloride of silver are soluble in cyanide of potassium up to a certain point; viz., until the double compound consisting of equal equivalents of cyanide of potassium and cyanide of silver is formed, which compound is not decomposed by excess of potash. To the liquid containing the prussic acid, caustic potash is added until it has a strong alkaline reaction, and then a few drops of chloride of sodium. A solution of nitrate of silver of known strength is then added, drop by drop, from a burette until a slight milkiness is perceptible. The quantity used is noted, every equivalent of silver consumed exactly corresponds to two equivalents of prussic acid. The presence of formic or hydrochloric acid has no influence on the result. The method may be employed advantageously to test the purity of commercial cyanide of potassium.—*Liebig's Annalen*, Jan., 1851.

NITROGEN; NITRIC ACID.

Estimation of Nitrogen—Nöller, Schmidt.—The substance under examination is heated in a tube with a mixture of caustic lime, as in *Will* and *Varrentrapp's* process (p. 258, col. 2), and the ammonia that is evolved, is conducted by a tube into a light bottle containing a solution of pure tartaric acid in absolute alcohol. The tube conveying the ammonia is not allowed to dip into the liquid of the first bottle, but the bottle is furnished with a safety tube, and likewise with another second tube leading through the cork of the first into the same solution in a second bottle, which is, in like manner, connected with a third bottle. The whole of the ammonia is thus collected and precipitated in the form of bitartrate of ammonia, a salt which is perfectly insoluble in strong alcohol, with which it may therefore be washed, and when dried at a temperature of about 180°, yields the amount of ammonia in the original substance; 100 parts of the salt thus dried containing 10·2 per cent. of ammonia = 8·4 per cent. of nitrogen. The author recommends this process when a speedy result is desirable, as in cases of commercial analysis, in determining the relative values of manures, &c.—*Ann. der Chem. und Pharm.*, lxvi. 314.

Schmidt burns the substance as in *Will* and *Varrentrapp's* process, and passes the ammonia formed into a solution of one part of chloride of barium in eight parts of water; through this a constant stream of carbonic acid is passed, and from the precipitated carbonate of baryta, the nitrogen in the analyzed substance is calculated by equivalents. According to *Bunce*, however, (*Silliman's Journal*, May, 1851) this process is not capable of affording accurate results, since carbonate of baryta is partially decomposed by boiling with chloride of ammonia in a neutral solution.

New Tests for Nitrites and Nitrates—Schaffer, Price.—The process of the former chemist is the following:—To the solution supposed to contain a nitrite, one or two drops of solution of yellow prussiate of potash are added; there should not be enough to give a perceptible tinge to the liquid. A few drops of acetic acid are then added, and immediately, or in a few minutes, according to the quantity of nitrite present, the liquid assumes a rich yellow tint. As the reagents used give nearly the same colour, spontaneously, after some time, even in pure water, it is better, when testing for minute quantities, to use two similar vessels, one containing pure water, and the other the liquid under examination, to both of which the reagents are to be added in precisely equal quantities. The vessels should be equally exposed to the light, with a sheet of white paper behind them; with these precautions the author states that he has been able to detect the presence of one part in 617,000 parts of water. To test for nitrates, *Schaffer* directs to agitate the slightly-warmed liquid for a few minutes with shavings of lead, and then to proceed as before.—*Proceedings of the American Association, Newhaven*, 1851, p. 403.

The method of *Dr. Price* (*Quart. Journ. of Chem. Soc.*, vol. iv. p. 151) is founded on the reduction of hydriodic acid by nitrous acid, and on the well-known reaction of free iodine with starch paste. A few drops of a dilute aqueous solution of iodide of potassium (free from iodate) are mixed with a little starch paste, and then dilute hydrochloric acid of sp. gr. 1·006 added. The liquid suspected to contain a nitrite if alkaline must be slightly acidified with hydrochloric acid, and then added to the test-mixture, when, if much nitrite be present, a dark blue colour will be instantly produced; and if very small traces only, then the liquid first assumes a pale fawn colour, which gradually changes to that of violet, plum, and ultimately dark blue. In searching for minute traces in a very large bulk of liquid, it is advisable to add more iodide of potassium than where the volume of liquid is small. *Dr. Price* thinks that *De Richemont's* test for nitric acid by protosulphate of iron (p. 72, col. 1), by the employment of which, according to its author, $\frac{1}{24000}$th part of nitric acid may be detected in a solution, as well as *Liebig's* test by sulphate of indigo (p. 72, col. 2), are both, in fact, tests for *nitrous* and not *nitric* acid, the former acid being either contained in the original substance as nitrite, or produced by the action of sulphuric acid upon the nitrate. Dr. Price found that if care be taken to prevent the mixture from becoming heated, and pure nitrate of potash free from nitrite be employed, no reaction can be obtained with protosulphate of iron; but that if the mixture be warmed, the brownish colour will be immediately produced. A liquid containing the $\frac{1}{8000}$th part of nitrous acid in the form of a soda salt becomes immediately coloured green upon the addition of a small quantity of sulphuric acid and sulphate of iron; perceptible shades of green are produced when a liquid contains the $\frac{1}{500,000}$th, and a faint colouration with the $\frac{1}{1,000,000}$th. In like manner *Dr. Price* found that a solution of pure nitrate of potash, which has been treated in the cold with concentrated sulphuric acid, or decomposed with tartaric acid, has no action whatever upon a solution of sulphate of indigo, but that the presence of the smallest quantity of nitrous acid is sufficient to destroy the same. By applying heat to the mixture of sulphuric acid and solution of nitre, to which a few drops of indigo solution have been added, the colour of the latter is found rapidly to vanish, and the test then becomes an exceedingly delicate one for nitrates, and in the absence of chlorates and organic matter may be most advantageously employed for them. By all these tests it will be found, according to *Dr. Price*, that the sulphuric acid of commerce, as well as most kinds of carbonate of potash, contain a trace of nitrous acid.

Silicic Acid.

Analysis of Silicates.—Wurtz (*Silliman's Journal*, Nov., 1850) proposes to fuse the finely-powdered mineral with a mixture of chloride of barium and chloride of strontium, instead of with hydrate or carbonate of baryta, as in *Abich's* method (p. 221, col. 2), the decomposition taking place at a lower temperature, and the crucible not being acted upon. He employs four parts of chloride of barium to three of chloride of strontium, and uses four or five parts of such a mixture to one part of the mineral. After the fusion, the excess of the earthy chlorides is dissolved out with water, and the residue is decomposed by hydrochloric acid, in the usual manner.

Iodine.

Detection of Iodine—Rabourdin, Lassaigne, Price, Grange.—According to the first author, the presence of iodine may be detected by chloroform in a liquid containing less than $\frac{1}{100,000}$th of its weight. To 150 grains of liquid to be tested are added 2 drops of nitric acid, 15 to 20 drops of sulphuric acid, and 15 grains of chloroform; the latter, after agitation, acquires a very distinct violet tint. To detect iodine in cod-liver oil *Rabourdin* proceeds as follows:—700 grains of the oil are well agitated with 75 grains of caustic potash dissolved in 230 grains of distilled water. The mixture is heated in a large iron spoon, in order to destroy the whole of the organic matter; the cinder is exhausted with distilled water, filtered, and 10 drops of a mixture of nitric and sulphuric acid added, taking care to cool the mixture. About 60 grains of chloroform are then well agitated with the mixture, when, after a time, the chloroform is deposited, coloured violet. *Lassaigne* states (*Journ. de Pharm. et de Chim.*, vol. xix. p. 425) that chloroform is less sensitive than starch, and greatly inferior to chloride of palladium, by which $\frac{2}{1,000,000}$ths of iodide of potassium may be detected in two pints of water; and, according to *M. Grange*, the presence of bromine hides the reaction of chlorine and iodine, and the chloroform assumes a yellow colour, whilst the least trace of sulphuret completely destroys the reaction. *Dr. Price* (*Quart. Journ. of Chem. Soc.*, vol. iv. p. 155) employs nitrite of potash as a test of iodine, and proceeds as follows:—The liquid suspected to contain an iodide is mixed with starch paste, and acidified with hydrochloric acid; a solution of nitrite of potash is then added, when, if much iodide be present, a dark blue colour will be instantly produced; if a very small quantity only, as for instance the $\frac{1}{2,000,000}$th or $\frac{1}{3,000,000}$th part, then a few seconds elapse before the blue colour makes its appearance. In this manner, *Dr. Price* states that he has detected the $\frac{1}{4,000,000}$th part of iodine dissolved in water, as iodine of potassium. *M. Grange* (*Comptes Rendus*, Dec. 7, 1851) pours into a test glass a small quantity of the liquid under examination, and adds to it, first, a few drops of solution of starch, and then a little nitric acid containing a large quantity of hyponitric acid in solution: the reaction is instantaneous, the liquid, acquiring a pale rose colour inclining to violet, for solutions which contain $\frac{5}{1,000,000}$ths of iodide, at the most, and when the experiment is made upon a liquid containing $\frac{1}{100,000}$th of its weight of iodide, it takes a bright blue colour.

ANALYSIS OF ASHES.

The method proposed by *Rosé*, for preparing and analyzing the ashes of organic substances (p. 284–288), has been submitted to a minute criticism by *Strecker*, *Staffel* (Liebig, *Annalen*, lxxiii. p. 539; and *Archer. der Pharm.*, lxiv. p. 1), and by *Way* and *Ogston* (*Journ. Royal Agricult. Soc.*, vol. ix., part 1). The two former chemists both agree that there is a loss of chlorine by this method, but that any loss of chlorine or of phosphorus may be avoided by burning the substances in a muffle, with the addition of hydrate of baryta, or still better, as *Rosé* suggests, with a weighed quantity of carbonate of soda.

Staffel adopts the following modification of the method previously proposed by *Wackenroder*:—

I. The organic substances are carbonized in a crucible, the lid of which is stuck on with starch paste. The lid has a hole through which the gases escape; these are inflamed. The charred mass is exhausted with water, and the aqueous extract (through which, if very alkaline, a stream of carbonic acid is passed) is evaporated to dryness and weighed. The solution of the weighed residue is acidified with nitric acid, and the silica being separated in the usual manner, the chloride is determined by nitrate of silver. The excess of silver being removed by hydrochloric acid, the solution is supersaturated with ammonia, and if no precipitate of phosphate of lime takes place the ammoniacal liquor is mixed with oxalic acid, for the separation of the lime. The liquid filtered from the oxalate of lime is precipitated with chloride of barium. The mixed oxalate, phosphate, and sulphate of baryta, after being dried and calcined, is digested with very dilute nitric acid, which leaves the sulphate of baryta undissolved. To the filtered liquid a slight excess of ammonia is added, and it is allowed to stand for some time. If any phosphate of baryta should be deposited, it is collected, dried, and calcined; and the phosphoric acid calculated according to the formula $5BaO + 2PO_5$, containing 27·16 per cent. of phosphoric acid. There is still the potash and soda to determine in the liquid filtered from the oxalate, sulphate and phosphate of baryta. The excess of baryta is removed by carbonate ammonia, and the alkalies are separated and estimated in the usual manner.

II. The charred and exhausted mass is reduced to ash in a Hessian crucible, placed in a slanting position. The ashes are weighed, and extracted repeatedly with water. The solution is divided into several parts: in one part, the chlorine is estimated; in another, acidified with nitric acid; the silica in a third; the sulphuric and phosphoric acids are thrown down by chloride of barium, and separated as above described. The solution freed from the mixed barytic precipitates serves for the determination of the alkalies. In a fourth portion the lime and magnesia are estimated.

III. The residue, insoluble in water, is digested with muriatic acid. The solution is evaporated to dryness, and again dissolved in warm muriatic acid; the silica and sand in the insoluble residue are separated by caustic potash. The muriatic solution is divided into two equal parts: in one, the alkalies are determined; the other serves for the estimation of the earth's peroxide of iron and phosphoric acid, which is effected according to the following plan:— The one-half is heated to boiling in a flask, mixed with acetate of soda and some acetic acid; the resulting precipitate, consisting of perphosphate of iron and phosphate of alumina, or of the first only, is collected on a filter, dried, calcined, and weighed. To separate the peroxide of iron from the alumina, the weighed precipitate is dissolved in muriatic acid, diluted with water, and heated to boiling for some time, with the addition of caustic potash. The separated peroxide of iron is collected on a filter and calculated for phosphate of iron according to the formula, $Fen\ O_3,\ PO_5$ proposed by *Wackenroder*. The alumina is precipitated from the filtered alkaline liquid by acetic acid as phosphate of alumina $= Al_2O_3,\ PO_5$ dried, calcined, and weighed. In this case we must not omit to examine the mixed precipitate obtained by acetate of soda from phosphate of lime, as frequently some is found in ashes which contain much phosphate of lime. If this precipitate be again dissolved in dilute muriatic acid, diluted with water, and heated to boiling with the addition of acetate of soda, it is obtained free from every trace of phosphate of lime. After the alumina and peroxide of iron have been precipitated by acetate of soda from the acid extract of the ash in the state of phosphate, the separated liquid is mixed with a solution of perchloride of iron (the amount of iron in which is known and equal in weight to about the tenth or twentieth part of the entire weight of the ash), in order to determine the phosphoric acid still contained in it; the liquid itself is diluted with a considerable amount of water, heated to boiling in a flask with the addition of 6 or 7 grains of chlorate of potash, somewhat neutralized with carbonate of soda, and the whole of the iron added to the liquid thrown down as basic phosphate by the further addition of acetate of soda. The precipitate is collected on a filter, washed, dried, and ignited in a platinum dish after having been moistened with a few drops of nitric acid, and in this way a basic phosphate of iron is obtained perfectly free from protoxide. The liquid filtered from the basic phosphate of iron is heated to boiling in a flask with carbonate of soda, in order to precipitate lime, magnesia, and protoxide of manganese as carbonates. The filtered liquid is mixed with some phosphate of soda and ammonia, and the crystalline precipitate of ammonio-phosphate of magnesia, obtained after twelve or twenty-four hours, added to that portion to be mentioned presently. The mixed precipitates of earthy carbonates are, after drying, heated to strong redness in a porcelain crucible, then dissolved in cold nitric acid. If any manganese be present it is left as $Mn_3\ O_4$. The separated liquid is mixed with oxalate of potash, the oxalate of lime calcined after drying, and calculated from the amount of carbonate. After separating the oxalate of lime, the liquid is mixed with ammonio-phosphate of soda, and the crystalline precipitate obtained, after standing is mixed with that previously obtained, calcined, and the weight of magnesia calculated from it. The other half of the liquid is examined for alkalies according to the usual method.

The conclusions to which *Messrs. Way* and *Ogston* have arrived, after a laborious series of experiments (*Journ. Royal Agricultural Society*, part i. vol. ix.) may be summed up thus:—It is impossible to burn a siliceous vegetable at any available temperature without a loss of carbonic acid; and in the absence of silica phosphates with less than three atoms of base will, to a greater or less extent, act upon the carbonates of the ash, and thus vitiate the results as far as this acid is concerned. The method proposed by *Rosé* of treating the charred vegetable by water, and estimating the alkaline carbonate in solution, can but partly remedy this defect, for it leaves the insoluble *earthy* carbonates quite undetermined. In fact, we know of no method of so burning the ash plants so as to obtain estimations of the carbonic acid of their ashes which shall be at all indicative of the organic acids present in the vegetable substance examined. But a knowledge of the proportion of carbonic acid for practical purposes is not required. In the ordinary method of burning there is a liability to loss of *sulphuric acid*, wherever silica is present, and where silica is not present there is always a loss of sulphur *not* existing in the plants as sulphuric acid, which loss is very variable in different experiments, depending on a variety of circumstances over which the operator can exercise no distinct control. The presence of phosphates do not appear to have any action upon the sulphates of the ash, and therefore the sulphuric acid afforded by an ordinary burning of a non-siliceous plant must represent the *full* quantity of that acid actually existing in the plant. There seems, at present, no method of distinguishing the *sulphuric acid* of the plant from its *sulphur*, but an exact estimation of the *total* sulphur is obtained by digesting the plant with strong nitric acid, till the substance of it has been broken down into one uniform pulp, when the free acid is neutralized with pure carbonate of soda, and the mixture evaporated and carefully burnt. The ash is then introduced into a deep flask, and treated very gradually with strong nitric acid till it becomes acid. It is important to employ strong nitric acid, and a deep rather than an open vessel; because without these precautions there is a very considerable liability to loss, sulphuretted hydrogen being evolved from the alkaline sulphurets produced in the last stages of the burning. The sulphuric acid in the nitric solution is estimated as sulphate of baryta in the usual manner. The ordinary methods of burning give perfectly accurate results for *phosphoric acid* both in siliceous and in non-siliceous ashes, provided an intense heat be not employed, in which case it is just possible that phosphorus may be reduced and dissipated, though from the tenacity with which phosphoric acid retains its last equivalent of base, such a result even then is more than questionable. Phosphates containing *two* atoms of a fixed base, with one of water, are not capable of decomposing chlorides at a high temperature, but phosphates with only *one* equivalent of a fixed base, and one or more of water, do decompose alkaline chlorides when treated with them, the chlorine escaping as hydrochloric acid; but there is good reason for believing that in the burning of plants this water is dissipated by the heat long before the mineral substances of the ash can have been brought in sufficient contact to enable them to act upon each other. Direct experiments proved that it was quite possible to obtain coincident results in regard to chlorine by careful burning, though when an unusually high temperature is employed a loss of greater or less extent occurs; but this loss does not seem to be increased by the presence in the ash of a large proportion of silica or of phosphates. With respect to the alkalies, as they could only be lost in the form of chlorides, the same observations which apply to chlorine apply to those ingredients as plant ashes also. It is, after all, a matter of temperature, and the authors think that the discrepancies in the results obtained by different ash analysts may, no doubt, be referable in many cases to this cause. The burning of a plant for analysis is plainly a process requiring considerable care—a process that should, in no instance, be hurried forward; but the authors submit that, on the whole, they have demonstrated that (with the exception of sulphur, which is obtained by a separate process) their method of burning crops affords an ash really and correctly representing the mineral matter of the plants under investigation.

Messrs. Way and Ogston have latterly found it convenient to adopt the following method for estimating the phosphoric acid in ashes; a method which a previous trial proved to give accurate results as respects the lime, phosphoric acid, and magnesia.

The hydrochloric solution of the ash is treated with acetate of ammonia, by which the oxide of iron is separated as phosphate. The lime is then thrown down by neutral oxalate of ammonia (the only free acid present being acetic acid); the liquid is then divided into two portions; to one ammonia is added (and, if necessary, phosphate of soda) to precipitate magnesia; and to the other portion, sulphate of magnesia and ammonia are added, and the phosphoric acid estimated as phosphate of magnesia. In all cases where much iron is present correct results will not be obtained, for phosphoric acid by precipitating it as above described, by acetate of ammonia, and calculating the precipitate according to the formula of Fresenius, which requires

42·78 peroxide of iron,
57·22 phosphoric acid,
———
100·00;

for Way and Ogston found that the composition of this precipitate is by no means uniform, but greatly dependent on the relative quantities of the different reagents employed in its production. If an acid liquid containing a persalt of iron and an alkaline phosphate in excess be neutralized by ammonia, phosphate of iron more or less coloured is thrown down. The neutral phosphate of iron is robbed of phosphoric acid by a fixed alkali, such as potash, and reduced to the red-coloured subphosphate. The same occurs, though in a less degree, with caustic ammonia, and the yellowish-white phosphate of iron is soon reddened in an ammoniacal liquid. Indeed, so unstable is this compound that it will part with phosphoric acid even to some ammoniacal salts; thus if the phosphate of iron, even when almost colourless, be dissolved in hydrochloric acid and reprecipitated by ammonia, it will be soon found to have acquired a very decided red tint, and phosphoric acid will be detected in the filtered liquid. In cases, therefore, where much iron is present, the phosphate of iron must be converted into pyrophosphate of magnesia by one of the processes described (p. 215, col. 1).

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ERRATA.

Page xvii, 13 and 15 lines from bottom, for “(C_4H_3)” read “(C_2H_3).”
33, 21 lines from bottom, 2nd column, for “$2S_2Fl_3$” read “$2SiFl_3$.”
35, 19 lines from bottom, 2nd column, for “*redissolved*” read “*reprecipitated.*”
41, 7 lines from top, 2nd column, for “$2K_2Cfy$” read “$2(K_2Cfy)$.”
42, 18 lines from bottom, 1st column, for “$2FeCl$” read “$2Fe_2Cl_3$.”
46, 31 lines from bottom, 2nd column, for “*and*” read “*with.*”
50, 11 lines from top, 2nd column, for “*Carb. Soda*” read “*Carbonic Acid.*”
51, 5 lines from top, 1st column, for “$(2CaO, AsO, AsO_3)$” read “$2CaO, AsO_3$.”
62, 4 lines from top, 1st column, for “$(Bal\,SO_3)$” read “(BaO, SO_3).”
66, 16 lines from bottom, 1st column, for “$3CaO, SO_3$” read “$3(CaO, SO_3)$.”
67, 15 lines from top, 2nd column, read the equation thus:—
“$3(KO, CrO_3) + 3NaCl + 6(HO, SO_3) =$
$(CrCl_3, 2CrO_3) + 3(KO, SO_3) + 3(NaO, SO_3) + 6HO$.”
79, 29 lines from bottom, 1st column, for “*soluble*” read “*insoluble.*”
83, 12 lines from bottom, 2nd column, for “*baryta*” read “*lime;*” and for “*barium*’ read “*calcium.*”
144, 5 lines from top, 1st column, for “*two ounces perfect of soda*” read “47 *per cent. of soda.*”
149, 19 lines from bottom, 2nd column, for “SoO” read “SrO;” and for “SO_2” read “CO_2.”
154, 16 lines from top, 1st column, for “ZrO” read “Zr_2O_3.”
—— 18 lines from bottom, 2nd column, for “*recrimination*” read “*elimination.*”
160, 29 lines from bottom, 2nd column, for “*aid*” read “*acid.*”
166, 1st line, column 1st, for “C_2O_2” read “C_2O_3.”
173, 15 lines from bottom, 2nd column, for “*continued*” read “*consumed.*”
175, 24 lines from top, 1st column, for “74.26” read “75.26.
203, 16 lines from bottom, 2nd column, for “$6FeO, SO_3$” read “$6(FeO, SO_3)$.’
233, 24 lines from bottom, 1st column, for “$2FeO, SO_3$” read “$2(FeO, SO_3)$.”

TO THE BINDER.

In binding with this Supplement that portion of the work which was originally published in two parts, the binder must cancel the Tables which were given at the end of Part 1, pages 311 and 312 at the end of Part 2, and the former Titles and Advertisement.

G. Woodfall and Son, Printers, Angel Court, Skinner Street, London.

RECENTLY PUBLISHED BY

ROBERT BALDWIN, 47, PATERNOSTER ROW.

I.

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