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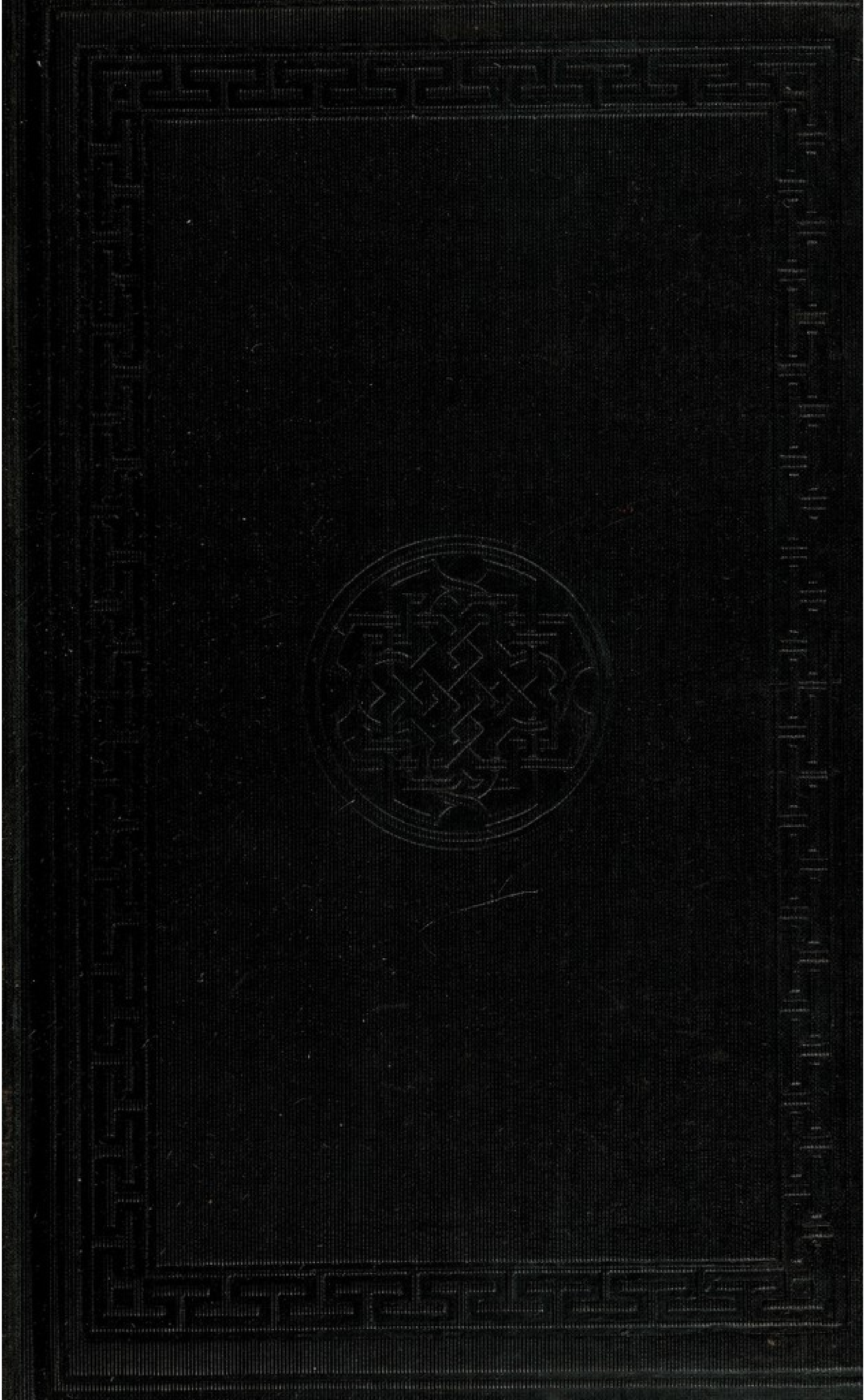

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INSTRUCTION

IN

CHEMICAL ANALYSIS.

(Quantitative.)

INSTRUCTION

IN

CHEMICAL ANALYSIS.

(Quantitative.)

BY

DR. C. REMIGIUS FRESENIUS,
PROFESSOR OF CHEMISTRY AND NATURAL PHILOSOPHY, WIESBADEN, LATE
ASSISTANT IN THE LABORATORY OF GIESSEN.

EDITED BY

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MEMBER OF THE CHEMICAL SOCIETY, LATE OF THE GIESSEN AND PARIS
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EDITOR'S PREFACE.

DR. FRESENIUS has prefaced his work in his own language with a few remarks which, however apposite, and suitable to German readers, I am unable to adopt without substituting for his description of *what is*, a statement of what *ought to be*, the state of chemical science. He observes, that the times are past when men who aspired to the title of CHEMISTS can be satisfied with a knowledge of mere results, without an acquaintance with the methods of research, and the power to pursue for themselves new discoveries. Whilst I am quite ready to acknowledge my belief that we have arrived at the dawn of the brighter period, I must confess myself unable to find in English scientific literature, any evidence of a wide-spread habit amongst those who undertake to teach, of qualifying themselves for the office by laborious application in the laboratory. The folly still prevails of supposing that chemistry can be learned by attendance on lectures; and so it can, equally with the manufacture of watches and steam engines, and the guidance of ships over the ocean. A course of lectures teaches more or less *about* chemistry; a few pretty experiments serve to give the student certain general notions which may be useful to him before entering upon its *study*. When he has resolved on this, he can find no guide comparable to Dr. Fresenius's work entitled " Elementary Instruction in Chemical Analysis." That work teaches him what experiments he must make to learn the characteristic properties of bodies; and when he has acquired this knowledge, what methods he must pursue to detect the presence of substances, existing together in combination or mixture. So that any kind of matter commonly met with, whether soil, mineral, or artificial production, falling into the hands of the student who has advanced thus far, he can analyse it qualitatively. He can discover infallibly what the materials are of which it is composed.

But the next step embraces a second capital division of the science. It now becomes the problem to determine the *quantities* of every ingredient present in any given compound. And the purpose of the present work is to teach

QUANTITATIVE ANALYSIS.

For the task of composing such a work, Dr. Fresenius is eminently qualified. He is well known throughout Europe as one of the most successful analysts of the age. The extensive acceptation of his first work induced him to proceed in composing the present, which, while it in one sense is a sequel to the former, (the two together constituting a manual of analytical chemistry,) is in itself a complete work.

The author very properly and justly observes, that his system is calculated to abridge and facilitate the labours of professors in practical teaching, whilst it enables a student to make safe and satisfactory progress, even when he is unable to obtain professional instruction. He says, that in the progress of his task he found most works on chemistry far more at variance with truth than he had previously imagined, and therefore he was compelled to institute a vast number of experiments, to satisfy himself respecting the true value of methods and processes. To verify every statement by actual experiment, was of course out of the question, but he has done so with by far the greater majority.

I confess that I am proud of the honour of presenting such a work as the present to the English student of chemistry. Its merits are of the highest order. The arrangement is simple, methodical, and consecutive. The theoretical explanations are appropriate, clear, and intelligible; the language plain, and the directness and honesty of purpose which are displayed throughout, must commend it to every one who proceeds far enough in chemistry to meet with difficulties, and who can appreciate a qualified guide to conduct him through them. The special methods, for analysing soils, ashes of plants, mineral waters, &c. will, I am sure, be very acceptable to English chemists.

In conclusion, I must express my regret that my business avocations have caused a rather longer list of errata than usual; a few errors of the press remain uncorrected, but they do not affect the sense of the context. The reader may correct the text in a very short time; and I can only beg his indulgence on the ground of the severity of the task imposed on a translator and editor of so extensive and profound a work.

J. LLOYD BULLOCK.

22, *Conduit Street,*
May, 1846.

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CHAPTER II.

APPENDIX TO I.

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PART III.

INTRODUCTION.

In my treatise entitled, "Elementary Instruction in Qualitative Chemical Analysis," I have stated that ANALYTICAL CHEMISTRY comprehends two branches, viz., "*qualitative analysis*" and "*quantitative analysis*," and that the object of the former is to ascertain the individual *kind and nature*, that of the latter to determine the absolute and relative *quantity or proportion* of the several component parts of any given compound.

By QUALITATIVE ANALYSIS we convert the *unknown* constituents of a given compound into certain forms or combinations, with the properties of which we are acquainted; and we are thus enabled to draw correct inferences respecting the nature of *every individual constituent* of the compound in question.

QUANTITATIVE ANALYSIS consists in converting the *known* constituents of a given compound into such forms or combinations as will, in the first place, admit of the most exact determination of their weight, and of which, moreover, the relative and combining proportions are accurately known. These new forms or combinations may be either *educts* from the analysed compound or mixture, or they may be *products*. In the former case we have simply to weigh the eliminated substance, since its ascertained weight, of course, supplies at once the direct expression of the quantity or proportion in which it existed in the compound under examination; whilst in the latter case, that is, when we have to deal with *products*, the quantity or proportion in which the eliminated constituent was originally present in the analyzed compound, has to be deduced by calculation from the proportion in which it exists in its new combination.

The following example will serve to illustrate these points:—Suppose we wish to determine the proportional amount of mercury contained in the perchloride of that metal; now, we may do this either by precipitating the metallic mercury from the solution of the perchloride, by means of protochloride of tin, or we may attain our object by precipitating solution of perchloride of mercury with sulphuretted hydrogen, and weighing the precipitated bisulphuret of mercury. 100 parts of perchloride of mercury consists of 74·08 of mercury and 25·92 of chlorine; consequently, the precipitation of 100 parts of perchloride of mercury by protochloride of tin will yield 74·08 of metallic mercury, which is ascertained by simply weighing the precipitate. The precipitation of the same amount of perchloride of mercury, by means of sulphuretted hydrogen, yields 85·838 of bisulphuret of mercury.

Now, in the former case the figure 74·08 expresses *directly* the proportioned amount of mercury contained in the analysed perchloride; in the latter case we have to find this amount by calculation, which may be accomplished by means of the following simple equation:—100 parts of bisulphuret of mercury contain 86·29 parts of mercury; how much mercury do 85·838 contain?

$$100 : 86{\cdot}29 : : 85{\cdot}838 + : x = 74{\cdot}08$$

It will be readily understood from the preceding illustration, that all those forms and combinations into which the known constituents of a given compound are to be converted for the purpose of quantitative determination, must of necessity, in the first place, admit of most accurate weighing, and that, in the second place, their constitution must be correctly known. These two conditions are absolutely indispensable; for it is quite obvious, on the one hand, that accurate quantitative analysis must be altogether impossible if the substance, the quantity of which it is intended to ascertain, does not admit of correct weighing or measuring; and on the other, it is equally evident, that if we do not know the exact composition of a new product, we lack the most indispensable element for our subsequent deductions.

Having thus briefly defined the subject of quantitative analysis, this definition may suffice to explain its object and general method. We may now remark that certain qualifications are essential to those who would devote themselves successfully to its pursuit. These qualifications, are, 1. theoretical knowledge; 2. skill in manipulation; and 3, strict conscientiousness.

In the first place, the *theoretical knowledge* required, consists in an acquaintance with the qualitative branch of analytical chemistry; together with some practice in simple calculation. A previous knowledge of qualitative analysis enables us to understand all the various methods proposed for isolating substances in order to determine their weight, whilst practice in simple arithmetical calculations, enables us to deduce from our analytical results the composition of the substance examined, in equivalents, and to test the correctness of the method we have pursued. To this *knowledge* must be joined the *power of performing the necessary practical operations*. This is an axiom generally applicable to all practical sciences, but more particularly to quantitative chemical analysis. The most extensive and solid theoretical acquirements will not enable us, for example, to determine the amount of common salt present in a solution of this substance, if we have not the skill necessary for pouring a fluid from one vessel to another without the smallest loss. The various operations of quantitative analysis demand great aptitude and manual skill, which can be acquired only by practice. But the possession of the greatest practical skill in manipulation, joined to a thorough theoretical knowledge is insufficient to insure a successful cultivation of quantitative investigation and research, unless the man so qualified possesses also the *will*, and is animated by a sincere love of truth.

No one who has ever been engaged in quantitative analysis can deny, that cases will sometimes happen in which doubts may be entertained as to whether the results of the operation are correct, or even where the operator is positively convinced that the result of his process *cannot* be correct. Thus, for instance, a small portion of the substance under investigation may be spilled, or some of it lost by decrepitation, or he may justly doubt the accuracy of his weighing, or it may happen that two analyses of the same substance do not exactly agree. In all such cases it is indispensable that the operator should be conscientious enough to repeat immediately his whole process. He who is not animated with this sincere devotion to science and is afraid of encountering labor and difficulties in the pursuit of truth—he who would be satisfied with mere assumption and suppositions, and other guess work, when the attainment of positive certainty is the object, is just as deficient in the necessary qualifications for quantitative analytical researches, as he who is wanting in theoretical knowledge or in practical skill. He therefore who cannot himself firmly and fully rely upon the accuracy of his operations and labours—he who cannot *swear* to the correctness of his results, may indeed occupy himself with quantitative analysis for his own *private* amusement and practice, but he ought never to *publish* as correct and *positive* the results of his operations and researches, nor ought he to apply these results to practical purposes of his own. In the latter case it would prove very little advantageous to himself; in the former, his error would be greatly detrimental to the interests of science, and might be eminently injurious to others.

The domain of quantitative analysis may be said to extend over all matter, that is, in other words, anything corporeal may become the object of quantitative investigation. The present work, however, is intended to embrace only the substances used in pharmacy, arts, trades, and manufactures.

Quantitative analysis may be subdivided into two branches, viz. into analysis of *mixtures*, and analysis of *chemical compounds*. This division may appear at first sight of very small moment, yet it is necessary that we should establish and maintain it, if we would form a clear conception of the value and utility of quantitative research. The quantitative analysis of mixtures has not the same aim as that of chemical compounds; and the method applied to secure the correctness of the results in the former is different from that adopted in the latter case. The quantitative analysis of chemical compounds rather subserves the theoretical purposes of science, whilst that of mixtures belongs to the practical purposes of life. If, for instance, I analyse thesalt, the result of the analysis will give me the constitution of the acid, its combining proportion, saturating capacity, &c. &c.; or, in other words, the results obtained will enable me to answer a series of questions, the solution of which is important for the theory of chemical science: but if, on the other hand, I analyse gunpowder, alloys of metals, medicinal mixtures, &c. &c., I have a very different object in view; I do not want in such cases to apply the results which I may obtain, to the solution of any theoretical question of chemistry, but I want to render a practical service either to the arts, trades, and manufactures, or to some other science. If in the analysis of a chemical compound, I wish to control the results obtained, I may do this in most cases by means of calculations, but in the case of a mixture a second analysis is necessary to *confirm* the correctness of the results afforded by the *first*.

The preceding remarks clearly demonstrate the immense importance of quantitative analysis. It is owing to this branch, that chemistry has been raised to the rank of a science, since it has led us to discover and determine the laws which govern the combinations and transpositions of the elements. Stochiometry is entirely based upon the results of quantitative investigations; all rational views respecting the constitution of compounds rest upon them as the only safe and solid basis. Quantitative analysis, therefore, forms the strongest and most powerful lever for chemistry as a science, and not less so for chemistry in its application to the practical purposes of life, to trades, arts, manufactures, and likewise in its application to other sciences. It teaches the mineralogist the true nature of minerals, and suggests to him principles and rules for their recognition and classification. It is an indispensable auxiliary to the physiologist, and no one can doubt but that agriculture will shortly derive incalculable benefit from it. We need not expatiate here upon the advantages which medicine, pharmacy, and every branch of industry derive, either directly or indirectly, from the practical application of its results. Whilst stochiometry owes its establishment to quantitative analysis, stochiometrical laws afford us the means of controlling the results of our analyses so accurately as to insure their correctness, and to justify in most cases the reliance which we now generally place in them. Again, whilst quantitative analysis has advanced, and continues to advance the progress of arts and industry, our manufactures in return supply us with the most perfect platinum, glass, and porcelain vessels, without which it would be impossible to conduct our analytical operations with the minuteness and accuracy to which we have now attained.

But although the aid which quantitive analysis thus derives from stochiometry, the arts and manufactures, greatly facilitates its practice; yet it must be admitted that the pursuit of this branch of chemistry to any satisfactory purpose, requires considerable expenditure of time. I would therefore advise every one desirous of becoming an analytical chemist, to arm himself with a consideral share of patience, reminding him that it is not at one bound, but gradually, and step by step, that the student may hope to attain the necessary skill and precision in his operations, to enable him to rely upon the correctness of his results. However mechanical, protracted, and tedious the operations of quantitative analysis may appear, the attainment of accuracy will amply compensate for the time and labor bestowed thereon; whilst on the other hand, nothing can be more disagreeable than to find, after a long and laborious process, that our results are in-correct or uncertain. Let him, therefore, who would render the study of quantitative analysis agreeable to himself, from the very outset, endeavour by strict, nay scrupulous adherence to the rules and conditions of this science, to attain to correct results, at any sacrifice of time. There cannot be a better and more immediate reward of labor than that which springs from the attainment of accurate results and perfectly corresponding analyses. The satisfaction enjoyed at the success of our efforts is surely in itself a sufficient motive for the necessary expenditure of time and labor, even without looking to the practical benefits which we shall derive from our operations.

The following are the substances treated of in this work.

I. Metalloids.

Oxygen, Hydrogen, Sulphur, Phosphorus, Chlorine, Iodine, Bromine, Fluorine, Nitrogen, Boron, Silicon, Carbon.

II. Metals.

Potassium, Sodium, Barium, Strontium, Calcium, Magnesium, Aluminum, Manganese, Iron, Nickel, Cobalt, Zinc, Cadmium, Bismuth, Tin, Copper, Lead, Silver, Gold, Platinum, Mercury, Chromium, Antimony, Arsenic.

I have divided my subject into three parts. In the first, I treat of quantitative analysis generally; describing 1st, the methods of performing analytical operations and processes; and, 2nd, the calculation of results. In the second, I give a detailed description of several special analytical processes. And in the third, a number of carefully selected examples, which may serve as exercises for the ground work of the study of quantitative analysis.

The following table will afford the reader a clear and definite notion of the contents of the whole.

I. GENERAL PART.

A—PERFORMANCE OF THE ANALYTICAL METHOD AND PROCESSES.

1. Operations.
2. Reagents.
3. Forms and combinations in which substances are separated from others, or in which their weight is determined.
4. Determination of the weight of substances in simple compounds.
5. Separation of substances.
6. Organic elementary analysis.

B—CALCULATION OF THE RESULTS.

II. SPECIAL PART.

1. Analysis of mineral water.
2. Analysis of the ashes of plants.
3. Analysis of soils.
4. Analysis of the atmospheric air.

III. EXERCISES FOR PRACTICE.

APPENDIX.

1. Analytical notes.
2. Table, for the calculation of analytical results.

DIVISION I.

GENERAL PLAN OF THE WORK.

SECTION I.

ON THE METHODS OF PERFORMING ANALYTICAL PROCESSES.

CHAPTER I.

OPERATIONS.

§ 1.

THE operations performed in quantitative research are generally the same as in qualitative analysis—of these I have treated in my former work. I shall here describe such modifications as those may require which are common to both, and shall enter more minutely into such as belong exclusively to quantitative inquiries.

§ 2.

The amount of solids, and generally also that of fluids, is determined by *weight;* the amount of gases and sometimes fluids by *measure:* upon the care and accuracy with which these operations are performed, depends the value of all our results; I shall therefore dwell minutely upon them.

§ 3.

WEIGHING.

Our success in determining the weight of substances we are studying, depends, 1st, upon our possessing a good BALANCE, and 2d, WEIGHTS perfectly accurate.

1st. As to the balance,—there are several points which every chemist must understand, respecting the construction and properties of the balance. The usefulness of this indispensable instrument of quantitative chemistry depends upon two points: 1st, its accuracy, and 2d, its sensibility.

§ 4.

The ACCURACY of a balance depends upon the following circumstances:

a. The fulcrum must be placed above the centre of gravity of the beam.

This is a condition essential to every balance. If the fulcrum were placed *in* the centre of gravity of the beam, it would not vibrate, but remain in any position in which it is placed, assuming the scales to be equally loaded. If the fulcrum be placed below the centre of gravity of the beam, the balance will be overset by the slightest impulse.

When the fulcrum is above the centre of gravity of the beam the balance represents a pendulum, the length of which is equal to that of the line uniting the fulcrum with the centre of gravity, and this line forms right angles with the beam in whatever position the latter may be placed. Now if we impart an impetus to a ball suspended by a thread, the ball, after having terminated its vibrations, will invariably fall back into its original perpendicular position under the suspension point. It is the same with a properly adjusted balance—impart an impetus to it, and it will vibrate for some time, but it will *invariably* return to its original position; in other words, its centre of gravity will finally fall back into its perpendicular position under the fulcrum, and the beam must consequently reassume the horizontal position.

β. *The point of suspension of the scales must be on an exact level with the fulcrum*, since if the fulcrum be placed below the line joining the points of suspension, the loading of the scales being gradually increased, will continually tend to raise the centre of gravity of the whole system, so as to bring it nearer and nearer the fulcrum; the weight which presses upon the scales, combining in the relatively high-placed points of suspension; at last, when the scales have been loaded to a certain degree, the centre of gravity will take its position in the fulcrum, and the balance will consequently cease to vibrate—any further addition of weight will finally cause the beam to overset by placing the centre of gravity above the fulcrum. If, on the other hand, the fulcrum be above the line joining the points of suspension, the centre of gravity will become more and more depressed in proportion as the loading of the scales is increased; the line of the pendulum will consequently be lengthened, and a greater force will be required to produce an equal turn; in other words, the balance will grow the less sensible the greater the load. But when the three edges are placed on a level with each other, increased loading of the scales will, indeed, continually tend to raise the centre of gravity towards the fulcrum, but the former can in this case never *entirely* reach the latter, and consequently the balance will never altogether cease to vibrate upon the further addition of weight, nor will its sensibility be lessened; on the contrary, a greater degree of sensibility is imparted to it This increase of sensibility is, however, compensated for by other circumstances.

γ *The beam must be so strong and inflexible, that the greatest weight which the construction of the balance admits of, must not cause the slightest perceptible bend in it,* since the bending of the beam would of course depress the points of suspension so as to place them below the line of the fulcrum, and this would, as we have just seen, tend to diminish the sensibility of the balance in proportion to the increase of the load. It is therefore necessary to avoid this fault by a proper construction of the beam. The form best adapted for beams, is that of a rhomb, or of an equilateral obtuse-angled triangle.

δ. *The arms of the balance must be of equal length,* i. e., *the points of suspension must be equi-distant from the fulcrum or point of support,* for if the arms be unequal, the weights in equipoise will be unequal in the same proportion; *i. e.*, the weights in one scale acting upon the longer arm of the lever, will preponderate over the exact equivalent in the other scale, and this in direct proportion to the greater or less excess of length of one arm over the other.

§ 5.

The SENSIBILITY of a balance depends principally upon the following circumstances:

α. *The friction of the edges upon their supports must be as slight as possible.*

The greater or less friction of the edges upon their supports depends upon both the form and material of those parts of the balance. The edges *must* be made of good steel, the supporters *may* be made of the same material; it is better, however, that the centre edge should rest upon perfectly even stone (agate) supporters. To form a clear conception of how necessary it is that even the lateral edges should have as little friction as possible, we need simply imagine what would happen were we to fix the scales in immoveable points, by means of inflexible rods. Such a contrivance would at once altogether annihilate the sensibility of the balance, for if a weight were placed upon one side, this certainly would cause the loaded scale to sink, but at the same time being compelled to form constantly a right angle with the beam, it would incline inwards, whilst the other scale would turn outwards, and thus the weight would be made to act upon the shorter arm of the lever. The more considerable the friction becomes at the end edges of a balance, the more the latter approaches the state just now described, and consequently the more is its sensibility impaired.

β. *The centre of gravity must be as near as possible to the fulcrum.* The nearer the centre of gravity approaches the fulcrum, the shorter becomes the pendulum. If we take two balls, the one suspended from a short and the other from a long thread, and impart the same impetus to both, the former will naturally in the extent of its vibrations swing at a far greater angle from its perpendicular position than the latter. The same must of course happen with a balance; the same weight will cause the scale upon which it is placed to turn the more rapidly and completely, the shorter the distance between the centre of gravity and the fulcrum. We have seen above, that in a balance where the three edges are on a level with each other, increased loading of the scales will continually tend to raise the centre of gravity towards the fulcrum. A good balance will therefore become more delicate in proportion to the increase of weights placed upon its scales, but on the other hand, its sensibility will be diminished in about the same proportion by the increased friction attendant upon the increase of load; in other words, the sensibility of a good balance will remain the same whatever may be the load placed upon it, ranging from the minimum to the maximum that its construction will enable it to bear.

γ. *The beam must be as light as possible.*—The remarks which we have just now made will likewise show how far the weight of the beam may influence the sensibility of a balance. We have seen that it is necessary that a balance should increase in sensibility in proportion to the increase of load, since the increased friction tends to diminish its sensibility in the same proportion; and further, we have seen that this increase in sensibility is owing to the increased weight continually tending to raise the centre of gravity towards the fulcrum. Now it is evident, that the more considerable the weight of the beam is, the less will an equal load placed upon both scales alter the centre of gravity of the whole system, the more slowly will the centre of gravity approach the fulcrum, the less will the increased friction be neutralized, and consequently the less sensibility will the balance possess.

§ 6.

Having premised this much, we will in the first place proceed to give the student a few general rules to guide him in the purchase of a balance intended for the purposes of quantitative analysis, and in the second place to point out the best method of testing the accuracy and sensibility of a balance.

1. A balance able to bear 70—80 grammes in each scale, suffices for most purposes.

2. The balance must be enclosed in a glass-case to protect it from dust. This case must not be too small, and more especially its side-walls should not approach too near the scales. The anterior wall of such cases is generally made of one piece, and arranged in the form of a sliding-door, but it answers the purpose far better to have it made of three parts, *i. e.*, one centre part which is fixed, and two lateral parts which open like doors.

3. The balance must be provided with a proper contrivance to render it immoveable, whilst the weights are being placed upon the scales. This is most commonly effected by an arrangement which enables the operator to lift up the beam and thus to remove the fulcrum from its support, whilst the scales remain suspended; other contrivances fix the scales without removing the fulcrum from its support. The best arrangement is that which raises the fulcrum as well as the end edges from their supports, and keeps the scales fixed at the same time. A contrivance which enables the operator to perform this part of the process of weighing without opening the door of the glass-case is best.

4. It is necessary the balance should be provided with an index to mark its vibration.

5. The balance must be provided with a pendulum or with two hydrostatic scales, to enable the operator to place the three edges on an exactly horizontal level; it is best also for this purpose that the box should rest upon three screws.

6. It is very desirable that the beam should be graduated into decimals, so as to enable the operator to weigh the milligramme

and its fractions, by suspending a centigramme crotchet or hook, on or between the indicated points of the graduated line, instead of placing the weight on the scale.

7. The balance must be provided with a screw to regulate the centre of gravity, and likewise with two screws to regulate the equality of the arms.

§ 7.

The following experiments serve to test the accuracy and sensibility of a balance.

1. The balance is in the first place accurately adjusted (by means of tinfoil should the scales not be perfectly equal,) and a milligramme weight is then placed in one of the scales. A good and practically useful balance must turn distinctly with this weight; a delicate chemical balance should indicate the $\frac{1}{10}$ of a milligramme with perfect distinctness.

2. Both scales are loaded with the maximum weight the construction of the balance will admit of—the balance is then *accurately* adjusted, and a milligramme added to the weight in the one scale. This ought to cause the balance to turn the same degree as sub 1. (In most balances, however, it shows somewhat less on the index.)

3. The balance is accurately adjusted, (should it be necessary to induce a perfect equilibrium between the scales by loading the one with a minute portion of tinfoil, this tinfoil must be left remaining upon the scale during the experiment,) both scales are then equally loaded, say with about fifty grammes each, and if necessary, the balance is again adjusted (by the addition of small weights, &c.) The load of the two scales is then interchanged, so that the weight of the right scale is transferred into the left, and *vice versâ*. A balance, the arms of which are perfectly equal, must maintain its perfect equilibrium upon this interchange of the weights of the two scales.

4. The balance is accurately adjusted; it is then arrested, and subsequently set again into motion, until it recovers its equili-

brium ; the same process should be repeated several times. A good balance must invariably re-assume its original equilibrium. A balance the end edges of which afford too much play to the hook resting upon them, so as to allow the latter slightly to alter its position, will show differences in different trials. This fault, however, is possible only with balances of defective construction. A balance to be practically useful for the purposes of quantitative analysis, *must* stand the first, second, and last of these tests. A slight inequality of the arms is of no great consequence, since this may be readily and completely remedied by the manner of weighing.

§ 8.

The WEIGHTS usually accompanying the best balances, range from 50 grammes to 1 milligramme. The French gramme is the best standard for calculating from. With regard to the set of weights, it is generally a matter of perfect indifference in chemical experiments whether the gramme, its multiples and fractions, are really and perfectly equal to the accurately adjusted *normal* weights of the corresponding denominations; but it is *absolutely* and *indispensably necessary* that they should agree *perfectly* among and with each other, *i. e.* the $\frac{1}{100}$ gramme weight must be exactly the one hundredth part of the gramme weight of the set, &c. &c.

2. The whole of the set of weights should be kept in an appropriate well-closing box ; and it is desirable likewise that a distinct compartment be appropriated to every one even of the smaller weights.

3. As to the shape best adapted for weights, I think that of short cylinders, with a handle at the top, the most convenient and judicious form for the large weights ; small square pieces of platinum plate, turned up at one corner, are best adapted for the minute and fractional weights. The plate used for this purpose should not be too thin, and the respective compartments adapted for the reception of the several smaller weights in the box, should

be large enough to admit of their contents being taken out of them with facility, or else the smaller weights will soon get cracked, bruised, and indistinct. Every one of the weights (with the exception of the milligramme* and lower fractions) should be distinctly marked.

4. With respect to the material most fitting for the manufacture of weights, I think that although rock crystal is admirably adapted for normal weights, yet its high price, and the inconvenient form of the pieces, render it far less so for weights intended to serve in the processes of quantitative analysis. Platinum weights would be universally adopted, were the metal not too expensive; but as it is, we commonly rest satisfied with having the smaller weights only, from one gramme downwards, made of platinum plate, using brass weights for all the higher denominations. Brass weights must be carefully shielded from the contact of acid or other vapors, or else their correctness will be impaired. But it is an erroneous notion to suppose that weights slightly tarnished are unfit for use. (It is hardly possible, moreover, to prevent weights for any very great length of time from getting slightly tarnished.) I have carefully examined many weights of this description, and have found them as exactly corresponding with one another in their relative proportions as they were when first used. The tarnishing coat or incrustation is in many instances so extremely small, that even a very delicate balance will generally fail to point out any perceptible difference in weight. It will, however, be found very advantageous to gild the brass weights (by the electro-galvanic process) previous to adjusting them.

The exact accordance of the several denominations of weights of the same set, may be fully tested and assayed in the following manner:—

The one scale of a very delicate balance is loaded with a one gramme† weight, and the balance is then completely equipoised by

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* One milligramme = ·0154 grains Troy.
One centigramme = ·1543 " "
One decigramme = 1·5434 " "

† One gramme . . =15·4336 grains Troy.

placing an exactly equivalent weight in small pieces of brass, and finally tinfoil, (but no paper, since this absorbs moisture,) upon the other scale. The weight is then removed, and replaced successively by the other gramme weights which the operator may happen to possess, and afterwards by the same amount of weight in pieces of lower denominations.

The balance must be carefully scrutinized every time, when required for use, and any departure from the exact equilibrium marked. The several pieces of higher denominations are then tested, and assayed in the same way. The smaller weights must not show the slightest perceptible difference on a balance turning with $\frac{1}{10}$ of a milligramme in the comparison of the larger weights with the smaller ones; differences, however, of from the $\frac{1}{10}$ to $\frac{2}{10}$ part of a milligramme may be passed over, since this will not materially impair their usefulness. If you wish them to be more accurate, you must adjust them yourself. In the purchase of weights, chemists ought always to bear in mind, that an accurate weight is in reality of great value, whilst an inaccurate one is worthless. Experience has taught me that it is invariably the safest way for the analytical chemist to test and assay for himself every weight he purchases, regardless of the reputation of the maker.

§ 9.

THE PROCESS OF WEIGHING.

We have two different methods of determining the weight of substances; the one is termed "*direct weighing*," the other is called "*weighing by substitution*."

In *direct weighing*, the substance is placed upon one scale, and the weight upon the other. If we possess a balance, the arms of which are of equal length, and the scales in a perfect state of equilibrium, it is indifferent upon which scale the substance is placed in the several weighings required during an analytical process; *i. e.* we may weigh upon the right or upon the left side, and change sides at pleasure, without endangering the accuracy of our results. But if, on the contrary, the arms of our balance are not perfectly equal, or if the scales are not in a state of perfect equilibrium, we are compelled to weigh invariably upon the same scale, otherwise the correctness of our results will be more or less materially impaired.

Suppose we want to weigh one gramme of a substance, and to divide this amount subsequently into two equal parts. Let us assume our balance to be in a state of perfect equilibrium, but with unequal arms, the left being 99 millimetres* long, whilst the right is 100 millimetres long; we place first a gramme weight upon the left scale, and against this the substance we want to weigh, until the balance recovers its equilibrium.

According to the axiom, " masses are in equilibrium upon the lever, if the distance of their products from the point of support is equal," we have consequently upon the right scale 0.99† grammme of substance, since 99 : 1,00=100 : 0.99. If we now, for the purpose of weighing one half the quantity, remove the whole weight from the left scale, substituting 0.5 gramme weight for it, and then take off part of the substance from the right scale, until the balance recovers its equilibrium, there will remain 0.495 gramme; and this is exactly the amount we have removed from the scale: we have consequently accomplished our object with respect to the relative weight; and, as we have already remarked, the absolute weight is not generally of so much importance in chemical experiments. But if we attempted to halve the substance which we have on the right scale, by first removing both the weight and the substance from the scales, and placing subsequently a 0.5 gramme weight upon the *right* scale, and the substance upon the *left*, until the balance recovers its equilibrium, we should have 0.505 of substance upon the left scale, since 100 : 0.500=99 : 0.505; and consequently, instead of exactly equal halves, we shall have one part of the substance amounting to 0.505, only to 0.495.

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* One millimètre= ·0394 inch.
† One centimètre= ·394 inch.
One decimètre = 3·937 inches.
One mètre . . =39·37 inches.

If the scales of our balance are not in a state of absolute equilibrium, we are obliged to weigh our substances in vessels, to ensure accurate results, (although the arms of the balance be perfectly equal). It is self-evident that the weights in this case must likewise be invariably placed upon one and the same scale, and that the difference between the two scales must not undergo the slightest variation during the whole course of a series of experiments.

From these remarks result the two following rules:

1. It is, under all circumstances, advisable to weigh substances invariably upon one and the same scale.

2. If the operator happens to possess a balance for his own private and *exclusive* use, there is no need that he should adjust it at the commencement of every analysis; but if the balance be used in common by several persons, it is absolutely necessary to ascertain before every operation, whether its state of absolute equilibrium be not disturbed.

Weighing by substitution, yields not only *relatively* but also *absolutely* accurate results; no matter whether the arms of the balance be of exactly equal lengths or not, or whether the scales be of equal weight or not.

The process is conducted as follows: the substance to be weighed—say a platinum crucible—is placed upon one scale, and the other scale is accurately counterpoised against it. The platinum crucible is then removed, and the equilibrium of the balance restored, by substituting weights for the removed crucible. It is perfectly obvious that the substituted weights will invariably express the real weight of the crucible with absolute accuracy. We weigh by substitution whenever we wish to obtain *absolutely* accurate results; as for instance, in the determination of atomic weights. The process may be materially shortened by accurately fixing in the first place a certain standard weight, (which must be heavier than the substance we are about to weigh,) then removing this weight, and substituting for it the body to be weighed; and finally adjusting the latter against the counterpoise, by the addition of smaller weights. The sum of the weights added is then subtracted from the known amount of the counterpoise: the remainder will at once indicate the exact weight of the substance we are dealing with. This counterpoise may be applied for the same purpose in all subsequent weighings.

§ 10.

The following rules will be found useful in performing the process of weighing:

1. The safest and most expeditious way of ascertaining the exact weight of a substance, is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns ought to be 6.627 grammes; well, we place 10 grammes in the other scale, and we find this is too much; we place the weight next in succession, *i. e.* 5 grammes, and find this too little; next 7, too much; 6 too little; 6,5 too little; 6,7 too much; 6,6 too little 6,65 too much; 6,62 too little; 6,63 too much; 6,625 too little; 6,627 right.

I have selected here for the sake of illustration a most complicated case; but I can assure the student of quantitative analysis, that this systematic way of trying the counterpoising of substances will in most instances lead to the desired end, in half the time required when weights are tried at random. In a few minutes we ought to be able thus to weigh to $\frac{1}{10}$ of a milligramme.

2. I have already had occasion to observe, that the placing of small crotchets or hooks, weighing 1 centigramme, on or between the points of the decimal division of the beam, is a more expeditious way to determine a milligramme and its decimal divisions, than the use of the corresponding weights upon the scale.

3. The balance ought to be arrested every time any change is

contemplated, (such as removing weights, substituting one weight for another, &c. &c.) or else it will soon get spoiled.

4. Substances must never be placed *directly* upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, &c. &c., never in paper or card, since these, being liable to attract moisture, are apt to alter their weight. The most common method is to weigh in the first instance the vessel by itself, and to introduce subsequently the substance into it; to weigh again, and subtract the former weight from the latter. In many instances, and more especially when several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then taken out, and the vessel weighed again; the difference between the latter and the original weight expresses the amount of the portion taken out of the vessel.

5. Substances liable to attract moisture from the air, must be weighed invariably in closed vessels, (in covered crucibles, for instance, or between two watch glasses, or in a stoppered glass tube;) fluids are to be weighed in small bottles, closed with glass stoppers.

6. A vessel ought never to be weighed whilst hot, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and of moisture, the quantity of which depends upon the temperature, and the hygroscopic state of the air, and likewise on its own temperature. Now suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again whilst hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract for this purpose the weight of the cold crucible, ascertained in the former, from the weight found in the latter instance, we shall subtract too much, and consequently we shall set down less than the real weight for the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around

them; the heated air expands and ascends, and the dense and colder air flowing towards the space which the former leaves, produces a current which tends to raise the scale, and thus making it appear lighter than it really is.

7. If we suspend from the end edges of a correct balance, 10 grammes of platinum and 10 grammes of glass, by wires of equal weight, the balance will assume a state of equilibrium; but if we subsequently immerse the platinum and glass completely in water, this equilibrium will at once cease, owing to the different specific gravity of the two substances; since we know that substances immersed in water lose of their weight a quantity precisely equal to the weight of their own bulk of water. If this be borne in mind it must be obvious to every one that weighing in the air is likewise defective, inasmuch as the bulk of the substance weighed is not the same with that of the weight. This defect, however, is so very insignificant, owing to the trifling specific gravity of the air in proportion to solid substances, that we may generally disregard it altogether in analytical experiments. In cases, however, where *absolutely* accurate results are required, the bulk both of the substance examined and of the weight, is taken into account, and the weight of the corresponding volume of air is added respectively to that of the substance and of the weight, making thus the process equivalent to weighing in vacuo.

§ 11.

2. MEASURING.

We generally measure only gases in analytical researches, and prefer the process of weighing for the determination of fluids, since as a general rule the latter process yields more accurate results than the determination by measure. We shall therefore confine ourselves here, to the measuring of gases, simply adding a few words with respect to that of fluids. The accuracy of the results obtained by measuring depends upon the proper construction of the measuring apparatus (meters), and also upon the manner in which the process is conducted.

a. APPARATUS FOR MEASURING.

We use for the measuring of gases graduated tubes of greater or less capacity, made of strong glass, and hermetically sealed at one end, (which should be rounded.) The following will be found sufficient for all the processes of measuring which we shall have occasion to treat of in this work.

1. A bell-glass capable of holding from 150 to 250 cubic centimetres, and about one and a-half inch in diameter; this bell-glass should be graduated into double cubic centimetres; that is, every divisional line is to correspond to two centimetres.

2. From five to six glass tubes capable of holding from 30 to 40 cubic centimetres, about half an inch diameter, divided into double cubic millimetres, so that every line corresponds to two cubic millimetres. The walls of these tubes should be pretty thick, as they are very liable to break, especially when used to measure over mercury.

The most important point, however, is that the tubes be correctly graduated, since upon this of course depends the accuracy of the results.*†

The practical usefulness of the measuring tubes depends principally upon the fulfilment of three conditions.

1. The divisions of the tube must *exactly* correspond with and among each other.

2. The divisions of every one of the tubes must exactly correspond with those of the other tubes. And

3. The volumes marked on the graduation line, must exactly correspond with our weights.

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* One centimètre=·397 inch.

† For the manner of graduating the tubes, the student may consult Berzelius' Manual of Chemistry, 4th edition, vol. x., article Measuring, or Faraday's Chemical Manipulations.

The following experiments serve to test our gasometers.

a. The tube which it is intended to examine is placed upon a tolerably large and sufficiently delicate balance and accurately counterpoised, (the tube is either to be placed upright upon the balance, by means of some appropriate contrivance or is suspended by a piece of wire.) It is then filled to about one-tenth of its capacity—with mercury, if one of the smaller tubes, or with water if the large bell jar is used—the divisional mark to which the liquid reaches in the tube is accurately noted, and the fluid determined by counterpoising the other scale until the equilibrium is restored; a further amount of fluid is then poured into the tube, and its weight ascertained in the same manner, and this operation is repeated until the tube is completely filled. If the divisions of the tube are exactly equidistant, the relative proportion which they bear to the corresponding weight must remain invariably the same. *Absolute* correctness in this respect cannot be demanded, of course, since it is impracticable to note the divisional marks of the tube with that degree of accuracy which is attained by weighing.

b. Different quantities of mercury are measured successively in one of the smaller tubes, and subsequently transferred into the other tubes. The tubes may be considered in perfect accordance with one another, if the mercury reaches invariably the same divisional point in every one of the tubes.

Such tubes as are intended simply to determine the relative volume of different gases, need only correspond individually and collectively in the divisions of their graduated scales; but in cases where we want to calculate the weight of a gas by inference from its *volume* it is necessary moreover to ascertain whether the volumes indicated by the degrees of the graduation scale correspond with the weights in our possession. For this purpose one of the tubes is filled with distilled water of 39.2, temperature, to the last mark of the graduated scale, and the weight of the water accurately determined. If the tubes be correctly graduated and the weights correctly adjusted, the number of cubic centimetres of this scale will be equal to that of the gramme weights placed against the water. In this case the weight of gases may be calculated at once from their measured volumes. But should it happen that the accordance between the divisions of the tubes and the weights of the balance be not so perfect, no matter whether the error lies with the graduation of the tube or with the adjustment of the weights, we cannot proceed at once to calculate the weight of a gas from its ascertained volume, but have in the first place, to reduce the latter in proportion to the difference existing between the divisions of our graduated scales and our weights. Let us suppose, for instance, that upon examining our gasometer tubes, we find 99 cubic centimetres of water as indicated by the graduated scale of the tubes to weigh 100 grammes and to correspond consequently to 100 grammes, according to our weights; to convert in this case the measured volume of a gas into weight, we must, in the first place, multiply by $\frac{100}{9}=1.0101$; the number of cubic centimetres found.

If, therefore, you wish to employ such tubes you must have a table, reducing the measures to their corresponding weights for every tube you employ.

b. THE PROCESS OF MEASURING.

In the measuring of gases we must have regard to the following points.

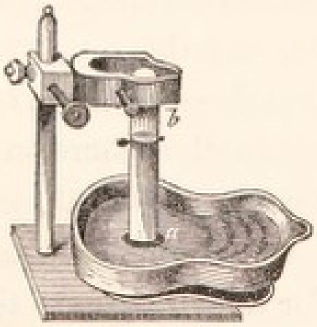
1. We must endeavour to determine as accurately as possible the exact division to which the water or mercury subsides. 2. We must take into consideration the temperature of the gas. And 3. The degree of pressure operating upon it. The two latter points will be readily understood, if it be borne in mind that any alteration in the temperature of gases or in the pressure acting upon them involves likewise a considerable alteration in their respective volumes.

With regard to the first point, it is somewhat difficult to decide with absolute accuracy the exact degree of the scale at which the mercury or water may happen to stand in the gasometer, since mercury in a jar or cylinder (more especially in a narrow one) has a convex surface owing to its own cohesion, whilst water, on the other hand, under the same circumstances has a concave surface, owing to the attraction which the walls of the tube exercise upon it. To ascertain the exact position of the mercury or water, the jar or cylinder should invariably be placed in a perfectly perpendicular position, and the eye directed on a level with the surface of the fluid. Graduating the cylinder on two sides will materially facilitate this process. But if the tube be graduated on one side only, the easiest method is to place a small looking-glass firmly against it, and to direct the eye on a level both with the real surface of the fluid in the tube, and with its reflection in the mirror. If water be used as the confining fluid, the middle of the dark zone formed by the water around the inner walls of the tube, in obedience to the attraction exercised upon it by their walls, is assumed to be the real surface; whilst when operating with mercury we have to place the real surface in a line drawn exactly in the centre between the highest point of the surface of the mercury and the points at which the latter is in actual contact with the walls of the tube.

With regard to the second point, the temperature of the gas is made to correspond with that of the confining fluid, which latter may be readily ascertained.

If the construction of the pneumatic apparatus is such as to permit the total immersion of the cylinder into the confining fluid, a corresponding temperature between the latter and the gas, which it is intended to measure, is most readily induced,—but if the construction of the apparatus will not allow this total immersion of the cylinder, it is necessary that the surrounding air should have the same temperature with the fluid, and we are consequently obliged in such cases to keep the cylinder for a considerable time exposed to the influence of both, before we can proceed to determine the exact degree of the scale at which the mercury or water stands. The operator should take care also to perform his experiment at an effectual distance from the heat of a stove, or the direct rays of the sun, &c.; and, moreover, he should not grasp the cylinder with his hand, but simply press it down with the finger, or better still, with a small wooden crotchet, or linen pin. Since if either of these rules be neglected, the gas will expand again, and of course inaccurate results will be the consequence. With regard to the third point, the gas is simply under the actual pressure of the atmosphere, if the confining fluid stands on an exact level both in and outside the cylinder, the degree of pressure exerted upon it may therefore be at once ascertained by consulting the barometer. But if the including fluid stands *higher* in the cylinder than outside, the gas is under *less* pressure,—if *lower*, it is under *greater* pressure; in the latter case, the perfect level of the fluid inside and outside the cylinder may readily be restored by raising the tube; if the fluid stands higher in the cylinder than outside, the level may be restored by depressing the tube; this however can only be done in cases where we have a trough of sufficient depth. When operating over water, the level may in most cases be readily effected—when operating over mercury, it is frequently impossible to bring the fluid to a perfect level inside and outside the cylinder.

PLATE I.



In the case illustrated here, we have the gas under the pressure of the atmosphere *minus*, the pressure of a column of mercury equal in length to the line $a\ b$. This pressure may be determined therefore by measuring the length of $a\ b$, with the greatest possible accuracy, and subtracting it from the actual state of the barometer. Suppose, for instance, the barometer marks twenty-six inches, and the length of $a\ b$, is $=3$ inches, the actual pressure upon the gas will be $26-3=23$ inches.

If we have water or some other fluid (potash ley, for instance) over the mercury, we proceed generally as if this were not the case; *i. e.*, we either place the mercury on a level inside and outside the cylinder, or measure the difference between the surface of mercury in the cylinder, and that in the trough. The pressure of the column of water, &c., &c., floating over the mercury, is mostly so trifling, that it may safely be disregarded altogether. The more correct way, of course, would be to measure the height of the column of water, &c., to reduce this upon mercury, and to subtract the resulting figure from the actual state of the barometer.

It is quite obvious from the preceding remarks, that volumes of different gases can be compared only, if measured at the same temperature, and under the same pressure. The temperature is generally reduced to 32°, and the pressure is maintained at 29.8 of the barometer. How this is effected, as well as the manner in which we deduce the weight of gases from their bulk, will be found in the chapter on the calculation of analytical results.

Fluids, likewise, are measured sometimes in analytico-technical investigations; we use for this purpose either graduated tubes or syphons, or if the fluid is to be poured out drop by drop, graduated dropping glasses.

In minute investigations, the weighing of fluids is invariably preferred to measuring them. If we wish simply to measure repeatedly the same volume of a fluid, we use either a bottle provided with a glass stopper rounded at the bottom, or a narrow-necked vial having a line mark cut or filed into the glass at a certain point of the neck.

CHAPTER II.

PRELIMINARY OPERATIONS.—PREPARATION OF SUBSTANCES FOR THE PROCESSES OF QUANTITATIVE ANALYSIS.

§ 13.

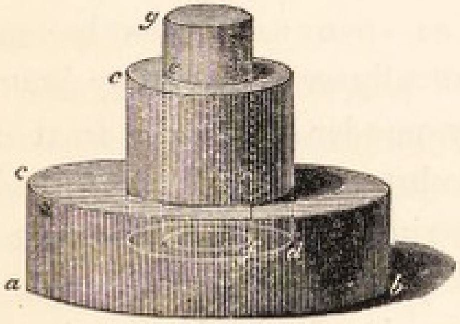
1. MECHANICAL DISINTEGRATION.

In order to prepare any substance for analysis, *i. e.*, in order to render it accessible to the action of solvents or fluxes, it is generally indispensable, in the first place, to divide it into minute parts, since this will create abundant points of contact for the solvent, and counteract and remove, as much as possible, the adverse influence of the power of cohesion, thus fulfilling the principal conditions necessary to effect a complete and speedy solution.

The means employed to attain this object, vary according to the nature of the different bodies we have to operate upon. In many cases, bruising or levigating is sufficient; in other cases it is necessary to reduce the levigated powder to the very highest degree of fineness, by sifting or by elutriation.

The operations of pounding and levigating are conducted in mortars, or levigating dishes; the first and most indispensable condition is, that the material of the mortar or dish be considerably harder than the substance to be pulverized, so as to prevent, as much as possible, the latter from being contaminated with any particles of the former. Thus, for the levigation of salts, and generally, of substances possessing no very considerable degree of hardness, porcelain dishes, may be used, whilst the pounding of harder substances (as of most minerals, for instance,) requires vessels of agate, chalcedony, or flint. In such cases the larger pieces are first bruised into a coarse powder; this is best effected by wrapping the pieces up in several sheets of paper, and beating them with a hammer upon an iron plate; the coarser powder thus obtained is subsequently triturated in small portions in an agate mortar, until it is completely reduced to the state of an impalpable powder. If we have but a small portion of a mineral to operate upon, and, in fact, in all cases where we are desirous of avoiding loss, it is advisable to use a steel mortar for the preparatory reduction of the mineral into coarse powder. Plate 2 represents a mortar adapted for this purpose.

PLATE II.



a b and *c d* represent the two component parts of the mortar; these may be readily taken asunder. The substance to be pounded is introduced into the cylindrical cavity *e f*; the steel cylinder *f g*, which fits somewhat loosely into this cavity, serves as a pestle. The mortar is placed upon a solid support, and perpendicular blows are struck upon the pestle repeatedly, until the object in view is attained.

Minerals which are very difficult to pulverise, should be ignited, and whilst red hot plunged suddenly into cold water, and subsequently again ignited, if necessary. This process is, of course, applicable only to minerals which lose no essential constituent at a red heat, and which are perfectly insoluble in water.

In the purchase of agate mortars, especial care ought to be taken that they have no palpable fissures or indentations; very slight fissures, however, do not render the mortar useless, although they impair its durability.

In operating on minerals insoluble in acids, and which consequently require fluxing, we must have recourse to elutriation after pounding them, otherwise we cannot calculate upon complete decomposition. For this purpose we add some water to the pounded mineral in the mortar, and continue to triturate the paste until all crepitation ceases completely; (this end may be attained far more speedily by performing the latter operation with a mullar upon a plate of agate, flint, or porphyry,) the paste is rinsed off into a beaker glass by means of the syringe bottle, and mixed with distilled water; the contents of the glass are allowed to stand at rest for a minute or so; and subsequently the turbid supernatant fluid is poured off from the coarse sediment. The latter is then again triturated and elutriated, etc. The turbid fluid which has been thus successively decanted from off the sediment, is allowed to stand at rest until the minute particles of the pounded substance which it holds in suspension have subsided; the supernatant fluid is decanted as soon as it has become perfectly clear, a process which generally requires many hours for its completion; the sedimentary powder is finally dried in the beaker glass. If we prepare substances for fluxing which are partially soluble in water, we must in the first instance pound them as finely as possible, and subsequently sift them through a linen bag. In operating upon compound and mixed minerals, we must not analyse the powder obtained upon the first sifting or elutriation, since this will contain the most readily divided parts in a greater proportion to the harder than the original substance. In such cases it is indispensable to convert the whole into a fine and uniform powder, and to intermix the latter intimately before subjecting it to the subsequent operations of analysis.

§ 14.

2. EXSICCATION.

Every substance which we intend to analyse, must be submitted to the necessary operations and processes in a clearly and distinctly characterized and definite state, or form.

We have laid it down as a rule in our introductory remarks, that the *kind* and *nature* of *every individual constituent* of the compounds we wish to analyse must be *exactly* and *accurately known* before we can proceed to ascertain the absolute and relative amount of the several constituents. Now, the essential constituents of substances are generally accompanied by an unessential one, viz., a greater or less amount of water enclosed 1 within their lamellæ, 2 adhering to them from the mode of their preparation, or 3 which they have absorbed from the atmosphere. It is quite obvious that we cannot form any correct notion of the real quantity of a substance, if we do not first remove these variable amounts of water admixed with it. *Most solid bodies require, therefore,* to be dried before they can be quantitatively analysed.

The operation of drying is of the highest importance for the correctness of results; indeed it may be said that by far the greater number of the differences occurring in analyses, proceed from the different degree of dryness in which the analysed substances are operated upon. We must, of course, bear in mind that many substances contain water as an *essential* constituent; that is, the water which they contain in their perfectly normal state, forms either part or parcel of their *constitution,* or it is necessary for their crystallization. With this water we must not interfere. The operation of drying which we have here in view, is intended *only* to remove the *variable* amount of water which substances may contain in accidental admixture ;—this latter we will, the better to distinguish, term " moisture." Consequently the object of drying substances for quantitative analysis, is simply to remove all *moisture,* without interfering in the slightest degree with the *water*, or with any other *essential* constituent of the substance to be analysed. If, therefore, we want to dry a substance, we must positively know all the properties which it manifests in its *dry* state; we must know whether it loses water or other constituents at a red heat, or at 212°, or in dried air, or even when simply in contact with the atmosphere. From these data we may then, readily infer, in every case, what process of exsiccation is best suited to the substance we mean to operate upon.

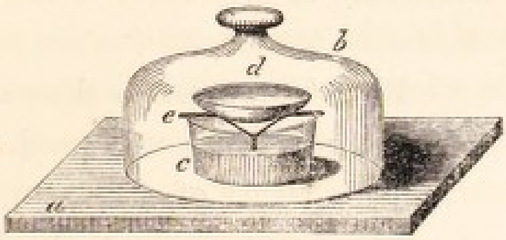
The following classification may accordingly be adopted:

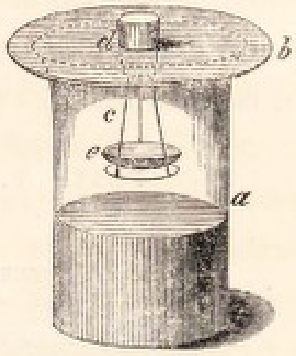
a. Substances which yield water even though simply in contact with the atmospheric air; such as sulphate of soda, carbonate of soda, etc. Substances of this kind turn dull and opaque when exposed to the air, and finally crumble wholly or partially into a white powder. They are more difficult to dry than many other bodies. The process best adapted for the purpose is, to press the levigated salts with some degree of force between thick layers of fine white blotting-paper, until the last sheets remain *absolutely dry.*

b. Substances which do not yield water to the atmosphere, provided the latter be not perfectly dry, but which, nevertheless, effloresce in artificially dried air; such as sulphate of magnesia, tartrate of soda, and potass, (Seignette's salt, or soda tartarisata,) etc. Salts of this kind are triturated as usual, and the powder, should it be very moist, pressed between blotting-paper; after pressing the powder, it must be allowed to remain for some time spread in a thin layer upon a sheet of blotting-paper, effectually protected against dust, and from the direct rays of the sun.

c. Substances which undergo no alteration in dried air, but lose water at 212°; tartrate of lime, for instance. These are finely levigated; the powder is put in a thin layer upon a watch-glass, (or into a small saucer,) and the latter placed inside a glass cover, in which the air is kept dry by means of sulphuric acid. This process may be conducted either in the apparatus illustrated by Plate III. or in that shown in Plate IV.

PLATES III. AND IV.





In Plate III., *a* represents a glass plate, (ground glass plates answer the purpose far better than polished ones,) *b* a bell-shaped glass cover, likewise ground at its inferior border, which is greased; *c* is a small vessel containing sulphuric acid; *d*, a watch-glass containing the substance which is to be dried, and resting upon a triangle made of wire.

In Plate IV., *a* represents a beaker-glass, ground at its superior border, which is greased, and filled to *one-third* or *one-fourth* with concentrated sulphuric acid; *b* is a glass plate likewise ground, and provided with an aperture in its centre; this aperture is closed by means of a cork stopper, *d*. *c* is a small wire support attached to the cork, and upon which rests *e*, a watch-glass, containing the substance under examination.

The body which it is intended to dry, is exposed to the action of the dry air until it no longer suffers any diminution of weight. Substances upon which the oxygen of the air exercises a modifying action, are dried in a similar manner under the exhausted receiver of an air-pump. Those which, although losing no water in dry air, yet yield up ammonia, are dried over calcined lime, mixed with some sal-ammoniac in powder, and thus in an anhydrous and ammoniacal atmosphere.

d. Substances which undergo no alteration at 212°, *but are decomposed at a red heat,* such as tartar, sugar, etc., are dried in a water-bath, either with or without the co-operation of a stream of dry air; the latter, however, is only resorted to when we have to operate upon substances opposing a more considerable resistance to drying than usual. Many substances do not completely lose their moisture at 212°, or at least require long-continued application of the water-bath; in such cases the air-bath, or the oil-bath, is resorted to.

PLATE V.

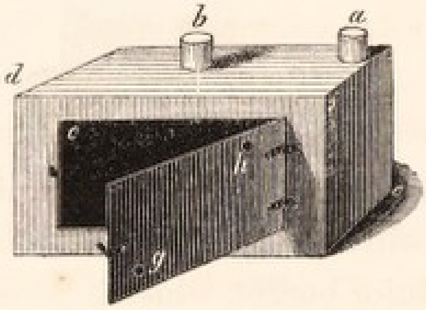


Plate V. represents the water-bath most commonly used. It is made either of sheet tin, or, more advantageously, of sheet copper, and soldered with brass, in order to render it equally fit to serve as an oil-bath, (in which case a thermometer is fixed into a by means of a cork.) The engraving renders any further explanation superfluous. The internal space c is surrounded on five sides by the external case d e, without communicating with it. The object of the apertures g and h is to occasion change of air; and this they completely effect. For use, the external space is filled to about one-half with rain water, the aperture b is entirely closed; and the aperture a, by means of a perforated cork, in which a glass tube is fitted. If the water-bath is to be heated over a coal fire, its length from d to f ought to be from 8 to 10 inches; but if over a spirit-lamp, or an oil-lamp, its length should be from about 5 to 6 inches only. The substances to be dried are placed within the interior c, upon watch-glasses. During the process of drying, the latter are placed one within another, but in weighing them, they ought to be placed covering one another. The glasses must be quite cold before they are placed on the scale of the balance. In cases where we have to deal with hygroscopic substances, the reabsorption of water by the latter, upon cooling, is prevented by selecting glasses that fit closely upon one another, and placing them for cooling under a glass cover, containing a vessel with sulphuric acid. (*Vide* plate III.)

The following apparatus serves to dry substances in a stream of air:—

PLATES VI. AND VII.

In plate 6 the stream of air is caused by heating the air; this apparatus is therefore extremely convenient for use.

PLATE VI.

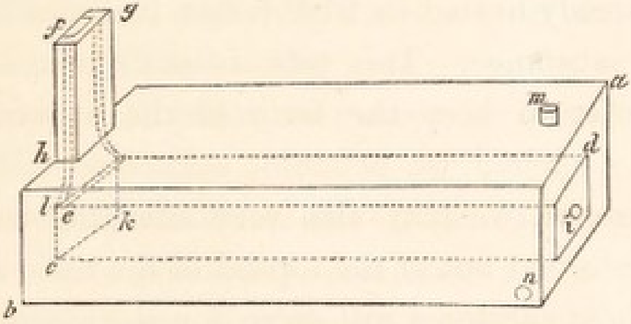


PLATE VII.

a b is a case of sheet copper, or sheet tin, into which the canal *c d* is soldered; the latter communicates with the ascending canal *e f*, which is surrounded on three sides by the cover *g h*, which communicates with *a b*. This cover is not provided with an aperture at top. At *i* we have a round aperture, leading into the canal, and which may be closed with a cork; *l k* is provided with a well-fitting sliding lid running in grooves.

The operation is commenced by filling the case *a b* to one-half with water, through the aperture *m*—(the aperture *n*, which serves to let off the water, is closed with a cork, and heat is then applied to raise the temperature of the water to the boiling point). The substances to be dried are placed upon watch-glasses, into the hollows of the sliding shelf represented in Plate VII.; and the latter is introduced into the canal *c d* at *l k*, which is then closed by the sliding lid.

The air in the canal becoming heated by the surrounding vapour, ascends, and this induces the cold atmospheric air to rush through the aperture *i*; and to stream on the drying substances, carrying away with it the evaporating moisture. There is a slight disadvantage attending this mode of proceeding, viz. the cold air which rushes through *i* keeps the drying substances constantly somewhat under 212° ; this may, however, be easily remedied, by conducting the air into the canal, through a long tube running along under the bottom of the canal down to *l k*, and returning thence to the other extremity, where it is finally fitted into *i* ; this tube must be soldered in its whole length to the external lower surface of the canal. The air which enters at *i* through this tube is already heated to 212° before it comes into contact with the drying substance. This tube is not represented in the engraving, in order to keep the form of the apparatus distinct.

Instead of the aperture *m*, we may also very advantageously substitute large round holes cut out of the top-lid of the case, and provided with covers; these apertures will serve for the reception of small evaporating dishes. A length of from 8 to 12 inches ought to be given to the apparatus, and a width and depth of about 4 inches; the canal *e d* should be two inches wide and one inch high.

PLATES VIII. AND IX.

PLATE VIII.

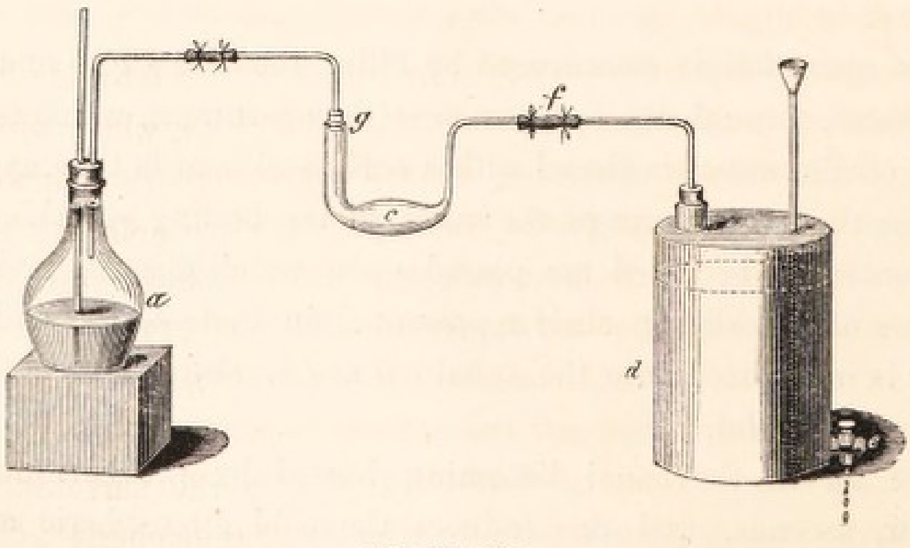
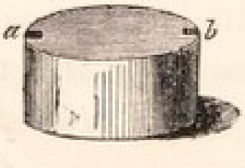


PLATE IX.



In the apparatus represented in Plate VIII., the stream of air is produced by the efflux of water.

a represents a flask filled to one-third with concentrated sulphuric acid; *c* a glass vessel; and *d* a tin vessel, provided with a stop-cock at *e*; and arranged in all other respects as the engraving shows.

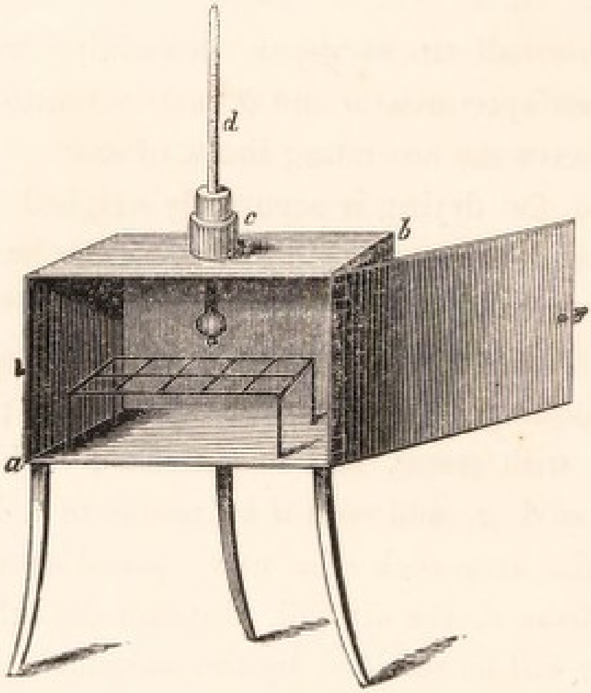
Plate IX. represents a small tin stew-pan, containing water, and covered with a lid; two apertures, *a* and *b*, are cut into the border of the latter, to receive the ascending limbs of *c*.

The substance intended for drying is accurately weighed, and placed in the tubular vessel, the exact weight of the latter having also been previously ascertained; *c* is then suspended into the little stew-pan represented in Plate IX., and the water contained in the latter is heated to boiling by means of a spirit-lamp; the tin vessel *d* is then filled with water, and *c* connected with the flask *a* by the perforated cork *g*, and with *d* by means of a little caoutchouc tube *f*. If the stop-cock *e* be now opened so as to cause the efflux of water from *d*, the air will, through the tube *h*, rush into *a*; its moisture will be retained by the sulphuric acid, and the dry air will then pass over the drying substance in *c*. After the operation has been continued for some time, it is interrupted for the purpose of weighing the vessel *e* and its contents, and then resumed again. The same course is then repeated and continued until the weight of *c c* and its contents is no longer diminished by the extrication of the latter, but remain invariable. The stream of cold air, exercising its constant cooling action upon the drying substance, the latter never really reaches a temperature of 212°. It is advisable, therefore, to substitute for the water in IX. a saturated solution of common salt.

If this substitution be adopted, the apparatus represented in Plates VIII. and IX. will be found to effect its purpose most expeditiously. It is not adapted, however, for the drying of such substances as have a tendency to fuse at 212°.

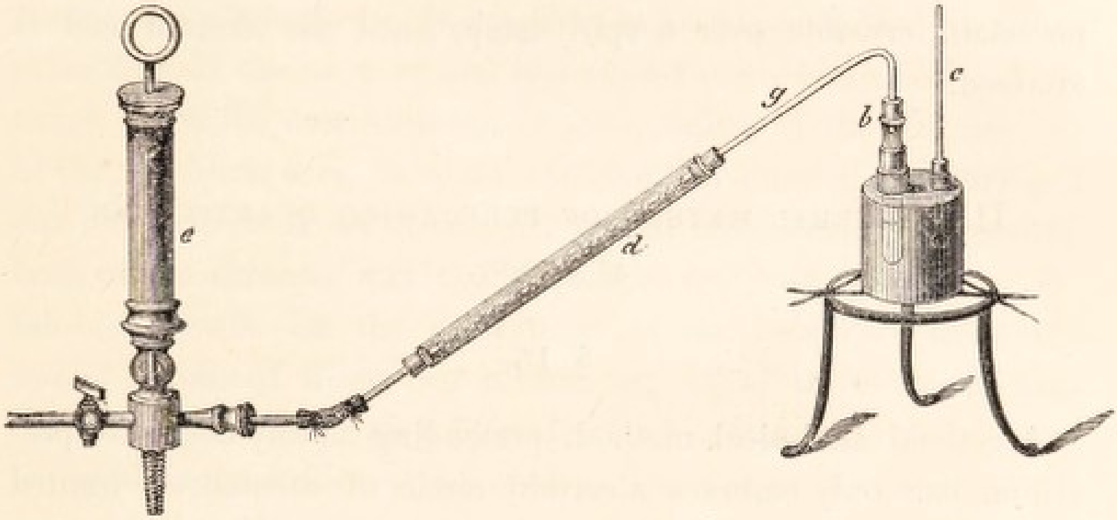
It has been stated above that many substances do not lose their moisture completely at 212°, but require for their perfect exsiccation from 230° to 250°, and more. In such cases an air-bath, or an oil-bath, are substitutes for the water-bath.

PLATE X.



This plate represents an air-bath of the simplest construction; *a b* is a case of strong sheet copper soldered with brass; the aperture *c* is intended to receive a perforated cork, into which a thermometer *d* is fitted, reaching into the internal space of the case; *e* represents a wire-stand adapted for the reception of the watch-glasses containing the substances intended for exsiccation. The case is heated by means of a small spirit, or oil-lamp. When the temperature has once risen to the intended point, it is easy to maintain it pretty constant, by regulating the flame. In order to lessen as much as possible the unavoidable outward refrigeration of the case, it is advisable to place over the whole apparatus a pasteboard cover open in front.

PLATE XI.



In the apparatus represented in this engraving, the exsiccation is promoted by repeated change of air, induced by the creation of a vacuum ; *a* represents a vessel of strong sheet copper, soldered with brass, and provided with two apertures at the top ; *b* is a small glass tube, containing the substance intended for exsiccation ; *c* a thermometer ; *d* a tube, with chloride of calcium ; *e* an exhausting syringe.

The operation is commenced by heating *a* to the desired degree ; *b* and *d* are then exhausted by working the syringe. After the lapse of a few minutes, fresh air is again admitted through the stop-cock *f*, and then repassing through *d*, is completely freed from moisture by the chloride of calcium contained in the latter. The same process of alternate exhaustion and re-admission of air is repeated over and over again, until the interior of the tube *g* ceases to exhibit even the faintest breath of moisture, when cooled by the application of cotton saturated with ether.

This apparatus may also be used as an oil-bath ; for this latter purpose, however, the apparatus represented in Plate V. is most frequently employed.

e. Substances which undergo no alteration at a red heat, such as sulphate of barytes, common salt, &c., are most readily freed from moisture. They are simply heated in a platinum or porcelain crucible over a spirit-lamp, until the desired end is attained.

III. General method of performing quantitative analyses.

§ 15.

A general analytical method, pretending to any degree of precision, can only embrace a certain circle of substances, limited and defined, at least, in its general outlines; for if we are making a road, it is necessary that we should know the points at which it is to touch. We deem it advisable, therefore, to premise, that the general analytical method which we propose to lay down here, is intended to embrace only the analysis and quantitative determination of the metals, and of their combinations with the metalloids; and also of the acids, and salt-compounds of inorganic nature. The quantitative analysis of other compounds—as the combinations of the metalloids with each other—does not readily admit of a universally applicable method, unless it be this, that their constituents generally require to be first converted into bases or acids, before their separation and quantitative determination can be attempted; this is the case, for instance, with sulphuret of phosphorus, chloride of sulphur, chloride of iodine, sulphuret of nitrogen, &c.

We have already stated, that the quantitative analysis of a substance requires, in the first place, a most accurate knowledge of the properties and nature of the substance, as well as of its individual constituents, since this will enable the operator at once to decide whether the direct proportional determination of each individual constituent is necessary or not; and, consequently, whether the analysis may be made simply upon one and the same portion, or whether he must analyse several portions separately. Let us suppose, for instance, that we have a mixture of chloride of sodium and anhydrous sulphate of soda, and wish to ascertain their exact proportion. It would be superfluous indeed to determine directly the proportional amount of every individual constituent, since the determination of the quantity of the chlorine, or of the sulphuric acid, is quite sufficient to answer the purposed end; moreover, if we determine, in this instance, the proportion both of the chlorine and the sulphuric acid, we possess an infallible control for the correctness of our analysis, since the united weight of these two substances, added to the known proportion of their respective equivalents of sodium and soda, must be equal to the weight of the analysed portion of the mixture.

Again, in this case we may perform our analysis upon one and the same portion of the mixture, by first precipitating the sulphuric acid with nitrate of barytes, and subsequently the hydrochloric acid contained in the liquid filtered off from the precipitated sulphate of barytes, with solution of nitrate of silver; or we may use a separate portion of the mixture for each of these two operations. The latter method, whenever it is at all admissible, is preferable to the former, in cases where we have to deal with perfectly homogeneous substances; and where we have a sufficient quantity of substance to act upon. It is more convenient than the former method, and leads to more correct results, since in cases where we operate upon one and the same sample of the substance under examination, the unavoidable washing of the first precipitate swells the amount of liquid so considerably, that the analysis is thereby protracted; and renders it, moreover, less easy to guard against loss of substance.

We will now proceed to describe the various operations constituting the actual process of quantitative analysis.

§ 16.

1. WEIGHING OF SUBSTANCES.

With respect to the amount of a substance necessary for its quantitative analysis, this depends entirely upon the nature of its constituents, and it is, therefore, impossible to lay down any general rule. One half gramme, and even less, of common salt, is sufficient to enable us to determine the proportion of chlorine which it contains. For the analysis of a mixture of common salt and sulphate of soda, one gramme would be sufficient; but if we have ashes of plants, complex minerals, etc., to deal with, it is necessary to take from three to four grammes or more. From one to three grammes may, however, in the great majority of cases, be considered sufficient for analysis.

The greater the amount of substances operated upon, the more accurate are the results of the analysis; the less their amount, the less time is required for the completion of the operation. We would advise the student of quantitative analysis, to endeavour to combine accuracy with economy of time. The less substance we take to operate upon, the more accurately we ought to weigh; the greater the amount of substance, the less harm can result from slight inaccuracies in weighing. In analyses of tolerably large proportions of substances, it is customary to limit the accuracy of weighing to about one milligramme; but in cases where we have very minute proportions to deal with, we must weigh accurately within the one-tenth of a milligramme.

If several different quantities of a substance are to be operated upon, it is most advisable to weigh the different portions successively; and this may be accomplished best by weighing the whole quantity intended for the analytical operations in a glass tube, or other appropriate vessel, the weight of which has, likewise, been previously accurately ascertained. From this tube, the portions required for the several operations are projected into the appropriate vessels, and the weight determined every time by the diminution in the weight of the tube. (Compare § 10, 4.)

§ 17.

2. DETERMINATION OF THE AMOUNT OF WATER CONTAINED IN SUBSTANCES.

If the substance to be examined contains water, it is usual, in the great majority of cases, to begin by determining the amount of this water. This operation is generally simple; in some instances, however, it has its difficulties. This depends upon various circumstances, viz. whether the compounds intended for analysis yield up their water readily or not; whether they can stand a red heat without undergoing decomposition, or whether, on the contrary, they yield up other volatile substances, besides their water, even upon the application of a less degree of heat.

The correct apprehension of the constitution of a substance depends frequently upon the accurate determination of the quantity of water contained in it; in many cases, such as, for instance, in the analysis of the salts of known acids, the determination of the amount of water contained in the analysed compound suffices to enable us to infer, and establish its formula. The determination of the amount of water contained in a substance, is, therefore, one of the most important, as well as most frequently occurring operations of quantitative analysis. The proportion of water contained in a substance may be determined in two ways, viz. 1. by the diminution of weight which the substance undergoes by the expulsion of the water; 2. by weighing the amount of water expelled.

A.—DETERMINATION OF THE PROPORTIONAL AMOUNT OF WATER CONTAINED IN A SUBSTANCE, BY THE DIMINUTION OF WEIGHT WHICH THE LATTER UNDERGOES UPON THE EXPULSION OF THE WATER BY HEAT.

This method is almost invariably adopted in the analysis of inorganic compounds, and is inadmissible only in very rare instances. The *modus operandi* and the apparatus, are exactly the same with those of exsiccation described in § 14.

If the substance intended for analysis will bear a red heat without losing any other constituent besides water, the operation may be conducted simply in a covered platinum or porcelain crucible, or in a small test tube, over the flame of a spirit-lamp, taking care to commence with a gentle heat, and to increase it gradually to the desired point. If the substance under examination does not admit of the application of a red heat without losing some other constituent besides water, (ammonia, carbonic acid, &c.) it is exposed to the temperature of a water-bath; or, should it be desirable to apply a higher degree of heat than 212° to the heat of an air-bath, or an oil-bath, provided with a thermometer, as we have seen in § 14.

Salts containing several distinct proportions of water, which separate at different temperatures, are first heated in the water-bath until they cease to lose weight, upon continuing the operation: they are subsequently exposed to temperatures of 302, 392, 482, &c. in the air,—or oil-bath; and finally heated over a free fire.

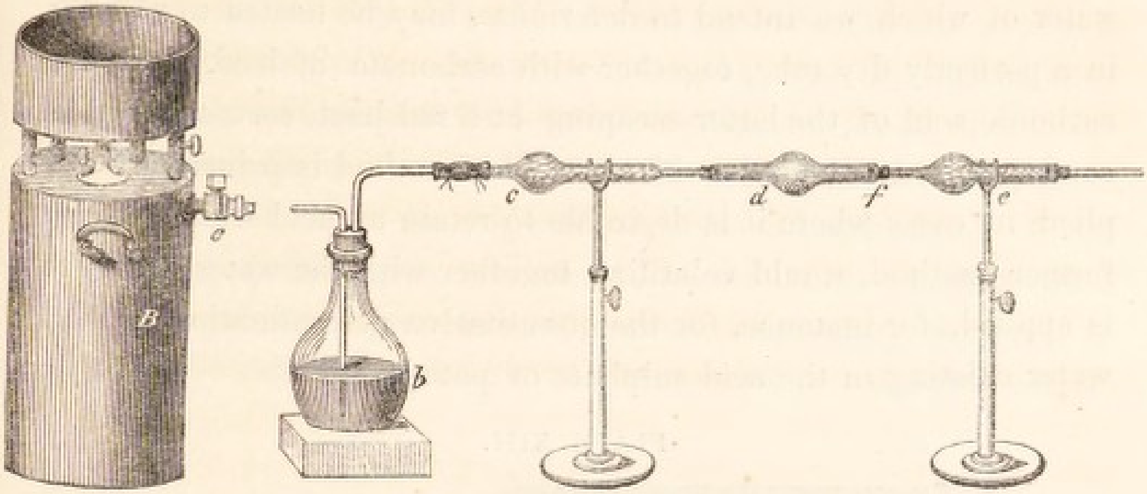
In this manner variously combined proportions of water may be distinguished, and their respective amounts correctly determined. Thus, for instance, the common perphosphate of iron, dried over sulphuric acid, contains 13 equivalents of water; 6 of which volatilize at 212°, 4 at between 392° and 572°, and 3, finally, at a red heat.

B.—DETERMINATION OF THE PROPORTIONAL AMOUNT OF WATER CONTAINED IN A SUBSTANCE, BY DIRECT WEIGHING OF THE WATER EXPELLED FROM THE LATTER BY HEAT.

The method which we have just described cannot be pursued in the analysis of substances which, upon the application of heat in the common way, lose other constituents besides water. Substances of this description must be freed from their water by the application of heat in such a manner as to admit of the condensation of the aqueous vapours, and of their transfer upon some hygroscopic substance, the exact weight of which has previously been accurately ascertained.

This operation may be conducted in various ways; the following, however, is one of the most appropriate:

PLATE XII.



B represents a gasometer, filled with air; *b* a flask, half filled with concentrated sulphuric acid; *c* and *e* are chloride of calcium tubes; *d* is a glass tube, expanded into a bulb in its centre.

The substance intended for examination is accurately weighed in the perfectly dry tube *d*; the weight of which is also to be previously ascertained; *d* is then connected, by means of sound and well-dried perforated corks, with the chloride of calcium tubes *c* and *e*; the latter of which must previously be accurately weighed.

The operation is then commenced by opening the stopcork *g* a little, so as to allow the air to pass through *b* and *c*, (where its moisture will be completely retained,) into *d*; the latter is then heated at *f*, beyond the boiling point of water, by means of a spirit-lamp, (always taking care not to burn or singe the corks;) and, finally, the bulb of the tube *d*, which contains the substance, is exposed to a slight red heat, whilst the above indicated temperature is maintained at *f*. After all the water is expelled, the air is still allowed, for a few moments, to pass through the apparatus; the latter is then taken asunder; and the chloride of calcium tube (after cooling) accurately weighed. The increase in its weight gained during the operation, indicates the amount of water originally contained in the substance examined.

The expulsion of the aqueous vapour from the tube containing the substance under examination, into the cloride of calcium tube, may also be effected by other means than a stream of air furnished by a gasometer; viz., the substance, the amount of water of which we intend to determine, may be heated to redness in a perfectly dry tube, together with carbonate of lead, since the carbonic acid of the latter escaping at a red heat, serves here the same purpose as a stream of air. This method is principally applied in cases where it is desirable to retain an acid which, in the former method, would volatilize together with the water; thus it is applied, for instance, for the quantitative determination of the water existing in the acid sulphate of potass, etc.

PLATE XIII.

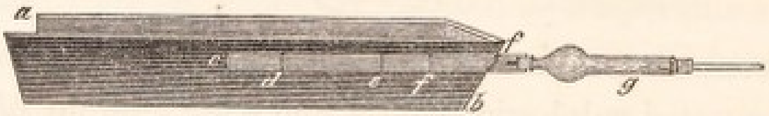


Plate XIII., represents the apparatus used for the application of this method.

a b is a common combustion furnace; *c f'* a tube filled from *c* to *d* with carbonate of lead, (this must have been heated to incipient decomposition, and subsequently cooled in a close tube;) from *d* to *e* is placed the substance to be analysed, intimately mixed with carbonate of lead; and from *e* to *f* pure carbonate of lead. The chloride of calcium tube *g*, after being accurately weighed, is connexed with the tube *c f* by means of a well-dried perforated cork *f*.

The operation is commenced by surrounding the tube *c f'* with red-hot charcoal, advancing from *f'* towards *c*; the inferior part of the tube which protrudes from the furnace, should, during the whole operation, be maintained at such a degree of heat as hardly to permit the operator to lay hold of it with his fingers. All further particulars of this operation will be found below in the chapter on organic elementary analysis. The mixing of the carbonate of lead with the substance to be analysed, is performed best with a piece of wire. The tube *c f* may be short and narrow.

These methods, however, do not suffice for all cases in which the application of the method described under *a* is inadmissible; they are applicable only where the substances evolved simultaneously with the water, are not of such a nature as to admit of condensation in the chloride of calcium tube (or in a potass tube, which might be substituted for the former). Thus they are perfectly well adapted for determining the amount of water in the basic carbonate of zinc, but they cannot be applied to determine the amount of water in sulphate of soda and ammonia. When we have to operate upon substances like the latter, we must either apply the rules and processes of organic elementary analysis, or we must be satisfied to determine the amount of water indirectly.

§ 18.

3. SOLUTION OF SUBSTANCES.

Previously to pursuing the analytical process further, it is in most cases necessary to dissolve the substance under examination. This operation is simple in cases when the substance to be analysed may be dissolved by directly acting upon it, either with water, or with acids or alkalies, etc.; but it is more complicated in cases where we have to operate upon substances requiring fluxing as an indispensable preliminary to their solution.

If we have mixed substances to operate upon, the several component parts of which comport themselves differently with solvents, it is not by any means necessary to dissolve the whole substance in mass; on the contrary, the separation may, in such cases, be effected in the most simple and expeditious manner by the different solvents required. Thus, for instance, a mixture of nitrate of potass, carbonate of lime, and sulphate of barytes, may be readily and accurately resolved into these three salts by dissolving out, in the first place, the nitrate of potass with water; and removing subsequently the carbonate of lime by means of hydrochloric acid, leaving the insoluble sulphate of barytes behind.

§ 19.

a. DIRECT SOLUTION.

This operation is conducted either in beaker glasses, or in flasks or dishes; and if required, may be aided by the application of heat. The water-bath is the best and safest method of applying heat for the promotion of solution. In cases where a free fire, or the sand-bath are used for the same purpose, it is necessary to guard against actual ebullition of the fluid, since this will render it almost impossible to avoid loss by the spirting of the liquid. Fluids containing a sediment either insoluble, or at least, not yet dissolved, when heated over a spirit-lamp, or oil-lamp, frequently begin to spirt even at temperatures far short of the boiling point.

If the solution of a substance be attended with evolution of gas, the operation should be conducted in a small flask or retort, placed obliquely so as to cause the spirting drops to be thrown against the walls of the vessel, since this will prevent their being carried off with the stream of the evolved gas.

§ 20.

b. RESOLUTION BY FLUXION.

According to the different nature and constituents of the substances to be fused, we employ as flux either carbonate of soda, or carbonate of soda and potass, or carbonate of barytes, hydrate of barytes, or, finally, acid sulphate of potass.

It may be laid down as a general rule, that carbonate of soda is used as the flux in the fusion of heavy spar, celestine, and gypsum, as well as of siliceous minerals, either actually free from alkalies, or in which we do not want to determine the amount of alkali they may contain. Carbonate of barytes, and hydrate of barytes serve to decompose silica compounds, containing alkalies, when we want to determine the amount of the latter; and the acid sulphate of potass is particularly well-adapted for the fluxion of certain alumina compounds insoluble in hydrochloric acid.

In almost every case of resolution by fluxion, it is indispensable to reduce the substance to be operated upon to the very highest degree of comminution by levigation and elutriation; if this preliminary operation be imperfectly performed, complete resolution can never be reasonably expected.

a. FLUXION WITH CARBONATE OF SODA.

The substance to be fluxed, after having been most finely pulverized, is mixed in a platinum crucible, with from three to four times its amount of effloresced and perfectly anhydrous carbonate of soda; the mixing is performed with a glass rod, rounded at one end; the minute particles adhering to the rod, are subsequently wiped off against a small proportion of carbonate of soda upon a card; and the contents of the latter are then likewise projected into the crucible. This is then well covered; and according to its size, exposed either to the flame of [redacted]lamp with double draught, or inserted into a hessian crucible filled with calcined magnesia to a charcoal fire. The heat applied must be gentle at first, and should be increased *gradually* to the most intense red heat; and the operation ought to be continued for from 30 to 60 minutes, when the mixture will be either in a state of complete, or at least of semi-fusion.

The contents of the crucibles, after cooling, are treated either with water, (in cases where we have to operate upon sulphates of the alkaline earths,) or with dilute hydrochloric acid, or nitric acid, (when we have to act upon silicates.)

In most cases, a gentle blow on the crucible will be sufficient to effect the liberation of the fused cake from its bottom and sides. In cases where we have to operate upon silicates, the fused mass (or even the crucible, together with its contents) is put into a beaker glass, and covered with from 10 to 15 times its amount of water; hydrochloric acid is then gradually added, taking care to cover the vessel with a glass plate; or, better still, with a large watch-glass, or a perfectly clean porcelain dish, so as to prevent the loss of the drops carried upwards by the carbonic acid evolved.

The solution is aided by the application of a gentle heat, which ought to be continued for some time, even after the whole mass is dissolved; since it will cause the perfect expulsion of the carbonic acid, and thus prevent any loss by efflorescence upon the subsequent evaporation of the solution. Should the fluid, when acted upon by the hydrochloric acid, deposit a powder, (chloride of sodium, or chloride of potassium,) this may be considered as a sign that the amount of water used is not sufficient; and, consequently, a fresh quantity of this menstruum should be added.

After the completion of the operation, minute drops of liquid adhering to the glass plate, (or watch-glass, or porcelain dish,) that has been used to cover the beaker glass, are rinsed off into the solution; and the crucible, likewise, is rinsed with dilute hydrochloric acid, and the rinsing, added to the solution.

If the [redacted] decomposition of the silicates acted upon, has been complete, the solution obtained by means of hydrochloric acid, will be perfectly clear; or slight flakes of silica only will appear floating in it. But if a heavy, gritty powder subsides to the bottom of the beaker glass, this may be looked upon as unresolved mineral, the non-resolution of which is generally owing to deficient elutriation. In such cases, it is indeed admissible to filter off from the sediment, and to dry and weigh the latter, subtracting its weight from the amount originally acted upon; but it is better to flux this sediment once more with carbonate of soda, or carbonate of soda and potass; better still to recommence the whole operation with an entirely fresh portion of the substance to be resolved; taking every possible care to levigate and elutriate this fresh portion to the very highest degree of comminution.

β.—FLUXION WITH HYDRATE OF BARYTES, OR CARBONATE OF BARYTES.

Fluxion with carbonate of barytes requires an extremely high temperature, to be attained only by a Sefström furnace, since this flux remains refractory in the very strongest heat that can be produced by a common wind furnace; and it is only in a state of fusion that it effects complete resolution. But once in fusion, the resolving power of carbonate of barytes is so energetic, that even the most difficultly decomposable fossils are readily and completely resolved by the action of this flux. From four to six parts of carbonate of barytes are used to one part of the mineral to be analysed. The fusion is conducted in a platinum crucible introduced into a fireproof crucible, which is filled with magnesia; the latter is left in the furnace for a quarter of an hour.

If we have to operate upon more readily decomposable minerals, we may attain our object more easily by using, instead of carbonate, hydrate of barytes, which has been freed from its water of crystallization. From four to five parts of the hydrate of barytes are intimately mixed with one part of the mineral to be analysed; this mixture may then be very advantageously covered with a layer of carbonate of barytes. The operation is best conducted in silver crucibles over a good spirit-lamp. Platinum crucibles are slightly acted on by it; the mixture gets either perfectly fused, or, at any rate, its particles agglutinate completely into a state of semi-fusion.

After the completion of the operation, no matter whether car bonate or hydrate of barytes has been used as the flux, the crucible is allowed to cool, and its outside is carefully washed; the crucible is then introduced into a beaker glass, and covered with from ten to fifteen parts of water; hydrochloric acid is then added, (or nitric acid,) and the further operation conducted exactly as stated, when we treated of fluxion with carbonate of soda, *at A.* Care should be taken not to add too much hydrochloric at once, since the chloride of barium formed is with difficulty soluble in that acid; and might, consequently, impede the further solution, by forming round the still undissolved portion of the fused mass, a kind of crust insoluble in the menstruum present.

γ. FLUXION WITH ACID SULPHATE OF POTASS.

One part of finely pulverized and elutriated mineral is mixed with from five to six parts of powdered acid sulphate of potass in a platinum crucible, which ought to be covered in order to avoid the too rapid evaporation of the excess of acid; the flame of a spirit-lamp is then applied until the contents of the crucible begin to fuse, and the same temperature is maintained until the whole mixture is fused into a transparent mass. This mass, after cooling, is mixed with water and heated to boiling. According to the nature of the mineral operated upon, either the whole mass will be dissolved by this process, or only a part of it; the rest remaining undissolved.

§ 21.

4. CONVERSION OF THE DISSOLVED SUBSTANCES INTO A PONDERABLE FORM.

The conversion of a substance in solution, into a form adapted for weighing, may be effected either by evaporation, or by precipitation. The former of these operations is applicable only in cases where the substance, the weight of which we are desirous to ascertain, either exists already in the solution in the form suitable for the determination of its weight, or may be converted into such form by evaporation with some re-agent. The substance must, moreover, be in solution, either by itself, or, at least, mixed only with such bodies as are expelled by evaporation, or at a red heat. Thus, for instance, the amount of sulphate of soda present in an aqueous solution of that substance may be ascertained by simple evaporation; whilst, if we wish to determine the amount of carbonate of potass present in a solution of this substance, it will be more advisable to convert this carbonate of potass into chloride of potassium, by mixing its solution with solution of sal ammoniac, and evaporating this mixture.

Precipitation may always be resorted to whenever the substance in solution admits of being transformed into a state or combination in which it is insoluble in the menstruum.

§ 22.

a. EVAPORATION.

In evaporation for pharmaceutical, or technico-chemical purposes, we have principally to consider the saving of time and fuel; but when this operation is undertaken for the purpose of quantitative analysis, these points are but subordinate; our chief care is to prevent loss, or contamination of the substance operated upon.

Fluids in a state of actual ebullition lose continually and unavoidably minute drops by bubbling and spirting. It is, therefore, advisable to use the water-bath at the boiling point for the evaporation of aqueous solutions; but for the evaporation of alcoholic or etherial solutions, the temperature of the water-bath may be more or less high, according to circumstances; of course always falling short of the boiling point. This arrangement will protect the solution from too high a temperature.

Should the operator possess a Beindorf's steam apparatus, or one similarly constructed, this may be advantageously substituted for the water-bath; otherwise we recommend a water-bath, constructed as follows.

PLATE XIV.

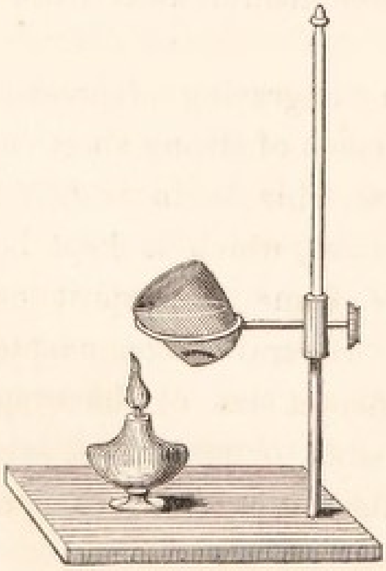
The engraving represents a basin made of strong sheet copper. For use, this basin is half filled with water, which is kept boiling by the flame of a spirit or oil-lamp. Several rings, adapted to the different size of the evaporating dishes or saucepans, serve to receive the latter. The contents of the vessel from *a* to *b* ought to be from four to six inches.

Larger quantities of fluids may be evaporated also in the sand-bath, or in a common stove, or even over a free fire, if we guard carefully against ebullition. Evaporation over a free fire, when properly and cautiously conducted, is a very convenient, expeditious, and clean process, which may be adopted in all cases where the fluids operated upon are clear, and not apt to deposit a precipitate during their evaporation. The operation is conducted most advantageously over a spirit or oil-lamp, the flame of which may easily be regulated, so as to maintain the temperature between 158° and 194°.

This species of evaporation ought, however, to be continued only as long as the fluid remains pretty dilute. The evaporation to dryness is invariably conducted best in a water-bath, or other bath of sufficiently low temperature.

The evaporation of fluids containing an insoluble sediment cannot well be conducted in the common way, in a dish over the free flame of a spirit or oil-lamp, even although but a very moderate degree of heat be maintained, since it would be hardly possible to prevent slight explosions of steam bubbles, arising from the sediment impeding the equal distribution of the heat. This may, however, be remedied by conducting the evaporation in a crucible, placed obliquely on the flame, as illustrated in Plate XV.

PLATE XV.



In this process the flame is guided in such a manner as to play upon the crucible above the level of the fluid.

Many salts have a tendency upon the evaporation of their solutions, to ascend efflorescing along the walls of the evaporating vessel; and, finally, to extend this efflorescence over the border of the latter; this tendency, of course, may cause a loss of the substance; however, if the solutions of such salts be evaporated in crucibles in the manner illustrated in Plate XV., there will be no danger of any loss arising from this tendency, since the upper parts of the vessel will be so hot as to cause the ascending liquid to evaporate immediately, leaving the salt behind. When the operation is conducted in dishes in the common way, the disadvantage just alluded to may generally be remedied, simply by covering the border and uppermost part of the internal surface of the dish with an *extremely* thin coating of tallow.

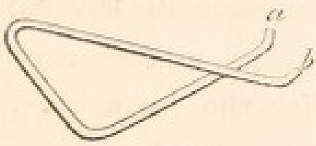
Fluids evolving gas bubbles upon evaporation require, in the first place, to be heated in an obliquely-placed flask until all the gas is expelled. If this necessary preliminary be neglected, it will be found impossible to evaporate such fluids without loss.

If the operator can manage to conduct his processes of evaporation in a private room, where he may easily guard against any occurrence tending to suspend minute particles of dust or ashes in the air, he will find it a very easy task to keep the evaporating fluid properly pure, even without covering the dishes or saucepans in which the operation is conducted.

But in a large laboratory, or in a room exposed to draughts of air, or in which a coal fire is burning, the greatest caution is required to shield the evaporating fluids from the contamination of dust, dirt, and ashes.

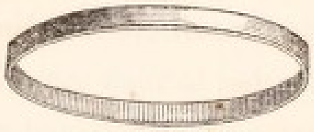
For this purpose the evaporating vessel is either covered with a sheet of blotting-paper, turned closely down over its borders, or a glass rod bent into a triangular shape, (Plate XVI.,) is placed upon the borders of the vessel, and a sheet of blotting-paper spread over it; and the position of the latter maintained by laying a glass rod across it, which is prevented from rolling down by the slightly turned-up extremities (*a* and *b*) of the triangle.

PLATE XVI.



The following method, however, may be recommended as the most advantageous.

PLATE XVII.



Order of any sieve-maker two small and thin wooden hoops, (Plate XVII.,) one of which must be made to fit loosely in the other; spread a sheet of blotting-paper over the smaller of the two, and push the larger over it. This will form a cover admirably adapted to the purpose for which it is intended. It will protect the evaporating fluid against any particles of dust floating in the air; it may be readily removed from the evaporating vessel; the paper does not come in contact with the fluid; and this kind of cover does not, in the slightest degree, impede or retard the process of evaporation. It is, moreover, very durable, and may at any time be readily renovated.

It is necessary sometimes to heat the salt residue remaining, upon evaporation in the water bath above 212°. For this purpose we may either use a sand-bath or an air-bath; the apparatus represented by Plate XIV is perfectly well adapted for the latter, (although it gets spoiled in course of time when put to this use;) during the process, the salt mass ought to be continually stirred with a glass rod, or platinum spatula.

Evaporation is usually conducted in platinum, silver, porcelain, or glass dishes; sometimes in beaker-glasses, flasks, or retorts; and also in crucibles, as I have already had occasion to mention. In cases where a fluid is to be evaporated with exclusion of the air, a tubulated retort is used, and, according to circumstances, either hydrogen gas, or carbonic acid gas, is introduced through a tube inserted into the tubular aperture of the retort, and reaching into the latter within a very short distance of the surface of the liquid. The question, which kind of vessels are best suited to the various substances? may, after the remarks which we have had occasion to make in the course of this paragraph, be left to the operator's judgment.

With respect to the material of the evaporating vessels, the first and most essential point for consideration is that the evaporating fluid does not act upon it. The method of testing glass and porcelain vessels, as to their applicability for the evaporation of acid fluids, is very simple. Pure hydrochloric acid, or pure nitric acid, is heated for some time in the glass or porcelain vessel in question, and evaporated to within a small amount; the remainder is then transferred into a platinum dish, and completely evaporated, when the fact of its leaving a residue or not will at once fully indicate whether the examined vessel is fit for the intended use or not.

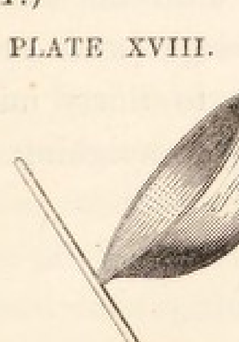
We have now to treat of the *weighing* of the dry residue remaining upon evaporation.

These residues are invariably weighed in the same vessel in which the evaporation has been *completed;* and here we may state, that platinum or silver dishes, of from two to three inches in diameter, are best adapted for the purpose, since with the same capacity they are lighter than porcelain vessels.

In most cases the amount of the fluid intended to be evaporated is so considerable that it cannot be evaporated at once in so small a vessel, and its gradual evaporation in portions would occupy too much time. In such cases the fluid is first concentrated in a larger vessel, and the evaporation finally completed in the small platinum or silver vessel in which the residue is to be weighed.

When transferring the fluid from the larger into the smaller dish, the lip of the former must be slightly smeared with tallow, and the fluid made to run down an inclined glass rod. (Plate XVIII.)

PLATE XVIII.



Finally, the dish is carefully rinsed by means of a syringe bottle until the last rinsing leaves no residue when evaporated upon a platinum plate. After the solution has been thus completely transferred into the smaller dish, the evaporation is completed in the water bath, and the residuary salt finally exposed to a red heat; provided always it will admit of this process. For this purpose the dish is covered with a lid of thin platinum plate, or with a thin glass plate, and then exposed to the flame of a spirit, or oil-lamp, heating gently at first, so as to expel all the water which may still adhere to the substance; and increasing the flame subsequently to such a degree as to heat the dish to redness. (If a glass plate be used as a cover, this must, of course, be first removed before the application of redheat can be resorted to.) The dish is then allowed to cool; if the contents are liable to absorb water, the process of refrigeration must be conducted under a glass bell by the side of a vessel containing concentrated sulphuric acid. (Vide Plate III.) After cooling, the covered dish is weighed with its contents. When we have to operate upon substances having water adhering mechanically, such as common salt, for instance, it is very advisable to expose them,—after their removal from the water-bath, and previously to the application of a free flame,—to a temperature somewhat above 212°, either in the air-bath, or in a sand-bath, or on a common stove.

If the residue does not admit of the application of a red-heat, as when we have to deal with organic substances, ammoniacal salts, &c., we have simply to dry the residuary mass at a temperature suited to its nature. In many cases the temperature of the water-bath is sufficiently high for this purpose, (for the drying of sal ammoniac, for instance;) in others, the air-bath or oil-bath must be resorted to. (Vide § 14.) Under any circumstances, the exsiccation is to be contiuued until the substance ceases to suffer the slightest diminution in weight after renewed exposure to the drying heat, for from fifteen to thirty minutes. The dish should invariably be covered during the weighing.

§ 23.

b. PRECIPITATION.

Precipitation is applied in cases of quantitative analysis far more frequently than evaporation, since it serves not merely to convert substances in ponderable forms, but also, and more especially to separate them from one another. The principal intention in precipitation, for the purpose of determining the amount of a substance in solution, is to convert this substance into a form in which it is insoluble in the menstruum present. The result will accordingly, *cæteris paribus*, be the more accurate the more the precipitated substance deserves the epithet *insoluble*; and in cases where a substance may be precipitated in several different forms, possessing the same degree of insolubility, *that* form will be least liable to loss which occurs with the least amount of solvent.

Hence it follows, first, that in all cases where other circumstances do not interfere with our choice, it is preferable to precipitate substances in their most insoluble form; thus, for instance, barytes should be precipitated as a sulphate, rather than as a carbonate; secondly, that when we have to deal with precipitates which are not altogether insoluble in the menstruum present, we must endeavour to diminish and remove this menstruum by evaporation as far as is practicable; thus a dilute solution of strontian should be concentrated before proceeding to precipitate the strontian with sulphuric acid; and thirdly, that when we have to do with precipitates slightly soluble in the liquid present, but altogether insoluble in another menstruum, into which the former may be converted by the addition of some substance or other, we ought to endeavour to bring about this modification of the menstruum. Thus, for instance, water should be converted into spirits of wine by the addition of alcohol when we wish to induce complete precipitation of chloride of platinum and ammonium, chloride of lead, sulphate of lime, &c.; thus again the basic phosphate of magnesia and ammonia may be rendered insoluble in water by adding ammonia to the latter, &c.

Precipitation is generally effected in beaker glasses. In cases, however, where we have to precipitate from fluids in a state of ebullition, or when the precipitate requires to be kept boiling for some time with the menstruum, small flasks, or dishes are substituted for beaker glasses. The separation of precipitates, from the fluid in which they are suspended, is effected either by *decantation* or by *filtration*.

§ 24.

a. SEPARATION OF PRECIPITATES BY DECANTATION.

When a precipitate subsides so completely and speedily in a fluid that the latter may be decanted off perfectly clear, and that the washing of the precipitate does not require a very long time, decantation is resorted to for its separation; this is the case, for instance, with chloride of silver, metallic mercury, &c.

Decantation will be found a very expeditious and accurate method of separation, if the process be conducted properly and carefully; it is necessary, however, in most cases, to promote and assist the speedy and complete subsidence of the precipitate; and it may be laid down as a general rule in this respect, that heating the precipitate with its menstruum will produce the desired effect. Nevertheless, there are instances in which the simple application of heat will not cause the precipitate to subside so speedily and completely as may be desirable; in some cases, as with chloride of silver, agitation of the fluid must be resorted to; in other cases, some re-agent or other is to be added—hydrochloric acid, for instance, in the precipitation of mercury, &c. We shall have occasion, subsequently, in the fourth section, to discuss this point more fully, when we shall likewise treat of the vessels best adapted for the performance of this process in its various modifications, according to the nature of the precipitate.

After having washed the precipitate with renewed quantities of the appropriate fluid, until there is no trace of a dissolved substance can be detected in the last rinsings, the precipitate is projected into an appropriate crucible or dish, (if it is not already in a vessel of that description) ; the fluid still adhering to it is poured off as far as is practicable, and the precipitate, according to its nature, is then either dried or heated to redness.

A far larger amount of water being required for washing precipitates separated by decantation, than is the case with precipitates washed upon filters, the former process can be expected to yield *accurate* results only in cases where the precipitates are *absolutely insoluble.* For this reason, decantation is not ordinarily resorted to in cases where, besides the amount of the precipitated substance, we have to determine the amount of other constituents contained in the decanted fluid.

§ 25.

B.—SEPARATION OF PRECIPITATES BY FILTRATION.

This operation is resorted to whenever decantation is impracticable ; and, consequently, in the great majority of cases.

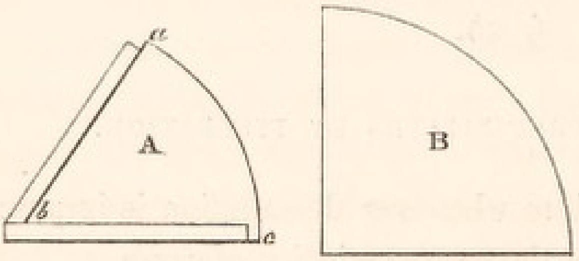
a a. FILTERING APPARATUS. Filtration, as a process of quantitative analysis, is almost exclusively effected by means of paper filters, supported by glass funnels.

Smooth and perfectly circular filters are invariably selected in quantitative analysis. Much depends upon the quality of the paper. To be perfect, this ought to combine the three following properties :—1. It should completely retain even fine precipitates ; 2. It should filter rapidly ; and 3. It should be as free as possible from any admixture of inorganic bodies, but more especially from such as are soluble in acid or alkaline fluids. *Swedish filtering paper* is the best. It is not very easy, however, to procure the article genuine, since many of the papers sold under this name are of greatly inferior quality, with respect to their filtering capacity, as well as with regard to their purity, containing as they do, in many instances, perceptible traces of lime, magnesia, and iron; and leaving upon incineration about 0.3 *per cent.* of ashes, which is considerably more than the genuine article does.

It is advisable, therefore, to treat filtering paper intended for minute experiments, with hydrochloric acid, in order to free it from the inorganic substances which it may contain; the paper is subsequently carefully washed with water to remove every trace of the acid, and finally dried, when it may be considered fit for use.

Ready-cut filters of various sizes should always be kept on hand. Filters are cut either by the pattern of circular pieces of pasteboard or tin, or the paper is folded doubly together, so that the borders form right angles, and placed between two tin plates, cut in the shape of segments. (Plate XIX.)

PLATE XIX.



That portion of the paper which projects from between the two plates, is cut off with the scissors. Filters cut in this manner are perfectly circular. Several pairs of tin plates of various sizes should be procured for this purpose.

In the selection of funnels, care should be taken that they be straight, and inclined at the proper angle (60°). Glass is the most suitable material for funnels.

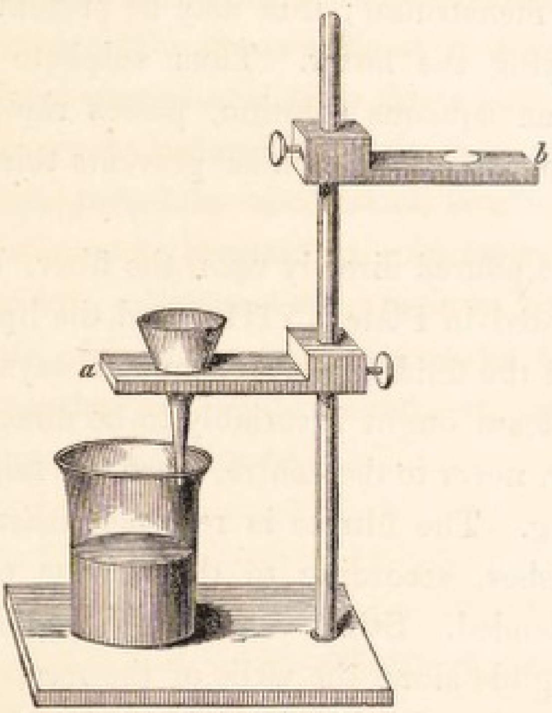
The filters should never be allowed to reach over the brim of the funnel; the best way is to select invariably a filter, the radii of which are by one or two lines shorter than those of the funnel into which it is to be inserted.

The filter is firmly pressed into the funnel, so as to get the paper at every point closely contiguous to the sides of the latter.

When the apparatus is to be used, the filter is moistened with water, which should be allowed to trickle off through the tube of the funnel; and under no circumstances whatever be poured off by inverting the latter.

The stand represented in Plate XX. completes the filtering apparatus.

PLATE XX.



This stand is very convenient, and may be easily carried about from one place to another, without interfering with the operation.

The aperture in the arm *a* must be cut sloping conically downwards, to keep the funnel steadily in its place; the arm *b* serves for the reception of a rinsing bottle. (Vide Plates XXIV. and XXV.) The stand should be made of solid hard wood. Stands having several arms on the same rod, and in each of these arms, several apertures for the reception of funnels, do not appear to me practically useful.

§ 26.

bb.—RULES AND PRECAUTIONS TO BE OBSERVED IN THE PROCESS OF FILTRATION.

Precipitates of a curdy, glutinous, flocculent, or crystalline nature, may be filtered immediately after precipitation, whenever there exists no special reason for the delay. But in cases where we have to deal with fine pulverulent precipitates, it is generally *necessary*, and always *advisable*, after allowing the precipitate to subside first, to filter the supernatant liquid, and finally to project the precipitate upon the filter. Substances which have been precipitated hot, are most properly filtered before cooling, (provided always there be no contra-indication to this course,) since hot fluids run through the filter more speedily than cold ones. Some precipitates have a very disagreeable tendency to be carried through the filter with their menstruum; this may be prevented in some instances by modifying the latter. Thus sulphate of barytes, when filtered from an aqueous solution, passes rapidly through the filter—the addition of sal ammoniac prevents this in a very great measure.

The fluid ought never to be poured directly upon the filter, but along a glass rod, as represented in Plate XVIII.; and the lip or brim of the vessel from which the fluid is poured, must always be greased with tallow. The steam ought invariably to be directed towards the sides of the filter, never to the centre, since this might occasion some loss by spirting. The filtrate is received either in flasks, beaker-glasses, or dishes, according to the various purposes for which it may be intended. Strict care should be taken to cause the drops falling to glide along the walls of the receiving vessel; they should never be allowed to fall into the centre of the collecting fluid, since this again might occasion loss by spirting. The best method in this respect is that illustrated in Plate XX., viz. to place the tube of the funnel against the upper part of the inner wall of the receiving vessel.

If the process of filtration is conducted in a place perfectly free from dust, there is no necessity to cover the funnel, nor the vessel receiving the filtrate; but since this is but rarely the case, it is generally indispensable to cover both the funnel and the receiving vessel. This is best effected with small panes of window-glass; a small aperture for the tube of the funnel is cut out at the border of the panes intended to cover the receiving vessel;—panes perforated in the centre are of no use for this purpose.

After the fluid and precipitate have been poured and projected upon the filter, and the vessel which originally contained them has been rinsed with water, (of course, likewise, upon the filter,) it happens generally that there still remain small particles of the precipitate adhering to the vessel. From beaker-glasses or dishes these particles may be readily removed by means of a quill prepared for the purpose, by tearing off nearly the whole of the feather, leaving only a small piece, which should be cut perfectly straight. But if the minute remainder of the precipitate happens to stick to the inner walls of a flask, as is sometimes with substances precipitated from fluids in a state of ebullition, (oxide of copper, for instance) ; or, in fact, wherever its removal cannot be accomplished by mechanical means, solution, and not precipitation, must be resorted to. In cases, therefore, where we have to deal with substances for which we possess no solvent, such as sulphate of barytes, we must avoid precipitating in vessels from which the precipitate cannot be readily and completely removed by mechanical means.

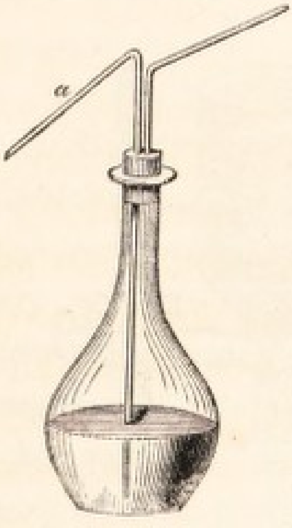
§ 27.

c c.—WASHING PRECIPITATES.

After having transferred the precipitate completely to the filter, we have next to perform the operation of washing or rinsing ; this is effected by means of a syringe bottle.

PLATE XXI.

PLATE XXII.



Care should be taken to regulate the stream properly, since too impetuous a flash of water might occasion some loss of substance.

It is frequently the best way to use the syringe-bottle represented in Plate XXI. simply as a dropping-bottle. As an invariable rule, the water ought to be conducted first around the brim, or margin, of the filter, so as to force the precipitate towards its extremity.

Substances precipitated from aqueous solutions may be washed most advantageously and expeditiously with hot water, provided there be no special reason against it. For this purpose we select either the syringe bottle represented by Plate XXII., or the dropping apparatus illustrated in Plate XXIII.

PLATE XXIII.

The construction of this apparatus does not require a minute explanation. The point *a* is drawn out of its extremity, and nipped off;—the handle *b*, which serves to render the use of the bottle more easy and convenient, is made of wood, and fastened with wire to the bottle.

PLATE XXIV.

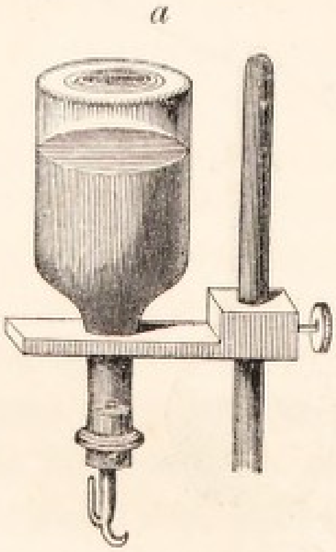
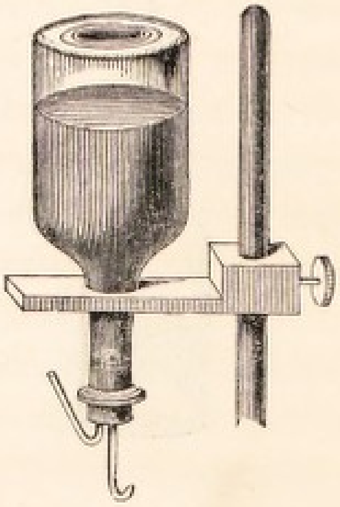


PLATE XXV.

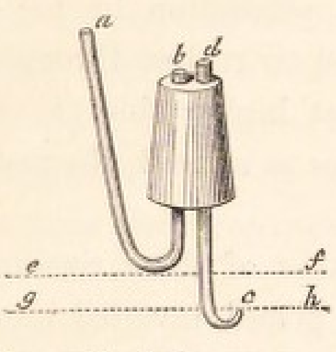


These two engravings represent washing or rinsing bottles adapted for the washing of gelatinous precipitates requiring a very protracted application of the process; such as hydrated alumina, for instance.

It will be seen from the engravings, that the principle is the same in both. There is only this difference between them, that in XXIV. the two tubes are fixed together into one piece, whilst in XXV. they are separate. The construction of XXIV. is somewhat more difficult of illustration than that of XXV. A brief exposition of the principle of the apparatus will show this very clearly. Plate XXVI. represents the cork with the tubes apart from the bottle.

The arrangement of these bottles is so contrived, that no water can flow out of them by a simple inversion, but it begins to flow immediately upon bringing the finger, or a small piece of paper, or some other substance, in contact with the water in the point *c*; the water now flows incessantly, whilst air rushes into the bottle through the tube *a b*; the efflux ceases upon removing the fingers or the piece of paper.

PLATE XXVI.



I deem it of great importance, for the proper construction and use of this rinsing apparatus, that the student should be enabled to form a clear and correct notion of the principle upon which its properties depend. I will, therefore, briefly explain this principle. In the first place, the non-efflux of water from *c* is owing to the circumstance that the pressure of the column of water, occupying the space between the lines *e f* and *g h* is not *altogether* but *nearly* sufficiently powerful to overcome the capillary attraction which the tube *a b* exercises upon the fluid; in the second place, the efflux of the water from *c*, upon being brought into contact with a substance to which it may adhere, is, owing to the draught of the water column *f h*, assisted now by the power of adhesion of the humiated substance overcoming the capillary attraction in *a b*. If the point *c* is placed completely under water, the efflux will likewise cease, since this shortens the column *f h*. If the tube *d c* be lowered, so as to place *c* below *g h*, the water will flow incessantly, the draught of the increased column of water overcoming by itself the capillary attraction in *a b*. But if, on the contrary, *c d* be moved upwards, the draught of the column *f h*, together with the power of adhesion of the substance in contact with it, will no longer be sufficiently powerful to overcome the capillary attraction in *a b*, and consequently no water will flow out. It will be readily conceived from the preceding remarks, that the construction, as well as illustration, of the joint-tube in XXIV. offers some difficulties, since it is not by any means easy to fill the extremity *c exactly* at the required distance from the point where the tube *a b* is united to *c d*. In XXV., the tube *c d* requires simply to be turned upward and downward until the desired point is attained. In the construction of the latter, care should be taken that the aperture *a* of *a b* be situated somewhat higher than *b*; if this precaution be neglected, water will be forced out every time the air rushes through this tube; moreover, *d* must abut somewhat higher than *b*, or else, as soon as the surface of the water ceases to close *b*, the rest will flow out in a continued stream.

The process of washing by means of either of these rinsing bottles is easily performed. The bottle is placed inverted into the aperture contrived for its reception in the second arm of the filter-stand, (*vide* plate XX. *b*.,) and kept suspended over the funnel in such a manner that *c just* dips under the surface of the fluid. If the apparatus is well arranged, the water will now flow out of *c* in the same measure as it runs off through the funnel. To substitute for these rinsing bottles, narrow-necked flasks, inverted directly into the funnel, is quite inadmissible in cases when we intend to determine the exact amount of the precipitated substance, since the air-bubbles which such a contrivance must unavoidably create, would invariably carry minute particles of the precipitate up into the flask.

Care should be taken whilst washing the precipitate (no matter whether with or without a rinsing apparatus) to prevent the formation of channels in it, through which the rinsing water might flow off at once, without previously pervading the whole mass of the substance. Should such channels have formed, however, the precipitate must be carefully stirred with a glass rod or platinum spatule.

The operation of rinsing may be considered complete when all soluble matter has been completely washed away; whether this end has been attained is generally ascertained by evaporating a drop of the last rinsing water upon a clean platinum plate, observing whether this leaves any residue behind or not. In some cases, however, when the precipitate is not absolutely insoluble in the rinsing water, (precipitated sulphate of strontian, for instance,) we have recourse to some more special tests which we shall subsequently have occasion to point out.

The operation of washing precipitates claims the greatest care and attention in the hands of the analytical chemist, since it is self-evident that the imperfect rinsing of a precipitate must materially interfere with the accuracy of his results. This operation should never be deemed concluded on the mere impression and judgment of the operator, the application of the appropriate test or tests alone can safely be relied on.

§ 28.

a. FURTHER TREATMENT OF PRECIPITATES PREPARATORY TO DETERMINING THEIR WEIGHT.

Before we proceed to weigh a precipitate, it is indispensable to convert it first into a state in which its composition is *perfectly* and *accurately known* to us. This is done either by drying or heating to redness. The former process is more protracted and tedious in its application than the latter, and is, moreover, liable to yield less accurate results. The application is therefore generally confined to precipitates which cannot bear exposure to a red heat without undergoing total or partial volatilization, and the residue of which remaining, in the latter case, are not of a kind to admit of any retrospective inference regarding the exact original composition of the precipitate; thus, for instance, drying is applied to sulphuret of mercury, sulphuret of lead, and other metallic sulphurets, and likewise to cyanide of silver, chloride of platinum, and potassium, &c., &c.

But whenever the nature of the precipitated substance leaves the operator at liberty to choose between drying and heating to redness, the latter is almost invariably preferred to the former, (thus precipitates of sulphate of barytes, sulphate of lead, and a great many more compounds, are heated to redness.)

§ 29.

γγ. *Drying of the precipitate.*

When a precipitate has been collected, washed, and dried on a filter, minute particles of it adhere so firmly to the paper that it is found impossible to remove them. The weighing of dried precipitates involves therefore the drying and weighing of the filter. In former times, chemists used to collect the precipitate upon two filters of equal size, the one placed within the other; after the precipitate was dried, the outer filter was taken off and placed on the balance as a counterpoise to the inner filter which contained the precipitate. It was at the time assumed that filters of equal size were likewise of equal weight. This assumption, however, is inadmissible in minute and accurate analysis, since every experiment shows that even small filters, although of equal size, yet differ in weight to the extent of twenty, thirty, and even more millegrammes. To obtain accurate results, it is necessary to dry and to weigh the filter previous to using it; the temperature at which the filter is to be dried must be the same to which it is intended subsequently to expose the precipitate. The filtering paper must not contain any substance liable to be dissolved by the fluid filtering through it.

The process of drying filters is conducted either in the water-bath, air-bath, or oil-bath, according to the degree of heat required. The dried filter must be weighed in vessels with a cover, platinum crucibles are generally used for this purpose. The filter, as soon as it appears dry, is introduced into the heated crucible, allowed to cool, (this may be done most advantageously by placing the crucible with the filter over a vessel of sulphuric acid under a bell-jar,) and weighed; the crucible with the filter is then again exposed for some time to the required degree of heat, and after cooling, weighed again. If the weight does not differ from that found the first time, the filter may be considered dry, and we have simply to note the collective weight of the crucible and filter.

After the rinsing of the precipitate has been concluded, and the water allowed to run off as much as possible, the filter with the precipitate is taken off the funnel, folded up, and placed upon blotting-paper, and is kept for some time in a moderately warm place, protected from dust; this, in some measure, dries it, and thus facilitates the further process. It is finally introduced into the same platinum crucible in which it has been weighed previously to the filtration, and the crucible is then exposed to the appropriate degree of heat, either in water, air, or oil-bath, according to the nature of the precipitate. The crucible with its contents is then repeatedly weighed, and the drying continued until the weight remains constant. From the collective weights of the precipitate crucible and filter thus ascertained, we have simply to subtract that of the crucible and filter which, as stated above, we had accurately determined previous to the commencement of the process; the remainder expresses the exact weight of the precipitate.

It happens sometimes that the precipitate nearly fills the filter, or retains a considerable amount of the rinsing water, or sometimes the paper is so thin that its removal from the funnel cannot

PLATE XXVII.

be well effected without tearing it. In all such cases the filter is allowed to get nearly dry in the funnel, and covering it with a piece of blotting-paper, turned closely over the brim, placing it in a broken beaker-glass or other similar utensil, and exposing the whole to the heat of a sand-bath or stove.

§ 30.

ββ. Heating the precipitate to redness.

It was customary formerly to dry precipitate, the weight of which it was intended to determine after previous exposure to a red heat, with the filter, by projecting the precipitate into a crucible, scraping the filter clean, and finally heating it to redness, thus separated from the filter. In this way the minute particles of the precipitate, which will always adhere to the filter, however cleanly scraped the latter may be, were calculated for as lost. This loss may be avoided by incinerating the filter upon which the precipitate has been collected and weighing the ashes together with the precipitate, subtracting from the sum the weight of the ashes remaining upon the incineration of a *clean* filter of the same size.

If we take care to cut our filters accurately, we determine at once the amount of ashes for different size of filters; for this purpose, ten filters (of the same size) are burnt in a platinum crucible, placed obliquely, or in a platinum dish, and red heat applied until the last trace of charcoal is consumed; the ashes are then weighed, and the amount is divided by ten, the quotient expresses with sufficient precision the average quantity of ashes which every individual filter leaves upon incineration.

All precipitates which it is intended to expose to a red heat, should be thoroughly dried in the first place—the best way of effecting this preliminary is to leave the filter in the funnel, to cover the latter with a piece of blotting-paper turned closely over the brim, and to expose the whole to the heat of a sand-bath or stove in the manner illustrated by plate 27.

The following two methods of heating precipitates to redness, with simultaneous incineration of the filters, seem to me the most appropriate.

§ 31.

FIRST METHOD.

The crucible destined to receive the precipitate is accurately weighed, and subsequently placed upon a sheet of glazed paper; the perfectly dry filter containing the precipitate is then taken out of the funnel and gently pressed together over the paper, so as to detect the precipitate from the filter, and emptied into the crucible. The filter is freed by friction as much as possible from the particles of the precipitate adhering to it, which are also transferred into the crucible. The filter is then cut into eight or ten small pieces, (with a pair of clean scissors over the glazed paper,) the cover of the crucible is heated to redness over a Berzelius lamp, and the pieces are placed one by one upon the red-hot cover, with a pair of small pincers—the application of a gentle red-heat is continued until the last trace of charcoal has been completely consumed. We have already stated that certain precipitates, the basic phosphate of magnesia and ammonia, for instance, are not absolutely insoluble in the rinsing water. The washing of precipitates of this kind consequently tends to soak the filter with a saline solution, although extremely dilute; in such cases the complete incineration of the filter frequently requires a long-continued application of red-heat. The incineration may be promoted by gently forcing the still unconsumed part of the filter against the red-hot cover, so as to bring them into the most intimate contact with the latter. The incineration of filters must, of course, be conducted in a spot entirely protected from draught. After having completed the incineration of the filter, the particles of the precipitate which may have chanced to fall upon the glazed paper are transferred into the crucible, and the cover of the latter is put on, taking great care not to lose any of the ashes which it contains. The covered crucible is then exposed to the action of a gradually increasing heat, until it gets red-hot. After being kept red-hot for some time, it is allowed to cool, (hygroscofic substances must be cooled under a bell-jar, by the side of a vessel with sulphuric acid). The crucible, when perfectly cool, must be weighed with its contents; should the operator have neglected to weigh the empty crucible at the commencement of the operation, this must be done now after the crucible has been carefully emptied of its contents. If the latter admit of a ready and complete removal, the emptied crucible may be weighed at once; but if the substance adheres so firmly to its bottom and walls, that it is necessary to have recourse to solvents, the crucible after being carefully washed with distilled water, must be again heated to redness, and allowed to cool before its weight can be accurately ascertained.

PLATE XXVIII.

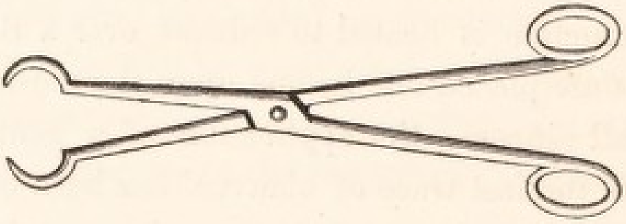


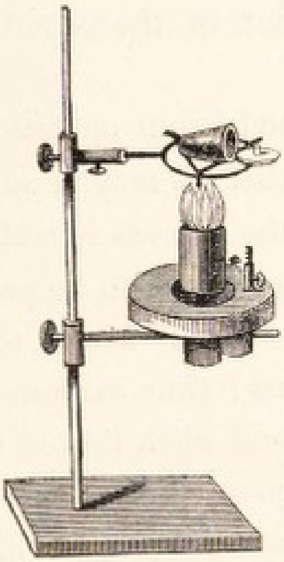
Figure 28 represents a pair of small pincers of iron or brass, well adapted for laying hold of red-hot crucibles.

§ 32.

SECOND METHOD.

This differs from the first only, inasmuch as the filter after having been freed from its contents, is loosely folded together and placed upon the precipitate in the crucible (instead of being cut in slips and consumed upon the cover of the crucible). The crucible is then covered and exposed to a gentle heat until the filter is completely charred—the cover is then removed, and the crucible heated to redness, so as to cause the charred filter to be completely consumed. To facilitate the latter part of the operation, the crucible is placed obliquely over the flame, and the access of air promoted by placing the cover against the crucible as illustrated Plate XXIX.

PLATE XXIX.



I have to mention still a third method which is applied in cases when the precipitate is intended for further analysis. This method consists, in collecting the precipitate upon a filter dried at 212°, the weight of which has been accurately ascertained; the precipitate is likewise dried at 212°, and a portion of it carefully weighed off into a crucible of known weight—this crucible is then heated to redness, and the diminution of weight, which the portion of the precipitate suffers in the operation is calculated for the whole precipitate. I think, however, that the application of this method, which requires so much weighing, may be altogether avoided, and the first method substituted for it, with this difference, that the cover of the crucible containing the ashes of the filter is placed inverted upon the crucible. This answers exactly the same purpose as the method just now described; that is, it permits us to weigh the whole of the precipitate without soiling it with the ashes of the filter, since only the minute particles which may have adhered to the filter are mixed up with the ashes.

Before dismissing this subject, I have to offer a few remarks on several points which deserve our particular attention in conducting the process of heating precipitates to redness.

In the *first* place we must endeavour to guard against any loss of substance; in this respect, particular care ought to be taken not to expose precipitates to the action of a red heat before they are perfectly dry; this rule applies more especially to substances which are loose and light when dry, such as silicic acid, for instance—since when these are subjected to the action of a red heat, whilst still retaining moisture, the aqueous vapours escaping with impetuosity would carry away minute particles of the precipitate; it applies with equal force to substances, which, like alumina or peroxide of iron, for instance, form into small hard lumps; some of these lumps retaining moisture, the application of intense heat will cause them to fly about in the crucible with great vehemence.

In the *second* place, we must know how to modify our operation according to the nature of the precipitate, or that we may be sure that the precipitate after the completion of the process is really the substance we suppose it to be. In this respect it is to be particularly observed, that certain precipitates must not be heated too intensely, or they will lose essential constituents; thus carbonate of lime, for instance, will yield up carbonic acid when heated to intense redness. On the other hand, many precipitates will require the protracted application of an intense red heat; if we are desirous to expel certain constituents, or to raise the substance to a certain degree of oxidation—the basic phosphate of magnesia and ammonia, protochromate of mercury, the oxides of manganese, &c. are examples of this kind. All such precipitates as suffer reduction when heated to redness, together with charcoal, must be heated according to the first method, since the second method would bring them into contact with the charcoal filter; the compounds of lead, copper, and zinc, sulphate of barytes, &c., are substances of this kind.

In the *third* place, care should be taken to incinerate the filter completely; we have already seen how the incineration of the filter may be promoted. In some instances, when the filters prove very refractory, the incineration may be aided by the action of nitric acid; providing always, other circumstances do not interfere with the application of this acid. The charred filtre is moistened with the acid slowly dried, and finally heated to redness. Nitrate of ammonia is sometimes used for the same purpose. A dilute solution of this salt is poured upon the filter, after the washing has been completed. The filter contains, consequently, after exsiccation, a small amount of this salt, which facilitates the incineration of the paper.

In the *fourth* place, we must avoid conducting the process in crucibles made of materials likely to be effected by the precipitate. We have already had occasion, in the qualitative analysis, to point out those cases in which the use of platinum crucibles ought to be avoided.

SECTION II.

REAGENTS.

§ 33.

For general remarks upon reagents necessary to the student, I would refer him to my volume on qualitative analysis.

We shall confine ourselves here to the preparation, tests, and most important uses of those chemical substances which subserve principally and more exclsively the purpose of quantitative analysis, simply enumerating the rest.

The same classification which I adopted in my qualitative anasis, is retained here, not because it is free from objection, but because upon the whole I deem it the best.

A.—REAGENTS IN THE HUMID WAY.

Which are,—I. General Reagents.

a. Reagents principally used as simple solvents.

§ 34.

1. DISTILLED WATER.

Water intended for quantitative investigations must be perfectly pure. Water distilled from glass retorts is not chemically pure, but leaves a minute residue upon evaporation. This defect renders it inapplicable in many experiments; thus, for instance, we cannot use it to determine the exact degree of solubility of substances which are only slightly soluble. (Vide experiment No. 1.) In many cases it is necessary to free the water by ebullition, from atmospheric air and carbonic acid.

2. ALCOHOL.

1. Absolute alcohol. 2. Spirits of wine of various degrees of strength.

3. ETHER.

The officinal ether of commerce is sufficiently pure. The application of ether as a solvent is very limited. It is more frequently mixed with spirits of wine, in order to diminish the solvent power of the latter for certain substances (e. g. chloride of platinum and ammonium).

β. Reagents which are principally used as chemical solvents.

§ 35.

1. HYDROCHLORIC ACID.

An acid of 1.12 sp. gr. suffices for most purposes; in some cases, however, it is required to be stronger.

2. NITRIC ACID.

An acid of 1.2 suffices for most purposes.

3. NITROSO-NITRIC ACID, (RED FUMING NITRIC ACID).

Preparation.—Two parts of pure and dry nitrate of potass are introduced into a retort, and one part of hydrated sulphuric acid is poured upon this salt, either through the tube of the retort, or if a common retort is used, through the neck of the latter by means of a long funnel tube bent at the lower extremity; this should be done carefully so as not to soil the neck of the retort. The latter is then placed in a sand-bath, and connected with a receiver, but not quite air-tight. The distillation is conducted at a gentle heat, and carried to dryness. The receiver must be constantly kept covered during the distillation.

Tests.—Red fuming nitric acid intended for analytical purposes, must be in a state of the greatest possible concentration and perfectly free from any admixture of sulphuric acid.

Uses.—This acid is a powerful solvent and oxidising agent; it serves more especially to convert sulphur and the sulphurets into sulphuric acid and sulphates.

4. AQUA REGIA.
5. ACETIC ACID.
6. CHLORIDE OF AMMONIUM.

γ. *Reagents which serve principally to separate substances into general classes or groups.*

§ 36.

1. SULPHURIC ACID.

a. CHEMICALLY PURE AND CONCENTRATED SULPHURIC ACID.

Preparation.—From three to four pounds of common sulphuric acid are introduced into a capacious glass retort, coated externally with a paste made with clay and cow-hair; a coil of platinum wire, or a few fragments of platinum, are thrown into the retort, and the latter is placed deep into a wind furnace, (which is subsequently to be covered with a cap;) the neck of the retort is then introduced into the body of a large globular receiver, without luting. The contents of the retort are gradually heated to boiling, by surrounding the latter with red-hot charcoal, taking care in the course of the operation to make the fire act principally upon the top and sides, and less upon the bottom, of the receiver.

If these instructions be strictly followed, the distillation will proceed quietly, and the operator need be under no apprehension of danger. The acid which passes over first is contaminated with nitric acid; it is necessary, therefore, to change the receiver after the lapse of some time, in order to obtain absolutely pure acid; the distillation is continued until about three quarters of the acid in the retort have passed over. The distillation may likewise be conducted in the sand-bath; in this case the bath should be so constructed that its bottom is covered with a considerable amount of sand, and that upon placing the retort into it, there remains but a small interval between the sides of the retort and the walls of the bath; the retort is covered with sand and a very inclined position given to the neck. The further operation is conducted exactly as the above. In this manner (i. e. in the sand-bath) ten pounds or more of sulphuric acid may be distilled at once without danger.

Tests.—If chemically pure, sulphuric acid will not leave the slightest residue when evaporated in a clean platinum dish.

b. COMMON SULPHURIC ACID.

c. DILUTE SULPHURIC ACID.

Dilute sulphuric acid, is prepared by mixing one part of concentrated sulphuric acid—(chemically pure or common, according to the circumstances of the case)—with five parts of water.

2. SULPHURETTED HYDROGEN.

a. Sulphuretted hydrogen gas.

PLATE XXX.

The cleaning of the tube through which this gas is conveyed, when needed for analytical purposes, may be materially facilitated by giving to the tube the construction illustrated by Plate XXX.

b. Sulphuretted hydrogen water.

3. HYDROSULPHURET OF AMMONIA.
4. SULPHURET OF POTASSIUM.
5. POTASS (pure potass ley.)
6. CARBONATE OF POTASS.
7. CARBONATE OF SODA.

One part of the anhydrous salt is dissolved in about ten parts of water. As a neutralizing and precipitating agent, this is in many cases preferable to carbonate of potass.

8. AMMONIA.
9. CARBONATE OF AMMONIA.
10. CHLORIDE OF BARIUM.
11. NITRATE OF BARYTES.
12. CYANIDE OF POTASSIUM.

This substance is extensively used in quantitative analysis to separate certain metals from one another. The aqueous solution of it must be prepared every time it is needed for use, since it does not keep, even in close vessels.

13. NITRATE OF SILVER.
14. CHLORINE.

II. SPECIAL REAGENTS IN THE HUMID WAY.

a. Reagents which serve principally to determine or to separate individual bases.

§ 37.

1. PHOSPHATE OF SODA.
2. OXALATE OF AMMONIA.
3. SUCCINATE OF AMMONIA.

Preparation.—Saturate succinic acid,—which has been purified by re-crystallization from its solution in nitric acid,—with dilute solution of ammonia, in such a manner that the reaction of the new compound is rather slightly alkaline than acid.

Uses.—This reagent serves to separate peroxide of iron from oxide of manganese, and other metallic oxides.

4. WATER OF BARYTES.

5. CARBONATE OF LIME.

Preparation.—Precipitate a heated solution of pure chloride of calcium with carbonate of ammonia, to which a little caustic ammonia has been added; allow the precipitate to subside; wash it carefully, and keep the pappy mass thus obtained in a close vessel for use.

Uses.—This reagent serves particularly to separate peroxide of iron from other metals which are not precipitated by carbonate of lime.

6. CARBONATE OF BARYTES.

Preparation. — This reagent is prepared from chloride of barium in the same manner as the preceding substance is prepared from chloride of calcium.

Uses.—Carbonate of barytes is used for the same purposes as carbonate of lime; but it is in many cases preferable to the latter.

7. PROTO-SULPHATE OF IRON.

8. PEROXIDE OF MERCURY.

This re-agent serves, in quantitative investigations, principally to decompose chloride of magnesium, in the process of separating magnesia from the alkalies.

9. PERCHLORIDE OF MERCURY.

10. PROTO-CHLORIDE OF TIN.

11. PERCHLORIDE OF GOLD.

12. CHLORIDE OF PLATINUM.

13. HYDROFLUO-SILICIC ACID.

14. TARTARIC ACID.

15. SULPHUROUS ACID.

16. COPPER.

The copper of commerce (with the exception of Japanese copper, which it is not always easy to procure) is not sufficiently pure for most analytical purposes.

The most convenient mode of preparing pure copper is that recommended by Fuchs; it consists in precipitating solution of blue vitriol with a piece or blade of clean iron; freeing the precipitated copper from the iron by boiling with hydrochloric acid, washing, drying, and fusing. The metal thus obtained is to be rolled out into thin sheets.

Tests. Pure copper must dissolve perfectly in nitric acid, and this solution must not yield the slightest trace of a precipitate upon addition of ammonia in excess, even after long standing, (iron, lead, etc.); nor should the addition of hydrochloric acid render it turbid (silver). Sulphuretted hydrogen must precipitate the copper completely from this solution.

Uses. This metal is frequently applied for the purpose of *indirect* analysis; thus, for instance, we use it to determine the amount of copper present in a fluid, or the amount of protoxide of iron existing by the side of the peroxide, etc.

17. TIN.

Preparation. Malacca tin, or English-grain-tin, is fused and poured out into slips. In cases where this cannot be readily procured, pure peroxide of tin is reduced by means of cyanide of potassium; the peroxide intended for this purpose should be prepared by oxidizing common tin with nitric acid, and washing, first with water containing a slight admixture of hydrochloric acid, and subsequently with pure water.

Tin is employed exclusively in the process of separating antimony from tin; it may be considered fit for that purpose if it dissolves in hot hydrochloric acid, forming a perfectly clear solution.

b. Reagents which serve principally to determine, or to separate, acids.

§ 38.

1. ACETATE OF POTASS.
2. CHLORIDE OF CALCIUM.
3. FLUORIDE OF CALCIUM.

This substance is used in quantitative analysis to expel and determine boracic acid; perfectly pure fluor spar, (like that of Derbyshire,) free from any admixture of silicic acid, is applicable for this purpose. Hydrofluoric acid, which is used in analytical investigations for the decomposition of silicates, may be prepared from a less pure kind of fluor-spar than the Derbyshire.

Tests. The best way of testing the purity of fluor-spar, in case of doubt, is to analyse it; the analysis is effected by levigating the fluor-spar finely, and treating a weighed amount of it with pure concentrated sulphuric acid, in a platinum crucible, at a gentle heat, which is gradually increased to redness:—this operation is to be repeated until the residue remains constant. The fluor-spar may be considered pure if the calculated amount of gypsum is obtained.

4. CHLORIDE OF MAGNESIUM.
5. PERCHLORIDE OF IRON.
6. OXIDE OF LEAD.
7. NEUTRAL ACETATE OF LEAD.
8. PROTOCHLORIDE OF PALLADIUM.

Preparation.—Dissolve palladium in aqua regia, evaporate to dryness, to expel the excess of acid; dissolve the residue in 20 parts of water, filter, if necessary, and keep the brown solution for use. This solution will contain a slight admixture of perchloride of palladium, which, however, is unimportant in the precipitation of iodine, the only purpose for which we use this reagent.

9. PROTOCHLORIDE OF ARSENIC.

Preparation.—Dissolve vitreous arsenious acid in pure and hot hydrochloric acid, and keep the solution for use.

Uses.—This reagent is employed for the determination of sulphuretted hydrogen.

B.—REAGENTS IN THE DRY WAY.

§ 39.

1. CARBONATE OF SODA.

2. HYDRATE OF BARYTES.

3. ACID SULPHATE OF POTASS.

Preparation.—Mix 87 parts of neutral sulphate of potass with 49 parts of pure hydrated sulphuric acid, in a platinum crucible, and heat to gentle redness, until the mass is in a state of uniform and clear fusion. Pour the fused mass into a platinum or porcelain dish, standing in cold water. After cooling, break the mass into pieces, and keep the latter for use.

Uses.—This reagent serves to resolve certain compounds of alumina, and of oxide of chromium, occurring in nature.

4. NITRATE OF POTASS.

5. CARBONATE OF AMMONIA, (solid).

Uses.—This reagent serves to convert the acid sulphates of the alkalies into neutral salts.

6. BIBORATE OF SODA—BORAX, (fused).

Preparation.—Heat crystallized borax in a platinum or porcelain dish, until it ceases to swell; reduce the porous mass to powder, and heat the latter in a platinum crucible, until the whole is fused into a transparent mass. Pour the more fluid portion of this mass upon a porcelain dish, remove the rest from the crucible by means of a platinum spatula, and keep the borax glass thus obtained in a stoppered bottle.

Uses.—This reagent serves to expel carbonic acid, and other volatile acids, at a red heat.

7. Hydrogen gas.

Preparation.—Hydrogen gas is evolved from dilute sulphuric acid by means of granulated zinc. It may be procured absolutely pure by transmitting it, in the first place, through a long glass tube loosely filled with cotton, soaked with solution of perchloride of mercury; subsequently through potass ley; and finally through hydrated sulphuric acid. In most cases, however, it is only necessary to transmit it through sulphuric acid, or through a chloride of calcium tube, for the purpose of drying it.

Tests.—Pure hydrogen gas is inodorous. It ought to burn with a colorless flame, which, when cooled by depressing a porcelain dish upon it, must deposit nothing on the surface of the dish except pure water, (free from acid re-action).

Uses.—Hydrogen gas is frequently used in quantitative analysis, to reduce oxides, chlorides, sulphurets, etc. to the metallic state.

8. Chlorine.

Chlorine gas is purified and dried by transmitting it, first, through a washing bottle, containing concentrated sulphuric acid, and, finally, through a chloride of calcium tube; the latter may, however, be omitted.

Uses.—Chlorine gas serves principally to produce chlorides, and to separate the volatile from the non-volatile chlorides; it is also used to expel, and indirectly to determine, bromine and iodine.

C.—REAGENTS APPLIED IN ORGANIC ELEMENTARY ANALYSIS.

§ 40.

1. Oxide of copper.

Preparation.—Mix pure copper scales with pure nitric acid, in a porcelain dish, so as to form a thick paste; after the effervescence has ceased, heat gently in the sand-bath until the mass is perfectly dry. Transfer the green basic salt produced into a hessian crucible, and heat to moderate redness, until no more fumes of hyponitric acid escape, which may be readily ascertained by introducing a small portion of the mass into a test-tube, closing the latter with the finger, and heating to redness, carefully looking through the tube in its whole length;—in most instances, the smell will sufficiently indicate whether the evolution of nitrous acid vapors continues, or not. The uniform decomposition of the salt in the crucible may be promoted by stirring the mass from time to time with a hot glass rod. After cooling, levigate the mass, which now consists of pure oxide of copper, into a tolerably fine powder, and keep this in a well-stoppered bottle for use. It will be found very advantageous to leave a small portion of the oxide in the crucible, and to expose this again to a most intense red heat. This portion is not to be levigated, but simply to be broken into small fragments, which must be kept in a separate bottle.

Tests.—Pure oxide of copper, prepared in this manner, is a dense, heavy, deep black powder, absolutely insoluble in water; upon exposure to a red heat, it should evolve no fumes of hyponitric acid, nor carbonic acid, (the latter would indicate contamination with fragments of charcoal, or with dust). That portion of the oxide which has been exposed to a very intense red heat, should be hard, and have a greyish black appearance.

Uses.—Oxide of copper serves to oxidize the carbon and hydrogen of organic substances, yielding up its oxygen wholly or in part according to circumstances. That portion of the oxide which has been heated to the most intense redness, is particularly useful in the analysis of volatile fluids.

The reduced copper may be again oxidised with nitric acid, and may thus be used again and again for the same purpose. Should it have been mixed with alkaline salts in the course of the analytical process, it may be freed from such admixture by digesting it with highly dilute nitric acid, and washing with water.

Chromate

2. [redacted], OF LEAD.

Preparation.—Precipitate a clean filtered solution of acetate of lead, slightly acidulated with acetic acid, by a small excess of bichromate of potass; decant from off the precipitate, and wash the latter completely upon a linen strainer; dry the washed precipitate, introduce it into a hessian crucible, and apply heat to bright redness until the mass fuses. Pour the fused mass upon a stone or iron plate, and levigate it into a fine powder.

Tests.—Chromate of lead prepared in this manner is a dirty yellow brown powder, insoluble in water. It must not evolve carbonic acid when heated to redness; (the evolution of carbonic acid would indicate contamination with organic matter, dust, etc.)

Uses.—Chromate of lead serves, like oxide of copper, for the combustion of organic substances. It is converted in the combustion process into chromic oxide and basic chromate of lead. It suffers the same decomposition, with evolution of oxygen, when heated by itself beyond the fusing point. This property renders chromate of lead, as an oxidizing agent, preferable to oxide of copper, in cases where we have to act upon substances difficult of combustion.

Chromate of lead which has been used once may be used a second time. It is for this purpose fused again, and the fused mass reduced to powder; if necessary, this second fusion is to be preceded by washing.

3. CHLORATE OF POTASS.

Preparation.—Commercial chlorate of potass is sufficiently pure. This is to be heated in a porcelain dish until it begins to enter into a state of complete fusion; the fused mass is then poured upon a porcelain dish, and broken into small pieces. The latter are kept for use in a well-stoppered bottle.

Uses.—Chlorate of potass yields up all its oxygen at a high temperature; it serves, therefore, for the complete oxidation of organic substances difficult of combustion. For the mode of its application, *vide infra.*

4. SODA-LIME, (mixture of caustic lime and hydrate of soda.)

Preparation.—Prepare, in the first place, a solution of soda from commercial crystallized carbonate of soda, in the manner prescribed for the preparation of potass ley, (*vide* 7 *a.*) ; ascertain the specific weight of the solution of soda prepared in this manner ; slake a weighed amount of the best caustic lime in the proportion of two parts of anhydrous caustic lime to one part of hydrated soda contained in the solution ; heat the mixture in a hessian crucible ; keep it for some time at a feeble red-heat, and levigate the mass, whilst still warm, into a tolerably fine powder ; keep this powder for use in a well-stoppered phial.

Tests.—This mixture of lime and soda must not effervesce too much when drenched with hydrochloric acid in excess. Mixed with pure sugar, and heated to excess, it must not evolve any ammonia ; the evolution of ammonia under these circumstances would render it entirely useless for the purpose for which it is intended in organic analysis.

Uses.—This mixture serves to analyse nitrogenous organic substances. For the manner and rationale of its action, *vide infra.*

5. BICARBONATE OF SODA.

In a certain method of organic elementary analysis of nitrogenous substances, bicarbonate of soda serves to evolve the carbonic acid by means of which the atmospheric air is expelled the combustion tube. The commercial bicarbonate is sufficiently pure for this purpose, provided it be perfectly dry.

6. COPPER TURNINGS.

These may be readily procured at any brazier's, but care should be taken to have them made of good copper ; if they are clean, pure, and free from any admixture of small fragments of wood, they are perfectly applicable to the purpose which they are intended to subserve in organic analysis. But if they have been already used, or are tarnished, or impure, it is necessary to purify them first ; for this purpose they are heated to nigrescence in a crucible, with free access of air, transferred subsequently into a glass or porcelain tube, and an uninterrupted stream of dry hydrogen gas passed over them; and, finally, when all atmospheric air has been completely expelled from the evolution apparatus and the tube, the latter is heated to redness in its whole length. The operator should be careful to wait until all atmospheric air has been *completely* expelled, before he proceeds to apply heat to the tube, since neglect in this respect may cause the apparatus to explode.

Uses.—Copper turnings serve in the analysis of nitrogenous substances for the reduction of the nitric-oxide gas which may have been formed.

7. POTASS.

a. SOLUTION OF POTASS.

Preparation.—The best way to prepare pure solution of potass, is to make a sufficiently dilute, cold prepared, solution of good potass, in the usual way, (by boiling with quick lime); to decant, and to evaporate the decanted fluid, in an iron kettle, with a rapid fire, until its specific gravity is 1.27. The fluid, whilst still warm, is poured into a bottle, and the latter being well closed, allowed to deposit every solid particle it contains; the clear solution is finally decanted from the sediment, and kept for use.

b. HYDRATE OF POTASS.

Preparation.—Pure solution of potass is introduced into a small silver kettle, and evaporated at a strong fire until the residuary hydrate begins to flow like oil, and to evaporate in white fumes; the fusing mass is then poured out on a clean iron plate, and broken into fragments, which are kept in a well-stoppered phial for use.

Uses.—Solution of potass serves for the absorption of carbonic acid, and consequently for the quantitative determination of this substance; in many instances, a tube filled with hydrate of potass is used in addition to the apparatus filled with the solution of potass.

8. CHLORIDE OF CALCIUM.

a. CRUDE FUSED CHLORIDE OF CALCIUM.

Preparation.—Digest with warm water the residue of chloride of calcium and lime which remains in the evolution of ammonia, filter and evaporate the filtrate to dryness in an iron caldron; fuse the residue in a hessian crucible, pour the fused mass out, break it into fragments, and keep them in well-stoppered phials.

b. PURIFIED CHLORIDE OF CALCIUM.

Preparation.—Dissolve the crude chloride of calcium of *a* in water, filter the solution, and should it manifest alkaline re-action, saturate it with a few drops of hydrochloric acid; evaporate to dryness in a porcelain dish, and expose the residue for several hours to a tolerably strong heat (about 392°) in the sand-bath. The white and porous mass obtained by this process consists of $\mathrm{Ca\,Cl} + \underset{\wedge}{\overset{2}{}}\mathrm{aq}$.

Uses.—The crude fused chloride of calcium serves to dry moist gases; the purified chloride is applied in elementary analysis for the absorption and determination of the water formed by the hydrogen of the analysed substance, and the oxygen of the reagent applied. Solution of purified chloride of calcium must not manifest an alkaline re-action.

SECTION III.

ON THE COMPOSITION AND PROPERTIES OF THE FORMS AND COMBINATIONS IN WHICH SUBSTANCES ARE SEPARATED FROM OTHERS, OR IN WHICH THEIR WEIGHT IS DETERMINED.

§ 41.

THE quantitative analysis of a compound substance requires, as the first and most indispensable condition, a correct and accurate knowledge of the composition and properties of the new combinations into which it is intended to convert its several individual constituents for the purpose of separating them from one another and determining their weight. Respecting the properties of these new compounds and their deportment, we have to inquire more particularly, in the first place, how they comport themselves with solvents; secondly, what is their deportment in the air; and, thirdly, what phenomena do they manifest when exposed to the action of a red heat? It may be laid down as a general rule that compounds are the better adapted for quantitative determination the more absolutely insoluble they are, and the less alteration they undergo upon exposure to the air, or to a high temperature.

The composition of bodies is expressed either in *per cent.* figures, or in a stœchiometrical or symbolic formulæ; by means of the latter, the constitution of the more frequently recurring compounds may be more easily committed to memory. With respect to its composition, a compound is the better adapted for quantitative determination the less it contains relatively of the substance which it is intended to determine, since the less the relative proportion of the latter, the less influence will any error or loss of substance that may occur in the course of the analytical process, exercise upon the accuracy of the results. Chloride of platinum and ammonium is, consequently, in this respect, better adapted for the determination of nitrogen than sal ammoniac, since 100 parts of the former contain only 6.28 of that element, whilst 100 parts of sal ammoniac contains 26.2 of it.

Suppose we have to analyse a nitrogenous substance: — we convert its nitrogen into chloride of platinum and ammonium, conducting the process with absolute accuracy, we obtain from 0.300 grammes of the analysed body, 1.000 gram. of chloride of platinum and ammonium: 100 parts of this double chloride contain 6.28 parts of nitrogen, 1.000 contains therefore 0.0628 of that element. These 0.0628 have been derived from 0.300 of substance; 100 parts of the analysed body, consequently, contain 20.93 of nitrogen.

We make a second analysis of the substance, in which we convert the nitrogen of the substance to be analysed into sal ammoniac, instead of chloride of platinum and ammonium; we conduct the process with absolute accuracy, and obtain from 0.300 of the substance under examination, 0.2396 of sal ammoniac, corresponding to 0.0628 of nitrogen, or 20.93 per cent.

Now, let us assume a loss of 10 milligrammes to have occurred in both processes ;—this will alter the result, in the first instance, from 1.000 to 0.990 of chloride of platinum and ammonium, corresponding to 0.062172 of nitrogen, or 20.72 per cent.; the loss of nitrogen will therefore be 20.93 minus 20.72=0.21.

In the second instance the result will be altered from 0.2396 to 0.2296 of sal ammoniac, corresponding to 0.0601 of nitrogen, or 20.05 per cent. The loss in this case will consequently amount to 0.88.

We see here that the same error occasions, in the one case, a loss of 0.21 per cent., with respect to the amount of nitrogen, whilst, in the other case, the loss amounts to 0.88 per cent.

We will now proceed to enumerate and examine all those combinations which are best adapted for the quantitative determination of every individual substance. The description of the external form and appearance of the new compounds relates to the state in which they are obtained in our analyses. With regard to the properties of the new compounds, we shall confine ourselves to enumerate those which bear upon the special object we have here more immediately in view.

A. FORMS AND COMBINATIONS, IN WHICH THE VARIOUS BASES ARE SEPARATED FROM OTHER BODIES, OR IN WHICH THEIR WEIGHT AND RELATIVE PROPORTION IS DETERMINED.

BASES OF THE FIRST GROUP.

§ 42.

1. POTASS.

The combinations best adapted for the weighing of potass are, SULPHATE OF POTASS, NITRATE OF POTASS, CHLORIDE OF POTASSIUM, CHLORIDE OF PLATINUM AND POTASSIUM.

a. Sulphate of potass (which, when its crystallization proceeds undisturbed, forms usually small, hard, oblique, four-sided prisms, or double pyramids of six faces) is obtained in analysis as a white crystalline mass. It dissolves pretty readily in water; it is nearly altogether insoluble in pure alcohol, but in a slight degree more soluble in alcohol containing sulphuric acid in admixture. (Experiment No. 2.) It does not alter vegetable colors; it is unalterable in the air. The crystals decrepitate strongly when heated, yielding at the same time a little water (which is mechanically confined between their plates). The decrepitation of crystals that have been kept long drying is less marked. At a strong red heat, sulphate of potass fuses unaltered and without volatilizing.

COMPOSITION.

$K\,O$	= 588.94	54.08
$S\,O_3$	= 500.00	45.92
	1088.94	100.00

The acid sulphate of potass, (hydrated bi-sulphate of potass,) ($K\,O, S\,O_3 + H\,O, S\,O_3$) which is uniformly produced when a solution of neutral sulphate of potass, impregnated with free sulphuric acid, is evaporated to dryness, is fusible even at a moderate heat. At a red heat, it loses half its sulphuric acid, together with the basic water, but not readily; the complete re-conversion of the acid into the neutral salt requiring the long-continued application of an intense red-heat. If heated, however, in an atmosphere of carbonate of ammonia,—(this may be readily procured by throwing a fragment of pure carbonate of ammonia into a crucible when heated to feeble redness, and putting the cover on,)—the acid salt changes readily and quickly into the neutral sulphate. This transmutation may be considered complete as soon as the salt, although kept simply at a feeble red-heat, has perfectly re-assumed the solid state.

b. Nitrate of potass crystallizes generally in long striated prisms. In analysis it is obtained as a white crystalline mass; it is readily soluble in water, nearly altogether insoluble in absolute alcohol, and scantily soluble in spirits of wine. It does not alter vegetable colors, and is unalterable in the air. On being exposed to a gentle heat, far below redness, it fuses unaltered and without diminution of weight; upon the application of a stronger heat, it changes into nitrite of potass, with evolution of oxygen, and if the heat be increased to intense redness, it becomes converted into caustic potass, and peroxide of potassium, with evolution of oxygen, and of nitrogen.

COMPOSITION.

KO	588.94	46.59
NO_5	675.25	53.41
	1264.19	100.00

c. Chloride of potassium crystallizes usually in cubes and rectangular prisms, rarely in octahedrons; in analysis we obtain it either in the former shape or as an amorphous mass. It is readily soluble in water, nearly insoluble in absolute alcohol, and but scantily soluble in spirits of wine. It does not change vegetable colors, and is unalterable in the air. When heated, it decrepitates, (if it has not been kept long drying,) yielding a little water (which is mechanically confined in it). At a feeble red-heat it fuses unaltered, and without diminution of weight, but when exposed to a higher temperature, it volatilizes in white vapors; and this volatilization proceeds the more slowly and difficultly, the more effectually and completely the access of air is prevented. (Experiments No. 3.)

COMPOSITION.

$K = 488.95$		52.45
$Cl = 443.20$		47.55
932.15		100.00

d. Chloride of platinum and potassium presents either small reddish-yellow octahedrons, or a lemon-yellow powder. It is difficultly soluble in cold, but more readily in hot water; nearly insoluble in absolute alcohol, and but scantily soluble in spirits of wine, 1 part requiring for its solution 12083 parts of absolute alcohol,—3775 parts of spirits of wine of 76 per cent,—1053 parts of spirits of wine of 55 per cent. (Experiment No. 4 *a.*) Presence of free hydrochloric acid sensibly increases its solubility.

Lee

(Experiment No. 4 *b*) It dissolves completely in caustic potass; the color of this solution is yellow. It is unalterable in the air, and at 212°. Upon being exposed to an intense red heat, that portion of the chlorine which is combined with the potassium escapes completely, and metallic platinum and chloride of potassium remain; but there still remains some chloride of platinum and potassium undecomposed, even after the mass has been kept in fusion for a long time. Complete decomposition takes place, however, if the salt is heated to redness in a stream of hydrogen gas.

COMPOSITION.

K	= 488.94	16.02
Pt	=1233.50	40.42
3 Cl	=1329.60	43.56
	3052.04	100.00

K Cl	= 932.14	30.54
$Pt\,Cl_2$	=2119.90	69.46
	3052.04	100.00

§ 43.

2. SODA.

Soda is usually weighed as SULPHATE OF SODA, NITRATE OF SODA, CHLORIDE OF SODIUM, OR CARBONATE OF SODA.

a. Anhydrous neutral sulphate of soda occurs as a white powder, or a white, very friable, mass. It dissolves readily in water; in absolute alcohol it is sparingly soluble, but somewhat more readily in spirits of wine; (Experiment No. 5;) the presence of free sulphuric acid increases its solubility in absolute alcohol. It is neutral to vegetable colors; exposed to a moist atmosphere, it slowly attracts water. (Experiment No. 6.) It remains unaltered at a gentle heat, but when exposed to an intense red heat, it fuses without decomposition or diminution of weight.

COMPOSITION.

Na. O.	=390.90	43.88
$S.\,O_3$.	=500.00	56.12
	890.90	100.00

Err.

The acid sulphate of soda (bisulphate of soda).

($Na\,O, S\,O_3 + H\,O, S\,O_3$) is uniformly produced when a solution of the neutral salt impregnated with sulphuric acid in excess is evaporated to crystallization; this acid salt fuses even at a gentle heat; it may be readily converted into the neutral salt in the same manner as the bisulphate of potass is reconverted into the neutral sulphate (vide § 42 *a*).

b. Nitrate of soda crystallizes in obtuse rhomboidal cubes. In analysis it is mostly obtained as an amorphous mass. It dissolves readily in water, but is nearly altogether insoluble in absolute alcohol, and but little more soluble in spirits of wine. It is neutral to vegetable colors, and unalterable in the common atmosphere; but when exposed to a very moist air, it absorbs water. It fuses without decomposition at a temperature far below red heat; at a higher temperature it undergoes the same decomposition as nitrate of potass. (Vide § 42 *b.*) (Comp. Experiment No. 7.)

COMPOSITION.

$Na\,O$ = 390.90	36.66
$N\,O_5$ = 675.25	63.34
1066.15	100.00

c. Chloride of sodium crystallizes in cubes, octahedrons, and hollow square pyramids. In analysis it is frequently obtained as an amorphous mass. It dissolves readily in water; it is hardly soluble in absolute alcohol, and but sparingly so in spirits of wine. It is neutral to vegetable colors. Exposed to a somewhat moist atmosphere, it slowly absorbs water. (Experiment No. 8.) Crystals of this salt that have not been kept long drying decrepitate when heated, yielding a little water, which they hold confined between their plates. At a red heat, it fuses without decomposition; at a white heat, and in open vessels, even at a bright red heat, it volatilizes in white vapors. (Experiments No. 9.)

See

COMPOSITION.

$Na = 290.90$	39.63
$Cl = 443.20$	60.37
734.10	100.00

d. Anhydrous carbonate of soda exists as a white powder, or a white, very friable mass. It dissolves readily in water, but is insoluble in alcohol. Its reaction is strongly alkaline. Exposed to the air, it absorbs water very slowly. At a strong red-heat it fuses without decomposition, and without volatilizing.

COMPOSITION.

$Na\,O = 390.90$	58.70
$C\,O_2 = 275.00$	41.30
665.90	100.00

§ 44.

3. AMMONIA.

Ammonia is most advantageously weighed as CHLORIDE OF AMMONIUM, AND CHLORIDE OF PLATINUM AND AMMONIUM.

Under certain circumstances, ammonia may likewise be determined from the volume of nitrogen separated from it.

a. Chloride of ammonium crystallizes in cubes and octahedrons, but more frequently in feathery crystals. In analysis we obtain it uniformly as a soft white mass. It dissolves readily in water, but is difficultly soluble in spirits of wine. It does not alter vegetable colors, and is persistent in the air. Solution of sal-ammoniac when evaporated in the water-bath, loses a small proportion of ammonia, and becomes slightly acid. The diminution of weight occasioned by this loss of ammonia is very trifling. (Experiment No. 10.) At 212° sal ammoniac loses nothing, or next to nothing, of its weight. At a higher temperature it volatilizes readily, and without undergoing decomposition.

COMPOSITION.

NH_4	=225.25 . . .	33.69
Cl	=443.20 . . .	66.31
	668.45	100.00

NH_3	=212.75 . . .	31.63
Cl H	=455.70 . . .	68.17
	668.45	100.00

b. Chloride of platinum and ammonium occcur either as a heavy lemon-yellow powder, or in small, hard, octahedral crystals of a bright yellow color. It is difficultly soluble in cold, but more readily in hot water. It requires for its solution 26535 parts of absolute alcohol; 1406 parts of spirits of wine of 76 per cent., 665 parts of spirits of wine of 55 per cent. The presence of free acid sensibly increases its solubility. (Experiment No. 11.) It is unalterable in the air, and at 212°. When heated to redness, chlorine and chloride of ammonium escape, and metallic platinum remains behind as a spongy mass.

COMPOSITION.

NH_4	=225.25 . .	8.08
Pt	=1233.50 . .	44.24
3 Cl	=1329.60 . .	47.68
	2788.35	100.00

N H Cl.	= 668.45 . .	23.97
$Pt\ Cl_2$	=2119.90 . .	76.03
	2788.35 .	100.00

NH_3	= 212.75 . . .	7.63
Cl H	= 455.70 . . .	16.34
$Pt\ Cl_2$	=2119.90 . . .	76.03
	2788.35	100.00

N	= 175.25 . . .	6.28
H_4	= 50.00 . . .	1.79
$Cl._3$	=1329.60 . . .	47.69
Pt	=1233.50 . . .	44.24
	2788.33	100.00

c. Nitrogen gas is colourless, tasteless, and inodorous, miscible with air without producing the slightest coloration; it is indifferent to vegetable colors; its specific gravity is 0·9706. (Air=1). One litre (one cubic decimeter) weighs at 32. and 0.76 metres atmospheric pressure (29.8 of the barometer) 1.2609 grammes.

It is difficultly soluble in water; one volume of gas requiring, at 64.4° 24 volumes of water.

BASES OF THE SECOND GROUP.

§ 45.

1. BARYTES.

Barytes is generally weighed as SULPHATE OF BARYTES, CARBONATE OF BARYTES, FLUORIDE OF SILICIUM AND BARIUM.

a. Sulphate of barytes, artificially produced, is a fine white powder. It is almost absolutely insoluble in cold as well as in hot water; the presence of free acid hardly increases its solubility. It is quite unalterable in the air, at 212°, and even at a red heat. When heated to redness, together with charcoal, it is transformed into sulphuret of barium. This reduction, however, takes place only if the access of air is precluded.

COMPOSITION.

BaO	=954.85	65.64
SO_3	=500.00	34.36
	1454.85	100.00

b. Carbonate of barytes, artificially produced, is a white powder. It dissolves in 14137 parts of cold, and in 15421 parts of boiling water, (experiment No. 12); it dissolves far more readily in solution of chloride of ammonium, or nitrate of ammonia. From these solutions it is, however, precipitated again by caustic ammonia. Water containing free carbonic acid dissolves carbonate of barytes as a bi-carbonate. It is almost absolutely insoluble in water impregnated with ammonia and carbonate of ammonia, one part requiring about 141000 parts. (Experiment No. 13.)

Solution of carbonate of barytes has a feebly alkaline reaction.

Carbonate of barytes is unalterable in the air, and at a red-heat. Upon heating it to redness, together with charcoal, caustic barytes is formed, whilst carbonic oxide gas escapes.

COMPOSITION.

$Ba\,O$	=954.85 . . .	77.64
$C\,O_2$	=275.00 . . .	22.36
	1229.85	100.00

c. Fluoride of silicium and barium exists in small, hard, and colorless crystals; more frequently still, as a crystalline powder. It dissolves in 3800 parts of cold, but more readily in hot water. (Experiment No. 14.) The presence of free hydrochloric acid increases its solubility considerably. (Experiment No. 15.) It is unalterable in the air, and at 212°; when heated to redness, it is decomposed into fluosilicic gas, which escapes, and fluoride of barium which remains behind.

COMPOSITION.

$Ba\,Fl$	=1090.56 . . .	62.43	Ba	=854.85 . . .	48.94
$Si\,Fl_2$	= 656.30 . . .	37.57	Si	=184.88 . . .	10.58
			Fl_3	=707.13 . . .	40.48
	1746.86	100.00		1746.86	100.00

§ 46.

2. STRONTIA.

Strontia is determined either as SULPHATE OF STRONTIA, OR AS CARBONATE OF STRONTIA.

a. Sulphate of strontia, artificially prepared, is a white powder. It dissolves in 6895 parts of cold, and 9638 parts of boiling water. (Experiment No. 16.) It is less soluble in water containing sulphuric acid, requiring as much as 11000 or 12000 parts. (Experiment No. 17.) It dissolves in solution of common salt, but is precipitated again by sulphuric acid. It is nearly altogether insoluble in alcohol as well as in spirits of wine. It does not alter vegetable colors; and is unalterable in the air, and at a red-heat. When exposed to a very intense red-heat, it fuses without undergoing decomposition. When heated to redness, together with charcoal, access of air being precluded, it is transformed into sulphuret of strontium.

COMPOSITION.

$Sr\,O$=	645.60	56.35
$S\,O_3$=	500.00	43.65
	1145.60	100.00

b. Carbonate of strontia, artificially produced, is a white delicate loose powder. It dissolves at the common temperature in 18045 parts of water. (Experiment No. 18.) The presence of ammonia diminishes its solubility. (Experiment No. 19.) It dissolves readily in solutions of sal-ammoniac and nitrate of ammonia, but is precipitated again from these solutions by ammonia. Water impregnated with carbonic acid dissolves it as a bi-carbonate. Its re-action is very feebly alkaline. It remains unaltered in the air, and even at a red-heat; but when exposed to a very intense red-heat, it fuses, and gradually loses its carbonic acid. Upon heating it to intense redness together with charcoal, caustic strontia is formed, whilst carbonic oxide gas escapes.

COMPOSITION.

$Sr\,O$=	645.60	70.12
$C\,O_2$=	275.00	29.88
	920.60	100.00

§ 47.

3. LIME.

Lime is determined either as SULPHATE OF LIME or as CARBONATE OF LIME; for the latter purpose, it is precipitated first as OXALATE OF LIME.

a. Anhydrous sulphate of lime, artificially produced, is a loose white powder. It dissolves at the common temperature in 430 parts, and at 212° in 460 parts of water. The presence of sal ammoniac, sulphate of soda, and common salt increases its solubility. The aqueous solution of gypsum does not alter vegetable colors. Sulphate of lime is nearly altogether insoluble in alcohol, as well as in spirits of wine. Exposed to the air, it slowly absorbs water; it remains unaltered at a dull red-heat. When heated to a bright redness, it fuses without undergoing decomposition. Upon being heated to redness together with charcoal, access of air being precluded, it is reduced to sulphuret of calcium.

COMPOSITION.

CaO	$=350.00$	41.18
SO_3	$=500.00$	58.82
	850.00	100.00

b. Carbonate of lime, artificially prepared, is a white fine powder. It dissolves in 10601 parts of cold, (Experiment No. 20,) and in 8834 parts of boiling water, (Experiment No. 21). Its solution has a hardly perceptible alkaline reaction. Water impregnated with ammonia and carbonate of ammonia dissolves it far more sparingly, one part requiring about 65000 parts for its solution. (Experiment No. 22.) This solution is not precipitated by oxalate of ammonia. It dissolves more readily in solutions of sal ammoniac and nitrate of ammonia, but is precipitated again from these solutions by ammonia. Neutral potass and soda salts likewise increase its solubility. Water impregnated with carbonic acid dissolves carbonate of lime as a bicarbonate. Carbonate of lime is unalterable in the air at 212°, and even at a red-heat; but upon the application of a more intense heat, it gradually loses its carbonic acid, more especially with free access of air. Attempts at calcining carbonate of lime completely, in a platinum crucible over a spirit-lamp, with double draught, have, however, failed. (Experiment No. 23.) It yields up its carbonic acid, (as carbonic oxide gas,) far more readily when heated to redness together with charcoal.

COMPOSITION.

$Ca\,O$	$= 350.00$	56.00
$C\,O_2$	$= 275.00$	44.00
	625.00	100.00

c. Oxalate of lime is a fine white powder, nearly absolutely insoluble in water. The presence of free oxalic acid and acetic acid increases its solubility slightly; but ammoniacal salts exercise no influence whatever in this respect. The stronger acids (hydrochloric acid, nitric acid) dissolve oxalate of lime readily; and from these solutions it is precipitated again unaltered by alkalies; and likewise (provided the excess of acid be not too great) by the addition in excess of alkaline oxalates, or of alkaline acetates. It is unalterable in the air, and at 212°; dried at 212°, its composition is as follows:—(Experiment No. 24.)

$Ca\,O$	$= 350.00$	38.36
$C_2\,O_3$	$= 450.00$	49.32
aq	$= 112.50$	12.32
	912.50	100.00

At a temperature of from 356° to 392°, oxalate of lime loses its water without undergoing decomposition; when heated to incipient dull redness it is decomposed, without actual separation of carbon, into carbonic oxide, which escapes, and carbonate of lime, which remains behind. The powder, which was previously of snowy whiteness, transiently assumes a grey color in the course of this process, even though the oxalate be of the most perfect purity. Upon the continued application of heat this grey color disappears again. If the oxalate of lime is heated in small coherent fragments, such as are obtained upon drying the precipitated salt upon the filter, the commencement and progress of the decomposition can be readily marked by this transient appearance of grey. If the process of heating be conducted properly and cautiously, the residue will not contain a trace of caustic lime.

§ 48.

4. MAGNESIA.

Magnesia is determined either as SULPHATE OF MAGNESIA, PYROPHOSPHATE OF MAGNESIA, OR AS PURE MAGNESIA. To transform it into the pyrophosphate, it is precipitated as BASIC PHOSPHATE OF AMMONIA AND MAGNESIA.

a. Anhydrous sulphate of magnesia is a white opaque mass. It dissolves readily in water. It is nearly altogether insoluble in absolute alcohol; and but very sparingly soluble in spirits of wine. It does not alter vegetable colors. Exposed to the air, it absorbs water rapidly. It does not undergo decomposition at a moderate red-heat, but it is partially decomposed when heated to very intense redness. It loses part of its acid in this process of decomposition, and is afterwards no longer completely soluble in water. (Experiment No. 25.)

COMPOSITION.

$Mg\,O = 257.75$ 34.01
$S\,O_3 = 500.00$ 65.99
757.75 100.00

b. Basic phosphate of magnesia and ammonia occurs as a white crystalline powder. It dissolves at the common temperature in 15293 parts of cold water. (Experiment No. 26.) It is far more insoluble in water impregnated with ammonia, one part requiring about 45000 parts. (Experiment, No. 27.) Sal ammoniac slightly increases its solubility. (Experiment Nos. 28 and 29.) The presence of phosphated alkalies is without influence in this respect. It dissolves readily in acids, even in acetic acid. Its composition is expressed by the formula $P\,O_5$, $2\,Mg\,O, N\,H_4, O + 12$ aq. When this salt is dried at 212°, ten equivalents of water escape; upon being heated to redness, all the water escapes, together with the ammonia, leaving $P\,O_5$, $2\,Mg\,O$ behind. The transition of the common phosphoric acid into pyrophosphoric acid is indicated by a lively incandescence of the heated mass.

c. Pyrophosphate of magnesia occurs as a white mass, frequently slightly inclining to grey. It is barely soluble in water, but readily so in hydrochloric acid, and in nitric acid; it is unalterable in the air, and even at a red-heat. It fuses without undergoing decomposition when exposed to a very intense degree of heat. It does not alter moist turmeric paper, nor reddened litmus paper.

COMPOSITION.

$P\,O_5 = 891.55$ 63.36
$2\,Mg\,O = 515.50$ 36.64
1407.05 100.00

d. Pure magnesia is a white, light, loose powder. It dissolves in 55368 parts of cold, and in the same proportion of boiling water. (Experiment No. 30.) Its solutions in water have a very feeble alkaline reaction. Magnesia dissolves in hydrochloric acid, and in other acids, without evolution of gas. Exposed to the air, it slowly absorbs carbonic acid and water. Magnesia is highly infusible, remaining unaltered at a strong red heat, and fusing superficially only at the very highest temperature.

COMPOSITION.

Mg O=157.75 . . . . 61.20
O=100.00 . . . . 38.80
257.75 100.00

BASES OF THE THIRD GROUP.

§ 49.

1. ALUMINA.

Alumina is usually precipitated as HYDRATE OF ALUMINA, and uniformly weighed in its pure state.

a. Hydrate of alumina, recently precipitated, is a gelatinous mass which retains invariably a minute proportion of the acid with which the alumina was combined previously to its precipitation, as well as of the alkali which has served as precipitant; it is freed with difficulty from these admixtures by repeated washings.

Hydrate of alumina is insoluble in pure water; but readily soluble in solutions of soda and potass, and in acids; it is sparingly soluble in caustic ammonia, and altogether insoluble in carbonate of ammonia, and also in caustic ammonia, if ammoniacal salts are present. (Experiment No. 31.) Hydrate of alumina shrinks considerably upon exsiccation, and when dry, becomes a hard, transparent, yellowish, or a white earthy mass. When heated to redness it loses its water, and this loss of water is frequently attended with slight decrepitation, and invariably with considerable diminution of bulk.

b. Alumina, prepared by heating the hydrate to redness, (vide *a*,) is a loose and soft mass, if a moderate degree of heat has been applied: but if this substance has been heated to a very intense degree of redness, it forms small hard fragments. At the most intense degree of white heat, (before the oxihydrogen blow-pipe,) it fuses into a colorless glass. Ignited alumina is dissolved by acids with very great difficulty. Placed upon moist reddened litmus paper, it does not turn the color of this paper into blue.

COMPOSITION.

2 Al	=340.84	. . . . 53.19
3 O	=300.00	. . . . 46.81
	640.84	100.00

§ 50.

2. OXIDE OF CHROMIUM.

Oxide of chronium is usually precipitated as HYDRATED OXIDE OF CHROMIUM, and uniformly weighed in its pure state.

a. Hydrated oxide of chromium, recently precipitated, is a greenish grey gelatinous mass, insoluble in water; it dissolves readily in solution of potass, at a low temperature, imparting a dark green tint to the solution; it dissolves likewise in solution of ammonia, at a low temperature, but only to a moderate extent, imparting a bright violet-red tint to the solution; in acids it dissolves readily, with dark green coloration. The presence of sal ammoniac does not exercise any influence upon the greater or less solubility of hydrated oxide of chromium in ammonia. Upon boiling solutions of hydrated oxide of chromium in potass and in ammonia, all the oxide separates. (Experiment No. 32.) Hydrated oxide of chromium, when dried, is a greenish-blue powder, which loses its water of hydration at a gentle red-heat.

b. Oxide of chromium, produced by heating the hydrate to dull redness, become as dark green powder, which, upon the application of a stronger degree of heat, assumes a brighter tint, with vivid incandescence, and without undergoing any diminution of weight. The feebly ignited oxide is difficultly soluble in hydrochloric acid, and the strongly ignited oxide is altogether insoluble in this acid.

COMPOSITION.

2 Cr	=703.63	70.11
3 O	=300.00	29.89
	1003.63	100.00

BASES OF THE FOURTH GROUP.

§ 51.

1. OXIDE OF ZINC.

The oxide of zinc is *precipitated* as BASIC CARBONATE OF ZINC, or as SULPHURET OF ZINC, but it is uniformly *weighed* as the pure oxide.

a. Basic carbonate of zinc, recently precipitated, is a white, flocculent precipitate, which is nearly insoluble in water, — (one part requires 44600 parts, Experiment No. 33,)—but readily soluble in solutions of potass, ammonia, carbonate of ammonia, and in acids. When a neutral solution of zinc is precipitated with carbonate of potass, (or carbonate of soda,) carbonic acid is evolved, under all circumstances, since the precipitate formed is not $Zn\,O,\,C\,O_2$, but consists of a mixture of $2\,(Zn\,O,\,C\,O_2)+3\,(Zn\,O,\,H\,O,)$ with carbonate of zinc and potass. (Potassio-carbonate of zinc.) Owing to the presence of this carbonic acid, as well as to the circumstance that *the carbonate of zinc and potass* is not insoluble in water, part of the oxide of zinc remains in solution; the cold filtered fluid yields, therefore, a precipitate when acted upon by sulphuret of ammonium.

If, however, the solution of zinc be heated to boiling, previously to the addition of the carbonate of potass, and then kept boiling for some time after, (which will prevent the formation of *carbonate of zinc and potass*, and will, moreover, cause the expulsion of every trace of free carbonic acid from the fluid),—the precipitation of the zinc will be complete, in so far as the filtrate will not be rendered turbid by the addition of hydrosulphuret of ammonia;—however, after allowing the filtrate, mixed with hydrosulphuret of ammonia, to stand at rest for many hours, minute and almost imponderable flakes of sulphuret of zinc will separate from the fluid. The precipitate of carbonate of zinc, obtained in the manner just now described, may be completely freed from all admixture of potass by washing with hot water. If ammoniacal salts be present, every trace of ammonia must be expelled first, before the complete* precipitation of the zinc can be achieved. If the solution of a zinc salt be mixed with carbonate of potass in excess, and the mixture be

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* That is, complete within the limits indicated just now, so that hydrosulphuret of ammonia occasions no turbidity in the filtrate, although it may produce subsequently and after long standing some slight and almost imponderable flakes of sulphuret of zinc.

evaporated to dryness, at a gentle heat, and the residue treated with cold water, a pretty considerable proportion of the zinc will be obtained in solution as *carbonate of zinc and potass;* but if the mixture be evaporated to dryness, at a boiling heat, and the residue be treated with hot water, all the zinc will be obtained as carbonate of zinc, (with the exception of an extremely minute proportion, as we have already had occasion to observe.) When dry, the basic carbonate of zinc is a shining, white, loose powder, which, upon being heated toredness, is transformed into oxide of zinc.

b. Oxide of zinc, produced by heating the carbonate to redness, is a white light powder, very slightly inclining to a yellowish tint. It assumes a yellow color at a high temperature, which disappears again upon cooling. Heating oxide of zinc to redness, together with charcoal, gives rise to the evolution of carbonic oxide gas, and of zinc vapor. Oxide of zinc is insoluble in water. Placed upon moist turmeric paper, it does not turn the color of this paper into brown. In acids, oxide of zinc dissolves readily, and without evolution of gas.

COMPOSITION.

Zn	=406.59	80.26
C	=100.00	19.74
	506.59	100.00.

c. Sulphuret of zinc, recently precipitated, occur as a white loose mass, ($Zn\,S, H\,O$,) insoluble in water as well as in caustic alkalies, carbonated alkalies, and alkaline sulphurets. It dissolves readily and completely in hydrochloric acid and nitric acid, but very sparingly in acetic acid. After drying, the precipitate becomes a white powder, which at 212° loses half, and at a red-heat the whole of its water. During the latter process, some sulphuretted hydrogen escapes, and the remaining sulphuret of zinc contains oxide of zinc in admixture.

§ 52.

1. PROTOXIDE OF MANGANESE.

Manganese is weighed either as MANGANOSO-MANGANIC OXIDE, (red oxide of manganese) [$(Mn\ O + Mn_2\ O_3) = Mn_3\ O_4$], or as PROTOSULPHATE OF MANGANESE. For the purpose of converting it into the first form, it is precipitated as PROTOCARBONATE OF MANGANESE, HYDRATED PROTOXIDE OF MANGANESE, and SULPHURET OF MANGANESE.

a. Protocarbonate of manganese, recently precipitated, forms a white flocculent precipitate, nearly altogether insoluble in pure water, but somewhat more readily soluble in water impregnated with carbonic acid. The presence of carbonate of soda or potass does not increase its solubility. Recently precipitated carbonate of manganese dissolves pretty readily in solution of sal ammoniac; it is owing to this property that a solution of protoxide of manganese cannot be completely precipitated by carbonate of potass or soda, in presence of sal ammoniac, (or of any other ammoniacal salt,) until the latter is completely decomposed. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, it slowly assumes a dirty brownish-white color, part of it becoming converted into hydrated manganic oxide. If the precipitate is dried, removed from the contact of air, it becomes a soft, white powder, persistent in the air, [$2\ (Mn\ O,\ C\ O_2) +$ [illegible] aq.], but when dried, with free access of air, the powder is of a more or less dirty white or brownish color. When heated to redness, with access of air, this powder first turns black, and is subsequently converted into brown manganoso-manganic oxide.

b. Hydrated protoxide of manganese, recently precipitated, forms a white, flocculent precipitate, insoluble in water and in the alkalies, but soluble in sal ammoniac; this precipitate immediately absorbs oxygen from the air, and turns brown, owing to the formation of hydrated manganic oxide. Upon drying the precipitate in the air, a brown powder is obtained, (hydrated manganic oxide,) the color of which strains off; this powder, when heated to intense redness, with access of air, becomes converted into manganoso-manganic oxide.

c. Protosulphuret of manganese, prepared in the humid way, forms a precipitate of a flesh tint; it is insoluble in water and alkalies. It is not altogether insoluble in the colorless hydrosulphuret of ammonia, but absolutely insoluble in the yellow hydrosulphuret or the penta-sulphuret of ammonium, (yellow sulphuretted hydrosulphuret of ammonia). The presence of sal ammoniac does not increase its solubility. In hydrated acids, (hydrochloric acid, sulphuric acid, &c.,) it dissolves with evolution of sulphuretted hydrogen. If the precipitate, while yet moist, is exposed to the air, or washed with water impregnated with air, its fleshy tint changes to brown, hydrated manganic oxide being formed, and, at the same time, some protosulphate of manganese. To avoid this, it is advisable to add to the washing water a slight portion of the yellow sulphuretted hydrosulphuret of ammonia.

*d. Manganoso-manganic oxide,** (red oxide of manganese), artificially produced, is a red-brown powder. If it is exposed to the action of heat, it assumes a black tint, but this is not attended with any variation in its weight. It is insoluble in water, and does not alter vegetable colors.

COMPOSITION.

3 Mn = 1033.32 . . . . 72.10
4 O = 400.00 . . . . 27.90
1433.32 100.00

e. Protosulphate of manganese, in its anhydrous state, such as is obtained upon exposing the crystallized salt to the action of

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* All the oxides of manganese are converted into the red oxide when ignited strongly in the open air.

heat, is a white, friable mass, readily soluble in water. It bears the continued application of a faint red heat, without undergoing decomposition; but when ignited to a greater degree of intensity, it is more or less completely decomposed. Oxygen, sulphurous acid, and anhydrous sulphuric acid, are evolved and expelled, and red oxide of manganese remains behind.

COMPOSITION.

Mn O	=444.44	47.05
SO_3	=500.00	52.95
	944.44	100.00

§ 53.

3. PROTOXIDE OF NICKEL.

Nickel is precipitated as HYDRATED PROTOXIDE OF NICKEL, and as SULPHURET OF NICKEL. It is uniformly weighed in the form of protoxide.

a. Hydrated protoxide of nickel occurs as an apple-green precipitate, nearly insoluble in water, but soluble in ammonia and carbonate of ammonia. It is completely precipitated, from these solutions, by the addition of potass in excess; this precipitation is promoted by heat. It is unalterable in the air. Upon ignition, it changes into protoxide of nickel.

b. Protoxide of nickel is a dirty greyish-green powder, insoluble in water, but readily soluble in hydrochloric acid. It does not affect vegetable colors. Its weight does not vary upon ignition in the air.

COMPOSITION.

Ni	=369.14	78.68
O	=100.00	21.32
	469.14	100.00

c. Hydrated *sulphuret of nickel*, prepared in the humid way, is a black precipitate insoluble in water. It is insoluble in an excess of sulphuret of ammonium, perfectly saturated with sulphuretted hydrogen, but it is slightly soluble in ammonia, and still more so in ammonia not fully saturated with sulphuretted hydrogen. When these solutions, which are of a more or less brown color, are exposed to the air, the sulphuret of nickel, contained in them, precipitates gradually. (Vide Experiments sub. No. 34). If sulphuret of nickel, in a moist state, is exposed to the air, it oxidizes slowly, and is converted into protosulphate of nickel. It is very sparingly soluble in acetic acid, but somewhat more so in hydrochloric acid. It is more readily soluble still in nitric acid, and most so in aqua regia. It loses its water upon the application of a red-heat; when ignited in the air, it becomes transformed into a basic compound of peroxide of nickel with sulphuric acid.

§ 54.

4. PROTOXIDE OF COBALT.

Cobalt is uniformly weighed in the pure metallic state. Beside the properties of METALLIC COBALT, we have to examine here those of HYDRATED PROTOXIDE OF COBALT, COBALTOSO-COBALTIC OXIDE, and SULPHURET OF COBALT.

a. Hydrated protoxide of cobalt.—Upon precipitating a solution of protoxide of cobalt with potass, a blue precipitate (a basic salt) is formed at first, which, upon boiling with potass in excess, removed from the contact of air, changes into bright red hydrate of protoxide of cobalt; if, on the contrary, this process be conducted with free access of air, the precipitate will become discolored, part of the hydrated protoxide being converted into hydrated peroxide. Hydrated protoxide of cobalt is insoluble in water, and likewise in potass; it is soluble in ammoniacal salts; when dried in the air, it absorbs oxygen, and assumes a brownish color *b.* If hydrated protoxide of cobalt is ignited in the air, it becomes transformed into either one or the other of the two following *compounds of protoxide with peroxide of cobalt,* (*cobaltoso-cobaltic oxide*).

$$Co_6 \ O_7$$

or,

$$Co_3 \ O_4$$

According to the greater or less degree of intensity of the heat applied, so that $Co_3 \ O_4$ is more particularly the result of a feeble heat, whilst $Co_6 \ O_7$ results from the application of an intense heat. Since it is difficult, however, to produce a constant oxygen compound in this manner, it is by far the safest way to reduce the compound thus obtained to the metallic slate, if it be intended to determine the cobalt.

c. Metallic cobalt, produced by reducing its oxide, by means of hydrogen, becomes a grey magnetic powder, of more difficult fusibility than gold. Cobalt that has been reduced at a gentle heat oxidizes at the common temperature; but when it has been reduced at an intense red-heat, it absorbs oxygen very slowly. Ignited in the air, it oxidizes into cobaltoso-cobaltic oxide. It dissolves readily and completely in nitric acid, and likewise in hot and concentrated hydrochloric acid.

d. Sulphuret of cobalt, produced in the humid way, is a black precipitate, insoluble in water, alkalies, and alkaline sulphurets. It is but sparingly soluble in acetic acid and dilute mineral acids, but more readily so in concentrated mineral acids; it dissolves most readily in hot aqua regia. When sulphuret of cobalt, in a moist state, is exposed to the air, it slowly absorbs oxygen, and becomes converted into protosulphate of cobalt.

§ 55.

5. PROTOXIDE OF IRON; and 6, PEROXIDE OF IRON.

Iron is uniformly weighed in the form of PEROXIDE. Besides the peroxide, we have to examine the HYDRATED PEROXIDE OF IRON, SULPHURET OF IRON, and PERSUCCINATE OF IRON.

a. Hydrated peroxide of iron, recently precipitated, is a red brown precipitate, insoluble in water, in the alkalies, and in ammoniacal salts, but readily soluble in acids; the process of drying reduces the bulk of this precipitate amazingly. When dry, it becomes a brown hard mass, the fracture of which exhibits a glossy appearance similar to shell. In the precipitation of persalts of iron by ammonia and the alkalies, (in excess,) a portion of the precipitated alkali is invariably carried down in combination with the peroxide of iron, and cannot be entirely removed by washing. When ammonia is used, however, the excess of the precipitant may be expelled by ignition. We use, therefore, ammonia alone to precipitate persalts of iron, for the purpose of analysis.

b. The hydrated peroxide of iron, upon being ignited, changes into the *anhydrous peroxide.* Pure peroxide of iron, when placed upon moist reddened litmus paper, does not color the latter blue. It dissolves slowly in dilute, but more rapidly in concentrated hydrochloric acid; the application of a moderate degree of heat promotes this solution more than that of ebullition heat.

Its weight does not vary, upon ignition in the air; when ignited together with sal ammoniac, perchloride of iron escapes. Ignition in contact with charcoal, shielded from the access of air, reduces it more or less.

COMPOSITION.

2 Fe	=700.00	70.00
3 O.	=300.00	30.00
	1000.00	100.00

c. Sulphuret of iron, produced in the humid way, is a black precipitate, slightly soluble in aërated water, (with decomposition,) insoluble in water containing alkaline sulphurets, but readily soluble in mineral acids (even in dilute mineral acids). When precipitated from a highly dilute solution, it remains suspended a long time, imparting a blackish green tint to the fluid; it subsides, however, completely, after the lapse of some time. When moistened and exposed to the air, it absorbs oxygen, and assumes a brown tint, being transformed into hydrated peroxide of iron and protosulphate of iron.

d. When a neutral solution of a persalt of iron is mixed with a neutral solution of a succinate of ammonia, a cinnamon-colored precipitate of a brighter or darker *hue* is formed; this is *persuccinate of iron* ($Fe_2\,O_3,\ \bar{S}_2$). It results from the nature of this precipitate, that its formation must set free an equivalent of acid, (of succinic acid, if the succinate of ammonia is used in excess); *e. g.*, $Fe_2\,O_3,\ 3\,S\,O_3 + 3\,N\,H_4\,O,\ \bar{S} = Fe_2\,O_3,\ \bar{S}_2 + 3\,N\,H_4\,O,\ S\,O_3 + \bar{S}$. This free succinic acid does not exercise a clearly perceptible solvent action upon the precipitate, in a cold and highly dilute solution, but it redissolves the precipitate more copiously in a hot solution. The precipitate must therefore be filtered cold, if we want to guard against its redissolution. Formerly the precipitate was erroneously supposed to consist of a neutral salt, decomposable by hot water into an insoluble basic and soluble acid compound. Persuccinate of iron is insoluble in cold, and but sparingly soluble in hot water. It dissolves readily in mineral acids. Ammonia deprives it of the greater portion of its acid, leaving compounds similar to the hydratid peroxide of iron, and which contain from nine to fifteen equivalents of peroxide of iron to one equivalent of succinic acid. (Döpping.) Hot ammonia withdraws the acid more completely than cold ammonia.

BASES OF THE FIFTH GROUP.

§ 56.

1. OXIDE OF SILVER.

Silver may be weighed in its METALLIC state, and likewise as CHLORIDE OF SILVER, SULPHURET OF SILVER, and CYANIDE OF SILVER.

a. Metallic silver, obtained by the ignition of salts of silver with organic acids, etc., is a light, white, glittering mass of metallic lustre; but when obtained by reducing chloride of silver, etc., in the humid way, by the agency of zinc, it forms a dull grey powder. It is not fusible over a Berzelius' lamp; ignition produces no alteration in its weight. It dissolves readily and completely in dilute nitric acid.

b. Chloride of silver recently precipitated, occurs as a white curdy mass, which, upon drying, becomes pulverulent. It is wholly insoluble in water and in nitric acid, but slightly soluble in concentrated hydrochloric acid; however, upon diluting this solution, the dissolved chloride precipitates again almost completely. It is likewise slightly soluble in solution of sal ammoniac, (but not of any other ammoniacal salt,) chloride of sodium and chloride of potassium, especially when these solutions are concentrated. It dissolves readily in caustic ammonia. Exposed to the light, it acquires first a violet, and finally a black color, owing to the escape of chlorine. This modification of the chloride of silver is, however, so very superficial, that the loss of chlorine cannot be determined, even though a very delicate balance be used. When heated, chloride of silver acquires a yellow tint, and at about 500° it fuses, forming a transparent yellowish liquid, which, after cooling, appears as a colorless or slightly yellowish mass. Chloride of silver, when very strongly ignited, volatilizes unaltered. When fused in chlorine gas, it absorbs a small proportion of the latter, but loses this again completely upon cooling. Ignition in contact with charcoal fails to reduce chloride of silver; but this substance is readily reduced to metallic silver by igniting it in a stream of carbonic oxide gas.

COMPOSITION.

Ag	=1349.01	75.28
Cl	= 443.20	24.72
	1792.21	100.00

c. Sulphuret of silver, formed in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies and alkaline sulphurets; this precipitate is unalterable in the air, and may be dried at 212° without suffering decomposition. It dissolves in concentrated nitric acid, with separation of sulphur.

COMPOSITION.

Ag	=1349.01	87.08
S	= 200.00	12.92
	1549.01	100.00

d. Cyanide of silver, recently precipitated, is a white curdy mass, insoluble in water and dilute nitric acid, soluble in cyanide of potassium, and likewise in ammonia; this precipitate may be dried at 212°, without suffering decomposition; when exposed to light, it does not acquire the slightest shade of black. When ignited, it is decomposed into cyanogen gas, which escapes, and metallic silver which remains behind, mixed with a small portion of paracyanide of silver.

COMPOSITION.

Ag	=1349.01	80.58
C_2N	= 325.25	19.42
	1674.26	100.00

§ 57.

2. PROTOXIDE OF LEAD.

Lead is weighed as PROTOXIDE, SULPHATE, CHLORIDE, and SULPHURET OF LEAD. Besides these four, we have likewise to examine the CARBONATE AND OXALATE OF LEAD.

a. Neutral carbonate of lead forms a heavy white pulverulent precipitate. It is but very slightly soluble in perfectly pure water, (one part requiring 50550 parts of pure water; vide Experiment No. 35 *a*,) but it dissolves somewhat more readily in water containing ammonia and ammoniacal salts. (Experiments No. 35 *b* and *c*).—It dissolves likewise somewhat more readily in water impregnated with carbonic acid, than in pure water. It loses its carbonic acid when ignited.

b. Oxalate of lead is a white powder very sparingly soluble in water. The presence of ammoniacal salts slightly increases its solubility. (Exper. No. 36). When heated in close vessels, it leaves suboxide of lead behind, but when heated, with access of air, the protoxide remains instead of the suboxide.

c. Protoxide of lead, produced by igniting the carbonate or oxalate of this metal, is a lemon-yellow powder, inclining sometimes to a reddish yellow, or to a pale yellow. When this yellow protoxide of lead is heated, it assumes a brownish red color, without the slightest variation in its weight. It fuses at an intense red heat. Ignition in contact with charcoal reduces it. When exposed to a white heat, it rises in vapor. Placed upon moist, reddened litmus-paper, it turns the color of this paper into blue. When exposed to the air, it slowly absorbs carbonic acid.

COMPOSITION.

Pb	=1294.50	92.83
O	= 100.00	7.17
	1394.50	100.00

d. *Sulphate of lead* forms a heavy, white powder. It dissolves, at the common temperature, in 22800 parts of pure water, (Experiment No. 37) ; it is less soluble still in water containing sulphuric acid, (one part requiring 36500 parts—Experiment No. 38) ; it is far more readily soluble in water containing ammoniacal salts; from this solution it may be readily precipitated again by adding sulphuric acid in excess, (Experiment No. 39) ; it is nearly altogether insoluble in alcohol and spirits of wine. It dissolves in concentrated hydrochloric acid, upon heating. It dissolves in nitric acid the more readily, the more concentrated and hotter the acid ; water fails to precipitate it from the solution in nitric acid ; but the addition of a copious amount of dilute sulphuric acid causes its precipitation from this solution. The quantity of sulphuric acid required for this precipitation increases in proportion to the amount of nitric acid present. It dissolves sparingly in concentrated sulphuric acid, and the dissolved portion precipitates again upon diluting the acid with water, (and more completely still, upon the addition of alcohol). Sulphate of lead is unalterable in the air and at a gentle red heat ; when exposed to a higher degree of heat, it fuses without suffering decomposition. (Experiment No. 40.) When sulphate of lead is ignited in contact with charcoal, sulphuret of lead is formed at first, and the sulphur of this reduces the sulphuric acid of a not yet decomposed portion of the sulphate, to sulphurous acid, giving thus, on both sides, rise to the separation of metallic lead.

COMPOSITION.

PbO =	1394.50	73.56
SO_3 =	500.00	26.44
	1894.50	100.00

e. *Chloride of lead* appears either in the form of small brilliant crystalline needles, or as a white powder ; it dissolves, at the common temperature, in 135 parts of water ; and is still far more readily soluble in hot water; it dissolves less readily in water impregnated with nitric acid, (1 part requiring 1636 parts.—Bischof); it dissolves copiously in concentrated hydrochloric acid, and may be precipitated again from this solution by the addition of water. It is extremely sparingly soluble in spirits of wine of from 70 to 80 per cent., and quite insoluble in absolute alcohol. It is unalterable in the air. It fuses at a temperature below red-heat, without suffering any diminution of weight. When exposed to a higher temperature, with access of air, it volatilizes slowly, with partial decomposition. Chlorine gas escapes, and a mixture of protoxide and chloride of lead remains behind.

COMPOSITION.

Pb=1294.50 . . . . . 74.49
Cl= 443.20 . . . . . 25.51
1737.70 100.00

f. Sulphuret of lead, prepared in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies and alkaline sulphurets. This precipitate is unalterable in the air, and may be dried at 212°, without suffering decomposition. It dissolves in concentrated and hot hydrochloric acid, with evolution of sulphuretted hydrogen. In moderately concentrated nitric acid, sulphuret of lead dissolves, upon the application of heat, with separation of sulphur, (when the acid is tolerably concentrated, a small portion of sulphate of lead is likewise formed). When sulphate of lead is acted upon by fuming nitric acid, it becomes converted into sulphate of lead, without separation of sulphur; the action of the fuming nitric acid upon the sulphuret, is very energetic. (Experiment No. 41.)

COMPOSITION.

Pb=1294.50 . . . . . 86.61
S = 200.00 . . . . . 13.39
1494.50 100.00

§ 58.

3. PROTOXIDE OF MERCURY; and 4. PEROXIDE OF MERCURY.

Mercury is weighed either in its METALLIC state, or as PROTOCHLORIDE, or as SULPHURET OF MERCURY (CINNABAR).

a. Mercury in its *metallic* state is liquid at the common temperature; its color is white like tin. When pure, its surface is perfectly clean, and does not tarnish in the air. It is unalterable in the air, at the common temperature. It boils at 680°. Mercury emits a sensible vapor at from between 68 and 80°; this species of vaporization proceeds, however, very slowly. Upon protracted boiling with water, a small portion of mercury vaporizes, and traces of it escape in conjunction with the aqueous vapor, whilst a very minute proportion remains suspended in the water. (Experiment No. 42.) This suspended portion of mercury subsides completely after long standing at rest. When metallic mercury is precipitated from a fluid, in a very minutely divided form, the small globules will readily unite into a large one, if the mercury be perfectly pure; but if even the slightest trace of extraneous matter, such as fat, etc., should adhere to the mercury, the confluence of the minute globules of this metal will be prevented. Mercury does not dissolve in hydrochloric acid, even though the acid be concentrated; it is barely soluble in dilute cold sulphuric acid, but it dissolves readily in nitric acid, and in concentrated boiling sulphuric acid.

b. Protochloride of mercury, prepared in the humid way, is a heavy white powder. It is almost absolutely insoluble in cold water; in boiling water it is gradually resolved into chlorine and mercury, and upon continued boiling the residue acquires a grey color. Highly dilute hydrochloric acid fails to dissolve the protochloride of mercury, at the common temperature, but dissolves it slowly at a higher temperature, and completely, by degrees, upon boiling the fluid, with access of air; the solution contains perchloride of mercury, ($Hg_2\,Cl + Cl\ H + O = 2\ Hg\,Cl +$

H O). When protochloride of mercury is acted upon by boiling concentrated hydrochloric acid, it is speedily decomposed into mercury, which remains undissolved, and perchloride of mercury, which dissolves in the menstruum. Boiling nitric acid dissolves protochloride of mercury, transforming it into perchloride and pernitrate of mercury. Chlorine-water and aqua regia dissolved it as perchloride, even at a low temperature. Solution of sal ammoniac, chloride of sodium, and chloride of potassium, resolve protochloride of mercury into metallic mercury and perchloride of mercury, which latter dissolves in the menstruum; at a low temperature this resolution is confined to a small portion of the protochloride, but it proceeds to a greater extent at a high temperature. Protochloride of mercury does not affect vegetable colors; it is unalterable in the air; it may be dried at 212°, without suffering any diminution of weight; when exposed to a higher degree of heat, (although still below redness,) it vaporizes completely, without fusion.

COMPOSITION.

2 Hg	=2501.80	84.95
Cl	= 443.20	15.05
	2945.00	100.00

c. Sulphuret of mercury, prepared in the humid way, is a black powder, insoluble in water. Dilute hydrochloric acid, and dilute nitric acid, fail to dissolve it, and it remains insoluble even in boiling hydrochloric acid; it is barely soluble in hot and concentrated nitric acid,—but it is dissolved by aqua regia. It is insoluble in boiling solution of potass, but dissolves readily in sulphuret of potassium. (Experiment No. 44). Sulphuret of ammonium and cyanide of potassium fail to dissolve it. It is unalterable in the air, and undergoes no change at 212°. When exposed to a higher temperature, it sublimes completely and unaltered.

COMPOSITION.

Hg	=1250.90	86.21
S	= 200.00	13.79
	1450.90	100.00

§ 59.

5. OXIDE OF COPPER.

Copper is usually weighed in the form of OXIDE. Besides the oxide, we have to examine SULPHURET OF COPPER, and METALLIC COPPER.

a. Oxide of copper. Upon mixing a dilute, cold, aqueous solution of a salt of copper with caustic potass in excess, a bright blue precipitate of hydrated oxide of copper is formed ; this precipitate is very apt to carry down a little of the precipitant alkali, which it is very difficult to remove completely by washing. If the precipitate be allowed to continue in the fluid, from which it has been precipitated, it will gradually acquire a dark brown tint, even at a temperature of from 68° to 80°, yielding up nearly the whole of its water of hydration. This transformation takes place immediately, if the fluid is heated nearly to boiling. The fluid filtered off from the black precipitate, is free from copper. If the solutions of the salt of copper and of caustic potass, are mixed in a concentrated state, the fluid, in addition to the formation of the blue precipitate, will acquire a blue color, owing to a portion of very minutely divided hydrated oxide remaining suspended in it. From a fluid of this description, even protracted boiling will fail to precipitate all the copper which it contains, except the fluid be previously diluted with water. If the solution of a salt of copper contains non-volatile organic substances in admixture, the action of potass in excess will not precipitate all the copper as oxide, not even upon boiling. The oxide of copper precipitated with potass from hot dilute solutions of salts of copper, retains a portion of the precipitant alkali, with great pertinacity; it may, however, be completely freed from this by washing with boiling water. Oxide of copper, prepared by the ignition of carbonate or nitrate of copper, is a dark brown or black powder, the weight of which remains invariable, upon strong ignition over the spirit-lamp. (Experiment No. 44.) The same powder is produced by igniting the oxide of copper prepared in the humid way. But if the oxide of copper (no matter whether prepared in the dry or humid way) is exposed to a heat approaching the fusing point of metallic copper, it fuses, yields up oxygen, and becomes converted into $Cu_5 O_3$. (Favre and Maumené.) Ignition in contact with charcoal succeeds very readily in reducing it; heated in the air, the metallic copper obtained, re-oxidizes. Oxide of copper, in contact with the atmosphere, absorbs water; oxide that has been but feebly ignited, absorbs the water more rapidly than such as has been strongly ignited. (Experiment No. 45.) Oxide of copper is nearly insoluble in water, but it dissolves readily in hydrochloric acid, nitric acid, etc.; it dissolves less readily in ammonia. It is indifferent to vegetable colors.

COMPOSITION.

Cu	=396.00 . . .	79.84
O	=100.00 . . .	20.16
	496.00	100.00

b. Sulphuret of copper, prepared in the humid way, is a dark brown or black precipitate, insoluble in water; when this precipitate, in a moist state, is exposed to the air, it acquires a greenish tint, and the property of reddening litmus paper, and becomes gradually altogether converted into sulphate of copper. Sulphuret of copper dissolves readily in boiling nitric acid, with separation of sulphur. Hydrochloric acid dissolves it with difficulty. It does not dissolve in solution of potass and of sulphuret of potassium, especially if these solutions be boiling; but it dissolves perceptibly in sulphuret of ammonium and readily in cyanide of potassium.

c. Copper, in its pure state, is a metal of a peculiar reddish-brown color; it requires a white heat for its fusion. Copper does not alter when exposed to dry air, or even to moist air, provided the air be free from carbonic acid; but when exposed to moist air, impregnated with carbonic acid, it gets gradually tarnished and coated with a film, at first of a dark grey, and finally of a blue-green color. When ignited in the air, it becomes covered with a stratum of black oxide. It does not dissolve in hydrochloric acid, not even upon boiling, if the air is excluded, but it dissolves slowly in this acid, if the air is freely admitted. It dissolves readily in nitric acid; it does not dissolve in ammonia, if the air is excluded, but, with free access of air, it dissolves slowly in this substance. Metallic copper, brought into contact with solution of chloride of copper, in hydrochloric acid, or with solution of oxide of copper in ammonia, converts the chloride into sub-chloride, and the black oxide into the red oxide, (sub-oxide,) one equivalent of metal being dissolved for every equivalent of chloride or of oxide.

§ 60.

6. PROTOXIDE OF BISMUTH.

Bismuth is invariably weighed in the form of PROTOXIDE. Besides this, we have to examine the basic CARBONATE and the SULPHURET OF BISMUTH.

a. Protoxide of bismuth, prepared by igniting the carbonate or nitrate of this metal, is a pale lemon-yellow powder which, when heated, assumes transiently a darker yellow or red-brown tint. When heated to intense redness, it fuses without any alteration in its weight. Ignition in contact with charcoal, or in a stream of carbonic oxide gas, reduces it to the metallic state. It is insoluble in water, and indifferent to vegetable colors.

It dissolves readily in those acids which form soluble salts with it.

COMPOSITION.

Bi=	2660.75	89.87
O_3=	300.00	10.13
	2960.75	100.00

b. Carbonate of bismuth.—Upon adding carbonate of ammonia in excess to the solution of a salt of bismuth, free from hydrochloric acid, a white precipitate of carbonate of bismuth (BiO_3 CO_2) is immediately formed; part of this precipitate, however, redissolves in the excess of the precipitant. But if the fluid with the precipitate be heated previously to filtration, the filtrate will be perfectly free from any trace of bismuth. Carbonate of potass likewise precipitates solution of salts of bismuth completely; but the precipitate in this case invariably contains traces of potass, which it is very difficult to remove by washing. Carbonate of soda fails to precipitate solutions of salts of bismuth as completely as the carbonate of ammonia and that of potass;—the precipitate is readily washed; it is nearly insoluble in water, but dissolves readily with effervescence, in hydrochloric acid and nitric acid. Upon ignition it loses its carbonic acid, leaving protoxide of bismuth behind.

c. Sulphuret of bismuth, prepared in the humid way, is a dark brown or black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. In moderately concentrated nitric acid it dissolves, at a high temperature, as a nitrate, with separation of sulphur. It is unalterable in the air, and may be dried at 212°, without undergoing any change.

COMPOSITION.

Bi =	2660.75	81.61
3 S=	600.00	18.39
	3260.75	100.00

§ 61.

1. OXIDE OF CADMIUM.

Cadmium is weighed either as OXIDE or as SULPHURET OF CADMIUM. Besides these, we have to examine CARBONATE OF CADMIUM.

a. Oxide of cadmium, produced by igniting the carbonate or nitrate of cadmium, is a powder, the color of which varies from a yellow brown to a red brown. The application of a white heat fails to fuse, to volatilize, or to decompose it; it is insoluble in water, but dissolves readily in acids; it does not alter vegetable colors. When ignited in contact with charcoal, it is readily reduced, and the metallic cadmium escapes in the form of vapor.

COMPOSITION.

Cd=696.77	87.45
O =100.00	12.55
796.77	100.00

b. Carbonate of cadmium is a white precipitate, insoluble in water and in the fixed carbonated alkalies, and extremely sparingly soluble in carbonate of ammonia. It loses its water completely upon exsiccation. Ignition converts it into oxide of cadmium.

c. Sulphuret of cadmium, produced in the humid way, is a lemon yellow, or orange yellow precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium, (Experiment No. 46). It dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen, and in moderately concentrated hot nitric acid, with separation of sulphur. It may be dried at 212°, without undergoing decomposition.

COMPOSITION.

Cd	=696.77	77.78
S	=200.00	22.22
	896.77	100.00

METALLIC OXIDES OF THE SIXTH GROUP.

§ 62.

1. PEROXIDE OF GOLD.

Gold is invariably weighed in its metallic state; besides METALLIC GOLD, we have here to consider SULPHURET OF GOLD.

a. Metallic gold, obtained by precipitation, exists as a blackish brown powder, destitute of metallic lustre, which it assumes, however, when pressed or rubbed; when coherent in a compact mass, it exhibits its characteristic and peculiar high yellow color. It requires a white heat for its fusion. It is wholly unalterable in the air and at a red heat, and is not in the slightest degree affected by water nor by simple acids. Aqua regia dissolves it as a perchloride.

b. Sulphuret of gold.—When sulphuretted hydrogen is transmitted through a dilute and cold solution of perchloride of gold, all the gold separates as auric sulphuret, ($Au\ S_3$,) in the form of a brown black precipitate. If this precipitate be allowed to continue in the fluid, it will gradually become converted into metallic gold and free sulphuric acid. Upon transmitting sulphuretted hydrogen through a hot solution of perchloride of gold, an *aurous sulphuret* ($Au\ S$) precipitates, with simultaneous formation of sulphuric acid and of hydrochloric acid.

$$(2\ Au\ Cl_3 + 3\ H\ S + 3\ H\ O = 2\ Au\ S + 6\ H\ Cl + S\ O_3.)$$

The auric sulphuret ($Au\ S_3$) is insoluble in water, hydrochloric acid, and nitric acid, but dissolves in aqua regia. It does not dissolve in the colorless hydrosulphuret of ammonia, but dissolves almost completely in the yellow sulphuretted hydrosulphuret of ammonia, and completely upon the addition of potass; it dissolves in potass with separation of gold; it dissolves completely in the yellow sulphuret of potassium: it loses its sulphur at a moderate heat.

§ 63.

2. PEROXIDE OF PLATINUM.

Platinum is invariably weighed in its METALLIC STATE; it is generally precipitated as CHLORIDE OF PLATINUM AND AMMONIUM, or CHLORIDE OF PLATINUM AND POTASSIUM, rarely as SULPHURET OF PLATINUM.

a. Metallic platinum, produced by igniting the chloride of platinum and ammonium, or of platinum and potassium, exists as a grey, lustreless, porous mass, (spongy platinum). Platinum requires the very highest degree of heat for its fusion; it is perfectly unalterable in the air, and in the most intense heat of our furnaces. It is wholly insoluble in water and simple acids, and nearly insoluble in solutions of the alkalies. It dissolves in aqua regia as a perchloride.

b. With regard to the properties of *chloride of platinum and potassium,* we refer to § 42; and for those of *chloride of platinum and ammonium,* to § 44.

c. Sulphuret of platinum—(Bisulphuret of platinum.)—Upon mixing a concentrated solution of perchloride of platinum with sulphuretted hydrogen water, or upon transmitting sulphuretted hydrogen gas through a more dilute solution of the perchloride, no precipitate is formed at first; after standing some time, however, the solution turns brown, and finally a precipitate subsides. But if the solution of perchloride of platinum, mixed with sulphuretted hydrogen in excess, is gradually heated to ebullition, all the platinum separates as platinic sulphuret, (free from any admixture of perchloride of platinum). The platinic sulphuret (or bisulphuret of platinum) is insoluble in water and in simple acids, but dissolves in aqua regia. It dissolves partly in caustic alkalies, (with a separation of platinum,) and completely in alkaline sulphurets. If sulphuretted hydrogen be transmitted through water holding minutely divided bisulphuret of platinum in mechanical suspension, the bisulphuret, absorbing sulphuretted hydrogen, will acquire a greyish brown color, (the sulphuretted hydrogen thus absorbed, separates again when the bisulphuret of platinum is exposed to the air). When moist bisulphuret of platinum is exposed to the air, it is gradually decomposed, being converted into metallic platinum and sulphuric acid. Bisulphuret of platinum, upon being ignited in the air, becomes reduced to metallic platinum.

§ 64.

4. OXIDE OF ANTIMONY.

Antimony is most generally weighed as SULPHURET OF ANTIMONY, more rarely as ANTIMONIOUS ACID, or in the METALLIC state.

a. Upon transmitting sulphuret of hydrogen through a solution of perchloride of antimony mixed with [redacted]tartaric acid, an orange red precipitate of *hydrated tersulphuret of antimony* is obtained, mixed at first with a small portion of basic chloride of antimony. However, upon saturating the fluid completely with sulphuretted hydrogen, and applying a gentle heat, the chloride of antimony admixed to the precipitate is decomposed, and the pure hydrated tersulphuret of antimony is obtained; which, subsequently loses its water of hydration upon drying. Sulphuret of antimony is insoluble in water and dilute acids; it dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. Brought into contact with fuming nitric acid mixed with a slight proportion of hydrochloric acid, it oxidizes with much violence, and is converted into sulphate of antimony. It dissolves readily in solutions of potass, hydrosulphuret of ammonia, and sulphuret of potassium, but is only sparingly soluble in ammonia. It may be dried at 212°, without suffering decomposition; when dried, it is unalterable in the air. When recently precipitated sulphuret of antimony is long boiled with water, it becomes transformed into oxide of antimony, which dissolves in the water, and into sulphuretted hydrogen. When sulphuret of antimony is exposed for some time to the air, water being present, the sulphuret absorbs oxygen, and dissolves gradually as sulphate of antimony. The higher sulphurets of antimony corresponding to antimonious and antimonic acid, are likewise insoluble in water; they dissolve, however, sparingly in water impregnated with sulphuretted hydrogen.

COMPOSITION.

$Sb = 1612.90$ 72.89
$S_3 = 600.00$ 27.11
2212.90 100.00

b. Antimonious acid is a white powder, which when heated, acquires transiently a yellow tint; it is fixed and infusible. It is barely soluble in water, and dissolves in hydrochloric acid with very great difficulty. It undergoes no alteration by the action of hydrosulphuret of ammonia. It manifests an acid reaction when placed upon moist litmus paper.

COMPOSITION.

$Sb = 1612.90$ 80.13
$4\,O = 400.00$ 19.87
2012.90 100.00

c. Metallic antimony, produced in the humid way, by precipitation, exists as a lustreless black powder. The metal antimony is insoluble in water; however, when it is exposed to the action of air, in presence of water, it oxidizes slowly, and the oxide formed dissolves in the water present. The powder of antimony may be dried at 212°, without suffering any alteration. It fuses at a moderate heat. It is hardly affected by even boiling concentrated hydrochloric acid. The action of nitric acid converts it into oxide of antimony, mixed with a greater or less proportion of antimonious acid, according to the greater or less degree of concentration possessed by the oxidizing acid.

§ 65.

4. PROTOXIDE OF TIN; and 5. PEROXIDE OF TIN.

Tin is generally weighed in the form of PEROXIDE; besides the peroxide, we have here to examine SULPHURET and BISULPHURET OF TIN.

a. Peroxide of tin.—Hydrated peroxide of tin is obtained in the form of a white precipitate, by the action of nitric acid upon metallic tin, or by evaporating a solution of a salt of tin, with nitric acid in excess. This precipitate consists of the insoluble modification of the peroxide; it does not dissolve in water, nitric acid, and sulphuric acid, and dissolves but sparingly in hydrochloric acid. It reddens litmus, even after being completely washed. It is deprived of its hydration water by ignition. The peroxide of tin prepared by the ignition of its hydrate, is a straw-yellow powder which, when heated, transiently assumes a different tint, varying from high yellow to brown. This powder is insoluble in water and acids, and does not alter the color of litmus paper.

COMPOSITION.

Sn	=735.30	78.62
2 O	=200.00	21.38
	935.30	100.00

b. Hydrated sulphuret of tin is formed as a brown precipitate, insoluble in water, sulphuretted hydrogen water, and diluted acids. It does not dissolve in ammonia, but dissolves readily—(as bisulphuret)—in the yellow sulphuretted hydrosulphuret of ammonium, and in sulphuret of potassium; it dissolves readily in hot concentrated hydrochloric acid. Heated, with exclusion of air, it loses its water of hydration, and becomes converted into anhydrous sulphuret of tin; when it is exposed to the continued action of a gentle heat, it becomes transformed into sulphurous acid, which escapes, and peroxide of tin, which remains behind.

c. Hydrated bisulphuret of tin is produced as a bright yellow precipitate, which, upon drying, assumes a darker tint. It is insoluble in water, but dissolves slightly in water impregnated with sulphuretted hydrogen; it dissolves with difficulty in ammonia, but readily in potass and alkaline sulphurets, and likewise in hot concentrated hydrochloric acid. When heated, with exclusion of air, it loses its water of hydration, and at the same time, according to the greater or less degree of heat applied, one-half or one equivalent of sulphur, becoming converted either into sesquisulphuret, or into sulphuret of tin; when heated very slowly, with free access of air, it becomes converted into peroxide of tin, whilst sulphurous acid escapes.

§ 66.

6. ARSENIOUS ACID; and 7. ARSENIC ACID.

Arsenic is weighed either in the form of ARSENIATE OF LEAD, or in that of SULPHARSENIOUS ACID.

a. Arseniate of lead, in a pure state, is a white powder, which begins to agglutinate into a semi-fused mass, when exposed to a gentle red-heat, at the same time transitorily acquiring a yellow tint; it fuses when exposed to a higher degree of heat. When strongly ignited, it suffers a slight diminution of weight, losing a small proportion of arsenic acid, which escapes as arsenious acid and oxygen. In analysis we have never occasion to operate upon the pure arseniate of lead, but upon a mixture of it with free oxide of lead.

b. Sulpharsenious acid forms a precipitate of a rich yellow color; it is insoluble in water, and but very sparingly soluble in sulphuretted hydrogen water. When boiled with water, or when kept in contact with water during several days, it undergoes a very superficial decomposition : a trace of arsenious acid dissolves in the water, and a minute proportion of sulphuretted hydrogen is disengaged. This does not interfere, however, with the washing of the precipitate. The precipitate may be dried at 212°, without undergoing decomposition ; all the water which it contains is expelled at that temperature. When exposed to a stronger degree of heat, sulpharsenious acid transitorily assumes a brown red color, fuses, and finally rises in vapor, without suffering decomposition. It dissolves readily in alkalies and alkaline sulphurets, and likewise in aqua regia, but it is barely soluble in concentrated boiling hydrochloric acid. When acted upon by red fuming nitric acid, it is transformed into arsenic acid and sulphuric acid.

COMPOSITION.

As =936.48 . . . . . 60.95
3 S=600.00 . . . . . 39.05
1536.48 100.00

B.—FORMS AND COMBINATIONS, IN WHICH INDIVIDUAL ACIDS ARE SEPARATED, FOR THE PURPOSE OF DETERMINING THEIR WEIGHT.

ACIDS OF THE FIRST GROUP.

§ 67.

1. ARSENIOUS ACID and ARSENIC ACID—vide § 66.

2. CHROMIC ACID.

Chromic acid is weighed either in the form of OXIDE OF CHROMIUM, or in that of CHROMATE OF LEAD.

a. Oxide of chromium.—Vide § 50 for the properties of this oxide.

b. Chromate of lead forms a precipitate of an intensely yellow color; this precipitate is insoluble in water and acetic acid, and barely soluble in dilute nitric acid, but readily so in potass ley. When chromate of lead is boiled with concentrated hydrochloric acid, it is readily decomposed, and its elements transposing with those of the decomposing acid, chloride of lead and protochloride of chromium are formed. (Addition of alcohol tends to promote this double decomposition.) Chromate of lead is unalterable in the air; it may be dried perfectly at 212°. When exposed to the action of heat, it transitorily acquires a red brown tint; it fuses at a red-heat; when heated beyond its point of fusion, it loses oxygen, and becomes transformed into a mixture of oxide of chromium and semichromate of lead. When heated in contact with organic substances, it readily yields up oxygen to the latter.

COMPOSITION.

$Pb\,O$	=1394.50	68.15
$Cr\,O_3$	= 651.82	31.85
	2046.32	100.00

3. SULPHURIC ACID.

Sulphuric acid is uniformly determined in the form of SULPHATE OF BARYTES, for the properties of which, vide § 45.

4. PHOSPHORIC ACID.

Phosphoric acid may be weighed as PHOSPHATE OF LEAD, PYROPHOSPHATE OF MAGNESIA, BASIC PERPHOSPHATE OF IRON, PHOSPHATE and PYROPHOSPHATE OF SILVER.

a. The *phosphate of lead,* ordinarily obtained in the course of analysis, is not quite pure, but intermixed with free oxide of lead. The basic phosphate of lead, (PO_5, 3 $Pb\,O$,) when in a pure state, exists as a white powder, insoluble in water and in acetic acid, and equally so in ammonia, but readily soluble in nitric acid; when exposed to the action of heat, it fuses without undergoing decomposition.

b. Pyrophosphate of magnesia.—Vide § 48.

c. Basic phosphate of peroxide of iron.—The white or yellowish white precipitate which is thrown down from solutions of phosphoric acid upon the addition of perchloride of iron in excess, in conjunction with that of an alkaline acetate is of variable composition, and therefore unfit to serve for the direct determination of the phosphoric acid. But when a solution containing peroxide of iron, and phosphoric acid, the latter in excess, is acted upon by an acetated alkali, a precipitate of constant composition is formed, exhibiting the same outward appearance with that obtained in the former instance. The composition of this precipitate, after ignition, is

$2\,Fe_2\,O_3$	=2000.0	42.78
$3\,PO_5$	=2674.6	57.22
	4674.6	100.00

This precipitate is insoluble in water, but readily soluble in ammonia, and likewise in acids; it is slightly soluble in peracetate of iron. Upon boiling the latter solution, all the phosphoric acid precipitates as *hyperbasic phosphate of peroxide of iron,* in conjunction with the basic peracetate of iron. The hyperbasic phosphate of peroxide of iron is invariably obtained (mixed with free hydrated peroxide of iron) when a solution containing phosphoric acid and peroxide of iron, the latter in excess, is precipitated with ammonia. This precipitate is wholly insoluble in water, and in ammonia.

d. Tri-basic phosphate of silver is a powder of a rich yellow color; it is insoluble in water, but readily soluble in nitric acid, and likewise in ammonia;—it is of difficult solubility in ammoniacal salts. It is unalterable in the air. When ignited, it acquires transitorily a red-brown color; when strongly ignited, it fuses without decomposition.

COMPOSITION.

3 Ag O	=4347.03	82.99
PO_5	= 891.55	17.01
	5238.58	100.00

e. Pyrophosphate of silver is a white powder, unalterable and insoluble in water, even upon ebullition, but readily soluble in ammonia, and likewise in nitric acid. It is unalterable in the air; at a heat, below ignition, it fuses without decomposition, forming a liquid of a dark brown color, which, upon cooling, solidifies into a white radiated mass.

COMPOSITION.

2 Ag O	=2898.02	76.48
PO_5	= 891.55	23.52
	3789.57	100.00

5. BORACIC ACID.

Boracic acid is usually determined in an *indirect* way. BORATE OF LEAD is the only form which interests us here.

Borate of lead, in a pure state, is a white powder, of difficult solubility in water. Exposed to the action of heat, it fuses into a clear glass, without suffering decomposition. In the course of analysis, borate of lead is never obtained in a pure state, but invariably mixed with oxide of lead.

6. OXALIC ACID.

Oxalic acid is usually precipitated in the form of OXALATE OF LIME, and its proportion is generally inferred from the carbonate of lime remaining when the oxalate is heated to incipient redness, by a spirit-lamp. For the properties of oxalate of lime and of carbonate of lime, vide § 47.

7. HYDROFLUORIC ACID.

The *direct* estimation of hydrofluoric acid is uniformly effected by weighing the FLUORIDE OF CALCIUM.

Fluoride of calcium forms a gelatinous precipitate, difficult of edulcoration. If it is digested with ammonia, previously to filtration, it becomes more dense and less gelatinous. It is wholly insoluble in water, and likewise in aqueous solutions of the alkalies; it is barely soluble in dilute, but more readily in concentrated hydrochloric acid. When acted upon by sulphuric acid, it is decomposed, and, its elements transposing with those of the decomposing acid, gypsum and hydrofluoric acid are formed. Fluoride of calcium is unalterable in the air and at a red heat; it fuses at a very intense red heat.

COMPOSITION.

Ca	=250.0	51.48
Fl	=235.7	48.52
	485.7	100.00

8. CARBONIC ACID.

The *direct* estimation of carbonic acid is usually effected by weighing the carbonate of lime. For the properties of this substance, vide § 47.

9. SILICIC ACID.

Silicic acid is uniformly weighed in its insoluble modification. The insoluble modification is artificially prepared by evaporating a solution of the soluble modification of silicic acid in water or in any volatile acid, (with the exception of hydrofluoric acid); in this process we obtain, at first, the silicic acid as a gelatinous hydrate, which, upon further evaporation to dryness and subsequent exsiccation, loses its water of hydration, and becomes converted into the insoluble modification. This forms a white powder, insoluble in water and in acids; it is soluble in potass ley, and likewise in solutions of the fixedc arbonated alkalies. It is perfectly unalterable in the air and at a red heat, and requires the very highest degree of heat for its fusion. It does not alter vegetable colors.

COMPOSITION.

$Si = 184.88$	48.03
$2O = 200.00$	51.97
384.88	100.00

ACIDS OF THE SECOND GROUP.

§ 68.

1. HYDROCHLORIC ACID.

Hydrochloric acid is almost uniformly determined in the form of CHLORIDE OF SILVER. For the properties of this substance, vide § 56.

2. HYDROBROMIC ACID.

Hydrobromic acid is uniformly determined as bromide of silver.

BROMIDE OF SILVER, prepared in the humid way, is a yellowish-white precipitate; it is wholly insoluble in water and in nitric acid, but tolerably soluble in ammonia; it dissolves in hot solution of sal ammoniac, but very sparingly in solution of nitrate of ammonia. When acted upon by chlorine, no matter whether in the dry or in the humid way, it is decomposed, chloride of silver is formed, and bromine separated. Exposed to light, it turns gradually grey, and finally black. Exposed to the action of heat, it fuses into a fluid of a reddish color which, upon cooling, solidifies, forming a yellow mass of horn-like appearance.

When brought into contact with zinc and water, bromide of silver is decomposed; a spongy mass of metallic silver subsides, and the solution contains protobromide of zinc.

COMPOSITION.

Ag	=1349.01	57.44
Br	= 999.63	42.56
	2348.64	100.00

3. HYDRIODIC ACID.

Hydriodic acid is usually determined in the form of IODIDE OF SILVER, and sometimes in that of PROTIODIDE OF PALLADIUM.

a. Iodide of silver, produced in the humid way, is a bright yellow precipitate, insoluble in water and in dilute nitric acid, and barely soluble in ammonia. It is decomposed by chlorine, both in the dry and in the humid way. Hot concentrated nitric and sulphuric acid convert it, but with difficulty, into the corresponding nitrate and sulphate of silver, with expulsion of the iodine. Iodide of silver acquires a black color when exposed to light. When heated, it fuses without decomposition into a reddish fluid which, upon cooling, solidifies, forming a yellow mass that may be cut with a knife. When brought into contact with zinc and water, it is decomposed; protiodide of zinc is formed, and metallic silver separates.

COMPOSITION.

Ag	=1349.01	45.96
I	=1585.57	54.04
	2934.58	100.00

b. The protiodide of palladium, produced by precipitating solution of the iodide of one of the alkali metals, with protochloride of palladium, is a deep brown-black flocculent mass. This precipitate does not dissolve in water; it is slightly soluble in saline solutions, (solution of chloride of sodium, chloride of magnesium, chloride of calcium, &c.,) it is insoluble in dilute hydrochloric acid. It is unalterable in the air; when dried simply in the air, it contains 1 equivalent of water=5.05 per cent. Dried at a high temperature, (158° to 176°,) or in vacuo, it loses this water completely, without suffering any loss of iodine. Dried at 212°, a trace of iodine escapes, and finally if the precipitate of protiodide of palladium is exposed to a heat of from 572° to 752°, all its iodine is completely expelled. It may be washed with hot water without losing its iodine.

COMPOSITION.

Pd=	662.54	29.47
I =	1585.57	70.53
	2248.11	100.00

4. HYDROCYANIC ACID.

The *direct* estimation of this acid is uniformly effected by weighing the CYANIDE OF SILVER. For the properties of this substance, vide § 56.

5. HYDROSULPHURIC ACID.

Sulphuretted hydrogen.

The forms into which sulphuretted hydrogen, or the sulphur in metallic sulphurets, are converted for the purpose of quantitative estimation, are SULPHARSENIOUS ACID, and SULPHATE OF BARYTES.

a. Sulpharsenious acid, vide § 66.

b. Sulphate of Barytes, vide § 45.

ACIDS OF THE THIRD GROUP.

§ 69.

1. NITRIC ACID, and 2. CHLORIC ACID.

These two acids are determined invariably in an *indirect* way.

We have had occasion already, in the preceding paragraphs, to treat of those compounds which serve for their indirect quantitative estimation.

SECTION IV.

In the preceding section, we have examined the composition and properties of the various appropriate forms and combinations in which substances are to be separated from others, or into which they are to be converted, for the purpose of determining their absolute and relative weight and proportion. We have now to consider the means of converting substances into these appropriate forms and combinations.

For the sake of greater clearness and simplicity, we will divide this part of the work into two sections, confining ourselves, in the first, to the exposition of the various methods applied to effect the *quantitative estimation of substances,* and deferring to the next section the consideration of the means best adapted for the *separation of substances from one another.*

QUANTITATIVE DETERMINATION OF SUBSTANCES.

§ 70.

We have to deal here exclusively with compounds consisting of *one base and one acid,* or of *one metal and one metalloid.*

In the quantitative estimation of substances, we have to study two points, viz., first, the most appropriate manner of dissolving the analysed substance, either in its isolated state, or in its various combinations,—ITS SOLUTION ; and secondly, the methods best adapted to convert the analysed substance into a ponderable form,—ITS ACTUAL DETERMINATION OF WEIGHT.

With regard to the latter point, we have to turn our attention to the *practical performance* of the several processes and operations constituting the special method or methods applied in every individual case, and second, to the greater or less degree of *correctness* of the several methods applied.

It happens very rarely in quantitative analyses that the amount of a substance, as determined by the analytical process, corresponds exactly with the amount theoretically calculated.

The cause of this almost invariably occurring discrepancy between the proportion calculated and that actually found, is to be ascribed either exclusively to *certain unavoidable defects inherent in the execution of the necessary processes and operations*, or it lies partly likewise in the *method itself*.

With regard to the *execution* of the analytical processes and operations, this can never be *absolutely* accurate, even though the greatest care and attention be bestowed on the most trifling minutiæ. To account for this, we need only bear in mind that our weights are never *absolutely* correct, nor our balances *absolutely* accurate, nor our reagents *absolutely* pure, and moreover, that we do not weigh *in vacuo*, and that, even if we infer the weight we might expect to obtain by weighing *in vacuo*, from the weight we actually obtain by weighing in the air, we can only *approximate*, but never *attain* absolutely accurate figures; that the hygroscopic state of the air is liable to vary between the moment of weighing the crucible whilst empty, and that of weighing the crucible after having introduced into it the substance to be analysed,—that we know the weight of the ashes of our filters only *approximately*,—that, upon the evaporation of many fluids, traces of salts will volatilize, which, in their solid state, are considered perfectly fixed,—that absolute perfection cannot be attained in the operation of washing and rinsing,—that we can never succeed in shielding the contents of dishes and crucibles, &c., *absolutely* against dust, &c. &c.

With regard to the *methods* themselves, many of them are not entirely free from certain unavoidable *sources of error*,—precipitates are not *absolutely* insoluble, compounds which require ignition are not *absolutely* fixed, others which require drying have a slight tendency to evaporize, &c., &c.

Strictly speaking, no method can be pronounced absolutely free from defect; (let it be borne in mind that even sulphate of barytes is not *absolutely* insoluble in water.)

We have therefore, in our analytical processes, invariably to contend against certain sources of inaccuracy which it is impossible to overcome entirely, although our operations may be conducted with the most scrupulous care and attention to established rules. It is evident that defects and sources of error, will in some cases *combine* to render the results less accurate than we desire them to be, whilst in other cases they will *compensate* one another, and thus enable us to attain a higher degree of accuracy. Owing to this circumstance, the results may be considered to waver between two points fixed on either side of *absolute accuracy*. In cases where the method itself is free from defects and sources of error, these points will very closely approximate the medium point of absolute accuracy; thus, for instance, in the quantitative estimations of chlorine, a careful operator will invariably be able to obtain between 99.9 and 100.1, instead of 100 parts of chlorine, as theoretically calculated.

Less perfect methods will exhibit far greater discrepancies; thus in the estimation of strontian, by means of sulphuric acid, even the most attentive and skilful operator may not be able to obtain, more than 99.0, (and even less,) instead of 100 parts of strontian, as theoretically calculated. When treating of the several methods individually, I shall take occasion to indicate in this manner their relative degree of accuracy, as resulting from direct experiments. The figures used refer invariably to the substance itself, (chlorine, nitrogen, barytes,) and not to the forms and compounds in which these substances are weighed (chloride of silver, chloride of platinum and ammonium, sulphate of barytes).

If the operator should happen to attain results *exactly* corresponding to those calculated, he is not invariably justified to assume for that reason, that his operations have been conducted with absolute accuracy, since it may happen in the course of the analytical process, that one error compensates another; thus, he may, at the commencement of his operations, spill a minute portion of the substance to be analyzed, whilst at a later stage of the process he may recover this loss by imperfect washing of the precipitates. It may be laid down as a general rule, that an analysis which exhibits a trifling loss, is more accurately and correctly performed, than one which yields an excess of substance.

To guard against inaccurate results, I would recommend the student of quantitative analysis to mark the appearance and properties of the weighed substance, and to compare them with those which this substance ought to exhibit, for which I refer to the preceding section.

I. QUANTITATIVE ESTIMATION OF BASES IN COMPOUNDS CONTAINING BUT ONE BASE AND ONE ACID, OR ONE METAL, AND ONE METALLOID.

FIRST GROUP.

POTASS—SODA—AMMONIA.

§ 71.

1. POTASS.

a. Solution.

Potass and those of its salts with inorganic acid, which we shall have to consider in this place, are disolved in water, in which menstruum they dissolve readily, or, at least, without any great difficulty. Potass salts, with organic acids, are first converted into carbonate of potass, by continued ignition in covered crucibles.

b. Determination of weight.

Potass is weighed either as *sulphate of potass* or *nitrate of potass*, or *chloride of potassium*, or *chloride of platinum and potassium.*

We may convert into

1. SULPHATE OF POTASS.

Potass salts with strong volatile acids; for instance, chloride of potassium, bromide of potassium, nitrate of potass, etc.

2. NITRATE OF POTASS.

Caustic potass, and the compounds of potass with such of the weak volatile acids as are decomposed by nitric acid; for instance, carbonate of potass, (potass salts, with organic acids.)

3. CHLORIDE OF POTASSIUM.

In general, salts of potass with such of the weak volatile acids as are decomposed by nitric acid, for instance, sulphuret of potassium.

Likewise, and more especially the sulphate, chromate, chlorate, and silicate of potass.

4. CHLORIDE OF PLATINUM, AND POTASSIUM.

4. Potass salts with such of the non-volatile acids as are soluble in alcohol; for instance, phosphate of potass, borate of potass; and, also, in general, all the salts of potass with acids soluble in alcohol. The form of chloride of platinum and potassium is more especially important here, since it is that in which potass is separated from soda, &c. &c.

The residue of carbonate of potassium which remains in the crucible upon the ignition of potass salts with organic acids, is liable to effervescence in the course of the subsequent processes,—to avoid this effervescence, it is advisable to heat the carbonate with solution of sal ammoniac slightly in excess. Upon evaporating this mixture and igniting the residue, we obtain chloride of potassium, whilst the carbonate of ammonia formed, and the excess of chloride of ammonium present, escape.

The potass in phosphate and borate of potass, may likewise be estimated in the same manner as the soda in the corresponding salts of soda. (Vide § 101 and § 102.)

1. *Determination as sulphate of potass.*

The aqueous solution of sulphate of potass is evaporated, the residue ignited and weighed. (§ 22.) The residue should be well dried previously to its ignition; the heat applied for the latter purpose, should be moderate at first, and increased very gradually; the crucible must be carefully covered—if any of these precautions be neglected, some loss of substance is likely to arise from decrepitation. If free sulphuric acid is present, we obtain, upon evaporation, bisulphate of potass. The excess of sulphuric acid is, in such cases, to be removed by the addition of bicarbonate of ammonia. Vide § 42.

Properties of the residue. Vide § 42.

This method, if *properly and carefully executed*, may be considered free from defects.

The most appropriate way of converting the above (sub. 1), enumerated salts, (chloride of potassium, bromide of potassium, etc.,) into sulphate of potass, is, to add to their aqueous solution a quantity of sulphuric acid, more than sufficient to combine with all the potass present, to evaporate the mixture, and finally, to ignite the residue. Platinum vessels should not be used when bromide of potassium and iodide of potassium are the salts operated upon. The sulphuric acid should not be added too greatly in excess.

2. *Determination of nitrate of potass.*

General method the same as described sub. 1. Nitrate of potass should be heated very gently, until it enters into fusion, or else some loss is likely to arise from the evolution of oxygen. Properties of the residue § 42. The method is easy of execution, and the results obtained by it are accurate. § 19 should be had regard to in the process of converting carbonate of potass into nitrate of potass.

3. *Determination as chloride of potassium.*

General method the same as described sub. 1. Chloride of potassium, like sulphate of potass, is to be carefully dried previously to ignition. It should be heated in well-covered crucibles, and should not be too strongly ignited, or else some loss is likely to arise from evaporation. No particular regard need be had to the presence of free acid. Properties of the residue, § 42. This method, if properly and carefully executed, yields accurate results.

The manner of converting the above (sub. 3) specified potass compounds into chloride of potassium, will be given in Part II. of this section, when treating of the corresponding acids.

4. *Determination as chloride of platinum and potassium.*

α. If a volatile acid is present, such as nitric acid, acetic acid, etc. the solution is to be mixed with hydrochloric acid; perchloride of platinum is then to be added in excess, and the mixture to be evaporated nearly to dryness, in the water-bath. The residue is then to be acted upon, for some time, with spirits of wine of about eighty per cent.; the undissolved chloride of platinum and potassium is finally to be placed upon a weighed filter, edulcorated with spirits of wine, dried at 212°, and weighed. (§ 29.)

β. If a non-volatile acid is present, such as phosphoric acid or boracic acid, the salt is first to be dissolved in water, as usual, taking care, however, to concentrate the solution. Hydrochloric acid, and perchloride of platinum, in excess, are then to be added to the solution, together with a pretty considerable proportion of the strongest possible alcohol; the mixture is then to be allowed to stand at rest for twenty-four hours, and is subsequently to be filtered, etc., in the same manner as described sub. *α.* Properties of the precipitate, vide § 42. The method, if properly and carefully executed, yields very satisfactory results; we meet, however, generally with a trifling loss, since chloride of platinum and potassium is not absolutely insoluble even in strong alcohol.

§ 72.

2. SODA.

a. Solution

All that has been stated in this respect, as applying to potass. (vide § 71,) applies equally to soda.

b. Determination.

Soda is determined either as *sulphate of soda* or *nitrate of soda*, or as *chloride of sodium*, or as *carbonate of soda*.

We may convert into—

1. SULPHATE OF SODA. 2. NITRATE OF SODA. 3. CHLORIDE OF SODIUM.	4. CARBONATE OF SODA.
In general those salts of soda which correspond to the potass salts specified under the same heads in § 71.	Caustic soda, bicarbonate of soda, and salts of soda with organic acids.

The proportion of soda in borate of soda, is best estimated by inference from sulphate of soda. (Vide § 102.)

The proportion of soda in phosphate of soda, is inferred from chloride of sodium. (Vide § 101.)

Soda salts with organic acids, are determined either as chloride or nitrate of soda, like the corresponding salts of potass, or they are weighed as carbonate of soda; the latter method is preferable with respect to soda—but it is less applicable to salts of potass.

1. *Determination as sulphate of soda.*

The aqueous solution of sulphate of soda is to be evaporated, and the residue to be ignited and weighed. (§ 22.) There is no risk of any loss by decrepitation, as in the ignition of sulphate of potass. Should free sulphuric acid be present, this is removed by means of carbonate of ammonia. (§ 42.) Properties of the residue. (Vide § 43.) This method is easy of execution, and yields accurate results.

2. *Determination as nitrate of soda.*

Same method as described sub. 1. What has been stated § 71, 2, applies equally here. Properties of the residue, vide § 43).

3. *Determination as chloride of sodium.*

Same method as described sub. 1. The rules laid down § 71-3, apply equally here. Properties of the residue, vide § 43.

The manner of converting sulphate, chromate, chlorate, and silicate of soda into chloride of sodium, will be given in Part II. of this section, when treating of the corresponding acids.

4. *Determination as carbonate of soda.*

The aqueous solution of carbonate of soda is evaporated, and the residue ignited and weighed. The method yields accurate results. Properties of the residue, vide § 43.

Caustic soda is converted into the carbonate by adding to its aqueous solution carbonate of ammonia in excess, evaporating at a gentle heat, and igniting the residue.

Bicarbonate of soda, when dry, is converted into the simple carbonate by ignition. The heat applied must be gentle at first, and increased very gradually; the crucible must be kept well covered. If we have the bicarbonate in solution, this is to be kept for some time in a state of ebullition, in a flask or retort placed obliquely; it is then to be evaporated to dryness, and the residue ignited as usual.

Salts of soda with organic acids are converted into the carbonate by igniting them in a platinum crucible, which is to be kept covered at first; after the lapse of some time, however, the lid is to be removed. A gentle heat is to be applied at first, and to be increased very gradually. When the mass has ceased to swell up, the crucible is to be placed obliquely over the flame, with the lid placed against it, (as illustrated Plate XXIX. § 32;) and a feeble red-heat is to be applied until the charcoal is consumed as completely as possible. The contents of the crucible are then to be heated with water, and the fluid is to be filtered off from the undissolved charcoal; the latter is to be carefully washed, adding the rinsing water to the filtrate, which is then to be evaporated to dryness, and the residue ignited. If the proportion of charcoal is very inconsiderable, (not exceeding a few milligrammes,) the crucible may likewise at once be weighed with its contents, after ignition, deducting the amount of charcoal from the resulting figure; the charcoal is collected for this purpose upon a small, weighed filter, carefully dried with the latter, and its weight ascertained. Both methods, if properly and carefully executed, yield accurate results. A direct experiment (No. 47) performed according to the latter method, yielded 99.7 instead of 100 parts of soda. If however, the amount of charcoal exceeds from 10 to 20 milligrammes, the former method is preferable, being less liable to errors of weighing.

§ 73.

AMMONIA.

a. Solution.

Ammonia is soluble in water, and so are all the salts which it forms with those acids that come under consideration here. It is not always requisite, however, to dissolve the ammoniacal salts, for the purpose of determining the absolute and relative proportion of ammonia contained in them.

b. Determination.

Ammonia is weighed either as *chloride of ammonium* or as *chloride of platinum and ammonium.* Into the latter form it may be converted, either *directly* or *indirectly.* Sometimes the proportion of ammonia is inferred likewise from the volume of nitrogen—the latter method is equally applicable to all ammoniacal salts.

We convert into

1. CHLORIDE OF AMMONIUM.

Caustic ammonia and ammoniacal salts, with weak volatile acids, such as carbonate of ammonia, sulphuret of ammonium, etc. etc.

2. CHLORIDE OF PLATINUM AND AMMONIUM.

a. Directly.	*b. Indirectly.*
Ammoniacal salts with acids soluble in alcohol, such as sulphate of ammonia, phosphate of ammonia, etc. etc.	Ammoniacal salts with acids insoluble in alcohol, or with acids that decompose alcohol; e. g. chromate of ammonia.

Besides, in the salts specified sub. *b.* the proportion of ammonia may be determined in all other ammoniacal salts, by converting them into chloride of platinum and ammonium, in the indirect way.

1. *Determination as chloride of ammonium.*

The aqueous solution of chloride of ammonium is evaporated in the water-bath, and the residue dried at 212°, until its weight ceases to diminish. (§ 22). This method yields very accurate results. The supposed volatilization of sal ammoniac is but very trifling. A direct experiment (No. 10) yielded 99.94 instead of 100 parts of ammonia. The presence of free hydrochloric acid does not render any modification of the process necesstary; the conversion of caustic ammonia and likewise of carbonate of ammonia into chloride of ammonium, may therefore be effected simply by supersaturating with hydrochloric acid, evaporating, and drying the residue at 212°; if we have carbonate of ammonia to operate upon, the process of supersaturation, and likewise the first stage of evaporation, are conducted in a flask or retort placed obliquely, (§ 22); the same applies to sulphuret of ammonium, with this addition, that should sulphur separate during the process, the supernatant liquid must be filtered off from this sulphur, immediately after the evolution of sulphuretted hydrogen has ceased, and before evaporating to dryness.

2. *Determination as chloride of platinum and ammonium.*

a. Direct determination.

Ammoniacal salts with volatile acids, are converted into chloride of platinum and ammonium, by the method described § 71, 4 *a.*; salts with non-volatile acids, by that described § 71, 4 *β.*

These methods yield accurate results: to control the accuracy of our operation, the filter containing the double chloride may be ignited, and the proportion of the ammonia inferred from the remaining platinum. The ignition must take place in a covered crucible; the heat applied should be gentle at first, and only very gradually increased. If this operation is not conducted very cautiously, some loss may arise from some portion of this double chloride being carried away with the vapor of sal ammoniac.

The best way is to expose the covered crucible containing the precipitate wrapped up in the filter, to a moderate heat at first, and finally to consume the charcoal of the filter at a gradually increased heat, taking care to remove the lid, and to place the crucible obliquely. (H. Rose.)

β. *Indirect determination.*

This is executed in the same manner as the determination of nitrogen in organic compounds; we refer therefore to § 149.

3. *Estimation of the ammonia from the volume of nitrogen.* We refer to § 147 and 148.

SECOND GROUP OF THE BASES.

Lime

BARYTES—STRONTIAN—[redacted]—MAGNESIA.

§ 74.

1. BARYTES.

a. Solution.

Many of the barytes salts are soluble in water, and so is caustic barytes. Those of the salts of barytes which are insoluble in water, dissolve readily in dilute hydrochloric acid, with the exception of sulphate of barytes, which is prepared for solution by fluxing with *carbonate of soda and potass,* etc. etc. Vide § 100.

b. Determination.

Barytes is weighed either as *sulphate* or as *carbonate.* (§ 45.) It is rarely converted into *silico-fluoride of barium,* (exclusively for the purpose of separating it from strontian. Vide § 117).

We may convert into

1. SULPHATE OF BARYTES.

a. By precipitation.	*b. By evaporation.*
All barytes compounds, without exception.	All barytes compounds with volatile acids, provided no other non-volatile body be present.

2. CARBONATE OF BARYTES.

a. All barytes salts soluble in water.

β. Salts of barytes with organic acids.

The method of precipitating as sulphate of barytes is the most frequently employed, since it is best adapted for the separation of barytes from other bases. The method of evaporating yields very accurate results, and is very convenient when we have to deal with small portions of fluid. The conversion into the carbonate is resorted to only in cases where the conversion into the sulphate is inadmissible or unadvisable.

1. *Determination as sulphate of barytes.*

a. By precipitation.

The compound of barytes which we have to operate upon, is to be dissolved, according to its nature, either in water or in hydrochloric acid, in a beaker-glass, taking care to render the solution moderately dilute; the solution is to be heated to 212°, and dilute sulphuric acid added, as long as the formation of a precipitate continues; the mixture is stirred with a glass rod, and the fluid adhering to the rod is rinsed off into the beaker-glass, with a little water; the glass is then to be covered, and allowed to stand at rest until the precipitated sulphate of barytes has completely subsided, and the supernatant fluid become perfectly clear, (this will require about twelve hours). The fluid is then cautiously decanted into another beaker-glass; if it is *perfectly* clear, it may be at once thrown away, if not, it is to be strained through a filter. The precipitate remaining in the first glass is mixed with a small portion of moderately diluted hot solution of sal ammoniac, and gradually projected upon a filter, (in case the fluid decanted at first from off the precipitate has required filtration, the same filter is to be used,) taking care, after the projection of every fresh portion of the precipitate, to wait until the fluid has completely drained off, and to add a fresh amount of hot solution of sal ammoniac to the precipitate remaining in the beaker-glass. If the filtering paper is tolerably good, this way of proceeding will separate the precipitate completely from its menstruum. The precipitate is washed, first with dilute hot solution of sal ammoniac, and finally with hot water, until chloride of barium produces no longer any turbidity in the washing water which runs off from the precipitate. The precipitate is then dried, and the further process conducted as stated § 31.

b. By evaporation.

Sulphuric acid in excess is added to the solution of the barytes compound, which it is intended to determine, and the mixture is evaporated in a weighed platinum dish, in the water-bath; the excess of sulphuric acid is then expelled in the air-bath or oil-bath, and the residue is ignited. The sulphuric acid used in this process must be perfectly pure, and should not be added too greatly in excess.

For the properties of sulphate of barytes, vide § 45. Both methods, if properly and carefully executed, yield *almost absolutely* accurate results.

2. *Determination as carbonate of barytes.*

a. In solutions.

The barytes salt, which it is intended to convert into the carbonate, is dissolved in water, in a beaker-glass, and the solution moderately dilute mixed with ammonia; carbonate of ammonia is then added in excess, and the mixture kept standing several hours in a moderately warm spot; the fluid is then filtered off from the precipitate formed, the latter is washed with water containing some ammonia in admixture, dried and finally ignited. (§ 31.) (Properties of the precipitate, vide § 45.) This method is liable to a trifling loss, since carbonate of barytes is not absolutely insoluble in water; it is, however, more expeditious and convenient of execution than the precipitation with sulphuric acid. The direct experiment, No. 48, yielded 99.79 instead of 100 parts of barytes.

b. Barytes salts with organic acids.

The salts of barytes with organic acids are slowly heated in a covered platinum crucible, until the escape of fumes ceases; the crucible is then placed obliquely, with the lid placed against it, (§ 32,) and a red heat is applied, until all the charcoal is completely consumed, and the residue has acquired a perfectly white appearance; the residue is then moistened with a concentrated solution of carbonate of ammonia, and again subjected to the action of an evaporation heat; it is finally gently ignited and weighed. The results obtained by this method are very satisfactory. The direct experiment No. 49 yielded 99.61, instead of 100 parts of barytes. The loss of substance which attends this method almost constantly, is owing to portions of the salt being carried off in the ignition, and is therefore the less considerable the more slowly and gradually the heat is increased at first. If the operator neglect to moisten the residue with solution of carbonate of ammonia, as directed above, he is likely to incur a further loss of substance, since the ignition of carbonate of barytes, in contact with charcoal, gives rise to the reduction of a portion of that salt into caustic barytes, whilst carbonic oxide gas escapes.

§ 75.

2.—STRONTIA.

a. Solution.

What we said regarding barytes, (§ 74,) applies equally to strontia.

b. Determination.

Strontia is weighed as *sulphate* or as *carbonate.* (§ 46.)

We may convert into

1. SULPHATE OF STRONTIA.

a. By precipitation.	*b. By evaporation.*
All compounds of strontia without exception.	All compounds of strontia with volatile acids, provided no other non-volatile substance be present.

2. CARBONATE OF STRONTIA.

α All those compounds of strontia which are soluble in water.

β. Salts of strontia with organic acids.

The method of determining strontia by converting it into the sulphate by precipitation, yields accurate results only in cases where the fluid from which the sulphate is to be precipitated, admits of being mixed with alcohol. In the contrary case, and if the conversion into the sulphate by evaporation is inadmissible, it is preferable to convert into the carbonate, if we have to operate upon soluble compounds of strontia, or upon salts of strontia with organic acids.

1. *Determination as sulphate of strontia.*

a. By precipitation.

The salt of strontia which it is intended to convert into the sulphate, is dissolved in a beaker-glass; the solution should not be too dilute; dilute sulphuric acid is added in excess, and beside this, a quantity of alcohol, at least equal to the amount of the fluid present. The mixture is allowed to stand at rest for the space of several hours, and subsequently filtered, washed with dilute spirits of wine, dried, and ignited. (§ 31.)

Should the particular circumstances of the case prevent the use of alcohol, care is to be taken to precipitate the fluid in a tolerably concentrated state; the fluid should, in such cases, be allowed to stand at rest for twelve hours in the cold, and the precipitate should be washed with cold water until the rinsing water ceases to leave any residue upon evaporation, and to manifest an acid reaction. Too long protracted washing of the precipitate gives rise to loss of substance. If traces of free sulphuric acid remain adhering to the filter, the latter will turn black, upon drying, and crumble into ashes.

The precipitate is then dried and ignited, taking care to get it *perfectly* dry before ignition; care should be taken, moreover, to leave as little as possible of the precipitate adhering to the filter, or else some loss of substance will be incurred; this may be clearly recognised by the filter burning with a carmine red flame. Properties of the precipitate, vide § 46.—The method yields very accurate results in all cases where the addition of alcohol to the solution is admissible; but if we have simply to deal with an aqueous solution, some loss is incurred, since sulphate of strontia is not absolutely insoluble in water; the direct experiments noted sub. No. 50, yielded only 98.12 and 98.02, instead of 100 parts of strontian. This inaccuracy may, however, in a great measure be remedied, by calculating the amount of sulphate of strontia dissolved in the filtrate and the rinsing water, basing this calculation upon the known degree of solubility of sulphate of strontia in acidified and in pure water. Vide Experiment No. 51, which yielded 99.77 instead of 100 parts of strontia.

b. By evaporation.

The same method as described § 74, 1 b.

2. *Determination as carbonate of strontia.*

a. In solutions.

The same method as described § 74, 2 a.—Properties of the precipitate, vide § 46.—This method yields very accurate results, since carbonate of strontia is nearly *absolutely* insoluble in water containing ammonia and carbonate of ammonia.—The direct Experiment No. 52 yielded 99.82 instead of 100 parts of strontia.

b. In salts with organic acids.

The same method as described § 74, 2 *b*.

§ 76.

3. LIME.

a. Solution.

What we stated with regard to barytes (§ 74) applies equally to lime. Fluoride of calcium is, by means of sulphuric acid, converted into sulphate of lime, and the latter, if necessary, is further resolved, by fluxing with carbonated alkali.

b. Determination.

Lime is weighed either as *sulphate*, or as *carbonate*. (§ 47.)

1. SULPHATE OF LIME.

a. By precipitation.	*b. By evaporation.*
All salts of lime, with acids soluble in alcohol, provided no other substances, insoluble in alcohol, be present.	All salts of lime with volatile acids, provided no non-volatile substance be present.

2. CARBONATE OF LIME.

a. By precipitation with carbonate of ammonia.	*b. By precipitation with oxalate of ammonia.*
All salts of lime soluble in water.	All salts of lime soluble in water or in hydrochloric acid.

c. By ignition.

Salts of lime with organic acids.

Of these two methods, that sub. 2 *b*, is the most frequently applied. This and the method sub. 1 *b*, yield the most accurate results. The method sub. 1 *a*, is usually applied only to separate lime from other bases, and that sub. 2 *a*, generally only in cases where we want to separate lime and other alkaline earths from the alkalies.

1. *Determination as sulphate of lime.*

a. By precipitation.

Dilute sulphuric acid in excess, is added to the solution of the salt of lime, which it is intended to convert into the sulphate—(this is to be done in a beaker-glass); two volumes of alcohol are then added to the mixture, and the whole is allowed to stand at rest for several hours; the fluid is then filtered off from the precipitate, and the latter is washed *completely* with spirits of wine, dried and ignited. (§ 31.) Properties of the precipitate, vide § 47. The results are very accurate. The direct experiment No. 53, yielded 99.64, instead of 100 parts of lime.

b. By evaporation.

The same method as described § 74, 1 *b*.

2. *Determination as carbonate of lime.*

a. *By precipitation with carbonate of ammonia.*

The same method as described § 74, 2 *a*. The precipitate should be ignited very gently, but the ignition should continue some time. Properties of the precipitate § 47. This method, if properly executed, yields very accurate results; but if the precipitate is washed with pure, instead of ammoniated water, a certain loss of substance is incurred; the direct experiment No. 54, executed in this manner, yielded 99.17, instead of 100 parts of lime.

b. By precipitation with oxalate of ammonia.

a. *The lime-salt which is to be determined is soluble in water.*

The lime salt which it is intended to convert into oxalate of lime, is dissolved in hot water, in a beaker-glass, and oxalate of ammonia added in excess, and moreover, a small portion of ammonia, so as to impart an ammoniacal smell to the fluid, the beaker-glass is then covered and placed in a warm spot until the precipitate has completely subsided. The precipitate is then placed upon a filter, in the manner described § 74, 1 *a*, (sulphate of barytes,)—simply substituting hot water for solution of sal ammoniac. Should it happen that minute particles of the precipitate adhere so firmly to the glass as to resist their removal by mechanical means, they must be dissolved in a few drops of highly dilute hydrochloric acid, and the solution subsequently precipitated with ammonia; this precipitate is to be added to the principal precipitate. After having washed the precipitate carefully, it is to be dried upon the filter in the funnel, and subsequently to be introduced into a platinum crucible; the filter is then incinerated upon the lid of the crucible; the lid with the filter ashes, is placed inverted upon the crucible, and the latter is exposed to a gentle heat, at first, but which is gradually increased until the bottom of the crucible begins to glow faintly; the crucible is kept at this temperature for the space of from ten to fifteen minutes, and subsequently allowed to cool; it is then weighed. If the whole of the process be properly and carefully executed, the results will prove exceedingly accurate; the direct experiment No. 55 yielded 99.99, instead of 100 parts of lime. To ascertain whether the operation has been perfectly successful, the contents of the crucible, which should appear white and hardly show the slightest inclination to grey, are, after weighing, moistened with some water, and the latter is tested with turmeric-paper. Should the paper turn brown, a sign that the heat applied was too intense, it will be necessary to correct the former operation by throwing a small fragment of pure carbonate of ammonia into the crucible, evaporating to dryness—(best in the water-bath), igniting very gently and weighing the residue; the amount obtained in the second operation will be a trifle higher than that of the first process; the slip of turmeric-paper that has been used as the test, must be washed with water, and the rinsings transferred into the crucible.

For the properties of the precipitate and residue, vide § 47.

Many chemists prefer collecting the oxalate of lime upon a weighed filter, to dry at 212°, and to weigh the dry precipitate of oxalate of lime, instead of converting it into the carbonate by ignition. The precipitate obtained in this manner is not, as is often erroneously supposed, $Ca\,O, C_2\,O_3$, but $Ca\,O,\ C_2\,O + aq.$ and ought therefore to be calculated as such. This method is more circumstantial and less accurate in its results than that of converting the oxalate of lime into the carbonate. The direct experiment No. 56, yielded 100.45, instead of 100 parts of lime.

β. The lime-salt which is to be determined is insoluble in water.

The salt which it is intended to convert into the oxalate, is dissolved in dilute hydrochloric acid. If the acid is of a nature to escape in this operation, such as carbonic acid, for instance, or of a nature admitting of its removal by evaporation, such as silicic acid, the process is, after the removal of the acid, conducted as described sub. *α*; but if the acid is of a more stable nature, such as phosphoric acid, for instance, it is necessary first to neutralize the free acid present, with ammonia, until a precipitate begins to form; this precipitate is to be redissolved by the addition of a drop of hydrochloric acid; oxalate of ammonia in excess is added, and finally acetate of potass; the precipitate formed is allowed to subside, and the further process conducted as sub. *a*. In this operation the free hydrochloric acid present combines with the potass and ammonia of the acetate and oxalate, liberating a corresponding amount of acetic acid and oxalic acid, in which acids oxalate of lime is nearly insoluble. This method yields very accurate results. In the direct experiment, No. 57, 99.78 parts of lime were obtained, instead of 100 parts.

c. By ignition.

The same method as described § 74, 2 *b*. The residue remaining upon evaporation with carbonate of ammonia, should be heated very gently. (It is advisable to repeat this operation.)

§ 77.

4. MAGNESIA.

a. Solution.

Many of the compounds of magnesia are soluble in water; those which are insoluble in that menstruum, dissolve in hydrochloric acid, with the exception of silicates.

b. Determination.

Magnesia is weighed either as *sulphate* or as *pyrophosphate*, or as *pure magnesia*.

We may convert into—

1. SULPHATE OF MAGNESIA.

a. Directly.

All compounds of magnesia with volatile acids, provided no other non-volatile substances be present.

b. Indirectly.

All those compounds of magnesia which are soluble in water, and likewise those which, insoluble in water, dissolve in hydrochloric acid, with separation of their original acid, (provided no ammoniacal salts be present.)

2. PYROPHOSPHATE OF MAGNESIA.

All compounds of magnesia without exception.

3. PURE MAGNESIA.

a. Salts of magnesia with organic acids, or with readily volatile inorganic oxygen acids.

b. Chloride of magnesium and those compounds of magnesia which admit of being converted into this salt.

The direct determination as sulphate of magnesia is the best in all cases where it is admissible. The method of indirect determination serves only to separate magnesia from certain bases, and its application is had recourse to as rarely as possible. The method of converting into pyrophosphate of magnesia is most frequently applied, especially also to separate magnesia from other bases. The method of reducing chloride of magnesium to pure magnesia is usually applied only to separate magnesia from the fixed alkalies. Compounds of magnesia and phosphoric acid are analysed as § 101 directs.

1. *Determination as sulphate of magnesia.*

a. Direct determination.

Dilute pure sulphuric acid is added to the solution of the magnesia salt which it is intended to convert into the sulphate; the acid is to be added to an amount more than sufficient to combine with the magnesia present; the mixture (in a weighed platinum dish) is evaporated to dryness in the water-bath; the dish is then covered, and cautiously heated in the air-bath or oil-bath until the excess of sulphuric acid is completely expelled;—the residue is finally heated to gentle redness over a spirit-lamp, allowed to cool, and weighed. Should no vapors of sulphuric acid escape, upon heating in the sand-bath, this may be considered a sure sign that the acid has been added in insufficient quantity; in such cases the mixture is allowed to cool, and a fresh portion of sulphuric acid is added to it. Care should, however, be taken not to add the acid too greatly in excess, since this tends to protract the process; the residue, moreover, should not be ignited too intensely, and should be speedily weighed. For the properties of the residue, vide § 48. The results obtained by this method are very accurate.

b. Indirect determination.

The salt of magnesia, which it is intended to determine, is dissolved in a flask; the solution is heated to 212°; and clear saturated water of barytes is added in excess; — the temperature is maintained for some time near the ebullition point;—the fluid is then filtered off from the precipitate, which latter is to be carefully washed with boiling water; the precipitate, after washing, is dissolved upon the filter by the action of hot and somewhat dilute hydrochloric acid; the filter is carefully washed, and the further operation is then conducted as directed, sub. *a.* Should a precipitate of sulphate of barytes form, upon the addition of the sulphuric acid, this may be considered a sign that the carbonic acid of the air had not been sufficiently excluded from contact with the water of barytes during the operation. In that case, we may either allow this precipitate to subside, filter off from it, and evaporate the filtrate, or we may evaporate at once, weigh the residue, act upon it with water, filter the solution off from the undissolved sulphate of barytes, ascertain the weight of the latter, (§ 74, 1 *a.*,) and subtract this from the the original residue.

The result obtained by this method falls somewhat short of 100, since hydrated magnesia is not quite insoluble in water. The method is, moreover, rather too complicated to yield perfectly accurate results. (Compare § 116 *a*).

2. *Determination as pyrophosphate of magnesia.*

The solution of the magnesia salt, which it is intended to convert into the pyrophosphate, is mixed with sal ammoniac, and ammonia added in excess. (Should the addition of ammonia cause any precipitate, this may be considered a sign that a sufficient amount of sal ammoniac has not been added; a fresh amount of this salt must consequently be added, sufficient to cause the re-solution of the precipitate formed.) The fluid is then to be mixed with a solution of phosphate of soda in excess, and the whole to be stirred with a glass rod, taking care to avoid touching the sides of the beaker glass with the stirring-rod; the mixture is then allowed to stand at rest for twelve hours; after the lapse of that time, the fluid is to be filtered off from the precipitate, taking care to collect every particle of the latter upon the filter; when the fluid has completely drained off, water mixed with $\frac{1}{8}$ of solution of ammonia, is poured upon the precipitate in the filter, and allowed to drain off; the same operation is to be repeated until the fluid running through the filter ceases to leave any residue when evaporated upon a platinum plate.

The precipitate is to be completely dried and, when dry, to be introduced into a platinum crucible (§ 31); the crucible is to be covered and heat applied; this should be very gentle at first; but should finally be increased to intense ignition. The filter, cut into small slips, is incinerated upon the lid of the crucible. This operation requires some patience, since the filter is difficult of combustion. The lid is then placed upon the crucible, and the latter is once more exposed to a red-heat; the crucible and its contents are finally allowed to cool, and their weight is ascertained.

For the properties of the precipitate and residue, vide § 48.

This method, if properly executed, yields exceedingly accurate results. It is indispensable that the washing water be mixed with ammonia.

The direct experiments, No. 58 *a.* and *b.*, yielded 100.14 and 100.03, instead of 100 parts of magnesia.

3. *Determination of pure magnesia.*

a. In salts of magnesia, with organic acids.

The salt of magnesia, which it is intended to reduce to the state of pure magnesia, is gently heated in a covered platinum crucible, increasing the temperature gradually, until the evolution of empyreumatic products ceases; the lid is then removed from the crucible, and the latter is placed in an oblique position, the lid leaning against it. (§ 32.) The crucible and its contents are then exposed to a red-heat until the residue has acquired a perfectly white appearance. For the properties of the residue, vide § 48.

The results obtained by this method are the more accurate the more slowly and gradually the operator increases the gentle heat applied at the commencement of the operation. Some loss of substance is generally sustained, owing to minute traces of the salt being carried away with the empyreumatic products. The direct experiment, No. 59, yielded 99.36 instead of 100 parts of magnesia. Salts of magnesia, with readily volatile oxygen acids, (carbonic acid and nitric acid,) may be easily reduced to pure magnesia, by ignition in the way just now described.

b. Conversion of chloride of magnesium into pure magnesia.

The concentrated solution of chloride of magnesium, in a porcelain crucible, is to be mixed with pure peroxide of mercury in such proportion that the amount of oxygen present is more than sufficient to convert the whole of the chloride of magnesium into magnesia; this mixture is to be evaporated in the water-bath, and well dried; the crucible is to be covered, and exposed to a red-heat until the complete expulsion of the perchloride of mercury formed, together with the excess of peroxide of mercury. (The operator should carefully guard against inhaling the vapors escaping from the mixture during ignition). The residue consists of pure magnesia, which may be either at once weighed in the crucible, or when the operation has for its end the separation of magnesia from the alkalies, is to be collected upon a filter, washed with hot water, dried, and ignited. (§ 31).

THIRD GROUP OF THE BASES.

ALUMINA—OXIDE OF CHROMIUM.

§ 78.

1. ALUMINA.

a. Solution.

Those of the compounds of alumina which are insoluble in water, dissolve, almost without exception, in hydrochloric acid. Crystallized alumina occurring in nature, (sapphire, ruby, &c.,) and many other alumina compounds likewise occurring in nature, as well as artificially prepared, strongly ignited alumina, require fluxion with carbonate of soda, caustic potass, or hydrated barytes, as a preparatory step to their solution in hydrochloric acid. There exists many other alumina compounds which are more advantageously fluxed with bisulphate of potass. (Compare § 20 g.)

b. Determination.

Alumina is invariably weighed in its pure state, § 49. The compounds of alumina may be converted into pure alumina, either by precipitation in the form of a hydrate and subsequent ignition, or by simple ignition.

We may change into

PURE ALUMINA.

a. By precipitation.

All those compounds of alumina which are soluble in water, as well as those of the insoluble compounds, the acid of which is evolved, and removed upon their solution in hydrochloric acid.

b. By ignition.

α. All the salts of alumina with readily volatile acids, (hydrochlorate of alumina, nitrate of alumina, &c.)

β. All the salts of alumina with organic acids.

The methods sub. *b.* are applicable only in cases where no other fixed substances are present. With regard to the estimation of alumina in its combinations with phosphoric acid, boracic acid, silicic acid, and chromic acid, we refer to Part II. of this section, where we shall have to treat of the estimation of these acids.

Determination as pure alumina.

a. By precipitation.

The alumina salt, which it is intended to reduce to the state of pure alumina, is to be dissolved in a beaker-glass, and the solution is to be moderately diluted; a tolerable large proportion of sal ammoniac is then to be added, together with ammonia *slightly* in excess, and heat applied for some time; the fluid is then filtered off from the precipitate formed, and the latter is washed with hot water, carefully dried, ignited, (§ 32,) and weighed. A gentle heat should be applied at first, and the crucible be kept well covered, or else some loss is likely to arise from the spitting of the gelatinous and still slightly moist hydrate of alumina. If we have sulphate of alumina to operate upon, it is necessary to dissolve the washed precipitate in hydrochloric acid, to re-precipitate with ammonia, and to weigh after ignition. If this second solution and re-precipitation are not attended to, the precipitate will, despite the most intense ignition, retain sulphuric acid. For the properties of the precipitate and residue, vide § 49. The method, if properly executed, yields very accurate results.

b. By ignition.

α. Compounds of alumina with volatile acids.

If the compound to be examined is in solution, this is evaporated in the water-bath, and the residue introduced into a platinum crucible, and exposed to a red-heat, gentle at first, but gradually increased to the very highest degree of intensity; the application of this heat is continued until the weight of the crucible ceases to vary. If the compound to be examined is in its solid state, it is to be introduced at once into the crucible. For the properties of the residue, vide § 49. The purity of the residue should be carefully examined. This method is entirely free from sources of error.

β. Compounds of alumina with organic acids.

The same method as described § 77. 3 *a*.

§ 79.

2. OXIDE OF CHROMIUM.

a. Solution.

Many of the compounds of chromium are soluble in water.

Hydrated oxide of chromium, and most of the salts of oxide of chromium which are insoluble in water, dissolve in hydrochloric acid. Ignition renders oxide of chromium and many of its salts insoluble in acids; this insoluble modification of the oxide and of the salts in question is to be prepared for solution in hydrochloric acid, by fluxing with carbonate of soda. (§ 20 *a.*) A small amount of oxide of chromium is in this process converted into chromic acid, owing to the action of the air; this is, however, reconverted into oxide upon heating with hydrochloric acid. Addition of alcohol promotes this reduction greatly.

b. Determination.

Oxide of chromium is invariably weighed in its pure state. (§ 50). The compounds of oxide of chromium are converted into the pure oxide either by precipitation as hydrated oxide and subsequent ignition, or by direct ignition.

We may convert into

PURE OXIDE OF CHROMIUM

a. By precipitation.	*b. By direct ignition.*
All the compounds of oxide of chromium which are soluble in water, as well as those of the insoluble compounds, the acid of which is liberated and removed upon their solution in hydrochloric acid.	*α.* All the salts of oxide of chromium with volatile oxygen acids, provided no non-volatile substances be present. *β.* Salts of oxide of chromium with organic acids.

For the analysis of the compounds of oxide of chromium with chromic acid, phosphoric acid, boracic acid, and silicic acid, we refer to the paragraphs treating of these acids, in the second part of this section.

Determination as oxide of chromium.

a. By precipitation.

The compound of oxide of chromium which it is intended to analyse is dissolved in the appropriate menstruum, in a beaker-glass; the solution should not be too concentrated. The solution is to be heated to 212°, and ammonia added slightly in excess; the mixture is then to be exposed, for the space of thirty minutes, to a temperature approaching ebullition; after this, it is to be filtered, edulcorated with hot water, well dried, and ignited, according to § 31 or § 32. The heat should be increased gradually, and the crucible kept covered, otherwise some loss is likely to arise from the spitting, attendant upon the incandescence of the oxide of chromium which marks the passing of the soluble into the insoluble modification. Care should be taken to continue heating the precipitated fluid until it is *perfectly colorless;* if this precaution be neglected, and the fluid be filtered whilst it yet retains a reddish appearance, a perceptible loss of substance will be incurred. Properties of the precipitate and residue, vide § 50. This method, if properly executed, yields very accurate results.

b. By direct ignition.

α. Salts of oxide of chromium with volatile acids.

The same method as described § 78 *b. α.* (Alumina).

β. Salts of oxide of chromium with organic acids.

The same method as described § 77 3 *α.* (Magnesia).

FOURTH GROUP OF THE BASES.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—PEROXIDE OF IRON.

§ 80.

1. OXIDE OF ZINC.

a. Solution.

Many of the salts of zinc are soluble in water. Metallic zinc, oxide of zinc, and the salts of zinc, which are insoluble in water, dissolve in hydrochloric acid.

b. Determination.

Oxide of zinc is invariably weighed as such. The conversion of the salts of zinc into the oxide is brought about either by precipitation as carbonate or sulphuret of zinc, or by direct ignition.

We may convert into

OXIDE OF ZINC.

a. By precipitation as carbonate of zinc.

All the salts of zinc which are soluble in water, and all those with organic volatile acids; likewise those of the insoluble salts, the acid of which is liberated and removed upon their solution in hydrochloric acid.

b. By precipitation as sulphuret of zinc.

All compounds of zinc without exception.

c. By direct ignition.

Salts of zinc with inorganic volatile oxygen acids.

The last method is to be recommended only for carbonate of zinc and nitrate of zinc. Sulphuret of zinc and sulphate of zinc (the former with access of air) require a white heat for their complete conversion into the oxide. The method *b.* is only applied in cases where *a.* is inadmissible. It serves more especially to separate oxide of zinc from other bases. Salts of zinc with organic acids are not to be converted into the oxide by ignition, since this process would cause a small portion of the oxide to become reduced to the metallic state, and to be dissipated as vapor. If the acids are volatile, the zinc may be determined at once according to method *a.*; if, on the contrary, the acids are non-volatile, the zinc may either be precipitated as sulphuret, or the salt under examination may be heated to gentle redness, the residue extracted with nitric acid, and the solution treated according to *a.* or *b.* For the analysis of chromate, phosphate, borate, and silicate of zinc, we refer to the paragraphs treating of the corresponding acids, in the second part of this section.

Determination as oxide of zinc.

a. By precipitation as carbonate of zinc.

The moderately dilute solution of the salt under examination is to be heated nearly to ebullition in a high and capacious flask, carbonate of soda (in excess) is to be added drop by drop; the retort is then placed in an oblique position, and its contents are heated to boiling for the space of a few minutes; the fluid is then filtered, the precipitate washed with hot water, dried, and ignited, as directed at § 31. Should the solution contain ammoniacal salts, the ebullition is to be continued until, upon a fresh addition of the carbonate of soda, the escaping vapor ceases to impart a brown tint to turmeric paper. The presence of certain ammoniacal salts renders it necessary to evaporate the fluid to dryness, by *ebullition* in the obliquely-placed flask; it is therefore in such cases more convenient to precipitate the zinc as sulphuret, (vide *b.*) It is always necessary to test the fluid filtered off from the precipitated carbonate of zinc with sulphuret of ammonium, to ascertain whether *all* the zinc has been precipitated. The application of this test yields *invariably* a slight precipitate; however, if the process is properly executed (§ 51) this precipitate is so insignificant that it becomes apparent only after the lapse of many hours, and even then only in extremely slight and imponderable flakes, so slight indeed that we may utterly disregard them without impairing materially the accuracy of our results. Should the precipitate be more considerable, it is necessary to treat it as directed sub. *b.*, and to add the weight of the oxide of zinc obtained to that of the first precipitate. (For the properties of the precipitate and residue, vide § 51). The figures resulting from the application of this method are a trifle below those found by theoretical calculation; this may be owing to several circumstances, viz., the precipitation is never *absolutely* complete; moreover a portion of the precipitate adhering to the filter may, during ignition, happen to get reduced to the metallic state, and to be dissipated as vapor. On the other hand, it may also occur that the precipitate is not thoroughly washed, and this may give rise to a *higher* result in figures than theoretically calculated. In such cases the residue will be found to possess an alkaline reaction.

b. By precipitation as sulphuret of zinc.

Ammonia is added to the solution of the salt under examination, until the precipitate which forms at first is re-dissolved; sulphuret of ammonium is then added in excess, and the precipitate which forms is allowed to subside; the supernatant fluid is then passed through the filter, and the precipitate is subsequently likewise placed upon the latter, and edulcorated with water impregnated with sulphuret of ammonium; — the filter whilst still moist is, together with the precipitate, introduced into a beaker-glass, and drenched with concentrated hydrochloric acid slightly in excess; —the solution is placed on a moderately warm spot until it smells no longer of sulphuretted hydrogen; it is then diluted with a small portion of water, filtered, and the filter carefully washed with hot water; the solution of chloride of zinc, obtained in this manner, is finally precipitated, &c., as directed sub. *a.*

From a solution of acetate of zinc, this metal may be precipitated completely, or very nearly so, by means of sulphuretted hydrogen gas, even though the acetic acid be present in excess, provided always no other acid be present. The precipitated sulphuret of zinc is, in this instance, washed with water, impregnated with sulphuretted hydrogen, and, for the rest, treated exactly like the sulphuret of zinc, precipitated by means of hydrosulphuret of ammonia. (Compare experiments, sub. No. 60).

c. By direct ignition.

The salt to be examined is introduced into a platinum crucible; the latter is then covered and exposed to a gentle heat at first, which is to be increased gradually to the very highest degree of intensity, and to be maintained until the residue ceases to suffer the slightest diminution of weight.

§ 81.

1. PROTOXIDE OF MANGANESE.

a. Solution.

Many of the salts of the protoxide of manganese are soluble in water. The pure protoxide, as well as those of its salts which are insoluble in water, dissolve in hydrochloric acid. The higher oxides of manganese dissolve likewise in this acid. Chlorine is evolved in this solution, and the fluid, after having been subjected to the application of heat, contains protochloride of manganese.

b. Determination.

Manganese is weighed either as *protosulphate,* or as *manganoso-manganic oxide.* Into the latter form it is converted either by precipitation as hydrated protoxide, or, as protocarbonate, and subsequent ignition,—(the application of the latter method is in some instances preceded by precipitation as sulphuret of manganese)—or, finally, by direct ignition.

We may convert into

1. MANGONOSO-MANGANIC OXIDE.

a. By precipitation as protocarbonate of manganese.

All the soluble salts of manganese with inorganic acids, and all the salts with volatile organic acids; likewise, all those of the insoluble salts, the acid of which is liberated and removed upon their solution in hydrochloric acid.

b. By precipitation as hydrated protoxide of manganese.

All the compounds of manganese, with the exception of its salts with organic non-volatile acids.

c. By precipitation as sulphuret of manganese.

All compounds of manganese without exception.

d. By direct ignition.

All the oxygen compounds of manganese; salts of manganese, with readily volatile acids, and likewise those with organic acids.

2. PROTOSULPHATE OF MANGANESE.

All the oxides of manganese, and likewise all its salts with volatile acids, provided no non-volatile substance be present.

The method 1 *d.* is the most simple and accurate, and is therefore preferred to all others, wherever it is admissible. The method 2, is convenient and expeditious, but its results are not absolutely accurate; the method 1 *c.* is applied only in cases where the application of none of the other methods is admissible. 1 *a.* is generally preferred to 1 *b.* in cases where the choice is permitted. If the solution of manganese contains sugar or any similar non-volatile organic substance, neither 1 *a.* nor 1 *b.* are applicable, and recourse must be had to 1 *c.* Protophosphate of manganese and protoborate of manganese are treated either according to the direction of 1 *b.* or to those of 1 *c.* The proportion of manganese in the silicate of this substance, is determined according to the directions given in 1 *a.* after the separation of the silicic acid. (§ 106.) Protochromate of manganese is treated like the corresponding salt of zinc. (§ 99.)

1. *Determination as manganoso-manganic oxide.*

a. By precipitation as protocarbonate of manganese.

The solution of the salt under examination is heated to 212°, and is then mixed with carbonate of soda in excess, and the application of heat is still continued for some time—(ebullition is not necessary); the fluid is then filtered off from the precipitate formed, and the latter is washed, dried, and ignited, as directed § 32. The lid is to be placed loose on the crucible, and the heat should be maintained at a high degree of intensity, until the weight of the residue ceases to vary, even to the slightest extent. Should the solution contain ammoniacal salts, it must be precipitated in a flask in the manner indicated at § 80 *a.* (Determination of zinc by precipitation as carbonate.) For the properties of the precipitate and residue, vide § 52. This method, if properly executed, yields very accurate results.

b. By precipitation as hydrated protoxide of manganese.

The method is the same as applied sub. *a.*, with this difference, that the precipitation is effected by means of solution of caustic potass instead of carbonate of soda. If phosphoric acid is present, or boracic acid, the precipitation is to be effected in a flask, and the precipitated fluid kept boiling for some time, with an excess of potass, since this will *completely* decompose the protophosphate or protoborate of manganese. Properties of the precipitate, vide § 52.

c. By precipitation as sulphuret of manganese.

The solution of the salt under examination is mixed with sal ammoniac, and subsequently with ammonia until the latter predominates; the yellow sulphuret of ammonium is then added in excess; the precipitate formed is allowed to subside, and the supernatant fluid is passed through the filter; the precipitate is finally placed upon the latter, and carefully washed with water containing a small portion of yellow sulphuret of ammonium in admixture. The moist precipitate and filter are then introduced into a beaker-glass, and drenched with dilute hydrochloric acid; the mixture is heated until it ceases to smell of sulphuretted hydrogen; the solution is then filtered, and both the filters are carefully washed; the filtrate is precipitated as directed sub. *a.*

d. By direct ignition.

The compound of manganese under examination is introduced into a platinum crucible, which is kept closely covered and exposed to a gentle heat at first; subsequently the lid is taken off and replaced loosely upon the crucible, and the latter is then exposed to the most intense heat until the weight of the residue ceases to vary. The conversion of the higher oxides of manganese into manganoso-manganic oxide requires a more intense heat and a more protracted application of this than the conversion of the protoxide and peroxide. When salts with organic acids are under examination, it is indispensable to ascertain whether all the charcoal has been completely consumed during ignition; should the contrary turn out to be the case, the residue should be either re-dissolved in hydrochloric acid, and precipitated, &c., as directed sub. *a.*, or it ought to be repeatedly evaporated with nitric acid until all the charcoal is oxidized. This method, if properly executed, yields very accurate results. The ignition with salts of manganese with organic acids generally causes a minute portion of the salt to volatilize; the results in such cases are therefore not strictly accurate.

2. *Determination as protosulphate of manganese.*

The same method as described § 77, 1. (Magnesia.) For the properties of the residue, vide § 52. Great care should be taken to ignite the residue very feebly, or else a small portion of sulphuric acid is likely to escape.

§ 82.

3. PROTOXIDE OF NICKEL.

a. Solution.

Many of the salts of protoxide of nickel are soluble in water. The pure protoxide and those of its salts which are insoluble in water, dissolve, without exception, in hydrochloric acid; metallic nickel dissolves slowly, with evolution of hydrogen gas, when heated with dilute hydrochloric acid or sulphuric acid; in nitric acid it dissolves with great readiness. Sulphuret of nickel is but sparingly soluble in hydrochloric acid, but it dissolves readily in aqua regia. Peroxide of nickel dissolves as a protochloride with evolution of chlorine, when heated with hydrochloric acid.

b. Determination.

Protoxide of nickel is invariably weighed as such. (§ 53.) The compounds of nickel are converted into the pure protoxide, either by precipitation as hydrated protoxide,—preceded, in some instances, by precipitation as sulphuret of nickel,—and subsequent ignition, or by direct ignition.

We may convert into

PROTOXIDE OF NICKEL

a. By precipitation as hydrated protoxide of nickel.

All the salts of nickel with inorganic acids which are soluble in water, and all the salts with volatile organic acids; likewise all those of its insoluble salts, the acids of which may be removed upon their solution in strong acids.

b. By precipitation as sulphuret of nickel.

All compounds of nickel without exception.

c. By direct ignition.

The salts of nickel with readily volatile oxygen acids, or with such of the oxygen acids as are decomposed at a high temperature, (carbonic acid, nitric acid, &c.) and likewise those with organic acids.

The method *c.* is preferable to all the other methods, in all cases where it is applicable, but more especially for salts of nickel with the inorganic acids indicated. The method *a.* is most frequently applied. Should sugar and other non-volatile organic substances be present, this method is inapplicable, and it is necessary, therefore, either to destroy such admixtures by ignition, or to have recourse to method *b*, which latter is generally used to separate nickel from other bases. For the analysis of the compounds of protoxide of nickel with chromic, phosphoric, boracic, and silicic acid, we refer to the paragraphs treating of acids, in the second part of this section.

Determination as protoxide of nickel.

a. By precipitation as hydrated protoxide of nickel.

The compound under examination is dissolved in its appropriate menstruum, in a beaker-glass, and pure solution of caustic potass is added in excess; the mixture is then heated to a point approaching ebullition, the fluid is filtered off from the precipitate formed, and the latter carefully washed with hot water, dried, and ignited. (§ 32.) Presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. For the properties of the precipitate and residue, vide § 53. This method, if properly executed, yields very accurate results.

b. By precipitation as sulphuret of nickel.

The moderately dilute solution of the compound under examination is neutralized (if necessary) with ammonia, (the reaction should be acid rather than alkaline) ; perfectly saturated colorless hydrosulphuret of ammonia is then added, as long as a precipitate continues to form, (the hydrosulphuret of ammonia should not be added too greatly in excess.) The mixture is then to be well stirred, passed through a moistened filter, and carefully washed with a continuous stream of distilled water, to which one or two drops of perfectly saturated colorless hydrosulphuret of ammonia have been added. (The filtrate and the rinsing water must be perfectly colorless.) The precipitate is then dried in the funnel, (§ 29,) and subsequently transferred into a beaker-glass. The filter is incinerated upon the lid of a platinum or porcelain crucible, and its ashes are added to the precipitate. The latter is then drenched with concentrated aqua regia, and digested at a gentle heat, until all sulphuret of nickel is dissolved, and the undissolved sulphur appears of a pure yellow ; the fluid is then diluted, filtered, and precipitated, &c., as directed sub. *a*. For the properties of the precipitate, vide § 53.—This method, if properly executed, yields very accurate results. If instead of the colorless hydrosulphuret of ammonia, the yellow sulphuret of ammonium be used to precipitate the original solution of the compound of nickel under examination, or if this solution contain free ammonia, the fluid filtered off from the precipitated sulphuret of nickel will invariably appear of a more or less brownish color, owing to its containing unprecipitated sulphuret of nickel, which it is very difficult to precipitate completely from it (by exposure to the air). Were the filter (instead of being incinerated) to be treated with aqua regia, it would be impossible subsequently to precipitate the nickel completely with potass, since the solution of the sulphuret would in that case contain organic substances.

c. By direct ignition.

The same method as described § 81, 1 *d.* (Manganese.)

§ 83.

4. PROTOXIDE OF COBALT.

a. Solution.

Protoxide of cobalt and its compounds deport themselves with solvents, like the corresponding compounds of nickel, metallic cobalt like metallic nickel.

b. Determination.

Cobalt is invariably weighed in its metallic state. (§ 54.) The reduction of the salts of cobalt to metallic cobalt is effected by precipitation as hydrated protoxide of cobalt,—preceded in some instances by precipitation as sulphuret of cobalt,—and subsequent ignition, or by direct ignition. The reduction of the impure protoxide into metallic cobalt is completed by means of hydrogen gas.

We may convert into

METALLIC COBALT.

a. By precipitation as hydrated protoxide of cobalt.

All the salts of cobalt with inorganic acids which are soluble in water, and all its salts with volatile organic acids; likewise those of its insoluble salts, the acid of which may be removed upon their solution in strong acids.

b. By precipitation as sulphuret of cobalt.

All the compounds of cobalt without exception.

c. By direct ignition.

The oxide of cobalt and their compounds with readily volatile acids, and likewise those with organic acids.

The method *b.* serves principally to separate cobalt from other metals; it is applied only when some obstacle opposes the application of method *a.*; for instance, when ammonia, ammoniacal salts, non-volatile organic substances, &c., happen to be present. Method *c.* is preferable to the other methods, in all cases where it is applicable. For the analysis of the compounds of protoxide of cobalt with chromic acid, phosphoric acid, and boracic acid, we refer to these paragraphs treating of the acids, in the second part of this section.

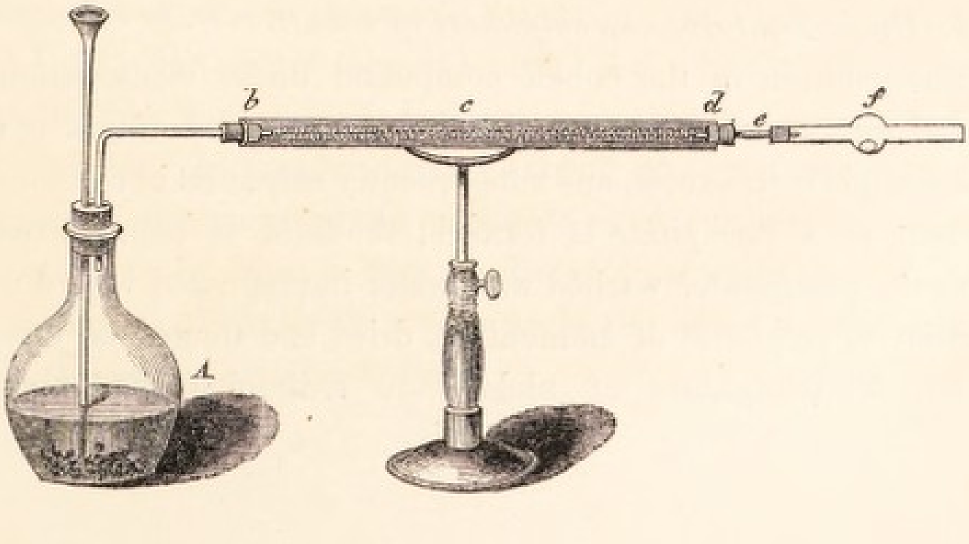
Determination as metallic cobalt.

a. By precipitation as hydrated protoxide of cobalt.

The cobalt compound under examination is dissolved in its appropriate menstruum, in a flask, and concentrated solution of caustic potass is added in excess; heat is then applied, until the precipitate formed, which was blue at first, has acquired a dirty light red, or brownish colour; the fluid is then filtered off from the precipitate, and the latter is carefully washed with hot water, dried, ignited, (§ 31,) and weighed, taking care to place the lid with the filter ashes inverted upon the crucible, so that the ashes do not get mixed with the contents of the crucible. Should ammoniacal salts be present, the operator must pursue the course recommended § 80, *a.* (Determination of zinc as carbonate.)

The contents of the crucible are then wholly or partially introduced into the bulb of a bulbous tube, (the weight of which has been previously ascertained,) and the amount of the oxide in the tube is determined by weighing the latter; the tube is then connected with an apparatus for the evolution of hydrogen gas, as illustrated by

PLATE XXXI.



A represents the evolution flask containing granulated zinc; *b d* is a long tube, filled up to *c* with blotting paper, and from *c* to *d* with chloride of calcium. The small tube *e* serves to connect, by means of two perforated corks, the bulbous tube *f* with *b d*. A slow stream of hydrogen gas is evolved by pouring dilute sulphuric acid into *A*; the operator should wait until all atmospheric air has been expelled the apparatus, and then apply a gentle heat to the bulb *f*, increasing this heat gardually to bright redness. The reduction may be considered completed when the formation of water ceases; the water which may still remain in the posterior part of the tube is expelled by means of a small spirit lamp, and the bulbous tube is then allowed to cool, whilst the transmission of hydrogen gas is continued; the tube is then taken off from *e*, and held obliquely for some time, so as to permit the air to replace the hydrogen; after this the tube is weighed. If the contents of the crucible (protoxide of cobalt) have been only partially introduced into the bulb of *f*, the operator has to calculate the amount of metallic cobalt obtained from the reduced portion, upon the whole amount of the protoxide. For the properties of the precipitate, of the ignited residue and the reduced cobalt metal, vide § 54.—This method, if properly executed, yields very accurate results. Care should be taken to ignite the reduced cobalt in *f* to a sufficient degree of intensity, since, if this be neglected, the cobalt is likely to take fire upon the access of air. Should it, notwithstanding intense ignition, show afterwards pyrophorous properties, this is a sign that the protoxide of cobalt was not pure.

b. By precipitation as sulphuret of cobalt.

The solution of the cobalt compound under examination, is mixed with a small portion of sal ammoniac; ammonia is then added slightly in excess, and subsequently sulphuret of ammonium, as long as a precipitate is formed; the fluid is then filtered off from the precipitate, washed with water impregnated with a small portion of sulphuret of ammonium, dried and treated as directed § 82, *b.* (Sulphuret of nickel,) to redissolve the sulphuret of cobalt. The cobalt in this solution is determined as described sub. *a*. For the properties of sulphuret of cobalt, vide § 54. This method, if properly executed, yields very accurate results, since it is free from all sources of error.

c. By direct ignition.

The same method as described § 81, 1 *d*. (Manganese.) The amount of cobalt in the oxide obtained by this method is determined by reduction with hydrogen, in the manner described sub. *a*.

§ 84.

5. PROTOXIDE OF IRON.

Many of the protocompounds of iron are soluble in water. The pure protoxide of iron and those of its compounds which are insoluble in water, dissolve nearly without exception in hydrochloric acid. The solutions, if not prepared with perfect exclusion of the air, and with solvents absolutely free from air, contain invariably more or less peroxide. Some natural compounds of iron require fluxing with carbonate of soda, as an indispensable preliminary for their perfect solution in hydrochloric acid. Solutions prepared in this manner, contain nearly exclusively perchloride of iron, and but little protochloride, or even none. Metallic iron dissolves in hydrochloric acid and dilute sulphuric acid, as protochloride or protosulphate, with evolution of hydrogen; in hot nitric acid, it dissolves as pernitrate, and in aqua regia as perchloride.

b. Determination.

Protoxide of iron is invariably weighed in the form of peroxide, (§ 55.) To convert it into this form, the solution of the protoxide is first peroxidized, and the peroxide is then treated as directed § 85. In some instances, (vide § 85,) and especially for the purpose of separating the protoxide of iron from other oxides, the protoxide of iron is first precipitated as sulphuret of iron. The method applied for this purpose is the same as that which will be found described § 85, *b*.

The following is the best method of peroxidizing the solution of a proto-salt of iron:—

The solution of the proto-salt of iron is mixed, in a flask, with a small amount of hydrochloric acid—(unless this acid be already present)—some nitric acid is added, and the mixture heated to incipient ebullition. The color of the solution will show whether a sufficiency of nitric acid has been added. In concentrated solutions, the addition of nitric acid produces a dark brown color, which disappears upon heating. This color is owing to the nitric oxide formed dissolving in the not yet decomposed solution of the proto-salt of iron.

The conversion of the protoxide into peroxide may likewise be effected by transmitting chlorine gas through the solution, or by adding to it chlorine water in excess.

With regard to the method of determining protoxide of iron from the amount of gold which it reduces from the perchloride of the latter metal, I refer to § 124, *β.*, *bb.*, since this method serves exclusively to separate the protoxide of iron from the peroxide.

§ 85.

PEROXIDE OF IRON.

a. Solution.

Many of the percompounds of iron are soluble in water. Pure peroxide of iron, and most of those of its compounds which are insoluble in water, dissolve in hydrochloric acid. In many instances, this solution proceeds with difficulty; it is necessary in such cases to use concentrated hydrochloric acid, and to reduce the compound to be analyzed to a state of the most minute division, previously to subjecting it to the action of the acid; this action is promoted by the application of a gentle heat; heating to ebullition is improper. Iron ores insoluble in hydrochloric acid are prepared for solution by fluxing with carbonate of soda.

b. Determination.

Peroxide of iron is invariably weighed as such. The compounds of iron are converted into this form either by precipitation as hydrated peroxide—preceded in some instances by precipitation as sulphuret or persuccinate of iron,—or by direct ignition.

We may convert into

PEROXIDE OF IRON.

a. By precipitation as hydrated peroxide of iron.

All persalts of iron with inorganic or volatile organic acids, which are soluble in water; and likewise those of the insoluble persalts, the acid of which may be removed upon their solution in hydrochloric acid.

b. By precipitation as sulphuret of iron.

All compounds of iron without exception.

c. By precipitation as persuccinate of iron.

All the compounds enumerated sub. *a.*

d. By direct ignition.

All persalts of iron with volatile oxygen acids.

The method *d.* is very expeditious and accurate, and is therefore preferred to the other methods in all cases where its application is admissible. The method *b.* serves principally to separate peroxide of iron from other bases; this method is applied moreover in certain instances where *a.* is inapplicable, and thus especially in cases where sugar or other non-volatile organic substances are present; and likewise to determine peroxide of iron in its compounds with phosphoric acid and boracic acid. The method *c.* is exclusively used to separate iron from other bases. For the determination of the peroxide of iron in perchromate and persilicate of Iron, I refer to § 99 and § 106.

Determination as peroxide of iron.

a. By precipitation as hydrated peroxide.

The iron compound under examination is dissolved in its appropriate menstruum, in a flask or beaker-glass, and ammonia is added in excess; the mixture is then heated nearly to ebullition, filtered, *carefully* washed with hot water, *thoroughly* dried, and ignited according to the method described § 32. The crucible should be kept closely covered at first, and exposed to a gentle heat; the lid should subsequently be removed, and placed against the crucible, in the manner illustrated by Plate XXIX., and a more intense heat should then be applied. This method, if properly and carefully executed, yields very accurate results, and is free from sources of error. Should the operator have reason to fear that part of the peroxide has suffered reduction by the charcoal of the filter, he need simply moisten the contents of the crucible with nitric acid, evaporate and ignite again; by this process he is sure to obtain all the iron present, in the form of peroxide.

For the properties of the precipitate and residue, vide § 55. The precipitate must, under all circumstances, be *carefully* washed, since, should it retain any sal ammoniac, a portion of the iron would volatilize in the form of perchloride.

b. By precipitation as sulphuret of iron.

The iron compound under examination is dissolved in its appropriate menstruum, in a beaker-glass, and ammonia added to complete neutralization of the free acid present. (If organic non-volatile substances be present, a little hydrated peroxide of iron will precipitate; however, this is not of any consequence.) Sulphuret of ammonium is then added in excess, and a gentle heat applied. The operator generally obtains, in this manner, a black precipitate in a colorless or yellowish fluid, in which case he may at once filter; but should the fluid exhibit a greenish color—which happens particularly with very dilute solutions, and is owing to extremely minute particles of sulphuret of iron remaining mechanically suspended in the fluid—the beaker-glass, covered with a glass plate, must be kept standing at rest on a moderately warm spot, until the fluid has acquired a yellow tint. The fluid may then be filtered. In either case, the precipitate is washed uninterruptedly with water, mixed with a small amount of sulphuret of ammonium, the funnel being kept well covered all the while. If any of these precautions be neglected, some loss of substance will arise from a portion of the sulphuret of iron oxidizing gradually in the air, and being carried into the filtrate as protosulphate. Since the protosulphate of iron which gets thus into the filtrate, is re-precipitated by the sulphuret of ammonium present, the fluid assumes in such cases a greenish color, and deposits gradually a black precipitate.

After having completed the washing of the precipitated sulphuret of iron, this, together with the filter, is introduced into a beaker-glass, and some water poured over it; hydrochloric acid is added until all the sulphuret of iron present is re-dissolved. Heat is then applied until the solution smells no longer of sulphuretted hydrogen; the solution is filtered into a flask, the filter is carefully washed, and the filtrate peroxidized by heating with nitric acid, (vide § 84;) the peroxidized solution is finally treated as directed sub. *a*.

c. By precipitation as persuccinate of iron.

The persalt of iron under examination is dissolved in the appropriate menstruum, in a flask, and very dilute solution of ammonia is added drop by drop until a small portion of the iron precipitates in the form of hydrated peroxide; a gentle heat is then applied to ascertain whether the precipitate will re-dissolve or not. If it re-dissolves, the addition of dilute ammonia is to be continued, until the application of heat causes no longer this re-solution of the precipitate formed. If, on the contrary, it does not re-dissolve, and the fluid continues to exhibit a brown-red color, all the conditions requisite for precipitation with succinate of ammonia are fulfilled. But should the fluid appear colorless, this is to be considered as a sign that too much ammonia has been added; in that case, it will be necessary to add a small portion of hydrochloric acid, and then again some ammonia until the desired point is attained. A perfectly neutral solution of succinate of ammonia is to be added to the fluid thus prepared, and this addition is to be continued as long as a precipitate is formed; a gentle heat is then applied, and the fluid is subsequently allowed to cool; when perfectly cold, it is filtered off from the precipitate, and the latter is washed first with cold water, and finally with a warm solution of ammonia; this operation, depriving the precipitate in a very great measure of its acid, causes it to acquire a deeper tint. The washed precipitate is dried upon the filter in the funnel, the filter and its contents are introduced into a platinum crucible, and the latter is heated, at first covered, subsequently uncovered, with a stream of air directed upon its contents, until the filter is completely incinerated, and the precipitate converted into red peroxide of iron. The object of washing the precipitate with ammonia is to remove part of the succinic acid, since, were this neglected, and the precipitate simply washed with water, part of the peroxide of iron might readily be reduced upon the ignition of the succinate. Properties of the precipitates, vide § 55. This method yields very accurate results.

d. By direct ignition.

The compound to be examined is exposed, in a covered crucible, to a gentle heat at first, which is gradually increased to the highest degree of intensity until the weight of the remaining peroxide ceases to vary, even to the slightest extent.

FIFTH GROUP.

OXIDE OF SILVER—OXIDE OF LEAD—PROTOXIDE OF MERCURY—PEROXIDE OF MERCURY—OXIDE OF COPPER—OXIDE OF BISMUTH—OXIDE OF CADMIUM.

§ 86.

1. OXIDE OF SILVER.

a. Solution.

Metallic silver and those of the silver compounds which are insoluble in water, are best dissolved in nitric acid (of course excepting those which are insoluble in this acid); dilute nitric acid suffices generally; sulphuret of silver, however, requires a more concentrated acid. It is best to make the solution in a flask. Chloride, bromide, and iodide of silver are insoluble in water and in nitric acid; but it is not necessary to dissolve these salts in order to analyse them (vide infra). The silver in the chloride, bromide, and iodide, may, however, be readily reduced by means of zinc or iron, and water acidulated with hydrochloric acid or sulphuric acid. It is most advisable, for this purpose, to introduce these salts into a porcelain crucible; to pour some water over the fused mass, to throw a piece of clean zinc or iron upon it, and to add some hydrochloric or sulphuric acid. The spongy silver obtained by these means is to be carefully washed, first with dilute sulphuric acid, and subsequently with water; it is then finally to be dissolved in nitric acid.

b. Determination.

Silver may be weighed as *chloride of silver, sulphuret of silver, cyanide of silver, or metallic silver.*

We may convert into

1. CHLORIDE OF SILVER. 2. SULPHURET OF SILVER.
3. CYANIDE OF SILVER.

All compounds of silver without exception.

4. METALLIC SILVER.

Oxide of silver and several of its compounds with readily volatile acids; salts of silver with organic acids; and, finally, chloride of silver.

The method 4 is the most convenient, and is preferred to the other methods in all cases, where its application is admissible. The method 1 is that most generally applied; 2 and 3 serve mostly to separate oxide of silver from other bases.

1. *Determination of silver as chloride of silver.*

a. In the humid way.

Two methods may be pursued to determine silver as chloride in the humid way.

The principle of the one of these methods is to weigh the precipitated chloride of silver; the principle of the other is to infer the proportion of silver present in a solution, by determining the quantity of common salt (in solution) which is required to precipitate the silver as chloride. The application of the latter method, however, is more exclusively confined to the workshops of the mint, and is but rarely had recourse to in the laboratory of the chemist; I deem it unnecessary, therefore, to describe it here more in detail.

With regard to the first method, the precipitated chloride of silver may be separated from the supernatant fluid either by decantation or by filtration; the former is generally preferred when we have a copious amount of precipitate before us, the latter answers better for small quantities.

a. Determination by decantation.

The moderately diluted solution of the compound under examination is introduced into a tall flask, with long neck and narrow mouth, and some nitric acid added to it; this mixture is heated to about 140°, and hydrochloric acid is added to it, as long as a precipitate is formed. The mouth of the flask is then closed with a perfectly smooth cork, (or, better still, with a well-ground glass stopper,) and the flask is forcibly shaken until the precipitated chloride of silver has subsided, united into coherent lumps, and the supernatant fluid has become clear. The minute particles of chloride of silver, which may still adhere to the sides of the neck of the flask, are then rinsed down by means of a syringe bottle, and the stopper is loosely replaced. The flask is then placed on a moderately warm spot in the sand-bath until the precipitate has *completely* subsided, and the supernatant fluid has become *perfectly* clear and transparent, which generally requires several hours. The clear fluid is then slowly and cautiously decanted into a beaker-glass, so as to retain every particle of the chloride in the flask, whence it is to be carefully transferred into a porcelain crucible, with steep and smooth sides; the last particles of chloride of silver which remain adhering to the bottom and sides of the flask are rinsed into the neck of the latter with a little water, (inverting the flask, and closing its mouth with the finger,) and thence likewise transferred into the crucible.

When the chloride of silver has completely subsided in the crucible, (which is greatly accelerated by exposing the latter to the heat of a water-bath,) the clear supernatant fluid is carefully decanted (with the aid of a glass rod) into the same beaker-glass which already contains the liquid of the first decantation. The chloride of silver in the crucible is moistened with a few drops of nitric acid, and subsequently drenched with hot distilled water; the chloride is again allowed to subside, the clear supernatant fluid again decanted, and the same operation repeated until the decanted fluid ceases to exhibit the slightest turbidity upon the addition of a few drops of solution of nitrate of silver. The last portions of supernatant fluid are then carefully and cautiously decanted or removed by means of a small syphon; the chloride is thoroughly dried in a water-bath, and subsequently heated to incipient fusion, over the flame of a spirit-lamp, taking care to apply a very gentle heat at first; as soon as the chloride begins to fuse round the border, the crucible is removed from the flame, allowed to cool, and finally weighed.

To remove the fused mass from the crucible, completely and without injury to the latter, a fragment of iron or zinc is placed upon the chloride, and highly dilute hydrochloric or sulphuric acid poured over it. The crucible is finally washed, dried, and weighed. Should the liquids successively decanted from the chloride of silver not be perfectly clear and transparent, they are to be kept standing in a warm place until the last particles of chloride have completely subsided, (which frequently requires several hours;) the clear supernatant fluid is then decanted, and the subsided chloride added to the bulk of the precipitate in the crucible.

β. Determination by filtration.

The chloride of silver is precipitated and allowed to subside as at *α.*; the supernatant fluid is then passed through a small filter to which the precipitate likewise is subsequently transferred, with the aid of a little hot water acidulated with nitric acid; the precipitate, when collected on the filter, is washed, first with water impregnated with nitric acid, and finally with pure water, thoroughly dried, ignited, (§ 31,) and weighed. For the properties of the precipitate, vide § 56.

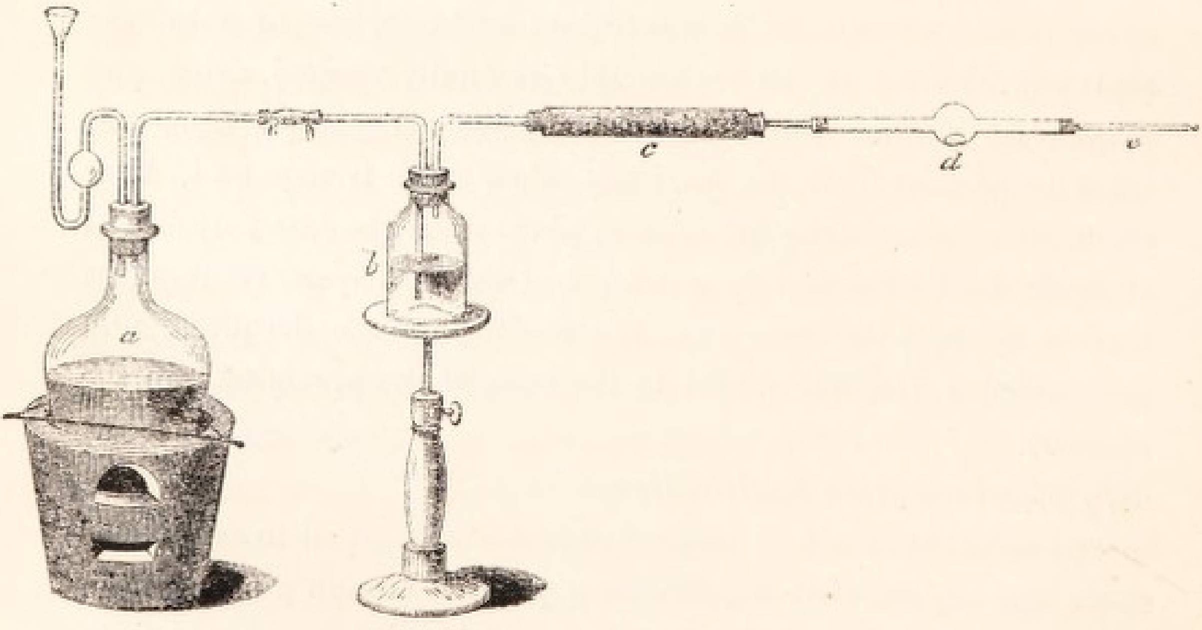
Both methods, if properly performed, yield very accurate results, although a trifling loss of substance is incurred in β., owing to part of the minute portion of chloride of silver which, notwithstanding the most careful scraping, will invariably adhere to the filter, being reduced upon the ignition of the ashes of the latter; this may be remedied, however, by adding the filter-ashes to the chloride in the crucible, pouring a little dilute nitric acid over them, heating for some time, adding a few drops of hydrochloric acid, evaporating, drying, and igniting as directed sub. *a*.

b. In the dry way.

This method serves more exclusively for the analysis of iodide and bromide of silver, although it is adapted likewise for the quantitative estimation of other salts of silver.

The process is conducted in the apparatus illustrated by Plate XXXII.

PLATE XXXII.



a is an apparatus for disengaging chlorine, *b* contains concentrated sulphuric acid, *c* chloride of calcium, *d* is intended for the reception of the iodide or bromide of silver, and *e* serves to conduct the chlorine gas out of the window. The operation is commenced by introducing the compound to be analysed into the bulb *d*, and applying heat to the latter until its contents are fused; when cold, the tube is weighed and connected with the apparatus. Chlorine gas is then evolved from *a*; when the evolution of the gas has proceeded for some time, the contents of *d* are heated to fusion, and kept in this state for about fifteen minutes, agitating now and then the fused mass in the bulb. The tube *d* is then removed from the apparatus, allowed to cool, and held in a slanting position to replace the chlorine by atmospheric air; it is subsequently weighed, and then again connected with the apparatus, and the former process repeated, keeping the contents of *d*. in a state of fusion for a few minutes. The operation may be considered concluded if the weight of the tube suffers no variation by the repetition of the process. This method, if properly executed, yields exceedingly accurate results.

2. *Determination as sulphuret of silver.*

Sulphuretted hydrogen precipitates silver completely from acid, neutral, and alkaline solutions; from neutral and alkaline solutions, however, this metal may likewise be precipitated by sulphuret of ammonium. Fresh and perfectly clear solution of sulphuretted hydrogen may be employed to precipitate small portions of silver; to precipitate larger quantities, the solution of the salt of silver is moderately diluted, and washed sulphuretted hydrogen gas (§ 36, 2) transmitted through it. The precipitated fluid is gently heated, the sulphuret of silver collected on a weighed filter, (§ 29,) washed, dried at 212°, and weighed. For the properties of the precipitate, vide § 56. This method, if properly executed, yields very accurate results. The operator must take care to filter quickly, and to prevent the access of air as much as possible during the filtration, since, if this precaution be neglected, sulphur is likely to separate from the sulphuretted hydrogen, and this, of course, would increase the weight of the precipitated sulphuret of silver. Should sulphur, nevertheless, have separated, in conjunction with the sulphuret of silver, owing either to the imperfect exclusion of the air during filtration, or to the presence of peroxide of iron or any other substance likely to decompose sulphuretted hydrogen; the precipitate, together with the filter, is digested at a gentle heat with moderately dilute nitric acid until complete decomposition ensues, and the undissolved sulphur appears of a pure yellow; the solution is filtered off from the sulphur, the latter carefully washed, and the filtrate, together with the rinsing water, treated as directed at 1.

3. *Determination as cyanide of silver.*

The neutral or acid solution of the salt to be analysed is mixed with cyanide of potassium until the precipitate which forms at first is completely redissolved; nitric acid is then added slightly in excess, and a gentle heat applied. The precipitated cyanide of silver is collected on a weighed filter, washed, dried at 212°, and weighed. For the properties of the precipitate, vide § 56. The results are perfectly accurate.

4. *Determination as metallic silver.*

Oxide of silver, carbonate of silver, &c., are easily reduced by simple ignition in a porcelain crucible; but salts of silver with organic acids are more advantageously heated first in a covered crucible; the lid being subsequently removed, and a more intense heat applied until the charcoal is completely consumed. For the properties of the residue, vide § 56. The results are absolutely accurate; in the analysis of salts of silver with organic acids, however, it happens frequently that the reduced silver is contaminated with a minute portion of charcoal, and thus the results are a trifle higher than theoretically calculated.

To convert chloride of silver into metallic silver, for the purpose of analysis, the former is introduced into the bulb of a bulbous-tube, fused, and weighed. The tube is then connected with an apparatus evolving dry hydrogen gas, (compare § 83, Plate

XXXI). When the apparatus is completely filled with hydrogen, and the evolution proceeds steadily and slowly, heat is applied to the bulb until the chloride of silver is in fusion; the fused chloride is maintained at a moderate heat until no more fumes of sal ammoniac are perceptible upon approaching the aperture through which the gas escapes with a glass rod moistened with ammonia. The apparatus is then allowed to cool, the bulbous tube is detached from it, held slantingly so as to expel the hydrogen by atmospheric air, and is then finally weighed. The results are most accurate.

§ 87.

OXIDE OF LEAD.

a. Solution.

Few of the salts of lead are soluble in water. Metallic lead, oxide of lead, and most of the insoluble salts of lead, dissolve in *dilute* nitric acid. Concentrated nitric acid effects neither complete decomposition nor complete solution, since, owing to the insolubility of nitrate of lead in concentrated nitric acid, the first portions of nitrate formed protect from further decomposition the yet undecomposed part of the salt to be analysed. For the degree of solubility of chloride and sulphate of lead, vide § 57.

Iodide of lead does not dissolve in cold dilute nitric acid; but upon heating, it dissolves readily in this acid, with separation of iodine. Chromate of lead dissolves without decomposition in potass alone, and is, for the purpose of analysis, most advantageously converted into chloride of lead.

b. Determination.

Lead may be weighed as OXIDE, SULPHATE, SULPHURET, or CHLORIDE, or finally also as OXIDE OF LEAD + LEAD.

We may convert most advantageously into

1. OXIDE OF LEAD.

a. By precipitation.

All salts of lead soluble in

b. By ignition.

α. Salts of oxide of lead with

water, and those of the insoluble salts, the acid of which is expelled and removed upon their solution in nitric acid.

readily volatile or decomposable inorganic acids.

β. Salts of lead with organic acids.

2. SULPHATE OF LEAD.

a. By precipitation.

Those of the insoluble salts of lead, the acid of which cannot be removed from their solution in nitric acid.

b. By evaporation.

α. All the oxides of lead, and likewise the salts of oxide of lead with volatile acids, and also iodide and bromide of lead.

β. Many of the organic compounds of lead.

3. CHLORIDE OF LEAD.

Chromate of lead, iodide, and bromide of lead.

4. OXIDE OF LEAD + LEAD.

Many of the organic compounds of lead.

5. SULPHURET OF LEAD.

All salts of lead in solution. This method serves principally to separate lead from other substances.

The application of these methods must not be understood to be rigorously confined to the compounds specially enumerated under their respective heads; on the contrary, the compounds enumerated sub. 1 may likewise be determined as sulphate of lead, and those enumerated sub. 1, 2, and 4, as sulphuret of lead, &c., &c. Chloride of lead may either be determined according to 1. *a.*, or it may be reduced to the metallic state in the manner described § 86 for the reduction of chloride of silver; the heat applied should not be too intense, since this might cause some of the chloride to volatilize.

The peroxides of lead are reduced by ignition to the state of simple oxide, and may thus be readily dissolved, and analysed.

Should the operator wish to avoid having recourse to ignition, the most simple mode of dissolving the peroxides of lead is to act upon them with dilute nitric acid, in conjunction with a small quantity of alcohol. For the methods of analysing sulphate, chromate, iodide, and bromide of lead, I refer to the paragraphs treating of the corresponding acids, in the second part of this section.

1. *Determination of lead as oxide.*

a. By precipitation.

α. By precipitation as carbonate of lead.

The moderately dilute solution of the compound to be analysed is mixed with carbonate of ammonia slightly in excess, some caustic ammonia added, a gentle heat applied, and the fluid, after the lapse of some time, filtered off from the precipitated carbonate of lead. The precipitate is washed with pure water, dried, and ignited in a porcelain crucible, the filter having previously been incinerated upon the lid of the latter. For the properties of the precipitate and residue, vide § 57. The results are satisfactory, although generally a trifle lower than calculated, owing to carbonate of lead not being absolutely insoluble in fluids impregnated with ammoniacal salts. (Experiment No. 35.) A small and thin filter should be selected, and every care taken to free this as much as possible from the carbonate adhering to it; otherwise the incineration of the filter might cause further loss of substance, owing to the reduction of the oxide to the state of metallic lead.

β. By precipitation as oxalate of lead.

The solution of the compound under examination is mixed with oxalate of ammonia in excess, and ammonia added until it begins to predominate; the precipitated oxalate is then allowed to subside, the fluid filtered off from it, and the further process conducted as directed at *α.*; the porcelain crucible is to be left uncovered during the ignition of the precipitate. Results as at *α*.

b. By ignition.

Compounds like carbonate or nitrate of lead are carefully ignited in a porcelain crucible until their weight ceases to diminish. For the manner of reducing salts of lead with organic acids, to the state of oxide, I refer to 4.

2. *Determination as sulphate of lead.*

a. By precipitation.

α. Moderately diluted pure sulphuric acid is added slightly in excess to the solution of the compound to be analysed, (this solution must not be too dilute); the fluid is then mixed with twice its volume of spirits of wine; the precipitated sulphate of lead is allowed several hours to subside, and the fluid is subsequently filtered off; the precipitate is washed with spirits of wine, dried and ignited. (§ 31). Although a careful operator may conduct the ignition in a platinum crucible, yet it is more advisable to use a thin porcelain crucible for this purpose. A small and thin filter should be selected, and the adhering sulphate of lead carefully scraped off. (Vide 1, *a.*, α.)

β. In cases where the addition of spirits of wine is inadmissible, the sulphuric acid should be added to a *perceptible* excess, and the precipitate, after subsidence, filtered at once, washed first with water very slightly acidulated with sulphuric acid, and finally with spirits of wine, the further process being conducted as at α.

For the properties of the precipitate, vide § 57. Both these methods, if properly and carefully executed, yield very accurate results. Of course, if the operator neglects to add the sulphuric acid sufficiently in excess, or to acidulate the washing water, he must not expect very accurate results, since, for instance, in presence of ammoniacal salts, nitric acid, &c., the lead does not completely precipitate if the sulphuric acid is not added *perceptibly* in excess, and since, on the other hand, sulphate of lead is not quite insoluble in pure water.

b. By evaporation.

α The substance to be examined, is weighed, introduced into a weighed dish, dissolved in dilute nitric acid, and moderately dilute pure sulphuric acid added slightly in excess; the mixture is carefully evaporated at a gentle heat, finally in a small sand-bath over a spirit-lamp, until the excess of sulphuric acid is completely expelled. In the absence of organic substances, this operation may be conducted in a platinum dish; but should organic substances be present, a porcelain dish is to be preferred. The results are perfectly accurate.

β. Organic compounds of lead are converted into the sulphate, by treating them, in a porcelain crucible, with pure concentrated sulphuric acid in excess, and evaporating carefully in a well-covered crucible, until the excess of sulphuric acid is completely expelled; the residue is then to be ignited and weighed. Should the residue not be perfectly white, it is to be moistened again with sulphuric acid, and the process repeated. This method, if properly executed, yields accurate results; a trifling loss is, however, usually incurred, since traces of the salt are liable to be carried away with the escaping sulphurous acid and carbonic acid gas.

3. *Determination as chloride of lead.*

In certain separations of lead from other substances, this metal is determined as chloride. For this purpose, the solution of the substance under examination is mixed with hydrochloric acid in excess, considerably concentrated in the water-bath, and the residue treated with absolute alcohol, mixed with some ether; the precipitated chloride of lead is allowed to subside, and the fluid subsequently filtered off; the precipitate is then dried and exposed to a gentle heat. Were the precipitate heated to redness, a small portion of the chloride would volatilize. A small and thin filter should be selected, and the adhering chloride of lead most carefully scraped off. (Vide 1, *a.*, α.)

4. *Determination as oxide of lead + lead.*

From one to two grammes of the organic compound of lead which it is intended to analyse, are weighed into a small porcelain dish, previously tared, and the latter is then exposed to a gentle heat, taking care to direct this first upon the brim of the dish, so as to cause the ensuing decomposition to commence on one side, and to proceed gradually. When the whole mass is perfectly decomposed, the heat is slightly increased and maintained thus until no more glowing particles are perceptible, and the residue forms a mixture of oxide of lead, with globules of metallic lead, and *perfectly* free from charcoal. This residue is weighed, and subsequently heated with acetic acid, until the oxide is completely dissolved; the solution is decanted from the metallic lead, the latter washed by repeated decantation, the last traces of water finally expelled by heat, and the remaining metallic lead weighed. By subtracting the weight of the metal from that of the whole residue, we find the proportion of oxide of lead which was present in the residue; by calculating the proportion of metal contained in the oxide, and adding the resulting figure to the weight of the metallic lead, we ascertain the total amount of this metal originally present in the analyzed compound. This method is very convenient, and, if properly and carefully executed, yields very accurate results. The operator must take care to conduct the decomposition of the organic compound very slowly, since the *rapid* combustion of its carbon and hydrogen at the expense of the oxygen of the oxide of lead, would produce so high a temperature as to volatilize a portion of the lead in visible fumes. If the residue is not perfectly free from charcoal—(which is detected while heating it with acetic acid)—this will tend to produce a higher result than calculated.

DULK has recently recommended the following modification of this method, which was originally introduced by BERZELIUS. According to the former chemist, the compound to be analyzed is gently heated, in a covered porcelain crucible, until the organic substance is completely carbonized; the lid is then removed, and the mass stirred with a piece of iron wire. Upon this, the mass begins to ignite, and forms a mixture of oxide of lead with metallic lead, and which may still contain unconsumed carbon. The crucible is then removed from the flame, a few crystals of nitrate of lead are introduced into it, and the crucible is again covered; the salt thus introduced melts, oxidizes the lead, and converts it partially into nitrate; the crucible is now exposed to a red-heat, until the evolution of hyponitric acid fumes ceases completely; the oxide thus produced is finally weighed, when cold. This modification of the original method yields very accurate results. It possesses this great advantage, that it ensures the complete combustion of the whole of the carbon present in the organic compound; some trouble is saved, moreover, in weighing and calculation.

5. *Determination of lead as sulphuret.*

α. The same method as is applied for the determination of silver as sulphuret of silver, may also serve for the determination of lead as sulphuret. (Vide § 86, 2.) For the properties of the precipitated sulphuret of lead, vide § 57.

β. Should the precipitated sulphuret of lead be contaminated with sulphur, it is to be converted into sulphate of lead. For this purpose the precipitate is dried upon the filter, and subsequently projected into a beaker-glass, into which the filter is then likewise introduced; pure fuming nitric acid is gradually dropped upon the contents of the glass, keeping the latter covered with a glass plate. When the oxidation of the sulphuret is completed, a gentle heat is to be applied for some time, and the contents of the beaker-glass are subsequently transferred *completely* into a small porcelain dish; a few drops of pure sulphuric acid are then added, the mixture is carefully evaporated, and the residue finally ignited. This method, if properly performed, yields accurate results. Should the operator attempt to oxidize with a less concentrated than the fuming nitric acid, separation of sulphur will be the consequence, and the oxidation of this will require long protracted heating with the nitric acid employed.

§ 88.

3. PROTOXIDE OF MERCURY.

a. Solution.

Protoxide of mercury and its salts should be peroxidized previously to their solution, since it is difficultto obtain a solution of protoxide entirely free from admixture of peroxide. The protoxide or protosalt of mercury is, for this purpose, heated for some time with nitric acid in excess, some hydrochloric acid added, and the application of heat continued until a perfectly clear solution is produced. All the proto-compounds of mercury, and also the metal itself, may be readily dissolved in this manner.

b. Determination.

It follows from the preceding remarks, that the determination of the protoxide is the same with that of the peroxide of mercury, which will be found in the next paragraph. For the separation of the protoxide from the peroxide, I refer to § 127.

§ 89.

4. PEROXIDE OF MERCURY.

a. Solution.

Peroxide of mercury and those of its compounds which are insoluble in water, dissolve in hydrochloric acid. Bisulphuret of mercury is heated with hydrochloric acid, and nitric acid added until complete solution ensues.

b. Determination.

Mercury may be obtained in the METALLIC state, or as PROTOCHLORIDE or BISULPHURET. In some instances, the mercury is expelled from the analyzed compound by ignition, and its amount inferred from the diminution of weight which the ignited compound suffers.

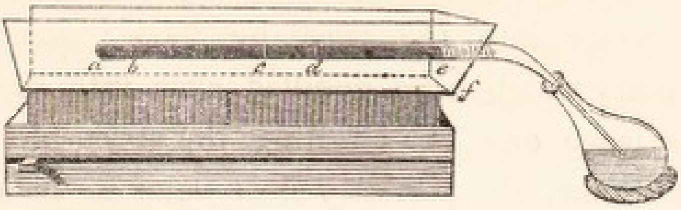
The methods of determining mercury as metal, protochloride, or bisulphuret, are applicable in all cases without exception; the latter, however, deserves the preference in most instances, on account of its accuracy, simplicity, and ready execution.

1. *Determination as metallic mercury.*

a. In the dry way.

The process is conducted in the apparatus illustrated by Plate XXXIII.

PLATE XXXIII.



The principal part of the apparatus consists of a tube made of difficultly fusible glass, and closed at one end; this tube should be $1\frac{1}{2}$ foot in length, and from 3 to 4 lines in diameter. Dry hydrate of lime is introduced into this tube, and pushed down to the end, so as to occupy about two inches in length (from *a* to *b*). The mercurial compound to be analyzed is intimately mixed in a mortar with an excess of *soda-lime,* (vide § 40, 4,) and then introduced into the tube, when it is made to occupy the place from *b* to *c*; those portions of the mixture which adhere to the mortar are removed from the latter with the aid of *soda-lime,* and the soda-lime which has been used for this purpose is likewise introduced into the tube, so as to occupy the place from *c* to *d*; a layer of pure *soda-lime* is then placed from *d* to *e,* and a loose stopper of pure asbestos is pushed down the tube, so as to occupy the place between *e* and *f*. The anterior end of the tube is finally drawn out, and bent at a somewhat obtuse angle. The manipulations requisite to perform these various processes, will be found described in detail, § 149, (elementary organic analysis). A few gentle taps upon the table suffice to shake together the contents of the tube in such a manner as to leave a free passage above them in the whole length of the tube.

The tube thus prepared and arranged is now introduced into a combustion furnace, and its point thrust into a receiving flask, filled to about one-half with water; the point is made to rest upon the surface of the water in the flask, in such a manner as partially to close the aperture of the tube. The tube is then surrounded with live coals, proceeding slowly from *e* towards *a*, as in organic analysis; the last traces of mercurial vapor are finally expelled the tube by heating the hydrated lime in the end of the tube. Whilst the tube still remains red-hot, the neck is cut off at *f*, and carefully rinsed with a syringe bottle, transferring the rinsing water into the receiving flask; the small globules of mercury which have distilled over into the latter, are united into a large one, by agitating the flask, and, after the lapse of some time, the perfectly clear water is decanted or removed by means of a syphon, and the mercury projected into a weighed porcelain crucible, when the water still adhering to it is removed with blotting-paper. The mercury is finally dried under a bell-jar, by the side of a vessel containing concentrated sulphuric acid, and this drying process continued—(but entirely without the application of heat)—until the weight of the mercury ceases to vary. For the properties of this metal, vide § 58. This method, if very properly and carefully executed, yields accurate results. This is more particularly the case with the somewhat more complicated modification adopted by Erdmann and Marchand for the determination of the atomic weight of mercury and of sulphur. (Journal für praktische Chemie XXXI. page 385.—Pharmaceutisches Centralblatt, 1844, page 354.)

b. In the humid way.

The solution of the compound under examination is, in the first place, treated with hydrochloric acid, and evaporated, and this process repeated several times, to ensure the expulsion of the nitric acid which may be present; the solution is then introduced into a flask, free hydrochloric acid added, and subsequently a clear solution of protochloride of tin in excess, which must likewise contain free hydrochloric acid; the mixture is then boiled for some time, and subsequently allowed to cool. After having been left standing at rest for some time, the perfectly clear supernatant fluid is decanted from the metallic mercury, which, if the process has fully succeeded, will be found united into one globule; should this be the case, the globule of mercury may be washed at once by decantation, first with water acidulated with hydrochloric acid, and finally with pure water. The washed mercury is then further treated and determined as sub. a. If, on the other hand, the particles of mercury have not united into one globule, they are (after the decantation of the clear supernatant fluid) to be kept boiling for a few minutes, with a small amount of moderately diluted hydrochloric acid, which will generally suffice to attain the desired end. For the properties of metallic mercury, vide § 58.

Phosphorous acid, sulphurous acid, and other reducing agents, may, in this process, be substituted for the protochloride of tin.

This method yields accurate results, but it requires the *very greatest* care in the performance of the various operations. The resulting figures fall generally somewhat short of what they ought to be, according to theoretical calculation. (Compare Experiment No. 61, made by one of my pupils.) This, however, is entirely owing to defective execution of the necessary operations, and not by any means to defects inherent in the method, and the generally received notion, viz. that a small portion of mercury escapes during the operations of boiling and drying, is quite erroneous. (Experiment No. 42.)

2. *Determination as protochloride of mercury.*

The solution of the compound under examination is mixed with hydrochloric acid, should it not already contain this acid; solution of potass is then added, until the excess of the acid is *nearly* neutralized; the solution is now mixed with formiate of soda in excess, and kept standing at rest for four days, at a temperature of from 140° to 176°. After the lapse of this time, the fluid is filtered off from the precipitated protochloride of mercury, and the latter collected upon a weighed filter, which has previously been dried at 212°. The filtrate is again kept standing for twenty-four hours, at a temperature of from 140° to 176°; and should a new precipitate form, this is added to the first, and the same process repeated, until the filtrate remains perfectly clear. The whole of the precipitate is then washed, dried at 212°, and weighed. This method is extremely tedious, and requires moreover the strictest care and attention in the performance of the various operations; its application is therefore almost exclusively confined to the separation of mercury from certain metals. The operator must take particular care to confine the temperature to 170°, since otherwise metallic mercury might separate; should this be the case, the precipitate will exhibit a greyish appearance, and the experiment must, under such circumstances, be considered a failure.

3. *Determination as bisulphuret of mercury.*

a. The solution of the persalt of mercury under examination is free from nitric acid.

The solution is slightly acidified with hydrochloric acid, should it not already be so, introduced into a flask with ground stopper, and mixed with a recently prepared clear saturated solution of sulphuretted hydrogen in slight excess, so that the odor of sulphuretted hydrogen is clearly perceptible, after agitating the flask; the latter is then stoppered, and the precipitated bisulphuret allowed to subside.

b. The amount of mercury present is so considerable, that its precipitation would require a very large portion of sulphuretted hydrogen water. Washed sulphuretted hydrogen gas (§ 36, 2) is substituted for the water; the gas is transmitted through the moderately dilute solution of the compound under examination.

c. The solution contains nitric acid.

Potass is added to the solution until the acid is *nearly* neutralized; the fluid is then mixed with a clear solution of cyanide of potassium in excess, and the mercury finally precipitated either with sulphuretted hydrogen water, or colorless hydrosulphuret of ammonia, or by transmitting sulphuretted hydrogen gas through it.

The precipitate formed in either case is allowed to subside, collected upon a weighed filter, quickly washed with cold water, dried at 212°, and weighed,

Should the precipitate happen to contain free sulphur, (owing to the presence of peroxide of iron, chromic acid, &c., &c., or to whatever other cause,) it is to be introduced, whilst still moist upon the filter, into a small flask, hydrochloric acid added, heat applied, and nitric acid dropped into the mixture until the sulphur which remains undissolved appears of a pure yellow color. The mixture is then diluted with water, the fluid filtered off from the sulphur, and the filtrate treated as directed sub. *c.*

For the properties of the precipitate, vide § 58.

This method, if properly and carefully conducted, yields exceedingly accurate results, and is in my opinion preferable to the other methods.

§ 90.

5. OXIDE OF COPPER.

a. Solution.

Most of the compounds of oxide of copper dissolve in water. Metallic copper, oxide of copper, and those of its salts which are insoluble in water, are to be dissolved in dilute nitric acid. Sulphuret of copper is heated with moderately dilute nitric acid until the sulphur which separates appears of a pure yellow color; the addition of hydrochloric acid promotes this decomposition greatly.

b. Determination.

Copper is usually weighed in the form of oxide, (§ 59.) Into this form it is either converted by *direct* precipitation or ignition; or it is, in the first place, precipitated as sulphuret of copper. The amount of copper present in a solution may also be determined by means of metallic copper; it is in this case, inferred from the amount of metal required to convert a solution of oxide into a solution of sub-oxide of copper.

We may determine

1. AS OXIDE OF COPPER.

a. By precipitation as such.

α. By direct precipitation.	*β. By precipitation after previous ignition of the compound.*
All salts of the oxide of cop-	The salts enumerated sub. *a.*,

per which are soluble in water, and likewise those of the insoluble salts, the acids of which may be removed upon their solution in nitric acid, provided no non-volatile organic substance be present.

if containing a non-volatile organic substance in admixture, (and thus particularly salts of copper with non-volatile organic acids).

b. By precipitation as sulphuret of copper.

All combinations without exception.

c. By ignition.

Salts of copper with readily volatile, or at a high temperature readily decomposable oxygen acids, (carbonate of copper, nitrate of copper.)

2. BY MEANS OF METALLIC COPPER.

All salts of oxide of copper without exception.

The method is particularly adapted for technico-chemical purposes.

1. *Determination as oxide of copper.*

a. By direct precipitation as such.

α. From neutral or acid solutions.

The *moderately dilute* solution of the compound under examination is heated (most advantageously in a porcelain dish) to incipient ebullition, and slightly diluted pure potass ley added until, upon further addition, it fails to cause the formation of a precipitate; the fluid is kept for a few minutes longer at a temperature approaching ebullition.

After allowing some time for the subsidence of the precipitate, the fluid is filtered off, the precipitate collected upon the filter, thoroughly washed with hot water, dried, and intensely ignited in a platinum crucible. (§ 31.) The filter-ashes are added to the contents of the crucible, which is then placed under a bell-glass, by the side of a vessel containing concentrated sulphuric acid; the crucible, whilst still slightly warm to the touch, is finally weighed with the greatest possible expedition.

Should particles of the oxide of copper adhere so pertinaciously to the porcelain dish, that mechanical appliances fail to remove them, the dish is to be thoroughly washed in the first place, and the adhering particles of oxide are subsequently to be dissolved with a few drops of nitric acid; the solution thus obtained is poured upon the principal mass of the precipitated oxide, and the latter again evaporated to dryness, previously to its ignition.

For the properties of the precipitate, vide § 59.

This method, if properly and carefully executed, yields very accurate results; defective performance of the various operations may produce figures either exceeding or falling short of those theoretically calculated. Thus, if the solution be not sufficiently dilute, the precipitate will fail to throw down the whole of the oxide of copper present; on the other hand, if the precipitate be not *thoroughly* washed with hot water, it will retain potass in admixture; if the ignited precipitate be not weighed quickly, but allowed to stand exposed to the air, its weight will be increased, &c. &c. (Compare § 59.)

The fluid filtered off from the precipitate should invariably be tested for copper with sulphuretted hydrogen water. Should (notwithstanding the strictest compliance with the above instruction) the addition of this reagent produce a precipitate or a brown coloration of the fluid, this may be considered a sign of the presence of organic matter. In this case the filtrate is to be concentrated by evaporation, and subsequently precipitated with sulphuretted hydrogen water; the precipitated sulphuret of copper is washed, treated as directed sub. *c.*, and the oxide of copper obtained, is added to the principal precipitate.

β. From alkaline solutions.

Ammoniacal solutions of oxide of copper may likewise be precipitated with potass. The process is the same with that described sub. *α.*, with this difference that, after the complete precipitation of the oxide of copper, the menstruum is to be heated until the supernatant fluid is perfectly colorless, when it is to be filtered off with the greatest possible expedition. Were the fluid allowed to cool while still containing the precipitate, part of the latter would redissolve.

b. By precipitation as oxide after previous ignition of the substance to be analysed.

α. The compound under examination is heated in a porcelain crucible until the organic substance present is completely destroyed; the residue is thus dissolved in dilute nitric acid, and the solution cleared by filtration, should this be required. The clear solution is finally treated as directed sub *a.*, *α.*, or it is evaporated, and the residue treated as directed sub. *d.*

β. In salts of copper with organic acids the determination of the copper may also frequently be effected in the following manner: the ignited residue is moistened with nitric acid, evaporated, moistened once more with nitric acid, evaporated again, and finally carefully ignited. The latter method, however, is generally attended with a trifling loss, owing to traces of the salt being liable to be carried off during ignition, (vide § 74, 2, *b.*)

c. By precipitation as sulphuret of copper.

The solution of the compound under examination is precipitated either with a saturated solution of sulphuretted hydrogen, or by transmitting sulphuretted hydrogen gas through it. The application of the one or the other method of precipitation depends upon the larger or smaller amount of copper present; the fluid is speedily filtered off from the precipitated sulphuret of copper, and the latter washed with water impregnated with sulphuretted hydrogen; the washed precipitate is then dried in the filter, and the latter subsequently, after the transfer of its contents into a beaker-glass, incinerated upon a small porcelain dish, and its ashes added to the precipitate in the glass; this is then drenched with moderately dilute nitric acid, some hydrochloric acid added, and a gentle heat applied until the precipitated sulphur appears of a pure yellow color; the fluid is then diluted with water, filtered off from the sulphur, and the filtrate precipitated as directed sub. *a.*

d. By ignition.

The salt to be analysed is introduced into a platinum or porcelain crucible, and the latter exposed to a gentle heat which is gradually increased to intense redness; the residue is finally weighed. This method, if properly executed, yields very accurate results.

2. *Determination by means of metallic copper.*

a. The solution of oxide of copper is introduced into a bottle provided with a glass stopper, and ammonia added in excess; the solution, upon this, will appear perfectly clear and of an azure blue color. The bottle is then nearly filled with water freed from atmospheric air by ebullition, and a perfectly clean, accurately weighed slip of copper placed into the bottle, which is then to be tightly stoppered, and kept standing at rest at the common temperature until the fluid is perfectly colorless. The slip of copper is now withdrawn, carefully washed, dried, and weighed. The diminution of weight which it has suffered in the process indicates the amount of copper originally present in the solution. The results are very accurate, provided the process be properly conducted. This method has, however, this great disadvantage, that it requires generally three or four days, and in many instances, even a longer period. It is obvious that it is utterly inapplicable in cases where the solution contains metals precipitable by copper.

b. The copper contained in a solution of chloride of copper free from nitric acid, may be determined also in the following manner. The moderately diluted solution is mixed with free hydrochloric acid; this mixture is introduced into a long-necked flask, and boiled therein in contact with an accurately weighed slip of clean copper until the solutions are perfectly colorless; the slip of copper is then withdrawn, carefully washed, dried, and weighed.

This method is more expeditious but less accurate than that described sub. 2 *a*.

§ 91.

6. OXIDE OF BISMUTH.

a. Solution.

Metallic bismuth, oxide of bismuth, and all other compounds of bismuth, are most advantageously dissolved in dilute nitric acid.

b. Determination.

Bismuth is invariably weighed in the form of OXIDE, (§ 60).

Into this form the compounds of bismuth are converted either by ignition, by precipitation as CARBONATE, or preceded, in some instances, by precipitation as SULPHURET.

We may convert into

OXIDE OF BISMUTH.

a. By precipitation as carbonate of bismuth.

All those compounds of bismuth which dissolve in nitric acid as nitrate of bismuth, yielding a solution perfectly free from any other acid.

b. By ignition.

α. Salts of bismuth with readily volatile oxygen acids.

β. Salts of bismuth with organic acids.

c. By precipitation as sulphuret of bismuth.

This method is applied in all cases where the direct application of *a.* or *b.* is inadmissible.

1. *Determination of bismuth as oxide.*

a. By precipitation as carbonate of bismuth.

Should the solution of the salt of bismuth under examination be too concentrated, it is, in the first place, to be diluted with water, no matter whether basic nitrate of bismuth precipitates upon their dilution or not. The dilute solution is then mixed with carbonate of ammonia in excess, heated for a short time, nearly to ebullition, and the fluid subsequently filtered off from the precipitated carbonate of bismuth, which latter is collected upon the filter, dried, and ignited, *exactly* as directed § 87. (Ignition of carbonate of lead.) The process of ignition converts the carbonate of bismuth into the pure oxide. For the properties of the precipitate and residue, vide § 60. This method, if properly executed, yields very accurate results, although a very trifling loss occurs in most instances, owing to the circumstance that carbonate of bismuth is not absolutely insoluble in carbonate of ammonia.

This method, as already stated, is inapplicable to solutions of salts of bismuth, which, besides the solvent, (nitric acid,) contain other acids. If it were attempted, for instance, to precipitate in this manner, a solution of bismuth containing sulphuric acid, or hydrochloric acid, the precipitate would contain, in the former case, an admixture of basic sulphate; in the latter, of basic chloride of bismuth. Were the precipitate filtered off, without previous application of heat, part of the basic carbonate of bismuth would remain in solution, and thus a considerable loss would be incurred. (Compare Experiment No. 62.)

b. By ignition.

α. Compounds like carbonate or nitrate of bismuth are ignited in a porcelain crucible until their weight ceases to diminish.

β. Compounds of bismuth with organic acids are treated like the correponding compound of oxide of copper, vide § 90, 1 *b*, *β*.

c. By precipitation as sulphuret of bismuth.

The solution of the compound under examination is diluted with water, slightly mixed with acetic acid, (to prevent the subsequent precipitation of basic salt,) and precipitated with sulphuretted hydrogen either as gas or in solution; the fluid is filtered off from the precipitated sulphuret of bismuth, and the latter carefully washed. Another method of precipitating bismuth as sulphuret is, to mix the diluted solution with ammonia to complete neutralization of the free acid present, and then to add sulphuret of ammonium in excess.

The precipitated sulphuret of bismuth may be weighed as such if the operator has every reason to be perfectly convinced that no free sulphur has been precipitated in conjunction with the sulphuret. But as the solutions of the salts of bismuth contain generally much free nitric acid, which may readily cause the decomposition of part of the sulphuretted hydrogen used as precipitant, it is invariably the safest way to convert the sulphuret into oxide.

For this purpose the filter, with the washed and still moist precipitate, is introduced into a beaker-glass, moderately concentrated nitric acid poured over it, and heat applied until the sulphuret of bismuth is completely decomposed; the solution is then diluted with water slightly acidulated with acetic or nitric acid, and filtered; the filter is washed with the same kind of acidulated water, and the filtrate finally precipitated as directed sub. *a.*

§ 92.

7. OXIDE OF CADMIUM.

a. Solution.

Cadmium, oxide of cadmium, and all those of its compounds which are insoluble in water, are dissolved in hydrochloric or nitric acid.

b. Determination.

Cadmium is weighed either as OXIDE, or as SULPHURET OF CADMIUM, (§ 61.)

We may convert into

1. OXIDE OF CADMIUM.

a. By precipitation.

All the compounds of cad-

b. By ignition.

Salts of cadmium with readily

mium soluble in water, and those of the insoluble compounds, the acid of which is removed upon solution in hydrochloric acid; likewise salts of cadmium with organic acids.	volatile or easily decomposable inorganic oxygen acids.

2. SULPHURET OF CADMIUM.

All compounds of cadmium without exception.

1. *Determination as oxide of cadmium.*

a. By precipitation.

The solution of the compound under examination is precipitated with carbonate of potass, and the precipitated carbonate of cadmium washed, dried, and ignited. The process of ignition converts the carbonate into the pure oxide of cadmium. For the details, accuracy, &c., of the method, vide § 80, (zinc.) For the properties of the precipitate and residue, vide § 61.

b. By ignition.

The same method is pursued as described § 80 *c.* (zinc.)

2. *Determination as sulphuret of cadmium.*

Neutral or acid solutions are precipitated with sulphuretted hydrogen gas, or with sulphuretted hydrogen water; alkaline solutions are precipitated with sulphuret of ammonium. The precipitate is collected upon a weighed filter, washed, dried at 212°, and weighed. For the properties of the precipitate, vide § 61. The results are accurate.

Should the precipitated sulphuret of cadmium contain an admixture of free sulphur, it must be converted into nitrate or chloride of cadmium, and subsequently precipitated as carbonate. For the details, vide § 80, *b.* (zinc.)

SIXTH GROUP.

PEROXIDE OF GOLD—PEROXIDE OF PLATINUM—OXIDE OF ANTIMONY—PEROXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS AND ARSENIC ACID.

§ 93.

1. PEROXIDE OF GOLD.

a. Solution.

Metallic gold and all those compounds of gold which are insoluble in water, are heated with hydrochloric acid, and nitric acid gradually added until complete solution ensues.

b. Determination.

Gold is invariably weighed in its pure metallic state, to which its compounds are reduced by ignition, or by precipitation as metallic gold, or lastly, by precipitation as sulphuret of gold with subsequent ignition.

We may convert into

METALLIC GOLD.

a. By ignition.	*b. By precipitation as metallic gold.*
All those combinations of gold, which contain no fixed acid.	All compounds of gold without exception.—This method is applied in all cases where the application of *a.* is inadmissible.

c. By precipitation as sulphuret of gold.

This method serves to separate gold in solution from certain other metals.

Determination as metallic gold.

a. By ignition.

The compound under examination is heated in a covered porcelain or platinum crucible, gently at first, finally to redness, and the residuary pure gold weighed. For the properties of this, vide § 62. The results are exceedingly accurate.

b. By precipitation as metallic gold.

α. The solution of gold is free from nitric acid.

The solution is mixed with some hydrochloric acid,—should it not already contain this acid in a free state,—and a clear solution of protosulphate of iron added in excess. A gentle heat is then applied, and maintained for several hours, until the precipitated fine gold powder has completely subsided; the fluid is then filtered off from the gold, and the latter washed, dried, and ignited. (§ 32.) The precipitation is most advantageously effected in a porcelain dish, as a vessel of this description permits the removal of the heavy and fine gold powder by rinsing more readily than a beaker-glass. This method, if properly executed, yields very accurate results

β. The solution of gold contains nitric acid.

The solution is evaporated in the water-bath to a syrupy consistence, adding from time to time, during the evaporation, a fresh amount of hydrochloric acid; the residue is dissolved in water acidulated with hydrochloric acid, and the solution treated as directed sub. *α*. It may happen that during the process part of the perchloride of gold is decomposed into protochloride and metallic gold; the latter will remain undissolved when the residue is treated with the acidulated water; this, however, does not require the slightest modification of the method.

γ In cases where it is desirable to avoid the presence of iron in the filtrate, the analysed compound of gold may be reduced with oxalic acid. For this purpose, the solution—(being previously freed from nitric acid, if necessary—vide *β*.)—is introduced into a beaker-glass, and mixed with oxalate of ammonia in excess; some hydrochloric acid is added,—should this not be present already,—and the vessel, covered with a glass plate, kept standing for two days in a moderately warm place; after the lapse of this time, the whole of the gold present will be found to have separated in small yellow scales; the supernatant fluid is then filtered off from the gold, and the latter washed, dried, and ignited.

c. By precipitation as sulphuret of gold.

Sulphuretted hydrogen gas is transmitted in excess through the dilute solution of the compound under examination; the precipitate formed is speedily filtered off, washed, dried, and ignited in a porcelain or platinum crucible. For the properties of the precipitate, vide § 62. The results are accurate.

§ 94.

2. PEROXIDE OF PLATINUM.

a. Solution.

Metallic platinum, and those of the platinum compounds which are insoluble in water, are dissolved by digestion with aqua regia, at a gentle heat.

b. Determination.

Platinum is invariably weighed in the pure metallic state to which its compounds are reduced, either by direct ignition or by precipitation as CHLORIDE OF PLATINUM AND AMMONIUM, CHLORIDE OF PLATINUM AND POTASSIUM, or SULPHURET OF PLATINUM, and subsequent ignition. All the compounds of platinum without exception may, in most cases, be reduced to the metallic state by either of these methods. Which is the most advantageous process to be pursued in special instances, depends entirely upon the circumstances of particular cases. The reduction of platinum compounds to the metallic state by simple ignition, is preferable to the other methods, in all cases where its application is admissible.* The method of converting into sulphuret of platinum is used exclusively to separate platinum from other metals.

Determination as metallic platinum.

a. By precipitation as chloride of platinum and ammonium. (*Ammonio-chloride of platinum.*)

The solution of the compound under examination is introduced into a beaker-glass, and mixed with ammonia, until the excess of acid—if there be any present—is *nearly* neutralized; sal ammoniac is then added in excess, and the fluid mixed with a considerable amount of absolute alcohol. Should the solution of the platinum compound be very dilute, it is to be concentrated previously to the addition of the alcohol. The vessel is then covered with a glass plate, and allowed to stand for the space of twenty-four hours, when the precipitated double chloride will be found to have completely subsided; the fluid is now filtered off from the precipitate, collected upon a filter, (which need not be tared,) thoroughly washed with spirits of wine of 80°, carefully dried, ignited, and weighed.

The process of ignition is conducted in the following manner: the dry precipitate, wrapped up in the filter, is introduced into a weighed platinum crucible, which is then covered, and exposed to a gentle heat, until the disengagement of fumes of sal ammoniac ceases completely; the lid is then removed, the crucible placed obliquely, (§ 32,) and the filter incinerated, which latter operation may be aided by moistening with a few drops of nitric acid. The process is finally concluded by applying an intense heat for some time. For the properties of the precipitate and residue, vide § 63. The results are very satisfactory, although a trifling loss is generally incurred, since ammonio-chloride of platinum is not entirely insoluble in spirits of wine. (Experiment No. 11.) If the operator be not particularly careful to apply only a moderate degree of heat during the first stage of the process of ignition, it may also happen that traces of the yet undecomposed double chloride are carried off with the fumes of sal ammoniac.

Were the precipitated ammonio-chloride of platinum weighed as such, the results would be inaccurate, since (as I have convinced myself by direct experiments) it is impossible to wash the double chloride with spirits of wine sufficiently to free it entirely from the sal ammoniac thrown down in conjunction with it, without dissolving, at the same time, a perceptible portion of the ammonio-chloride of platinum.

b. By precipitation as chloride of platinum and potassium, (potassio-chloride of platinum.)

The solution of the compound under examination is introduced into a beaker-glass, and mixed with potass, until the greater part of the excess of acid (if there be any) is neutralized; chloride of potassium is then added slightly in excess, and finally a considerable portion of absolute alcohol. The mixture is allowed to stand for the space of twenty-four hours, when the precipitated double chloride will be found to have completely subsided. The fluid is then filtered off, and the precipitate collected upon a weighed filter, washed with spirits of wine of 70°, thoroughly dried at 212°, and weighed. A portion of the dried precipitate is now introduced into a weighed bulbous tube, the ends of which are subsequently cleaned with the beard of a quill; the tube is weighed again, to ascertain the exact amount of potassio-chloride of platinum which it contains. The tube is now connected with an apparatus evolving dry hydrogen gas, (Plate XXXI.), and its contents are heated to redness, until the ensuing evolution of hydrochloric acid vapor ceases completely; (this may be readily ascertained by approaching the end of the tube with a glass rod, moistened with ammonia). The contents of the bulb are then allowed to cool, the tube is removed from the apparatus, and filled with water; the solution of chloride of potassium which is formed is carefully decanted, and the residuary platinum thoroughly washed. The tube is again connected with the apparatus, and heated in a stream of hydrogen gas; when perfectly dry, it is weighed. By subtracting the original weight of the empty tube from that which it is now found to possess, the exact weight of the platinum contained in it will be ascertained; and this is then to be calculated upon the whole of the precipitated potassio-chloride of platinum.

For the properties of the precipitate and residue, vide § 63. The results are more accurate than those obtained by method *a.*, since, on the one hand, the potassio-chloride of platinum is more insoluble in spirits of wine than the ammonio-chloride; and, on the other hand, because loss of substance is less likely to arise during ignition, than in method *a*. The results would be less accurate were the ignition effected in a crucible, since in that case complete decomposition would not ensue, at least not if the amount of substance operated upon be considerable. Were the precipitated potassio-chloride of platinum weighed as such, the results obtained would be inaccurate, since washing with spirits of wine fails to free this double chloride entirely from the chloride of potassium thrown down in conjunction with it.

c. By precipitation as sulphuret of platinum.

The solution of the compound under examination is precipitated—(according to its greater or less amount)—either with sulphuretted hydrogen gas, or with sulphuretted hydrogen water; the mixture is heated to incipient ebullition, the fluid filtered oft from the precipitate, and the latter collected upon the filter, washed, dried, and ignited. (§ 32.) For the properties of the precipitate and residue, vide § 63. The results are accurate.

d. By ignition.

The compound under examination is heated, in a porcelain or platinum crucible, gently at first, finally to ignition, and the residuary pure platinum weighed. For the properties of the latter, vide § 63. The results are exceedingly accurate.

§ 95.

3. OXIDE OF ANTIMONY.

a. Solution.

Oxide of antimony, and those of its compounds which are insoluble in, or decomposable by water, are dissolved in hydrochloric acid of a greater or less degree of concentration, according to circumstances; metallic antimony is most advantageously dissolved in aqua regia.

b. Determination.

Antimony is weighed either as SULPHURET or in the METALLIC state, or as ANTIMONIOUS ACID.

We may convert into

1. SULPHURET OF ANTIMONY.	2. METALLIC ANTIMONY.
All compounds of antimony without exception.	All compounds of oxide of antimony without exception.

3. ANTIMONIOUS ACID.

The oxides of antimony and their salts, with readily volatile or decomposable oxygen acids.

The method of determining antimony by reduction to the metallic state, is generally only had recourse to for the purpose of separating antimony from tin, and its detailed description belongs therefore more properly to the fifth section, where it will be found, at § 130.

1. *Precipitation as sulphuret of antimony.*

*a. The solution contains oxide of antimony or the corresponding chloride, and besides this, no other substance possessing the property of decomposing sulphuretted hydrogen.**

The solution of the compound under examination is mixed with some tartaric acid, and (if necessary) diluted with water. Sulphuretted hydrogen gas is then transmitted in excess through the clear solution. The beaker-glass is now covered with a glass plate, and kept standing at rest in a moderately warm spot, for the space of half an hour; the fluid is then speedily filtered off from the precipitate, and the latter collected upon a tared filter, thoroughly washed, dried at 212°, and weighed. For the properties of the precipitate, vide § 64. The results are generally a trifle too high, owing to traces of free sulphur precipitating in conjunction with the sulphuret of antimony. As a precautionary measure, it is invariably advisable to dissolve a small portion of the weighed precipitate in hydrochloric acid, at

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* This method is applicable in all cases where we have a salt of the oxide of antimony, or protosulphate of antimony, in hydrochloric solution, but never in presence of free nitric acid.

a high temperature. Should no sulphur, or at least only a trace, be left, the results may be considered accurate; on the other hand, should a perceptible amount of sulphur remain, the precipitated sulphuret of antimony is to be treated as directed sub. *b*.

b. The solution contains, besides oxide of antimony, also antimonious acid, or antimonic acid, or some substance possessing the property of decomposing sulphuretted hydrogen.

The solution is treated as directed sub. *a.*, with this difference, that, previously to filtration, the beaker-glass containing the precipitated fluid is covered with paper, and kept standing in a moderately warm spot until the odor of sulphuretted hydrogen has completely disappeared.

The precipitate is washed, dried, and weighed, as in *a.*; it consists of an unknown sulphuret of antimony mixed with free sulphur, or, in other terms, of antimony + x sulphur.

To determine the amount of the antimony present, it is necessary, therefore, either to separate this metal from the sulphur, or to ascertain the proportion of sulphur present in the precipitate.

To separate the antimony from the sulphur, the precipitate may be heated in a bulbous tube in a stream of hydrogen gas, until the formation of sulphuretted hydrogen ceases completely. But since a slight loss of antimony can hardly be avoided, in this process (the stream of hydrogen gas tending to carry off mechanically a small portion of the antimony) it is preferable to determine the amount of sulphur present in the precipitate, and to calculate from this the proportion of antimony.

For this purpose, the precipitate is dried upon the filter in a platinum crucible at a temperature of 212°, and subsequently weighed; as much of the contents of the crucible as may be detached without difficulty is then carefully projected into a flask; the filter, with the still adhering portion of the precipitate, is re-introduced into the crucible, and the latter again weighed; the difference between the weight which the crucible is now found to possess, and that which it exhibited when weighed, with the whole of the dry precipitate, shows at once the amount of precipitate contained in the flask.

Red fuming nitric acid (perfectly free from sulphuric acid) is now gradually dropped upon the contents of the flask. When the action of the acid has grown somewhat less energetic than at first, a larger portion is added, together with a small amount of hydrochloric acid, and a gentle heat applied and maintained for some time. Upon this, two different cases may occur, viz., either

α. The solution is perfectly clear, and contains no trace of separated sulphur.

If this be the case, the solution is to be mixed with a tolerably large portion of water, and, should this produce any turbidity or precipitate in the fluid, tartaric acid added drop by drop until the liquid appears again perfectly clear. Solution of chloride of barium is now added slightly in excess, and the sulphate of barytes, which precipitates upon the addition of this reagent, determined as directed § 74, taking particular care to wash the precipitate *thoroughly*, (compare § 100). The proportion of the sulphur present in the precipitated sulphate of barytes is accurately calculated, and from the result we may readily infer the proportion of sulphur present in the whole of the originally precipitated sulphuret of antimony, and this will at once show, by simple calculation, how much antimony the analysed compound originally contained. Or,

β. The solution is clear, but contains separated sulphur.

If this be the case, the solution is to be mixed (as in *α*.) with a tolerably large portion of water, and, should this produce any turbidity, tartaric acid added drop by drop until the fluid has cleared again. The solution is then passed through a small tared filter, and the separated sulphur collected upon the latter, washed, dried at 212°, and weighed. The filtrate is treated as in *α*. The weight of the free sulphur is added to that calculated from the sulphate of barytes, and the rest of the calculation made as in *α*.

2. *Determination as antimonious acid.*

The compound under examination is carefully evaporated with nitric acid, and the residue ignited until its weight ceases to vary. The process may be safely conducted in a platinum crucible. If the operator has to act upon antimonic acid, we need not evaporate it with nitric acid. For the properties of the residue, vide § 64. This method is free from sources of error.

§ 96.

4. PROTOXIDE OF TIN, and 5. PEROXIDE OF TIN.

a. Solution.

The water used to dissolve those compounds of tin which are soluble in this menstruum, is to be slightly acidified with hydrochloric acid to ensure a clear solution. Nearly all the insoluble compounds of tin dissolve in hydrochloric acid or in aqua regia. The insoluble modification of peroxide of tin, and the compounds of this modification must be prepared for solution by fluxing with carbonate of soda. Metallic tin is most advantageously dissolved in aqua regia. The determination of metallic tin is, however, generally effected by converting the metal into the peroxide without previous solution.

b. Determination.

Tin is usually weighed in the form of PEROXIDE, into which its compounds are converted either by ignition, or by evaporation with nitric acid, or by precipitation as SULPHURET OF TIN.

We may convert into

1. PEROXIDE OF TIN.

a. By ignition.	*b. By evaporation with nitric acid.*
All compounds of tin which contain volatile acids, (even sulphuric acid,) provided no fixed substance be present.	All compounds of tin which contain volatile acids.

c. By precipitation as sulphuret of tin.

All compounds of tin without exception.

It is a matter of perfect indifference in these methods whether the tin be present in the analysed compound in the form of protoxide or in that of peroxide. The application of method *c.* is mostly confined to cases where *a.* and *b.* are inapplicable, and serves particularly to separate tin from other metals. For the method of separating protoxide of tin from the peroxide, I refer to § 130, 5.

Determination of tin as peroxide.

a. By ignition.

The compound under examination is drenched with nitric acid in excess, and the mixture evaporated to dryness; the residue is finally ignited, and weighed. The process may be performed in a platinum crucible if no hydrochloric acid is present; but in presence of this acid, the operation is to be conducted in a porcelain crucible. Should sulphuric acid be present, the expulsion of this is accelerated by the addition of carbonate of ammonia, (compare § 42. Conversion of the acid sulphate of potass into the simple sulphate.) For the properties of the residue, vide § 65. This method is free from sources of error.

b. By evaporation with nitric acid.

The solution of the compound under examination is introduced into a flask, mixed with nitric acid in excess, and carefully evaporated to a state of high concentration. Should hydrochloric acid be present, the nitric acid is to be added in sufficient quantity to ensure its *complete* decomposition and expulsion. The residuary mass in the flask is diluted with water, the fluid filtered off from the peroxide of tin, and the latter washed, dried, and ignited in a platinum crucible, (§ 31). This method is free from sources of error.

c. By precipitation as sulphuret of tin.

The dilute neutral or acid solution of the compound under examination is precipitated with sulphuretted hydrogen gas or sulphuretted hydrogen water. If the tin was present in the solution in the form of protoxide, in which case the precipitate will consist of the brown protosulphuret of tin, the solution supersaturated with sulphuretted hydrogen, is to be kept standing for half an hour in a moderately warm spot, and subsequently filtered; if, on the other hand, the solution contained a persalt of tin, in which case the precipitate will consist of the yellow bisulphuret of tin,—the fluid is to be loosely covered and kept exposed to a gentle heat until the odor of sulphuretted hydrogen has completely disappeared; the fluid is then filtered off from the precipitate. The washed and dried precipitate is projected into a porcelain crucible, and the filter consumed upon the lid of the latter; the precipitate is heated gently, with free access of air until all evolution of sulphurous acid has ceased; a more intense heat is then to be applied. To ensure the expulsion of every trace of sulphuric acid which may perchance have remained, it is advisable finally to add a small fragment of carbonate of ammonia to the contents of the crucible. Were the precipitate heated intensely from the commencement of the operation, the bisulphuret of tin would change into the protosulphuret, with loss of sulphur. The protosulphuret of tin fuses readily, and becomes only slowly converted into the peroxide upon ignition in the air. However, as the atomic weight of the protosulphuret is absolutely the same with that of the peroxide of tin, it does not matter whether the latter is perfectly pure, or contains an admixture of the former. For the properties of the precipitate, vide § 65. The results are accurate.

§ 97.

6. ARSENIOUS ACID, and 7. ARSENIC ACID.

a. Solution.

Those of the compounds of arsenious and arsenic acid which are not soluble in water, are dissolved in hydrochloric acid, or in aqua regia. Some natural arseniates of metallic oxides require fluxing with carbonate of soda, as an indispensable preliminary to their solution. Metallic arsenic, and likewise metallic arseniurets are dissolved in aqua regia; those of the metallic arseniurets which are insoluble in this menstruum, are fluxed with carbonate of soda and nitrate of potass; this process gives rise to the formation of a soluble arseniated alkali and an insoluble metallic oxide. All solutions of compounds of arsenic which have been effected by heating with aqua regia in excess, contain arsenic acid.

Determination.

Arsenic is weighed either as ARSENIATE OF LEAD, or as SULPHARSENIOUS ACID; and in some instances also as ARSENIATE OF PEROXIDE OF IRON.

We may convert into

1. ARSENIATE OF LEAD.	2. SULPHARSENIOUS ACID.
Arsenious and arsenic acid when present singly either in aqueous or nitric acid solution.	All compounds of arsenic without exception.

3. The method of determining arsenic in the form of arseniate of peroxide of iron (Berthier) is executed like that used for the determination of phosphoric acid, vide § 101. I omit describing this method here, since it is, in every respect, inferior to that of precipitating as sulpharsenious acid.

1. *Determination as arseniate of lead.*

a. Arsenic acid in aqueous solution.

A weighed portion of the solution is introduced into a platinum or porcelain dish, and a definite amount of recently ignited pure oxide of lead added; the mixture is cautiously evaporated to dryness, and the residue heated to gentle redness, and maintained some time at this temperature. The residue, which consists of arseniate of lead + oxide of lead, is then weighed. The amount of arsenic acid present in the analysed solution is now readily found by subtracting the weight of the oxide of lead added, from that of the residuary mass, and calculating the result upon the whole solution. For the properties of arseniate of lead, vide § 66. The results are perfectly accurate, provided the residue be not heated beyond gentle redness.

b. Arsenious acid in solution.

The solution is mixed with nitric acid, a small portion of hydrochloric acid added, and the mixture evaporated to dryness in an obliquely-placed flask; the residuary arsenic acid is then heated somewhat more strongly, subsequently dissolved in water with the aid of a gentle heat, and the solution treated as in *a.*[*]

2. *Determination as sulpharsenious acid.*

a. The operater has in solution, arsenious acid, or an arsenite free from arsenic acid.

The solution is introduced into a bottle provided with a glass stopper; some hydrochloric acid is added, and the solution subsequently precipitated either with sulphuretted hydrogen water, or gas. The flask is then stopped, and allowed to stand for the space of an hour; after this, washed carbonic acid gas is transmitted through the contents of the flask until all odour of sulphuretted hydrogen has completely disappeared; the fluid is then filtered through a tared filter, and the precipitate collected upon the latter, washed, dried at 212°, and weighed. For the properties of the precipitate, vide § 66. The results are very accurate.

Should any other substance possessing the property of decomposing sulphuretted hydrogen, peroxide of iron, chromic acid, &c., be present in the analysed solution, free sulphur will precipitate in conjunction with the sulpharsenious acid. In this case, the free sulphur is to be determined as sulphate of barytes in the manner described § 95, 1. *b.*, *a.* (determination of antimony as sulphuret,)

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[*] If a solution containing nitric acid is evaporated directly with oxide of lead, it is difficult to avoid some loss of substance; since, in the first place, nitrate of lead decrepitates violently when heated, and, in the second place, the hyponitric acid disengaged during the decomposition of the nitrate of lead may readily carry off minute particles of the salt.

and the thus ascertained weight of free sulphur subtracted from the total weight of the precipitate. Another method has been recommended to separate the free sulphur from the sulpharsenious acid, viz. treating the precipitate with ammonia; by which means the sulpharsenious acid is dissolved, whilst the free sulphur remains undissolved;—however the results obtained by this method are only approximate, since the ammoniacal solution of the sulpharsenious acid dissolves a little free sulphur.

b. The operator has in solution arsenic acid, or an arseniate, or a mixture of the two degrees of oxidation of arsenic.

The solution is introduced into a flask, and mixed with a concentrated aqueous solution of sulphurous acid in considerable excess; the flask is placed in an oblique position over the flame of a spirit lamp, and its contents are heated slowly to incipient ebullition; the temperature is subsequently maintained a trifle below the boiling point, until the fluid ceases to smell of sulphurous acid. The solution, which now contains simply arsenious acid, is then treated as directed at *a*.

II. QUANTITATIVE DETERMINATION OF THE ACIDS IN COMPOUNDS CONTAINING BUT ONE BASE AND ONE ACID, OR BUT ONE METAL AND ONE METALLOID;—AND SEPARATION OF THE ACIDS FROM THE BASES.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—CARBONIC ACID—SILICIC ACID.

§ 98.

1. ARSENIOUS AND ARSENIC ACID.

For the quantitative determination of these two acids, I refer to the preceding paragraph;—the methods of separating them from the bases will be found §§ 129 and 130.

§ 99.

2. CHROMIC ACID.

I. DETERMINATION.

Chromic acid is determined either in the form of OXIDE OF CHROMIUM, or in that of CHROMATE OF LEAD.

a. Determination as oxide of chromium.

The chromic acid is reduced to the state of oxide, and the amount of the latter determined, (§ 79). The reduction is effected either by heating the solution gently with hydrochloric acid and alcohol—or by mixing hydrochloric acid with the solution, and transmitting subsequently sulphuretted hydrogen through it; or by adding to the solution a strong solution of sulphurous acid, and applying a gentle heat. Concentrated solutions are generally determined according to the first—dilute solutions according to one of the other two methods. With regard to the *first* of the three methods given, we have to remark here, that the alcohol which has been added in the process of reduction, must be expelled again previously to the precipitation of the oxide of chromium with ammonia;—and with regard to the *second*, that the solution when supersaturated with sulphuretted hydrogen is to be kept standing in a moderately warm place until the separated sulphur has completely subsided.

b. Determination as Chromate of lead.

The solution is mixed with acetate of soda in excess, and should it be necessary, acetic acid added, until the fluid acquires a feebly acid reaction; the solution is then precipitated with neutral acetate of lead; the precipitate is collected upon a tared filter, washed, dried in the water-bath, and weighed. For its properties, vide § 67. The results are accurate.

II. SEPARATION OF CHROMIC ACID FROM THE BASES.

a. OF THE FIRST GROUP.

α. The chromic acid is reduced to the state of oxide according to the directions given at I.; and the oxide separated from the alkalies, as directed § 118.

β. Chromate of ammonia is reduced to the state of chromic oxide by cautious ignition.

b. OF THE SECOND GROUP.

α. The compound under examination is fused together with four parts of a mixture of carbonate of soda and carbonate of potass. Upon extracting the fused mass subsequently with hot water, the chromic acid is dissolved as an alkaline chromate, whilst the alkaline earths remain as carbonates. The chromic acid in the former is finally determined as directed at I. The carbonates of the alkaline earth cannot be determined directly by simple weighing, since they contain an admixture of alkali.

β. The compound under examination is dissolved in hydrochloric acid, and the chromic acid reduced as directed at I.; the chromic oxide is finally separated from the alkaline earths according to the directions of § 119.

c. OF THE THIRD GROUP.

α. From alumina.

The alumina present in the solution is precipitated by ammonia, (§ 78,) and the chromic acid in the filtrate determined as directed at I.

β. From oxide of chromium.

aa. In solution.

The chromic acid is precipitated as directed at I. *b*, and the lead and oxide of chromium in the filtrate separated according to the directions given at § 126.

bb. The compound under examination is insoluble, (neutral chromate of oxide of chromium.)

The compound is ignited; oxygen is expelled, and oxide of chromium remains. The amount of chromic acid originally present in the analysed compound is calculated from the amount of oxygen expelled; in other words, from the loss of weight which the compound has suffered by ignition.

d. OF THE FOURTH GROUP.

α. The same method is applied as at *b. α.* Upon extracting the fused mass with hot water, the metals remain as oxides. To separate chromic acid from manganese, the fusion is to be effected in a bulbous tube, with transmission of a stream of carbonic acid gas over the fusing mixture.

β. The chromic acid is reduced as at I. *a.*, and the chromic oxide separated from the metals of the fourth group according to the directions which will be found at § 123.

e. OF THE FIFTH AND SIXTH GROUP.

α. The solution of the compound under examination is mixed with free acid, and subsequently precipitated with sulphuretted hydrogen. The metals of the fifth and sixth group are precipitated as sulphurets in conjunction with free sulphur, (compare from § 86 to § 97,) whilst the chromic acid, reduced to the state of oxide, is obtained in the filtrate, from which it is finally precipitated as directed at I. *a*.

β. The most appropriate method of decomposing chromate of lead, is to heat it with hydrochloric acid and a small amount of alcohol:—chloride of lead and protochloride of chromium are formed, which are subsequently separated by means of alcohol. (Compare § 126.)

§ 100.

3. SULPHURIC ACID.

I. DETERMINATION.

The best way of determining sulphuric acid is to convert it into SULPHATE OF BARYTES.

For this purpose the solution of the compound under examination is acidified with hydrochloric acid, (should this be necessary,) chloride of barium added in slight excess, and the further process conducted according to the directions given at § 74. Should the analysed solution contain nitric acid, some nitrate of barytes is likely to precipitate in conjunction with the sulphate; the removal of this admixture of nitrate of barytes from the precipitate, requires long protracted washing with hot water. It is, under all circumstances, necessary to continue the washing of the precipitate until the last rinsings remain perfectly clear upon testing with sulphuric acid.

II. SEPARATION OF SULPHURIC ACID FROM THE BASES.

a. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

The sulphuric acid is precipitated as at I. The filtrate contains, besides the chlorides of the bases originally combined with the sulphuric acid, the excess of the chloride of barium added; from which the bases are finally separated by the methods recommended in the fifth section, to effect the separation of the various bases from barytes.

b. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS INSOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

α. From barytes, strontia, and lime.

The compound under examination is very finely levigated and fused in a platinum crucible, together with four parts of mixed carbonate of soda and potass. The crucible with its fused contents is introduced into a beaker-glass or platinum or porcelain basin, where it is subsequently drenched with water, and heat applied until the alkaline sulphates and carbonates are completely dissolved; the hot solution is then filtered off from the undissolved carbonates of the alkaline earths, and the latter are thoroughly washed with hot water, and subsequently dissolved in hydrochloric acid, and determined according to the methods given from § 74 to § 76. The sulphuric acid in the filtrate is precipitated as at I. Finely levigated sulphate of lime may be completely decomposed also by boiling with a solution of carbonate of soda or carbonate of potass.

β. From oxide of lead.

The finely levigated compound under examination is fused, together with a mixture of carbonate of soda and potass, in a porcelain crucible, until the mass has entered into a state of semifusion; the mass is then digested with hot water to complete extraction of the alkaline sulphate formed, and of the excess of the alkaline carbonate added; the solution is then filtered off from the undissolved oxide of lead, (which is never quite free from admixed alkali,) and the latter thoroughly washed. The filtrate, which invariably contains a more or less copious admixture of oxide of lead, is now slightly acidified with nitric acid, (this should be done cautiously to avoid loss by spitting,) and the sulphuric acid precipitated as at I., with this difference, that nitrate of barytes is substituted for chloride of barium. The washed oxide of lead is dissolved in dilute nitric acid, and the solution added to the fluid filtered off from the sulphate of barytes; the lead is finally precipitated from this solution, with sulphuretted hydrogen, § 87.

§ 101.

4. PHOSPHORIC ACID.

I. DETERMINATION.

Phosphoric acid is determined as PHOSPHATE OF LEAD, PYROPHOSPHATE OF MAGNESIA, BASIC PERPHOSPHATE OF IRON, PHOSPHATE OR PYROPHOSPHATE OF SILVER.

a. Determination as phosphate of lead.

This is effected in the same manner as the determination of arsenic acid as arseniate of lead, vide § 97 1, *a.* The application of this method is admissible only when no other acid is present.

b. Determination as pyrophosphate of magnesia.

A mixture of sulphate of magnesia, sal ammoniac, and ammonia, is added to the solution as long as a precipitate continues to form; should the solution, after this, not smell strongly of ammonia, some more of the latter substance is to be added; the mixture is then kept standing at rest for several hours, the fluid subsequently filtered off from the precipitate, and the latter washed with water containing ammonia, until the last rinsings remain perfectly clear, upon testing with chloride of barium; the further process is then to be conducted exactly as directed at § 77. The mixture of sulphate of magnesia, sal ammoniac, and ammonia, should contain exactly as much sal ammoniac as will prevent the precipitation of the magnesia by the ammonia, and no more. The results are accurate, (Experiments sub. No 63,) although an exceedingly trifling loss is sustained, since the basic phosphate of magnesia and ammonia is not altogether insoluble, (Experiment No. 27.) For the properties of the precipitate and residue, vide § 48.

c. Determination as basic perphosphate of iron.

A weighed amount of pure metallic iron is dissolved in nitric acid, and the solution added to that of the compound under examination. Ammonia is then added in excess to the mixed fluid, (the addition of the ammonia must produce a red-brown precipitate; should the latter appear white, this is a sign that the amount of solution of iron added was insufficient,) and heat applied; after the lapse of some time, the fluid is filtered off from the precipitate, and the latter completely washed with hot water, thoroughly dried, and finally strongly ignited, (§ 31). The ignited precipitate consists of basic perphosphate of iron + peroxide of iron, or, in other words, of phosphoric acid + peroxide of iron. The quantity of the latter is calculated directly from the weight of the iron employed in the process, and the resulting figure subtracted from the weight of the ignited precipitate; the difference indicates the amount of phosphoric acid originally present in the analysed compound.

This method yields very accurate results; but its performance requires great care and attention, since any loss that may happen to be incurred in the process falls entirely upon the phosphoric acid. There is one disadvantage connected with this method, viz., even the purest iron of commerce is not absolutely pure, and consequently does not really yield the exact amount of peroxide theoretically calculated. This may, however, be remedied by taking a weighed sample of a large quantity of iron wire, and determining the exact amount of peroxide which this yields.

d. As phosphate of silver.

Phosphoric acid, in the free state, cannot be determined in this form.

II. SEPARATION OF PHOSPHORIC ACID FROM THE BASES.

a. From the fixed alkalies.

α. The method described at I. *c*. is applied, and the alkaline nitrates in the filtrate are determined by the appropriate methods.

β. The method I. *b.* is applied, and the magnesia in the filtrate is separated from the alkalies present, according to the directions given at § 116.

γ. Salts composed after the formula $P\,O_5$, $3\,M\,O$ (metallic oxide) are brought into aqueous solution, and the latter is precipitated directly with neutral solution of silver; the yellow precipitate formed ($P\,O_5$, $3\,Ag\,O$) is washed, dried, and ignited, (§ 31).

Phosphates, composed after the formula $P\,O_5$, $2\,M\,O$, $H\,O$, are to be ignited, the residue is to be dissolved in water, and the solution precipitated with neutral solution of silver. The fluid is then filtered off from the precipitate, (which, in this case, consists of pyrophosphate of silver, $P\,O_5$, $2\,Ag\,O$,) and the latter washed, dried, and ignited, (§ 31). For the properties of the precipitated phosphates of silver, vide § 67, 4.

The bases in the filtrates are determined after the removal of the silver, (viz., the excess of the nitrate of silver employed in the process,) vide § 126.

The results are very accurate; this method is particularly convenient, on account of the facility with which the alkalies in the filtrate may be estimated.

b. From the whole of the alkalies.

The aqueous solution is mixed with acetate of lead in slight excess; the precipitated phosphate of lead is allowed to subside, and the fluid subsequently filtered off; the alkalies in the filtrate are separated from the excess of the salt of lead employed in the process, according to the directions given at § 126. The proportion of the phosphoric acid originally present in the analysed compound may be inferred, in this case, from the difference of weight between the alkalies and the original phosphates; but it may also be determined directly by treating the washed precipitate of phosphate of lead according to § 101 *d.*, *β.*

c. From barytes, strontia, lime, and oxide of lead.

The compound under examination is dissolved in hydrochloric or nitric acid, and the solution precipitated with sulphuric acid in slight excess. In the separation of phosphoric acid from strontia, lime, and oxide of lead, alcohol is added in conjunction with the sulphuric acid. The phosphoric acid in the filtrate is determined according to I. *b.*, after having previously removed the alcohol by evaporation.

d. From the whole of the alkaline earths.

α. The compound under examination is dissolved in hydrochloric acid, (the acid should not be used in great excess,) some perchloride of iron added, and finally acetate of soda in excess. Should the solution, upon this, fail to acquire a red color, perchloride of iron is to be added drop by drop until the fluid assumes this color. The mixture is then heated to boiling in a capacious basin, and maintained in a state of gentle ebullition during five minutes. A reddish brown precipitate subsides, and the fluid becomes colorless; should this, however, not occur, it is a sign that the acetate of soda has not been used in sufficient quantity, and consequently that an additional amount of this reagent is required. The boiling fluid is subsequently filtered, and the precipitate thoroughly edulcorated with hot water. The phosphoric acid may now be determined by either of the two following methods, (I prefer *aa.* on account of its simplicity).

aa. The precipitate, while still moist, is dissolved in hydrochloric acid, tartaric acid added, and subsequently ammonia, until the precipitate which forms at first is completely redissolved in the excess of the ammonia added; the solution is clear, and exhibits a yellow color. The phosphoric acid in the solution is determined according to I. *b.*, care being taken to wash the precipitate *thoroughly*. Notwithstanding the most careful washing, the appearance of the precipitate will invariably slightly incline to yellowish, instead of being perfectly white. Upon ignition, the precipitate turns blackish, and the examination of the residue reveals the presence of traces of iron. The accuracy of the results is, however, but very slightly impaired by this defect, (generally about $\frac{2}{10}$ to $\frac{3}{10}$ per cent. too high. Compare Experiment No. 63, *b*.) This source of error may even be altogether removed by redissolving the washed precipitate in hydrochloric acid, and reprecipitating with ammonia.

bb. The precipitate is carefully dried, and subsequently ignited in a platinum crucible, with free access of air. The filter is burnt upon the lid of the crucible. The residue is accurately weighed, and subsequently moistened with strong nitric acid; the acid is then expelled by evaporation at a gentle heat, and the residue, after this, ignited again. It may happen that the weight of the residue exhibits a slight increase after this process; should this be the case, the operation (*i. e.* the moistening with nitric acid, evaporation, and subsequent ignition) must be repeated until the weight of the residue ceases to vary. The crucible and its contents are now introduced into a beaker-glass, and digested with strong hydrochloric acid until the latter are dissolved. The solution is transferred into another vessel, and the beaker-glass and crucible thoroughly rinsed with water (adding the rinsings to the solution). The whole fluid * is now mixed with tartaric acid, and subsequently with ammonia in excess. Sulphuret of ammonium is then added in excess, (no matter whether the addition of the ammonia has left the fluid quite clear, or caused the appearance of a slight turbidity in it,) and the further process conducted according to § 85 *b*. The weight of the peroxide of iron obtained is subtracted from the weight of the original residue; the difference expresses the amount of phosphoric acid originally present in the analysed compound.

The filtrate contains the alkaline earths in the form of chlorides, and likewise a hardly perceptible trace of iron. The alkaline earths are determined according to §§ 74, 75, 76, and 77. (Were the fluid not filtered off when quite hot, or were the precipitate not *uninterruptedly* washed with hot water, the filtrate would, instead of exceedingly minute traces, contain a very per-

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* The undissolved particles of the filter ashes which the solution contains are allowed to remain in it.

ceptible amount of iron.) This method yields very accurate results. It is frequently applied in the analysis of soils and ashes.* With respect to the *theory* of the process, we may assume that, upon mixing the hydrochloric solution of the phosphate of the alkaline earth with perchloride of iron, perphosphate of iron is formed, whilst the chlorine combines with the metal of the alkaline earth; the free hydrochloric acid present maintains the perphosphate of iron in solution. When acetate of soda is now added, the free hydrochloric acid combines with the soda; and since the liberated acetic acid has no solvent action upon perphosphate of iron, part of this salt precipitates, whilst a greater or less portion of it remains dissolved in the solution of the peracetate of iron, which is formed by the transposition of the constituents of the perchloride of iron, (that is, of the excess of the perchloride employed in the process,) with the constituents of acetate of soda. (It occurs sometimes, that the whole of the perphosphate of iron remains in solution, if the peracetate of iron thus formed is present in great excess.) Upon boiling the mixture, this peracetate of iron is decomposed, and the perphosphate of iron precipitates as a basic salt in conjunction with a basic peracetate of iron, whilst the *whole* of the alkaline earth present remains in solution, (which is not the case with method II. *a.* *α.*) The precipitate of *bb.* consists therefore of peroxide of iron + phosphoric acid, whilst the precipitate produced upon the decomposition of this with sulphuret of ammonium, consists exclusively of peroxide of iron; the difference between the respective weights of these two precipitates indicates consequently the amount of phosphoric acid originally present in the analysed salt. The addition of tartaric acid, which precedes that of the ammonia and sulphuret of ammonium, has for its object to prevent, at least partially, the precipitation of the perphosphate of iron by the ammonia which is subsequently added,

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* Compare Fresenius and Will. Untersuchungen über die unorganischen Bestandtheile der Vegetabilien—Annalen der Chemie und Pharmacie L., page 363.

and thus to promote the complete decomposition of this salt by the sulphuret of ammonium.

β. The compound under examination is dissolved in the least possible amount of nitric acid, and basic acetate of lead added in trifling excess; the precipitate which forms upon the addition of the reagent consists of phosphate and basic nitrate of lead; this is allowed to subside, filtered, washed, dried, ignited, (§ 31,) and finally weighed. The residue consists of phosphate of lead + oxide of lead, or, in other words, phosphoric acid + x oxide of lead. The residue is now introduced (in the crucible) into a beaker-glass, and digested at a gentle heat with moderately dilute nitric acid until dissolved. The solution is poured off into another glass, and both the crucible and beaker-glass washed, adding the rinsings to the solution, in which the oxide of lead is then determined (according to II. *c.*) as sulphate of lead. If the amount of oxide of lead calculated from the sulphate produced, is subtracted from the weight of the ignited residue of the first precipitate, the difference indicates directly the amount of phosphoric acid originally present in the analysed compound. The fluid filtered off from the mixed precipitate of phosphate and basic nitrate of lead contains the bases which were originally combined with the phosphoric acid, and moreover the excess of the basic acetate of lead used in the process; from the latter the bases are finally separated according to the directions of § 126. This method likewise yields very accurate results.

e. From alumina.

α. The phosphate of alumina, which it is intended to determine, is dissolved in hydrochloric acid, or in nitric acid, and the separation of the alumina from the phosphoric acid is then effected in the same manner as that of peroxide of iron from phosphoric acid, (vide II., *d. α αα.*) The alumina and magnesia in the filtrate are separated as directed at § 119. The results are very accurate. (Compare Experiment No. 63, *b.*)

β. The phosphate of alumina under examination is very finely levigated, and intimately mixed with about 1½ part of pure silicic acid, (best artificially prepared to ensure its purity,) and six parts of carbonate of soda. The mixture is introduced into a platinum crucible, and exposed during about thirty minutes to a most intense red-heat. The ignited mass is soaked with water, bicarbonate of ammonia added in excess, the mixture digested for some time, and the solution filtered off from the undissolved residue of silicate of soda and alumina, which is collected upon the filter and washed. The filtrate contains phosphate of soda, bicarbonate of soda, and carbonate of ammonia. (Were the solution filtered previously to the addition of the bicarbonate of ammonia, a small portion of the alumina compound would get into the solution.) The phosphoric acid in the filtrate is finally determined according to II. *a.*; the alumina in the insoluble residue is separated and determined as directed § 106. (Berzelius.)

f. From oxide of chromium.

α. The compound under examination is fused in conjunction with carbonate of soda and nitrate of potass, and the phosphoric and chromic acid separated according to the direction of § 131.

β. The same method as at II. *e. α.* (separation of phosphoric acid from alumina.) Vide likewise *g.*

g. From oxide of chromium and the metallic oxides of the fourth group.

α. The compound under examination is fused in conjunction with carbonate of soda, and the fused mass treated with water; the solution which is thus obtained contains the phosphoric acid in combination with soda; the phosphoric acid is finally determined according to II. *a.* The carefully washed residue, which generally retains an admixture of alkali, is dissolved in hydrochloric acid, and the metal present determined by the appropriate method. (vide from § 79 to § 85). In the analysis of phosphate of ~~magnesia~~ manganese or of chromium, these salts are to be fused in a bulbous tube, through which a stream of carbonic acid gas is transmitted during the operation.

β. (Inapplicable to phosphate of chromium.) The compound under examination is dissolved in hydrochloric acid; tartaric acid is added to the solution, subsequently ammonia, and finally sulphuret of ammonium. The fluid is then filtered off from the precipitated sulphuret, and the metal in the latter determined according to the directions given at §§ 80 to 85. The phosphoric acid in the filtrate may be either determined according to I. *b.*, or its proportion inferred from the difference between the weight of the metal and that of the original phosphate. This method is less appropriate than the former, for the analysis of phosphate of nickel.

β. From the metals of the fifth and sixth group.

The phosphate under examination is dissolved in hydrochloric acid or in nitric acid, and the solution precipitated with sulphuretted hydrogen; the fluid is filtered off from the precipitated sulphurets, and the metals in the latter determined according to the directions given at §§ 86 to 97. The phosphoric acid in the filtrate is determined as directed at I. *b.*

§ 102.

5. BORACIC ACID.

I. Determination.

Free boracic acid in solution may be determined in the same manner as free arsenic acid, (vide § 97); i. e by evaporating the solution with a weighed amount of pure oxide of lead, and igniting the residue. The determination of boracic acid cannot be effected by simply evaporating the solution containing the free acid, since, without the addition of a base, part of the boracic acid will volatilize in conjunction with the vapor of the solvent; nor can it be effected by precipitation with any of the metallic salts, or of the salts of the alkaline earths, since none of the borates are sufficiently insoluble for complete precipitation.

II. Separation of boracic acid from the bases.

The proportion of boracic acid present is generally inferred from the difference between the weight of the separated base and that of the analysed borate.

a. From the whole of the fixed bases.

A portion of the very finely levigated compound under examination is weighed into a platinum crucible, mixed with from three to four parts of perfectly pure fluor spar in powder, and pure concentrated sulphuric acid added, until the mixture is thoroughly moistened; a gentle heat is then applied for some time, which is finally increased to redness, and maintained at this degree of intensity until the disengagement of acid fumes ceases. In this operation the boracic acid goes off in the form of fluoride of boron. ($B\,O_3 + 3\,Fl\,H = B\,Fl_3 + 3\,H\,O$). The residue contains the bases in the form of sulphates, mixed with gypsum; the bases are determined by the appropriate methods which, will be found described in the fifth section—and the proportion of the boracic acid inferred from the difference between the weight of the separated base and that of the original borate. The application of this method presupposes, of course, that the analysed compound is anhydrous, and decomposable by sulphuric acid. Should the compound under examination contain lime, pure fluoric acid may be advantageously substituted for fluor spar.

b. From the alkalies.

The method of determining potass and ammonia in the borates of the alkalies, have been discussed already at §§ 71 and 73. Borate of soda may be converted into sulphate of soda. For this purpose the aqueous solution of borate of soda is mixed with pure sulphuric acid in excess, and the mixture evaporated in a flask, until sulphuric acid fumes begin to escape; the evaporated mass is now mixed with a tolerably large portion of absolute alcohol, the flask stoppered, and kept standing for twenty-four hours, during which period its contents are to be frequently agitated. The fluid is subsequently filtered off from the sulphate of soda, (which is insoluble in alcohol,) and the latter washed with alcohol until the rinsings fail to redden moistened litmus paper, dried and ignited, (§ 31). This method, if very carefully executed, yields sufficiently accurate results. But perfect precision is unattainable by it, since sulphate of soda is not altogether insoluble even in absolute alcohol, in the presence of free sulphuric acid.

c. From barytes, strontia, lime, and oxide of lead.

The same method as is applied for the determination of phosphoric acid under the same circumstances. (Vide § 101, II. *c.*) The proportion of the boracic acid present in the analysed compound, is inferred from the difference between the weight of the separated base and that of the original borate.

d. From metallic oxides of the fourth, fifth, and sixth group.

The solution of the compound under examination is precipitated with sulphuretted hydrogen, (or, sometimes, with sulphuret of ammonium,) and the metallic oxide determined by the appropriate method. (Vide §§ 80 to 97.) The boracic acid is determined from the difference between the weight of the separated oxide of metal and that of the original borate. In cases where the metal has been precipitated with sulphuretted hydrogen from acid or neutral solutions, the boracic acid may also be determined directly in the filtrate, according to I., after having previously expelled the sulphuretted hydrogen from the filtrate, by transmitting through it a stream of carbonic acid gas.

§ 103.

6. OXALIC ACID.

I. DETERMINATION.

Oxalic acid is either precipitated in the form of OXALATE OF LIME, and the latter determined as CARBONATE OF LIME, or the proportion of oxalic acid present in the compound under examination, is inferred from the amount of carbonic acid which the latter yields.

a. Determination as carbonate of lime.

The oxalate under examination is best precipitated with a solution of acetate of lime in excess, or with chloride of calcium in conjunction with acetate of soda. The precipitate is treated according to § 76.

b. Determination by inference from the amount of carbonic acid yielded by the oxalate under examination.

This may be effected either

α. By the method of organic elementary analysis, (§ 140); or

β. By bringing oxalic acid into contact with peroxide of manganese in excess, and subsequently with sulphuric acid, in an apparatus so constructed that the disengaged carbonic acid is perfectly dried previously to escaping.

The theory of this method may be illustrated by the following equation:

$$C_2\,O_3 + Mn\,O_2 + S\,O_3 = Mn\,O,\ S\,O_3 + 2\ C\,O_2.$$

Every equivalent of oxalic acid yields accordingly two equivalents of carbonic acid. With regard to the apparatus and execution of the process, I refer to §§ 105 and 125; and will here simply remark, that free oxalic acid must first be prepared for the process by slight supersaturation with ammonia, and also that 9 parts of free oxalic acid are required theoretically for 11 parts of pure peroxide of manganese. Since an excess of the latter substance does not interfere with the accuracy of the results, it is easy to determine by simple estimation the amount to be added. The peroxide of manganese need not be pure, provided it contain no carbonate. This method is very expeditious, and yields extremely accurate results, especially if the process is conducted in a light apparatus, so as to admit the use of a sensible balance.

II. SEPARATION OF OXALIC ACID FROM THE BASES.

a. The methods I. *b.* *α.* and *β.* are applicable to all oxalates as far as the acid is concerned; but the determination of the bases in the same portion of the analysed substance is not very easy in *α.*, and inconvenient in *β.*

b. In many neutral oxalates, the proportion of acid may be determined from the loss of weight which the salt undergoes upon ignition in the air and consequent reduction to the metallic state, (e. g. oxalate of silver); or to the state of pure oxide, (e. g. oxalate of lead); or to the state of carbonate, (the oxalates of the alkaline earths and of the alkalies). This method is particularly adapted to determine the bases in the oxalates.

c. In all soluble oxalates the acid may be determined according to I. *a.*, separating the bases subsequently from the excess of the precipitant salt of lime, by the methods of the fifth section.

d. All those oxalates, the bases of which are precipitated by carbonate of potass, and are insoluble in an excess of this reagent, may be decomposed, by boiling with solution of carbonate of potass, into oxide or carbonate on the one side, and oxalate of potass on the other.

e. All the salts of oxalic acid, with the oxides of the fourth, fifth, and sixth group, may be decomposed by means of sulphuretted hydrogen, or of sulphuret of ammonium.

§ 104.

7. HYDROFLUORIC ACID.

I. Determination.

Free hydrofluoric acid in aqueous solution is determined as FLUORIDE OF CALCIUM.

For this purpose, the solution is supersaturated with ammonia, chloride of calcium added in excess, heat applied, and the gelatinous precipitate which forms allowed to subside; the fluid is filtered off, and the precipitate washed, first with hot water, finally with a little dilute acetic acid; (to remove the carbonate of lime which may have been formed by the action of the carbonic acid of the atmosphere); the washed precipitate is finally dried, ignited, and weighed. For the properties of the precipitate, vide § 67, 7. The results are accurate.

II. SEPARATION OF FLUORINE FROM THE BASES.

a. Soluble fluorides.

The method given at I. is applied. The bases are determined in the filtrate by separating them from the excess of the precipitant salt of lime. (For the way in which this separation is effected, vide the fifth section.)

b. Insoluble fluorides.

α. Anhydrous insoluble fluorides.

The finely levigated and accurately weighed substance under examination is heated for some time with pure concentrated sulphuric acid; the residue is subsequently ignited until the free sulphuric acid is completely expelled. The residuary sulphate is weighed, and the metal contained in it calculated. The difference between the calculated weight of the metal and that of the original fluoride indicates directly the amount of fluorine originally present in the analysed compound. Should the fluoride contain a metal, the sulphate of which yields a part of its acid upon ignition, or should the residue contain several metals, it is necessary to analyse it further before this calculation can be made.

β. Hydrated insoluble fluorides.

A sample of the compound under examination is heated in a tube.

aa. The water expelled is perfectly neutral to litmus paper.

In this case the amount of water present is ascertained by igniting the hydrated compound, and the fluoride and metal are subsequently determined according to II., *b. α.*

bb. The water expelled manifests an acid reaction.

The hydrated fluoride under examination is, in the first place, treated according to II. *b. α.*, to determine the metal on the one hand and the water + fluorine on the other. Another weighed portion is then mixed in a small retort, with about six parts of recently ignited oxide of lead; the mixture is then covered with a layer of this oxide of lead, the retort weighed, and heat applied, which is gradually increased to redness; the water which is by this means completely expelled, is entirely free from any admixture of hydrofluoric acid. The retort is now weighed again, and the amount of water expelled calculated from the diminution of weight which the retort has undergone. The first operation having furnished us with the exact amount of the water + fluorine, we may now at once calculate the proportion of fluorine originally present in the analysed compound, by simply subtracting from the weight of the water + fluorine that of the water expelled in the second operation.

We shall have occasion in the fifth section to mention still another method of determining fluorine. (Separation of fluorine from silicic acid.)

§ 105.

8. CARBONIC ACID.

I. DETERMINATION.

Free carbonic acid in aqueous solution is determined in the following manner: a clear and transparent mixture of chloride of calcium, with ammonia in excess, is added to a measured or weighed solution, and the precipitate which forms allowed to subside; the fluid is filtered off from the precipitate, (the funnel being kept covered during the filtration, so as to exclude the access of air,) and the latter washed with water containing ammonia, dried, and ignited. (Compare § 76). Should the solution contain other substances precipitable by ammonia, the carbonic acid in the precipitate is to be determined according to II., *b.*, *β.*, *aa.* It is not necessary to dry the precipitate for this purpose.

II. SEPARATION OF CARBONIC ACID FROM THE BASES.

The methods of determining the amount of carbonic acid present in a compound have all the same principle in common, viz., expulsion of the carbonic acid by a stronger acid, the proportion of the carbonic acid being inferred either from the loss of weight which the analysed compound undergoes, or from the increase of weight of the fluid which has been made to absorb the disengaged carbonic acid.

a. Separation of carbonic acid from bases which yield up their carbonic acid readily and completely upon ignition.

Such are the carbonates of zinc, lead, copper, magnesia, &c.

α. The carbonate under examination is anhydrous.

A weighed portion of the carbonate is ignited in a porcelain crucible, and the same process repeated until the weight of the residue ceaes to vary. The loss of weight indicates the proportion of carbonic acid originally present in the ignited compound. The results are, of course, exceedingly accurate. Substances liable to absorb oxygen upon ignition in the air, are ignited in a bulbous tube, through which a stream of dry carbonic acid gas is conducted during the process.

β. The carbonate under examination is hydrated.

A weighed portion of the carbonate is ignited in a glass tube connected with a chloride of calcium tube and a potass apparatus; the extremity of the tube contains a little fused chlorate of potass. The process is the same as in organic elementary analysis, (§ 140). The chlorate of potass serves to expel the last traces of carbonic acid from the tube. The potass apparatus and chloride of calcium tube are weighed only after the lapse of about fifteen minutes, to permit the atmospheric air to replace by simple diffusion the oxygen gas present in them. In very minute and precise experiments the potass ley is saturated with oxygen gas before commencing the process, (compare § 142, *bb*). That the carbonate intended to be analysed by this method must be entirely free from admixture of organic substances, is self-evident.

b. Separation of carbonic acid from all bases without exception.

α. Anhydrous carbonates.

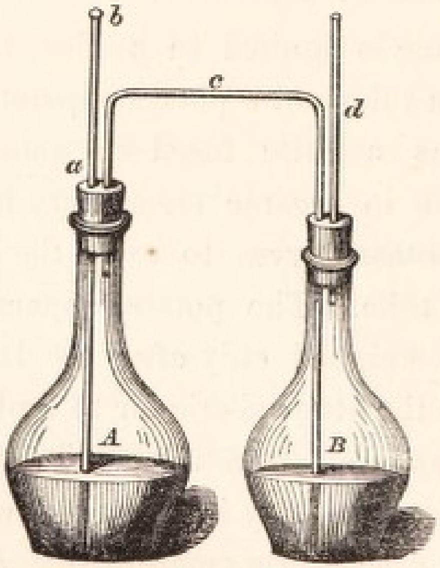
The carbonate under examination is weighed in a platinum crucible, and about four times its weight of fused perfectly anhydrous borax (§ 39, 6) added; heat is then applied, which is gradually increased to redness, and maintained at this degree of intensity until the contents of the crucible are in calm fusion. The crucible is weighed, after cooling. The loss of weight indicates the amount of carbonic acid originally present in the ignited compound. The results are accurate.

β. Carbonates readily and completely decomposable by acids.

aa. Carbonates, the bases of which form soluble salts with sulphuric acid.

The process is conducted in the apparatus illustrated by

PLATE XXXIV.



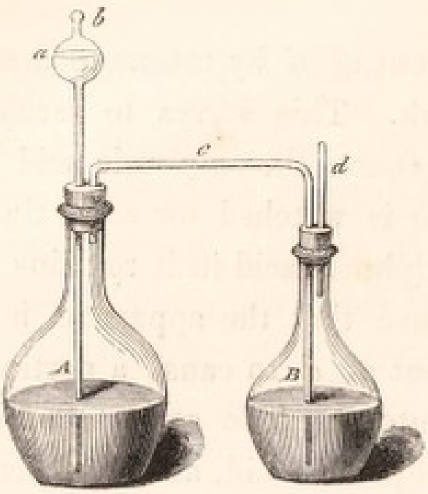
The size of the flasks depends upon the capacity of the balance which the operator may happen to possess. The tube *a* is closed at *b* by means of a small wax stopper; the other end of the tube *a* is open, and so are both ends of *c* and *d*. The flask B is to be nearly half filled with concentrated sulphuric acid; the tubes *a*, *c*, and *d* must fit air-tight in the perforation of the cocks, and the latter equally so in the mouths of A and B. A weighed portion of the carbonate under examination is introduced into A; this flask is then filled to about one-third with water, subsequently corked, and the whole apparatus placed in equilibrium upon the balance.

A few bubbles of air are sucked out of *d* by means of a small suction tube, or of a perforated cork. This serves to rarify the air in A likewise, and consequently causes the sulphuric acid in B to ascend in the tube *c*. This tube is watched for some time to ascertain whether the column of sulphuric acid in it remains perfectly stationary, since this will prove that the apparatus is airtight. Air is then again sucked out of *d*, to cause a portion of the sulphuric acid to flow over into A. The carbonate in the latter flask is decomposed by the sulphuric acid, and the liberated carbonic acid, completely dried in its passage through the concentrated sulphuric acid in B, escapes through *d*. As soon as the evolution of carbonic acid ceases, the same process is repeated until the carbonate is completely decomposed. A large amount of sulphuric acid is then made to pass over into A, by applying a greater degree of suction to *d*, than in the preceding part of the process; this influx of sulphuric acid into A causes the contents of this flask to become considerably heated; when all evolution of gas-bubbles has completely ceased the wax stopper on *a* is to be slighly opened and the suction applied to *d* until the air tastes no longer of carbonic acid. The apparatus, when cool, is replaced upon the balance; and the former equilibrium restored by adding weights to the apparatus. The sum of these weights expresses at once the amount of carbonic acid originally present in the analysed compound. The results are very accurate.

bb. Carbonates, the bases of which form insoluble salts with sulphuric acid.

In this case, the method *aa.* is not quite applicable, since the insoluble sulphate formed (gypsum, for instance,) will partially protect the not yet decomposed portion of the carbonate from decomposition. The construction of the apparatus is therefore modified as illustrated by Plate XXXV.

PLATE XXXV.



It will be seen from this engraving that the modification consists simply in the tube *a* being expanded at the upper end, into a tubulated bulb, and drawn out to a fine point at the lower end.

The process is conducted as follows:

The carbonate under examination is introduced into A, which is filled to about one third or one half with water. A certain amount of dilute nitric acid, more than sufficient for the decomposition of the carbonate, is introduced into the tube *a*, and prevented from flowing through the narrow aperture of this tube by a little wax stopper (*b*). The point of this tube must not dip into the water in A, but simply reach to its surface. The apparatus, when thus fully prepared, is placed in equilibrium upon the balance, and the tube *a* is then carefully and cautiously depressed, (by turning,) so that its point nearly touches the bottom of A. The wax-stopper *b* is then slightly and momentarily raised, so as to permit a small quantity of nitric acid to flow out of the tube *a*; and the same operation is repeated until the carbonate is completely decomposed. A is then placed in hot water, the little wax-stopper is partly removed, and suction applied to the tube *d*, until the air tastes no longer of carbonic acid. The diminution of the weight which the apparatus has undergone in this process, is ascertained when the apparatus has completely cooled.

§ 106.

β. SILICIC ACID.

1. Determination.

Silicic acid is invariably weighed in its insoluble state into which the soluble modification is converted by evaporation and subsequent ignition. In cases where we have to operate upon free silicic acid in aqueous or acid solution, this is to be evaporated to d yness, and the residue ignited and weighed.

II. SEPARATION OF SILICIC ACID FROM THE BASES.

a. Compounds which are soluble in water.

The solution is mixed with hydrochloric acid in excess, and the mixture evaporated to dryness in the water-bath ; the residue is heated in the air-bath, or sand-bath, with stirring, until all moisture is *completely* and *absolutely* expelled ; the dry residue is digested with hydrochloric acid, water added, a gentle heat applied, and the fluid filtered off from the silicic acid. The acid is washed with hot water, *carefully* and *thoroughly* dried and ignited. Properties of the residue, vide § 67, 9. This method yields accurate results. For the methods of determining the bases which we have as chlorides in the filtrate, I refer to the first part of this section.

b. Compounds which are decomposed by hydrochloric acid or nitric acid.

The compound under examination is very finely levigated, and dried at 212° (taking care not to raise the temperature higher). The powder is introduced into a platinum dish, or of genuine porcelain, and drenched with strong hydrochloric acid, or (in cases where the substance under examination contains lead or silver) with strong nitric acid. This mixture is digested at a very gentle heat, until the substance under examination is completely decomposed. To ascertain whether this point has been attained, the mixture is to be stirred from time to time with a glass rod, rounded and smooth at the lower end : the process may be considered at an end, when the stirring ceases to cause the slightest grating or crepitating noise, the glass rod moving smoothly along the sides, and over the bottom of the dish.

The various compounds of silica manifest some difference of deportment in this process; some of them, for instance, form a bulky gelatinous mass, whilst the silica of others separates as a light, pulverulent precipitate. Again, many of them are decomposed very readily, whilst others require long-protracted digestion at a high temperature.

When the decomposition is completed, the whole mixture is to be evaporated to dryness in the water-bath, and the residue heated until all moisture is completely and absolutely expelled; the dry residue is then again digested with hydrochloric acid, or nitric acid, until the base, or bases, which it contains are completely dissolved out. The further process is conducted exactly as directed sub. II. *a.*

c. Compounds which are not decomposed by hydrochloric acid or nitric acid.

α. Compounds of this kind are fluxed with carbonate of soda, hydrate of barytes, or carbonate of barytes, according to the nature of the bases with which the silicic acid may happen to be combined, (vide § 20, *b.*) They are then dissolved in hydrochloric acid or in nitric acid, and the solution is treated as directed sub. II. *b.*

β. The compound to be analysed is very finely levigated and elutriated, and one part of the powder obtained by these operations is mixed with about five parts of pure, finely powdered, fluor spar, in a platinum dish or in a capacious platinum crucible. The mixture is moistened with pure concentrated sulphuric acid, and stirred into an uniform paste with a small piece of platinum wire, which is then wiped clean against some powdered fluor spar, and the latter likewise projected into the dish or crucible. A gentle heat is then applied; fluoride of silic~~a~~on and hydro~~ch~~fluoric acid escape. The heat is finally increased to gentle redness, so as to expel the sulphuric acid completely. The residue, which is now perfectly free from silicic acid, is digested for some time with concentrated hydrochloric acid; the mixture is then diluted with water, and the fluid filtered off from the gypsum, the greatest part of which remains undissolved; the bases are finally determined according to the methods which will be found in the fifth section. This method should be pursued only in cases where we wish to determine the alkalies in compounds of which the other constituents have been determined already according to II. *c. α*. Pure fuming hydrofluoric acid is also applied very advantageously for the resolution of insoluble silicates, but as this method requires the possession of a small distilling apparatus of platinum, I will content myself with simply alluding to it. Brunner's lead apparatus for resolving insoluble silicates by means of hydrofluoric gas, is less expensive and greatly to be recommended to analytical chemists. (Vide POGGENDORFF's Annalen, xliv. p. 134.)

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID (SULPHURETTED HYDROGEN.)

§ 107.

1. HYDROCHLORIC ACID.

I. DETERMINATION.

a. Hydrochloric acid is almost invariably determined as chloride of silver. Solution of nitrate of silver containing a small amount of free nitric acid in admixture, is added in excess to the solution of the chloride under examination; the supernatant fluid is carefully decanted from off the precipitated chloride of silver, which is then washed, dried, and ignited. For the details of this method, we refer to § 86. The solution of the chloride should not be heated until the solution of nitrate of silver has been added to it.

The process of determining hydrochloric acid by means of silver is more readily executed than that of determining silver by means of hydrochloric acid, since, in the former, the chloride of silver will immediately and completely subside, upon agitating the vessel, as soon as the nitrate of silver begins to be present in excess, and the supernatant fluid will become perfectly clear after standing for a short time on a warm spot.

b. If we have hydrochloric acid alone in aqueous solution, it is simply necessary to mix a weighed amount of the fluid with ammonia in excess, to evaporate the mixture, to dry the residue in the water-bath, and to weigh the sal ammoniac. This method yields quite satisfactory results. (Compare experiment No. 10.)

II. SEPARATION OF CHLORINE FROM THE METALS.

a. Soluble metallic chlorides.

The same method as sub. I. *a.* For the method of separating the metals in the filtrate from the excess of nitrate of silver, we refer to the fifth section. Some of the metallic chlorides require certain precautionary modifications of the process; among them we have to notice more particularly perchloride of tin, and the chlorides of antimony. Were we to conduct the process exactly in the same way, we should obtain, besides chloride of silver, a precipitate consisting of a mixture of peroxide of tin with oxide of silver, or of a basic salt, (in the case of antimonial compounds). In the latter case we may readily prevent the precipitation of the basic salt by adding tartaric acid to the solution of the chloride of antimony. But when we have to deal with perchloride of tin, it is necessary to precipitate the metal with sulphuretted hydrogen; (vide § 96;) and to determine the hydrochloric acid in the filtrate, compare § 133. Great care should be taken not to heat this filtrate to the degree at which hydrochloric acid volatilizes.

b. Insoluble chlorides.

α. Chlorides soluble in nitric acid.

The chloride is dissolved in nitric acid without the application of heat, and the further process conducted as directed sub. I. *a.*

β. Chlorides which do not dissolve in nitric acid. (Chloride of lead, chloride of silver, protochloride of mercury.)

aa. Chloride of lead and chloride of silver are commonly analysed by reducing them to the metallic state by means of hydrogen gas, (vide § 86 and 87,) and determining the amount of chlorine from the diminution of weight. Chloride of silver may also be ignited in a porcelain crucible, with three parts of a mixture of carbonate of soda, and carbonate of potass, until the mass begins to enter into fusion. The mass, when cold, is treated with water, when the alkaline chlorides will be dissolved out, leaving the metallic silver behind. The solution of the alkaline chloride is to be treated as directed sub. II. *a.*

bb. Protochloride of mercury is decomposed by digestion with potass ley. The hydrochloric acid in the filtrate is determined as II. *a.* directs. The protoxide of mercury is dissolved in aqua regia and the mercury determined as directed § 89.

c. The soluble chlorides of the metals of the fourth, fifth, and sixth group, may be decomposed by sulphuretted hydrogen or hydrosulphuret of ammonia. The hydrochloric acid in the filtrate is determined as § 133 directs. This method is rarely applied.

d. In some metallic chlorides (for instance in those of the metals of the first and second group) the proportion of chlorine may be determined by evaporating with sulphuric acid, and then converting the base into a sulphate: this sulphate is subsequently ignited and weighed, and the proportion of chlorine inferred from the loss of weight. This method is inapplicable to chlorides of silver and of lead, which are decomposed by sulphuric acid imperfectly and with difficulty, and likewise to protochloride of mercury, perchloride of mercury, and perchloride of tin, which are altogether or nearly undecomposable by sulphuric acid.

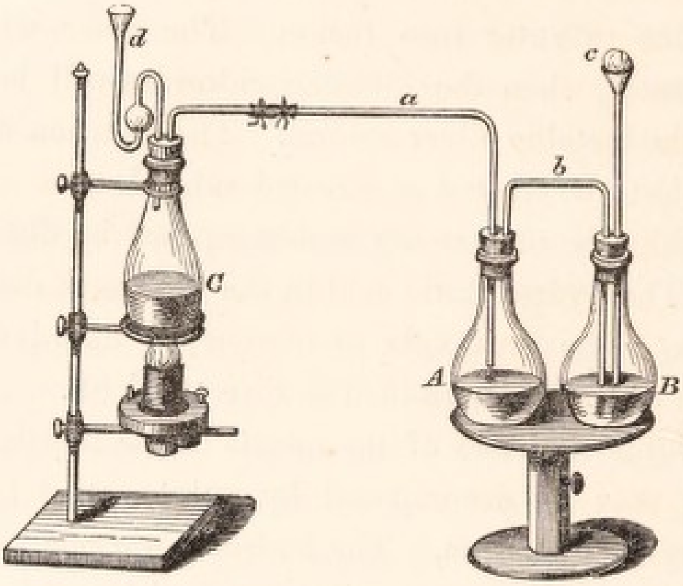
Determination of chlorine in a free state.

If we have the chloride in aqueous solution, this solution is to be mixed with ammonia in excess. Nitrogen gas escapes, and the solution contains chloride of ammonium, in which the chlorine is determined as directed.

$$(3\,Cl + 4\,NH_3 = N + 3\,[NH_4\,Cl.])$$

When the chlorine is evolved as gas, this is transmitted through dilute solution of ammonia, and the rest of the process conducted in the manner just now described. The apparatus illustrated by engraving XXXVI. is most appropriately adapted for the evolution of the chlorine and its absorption by ammonia.

PLATE XXXVI.



This apparatus scarcely requires any explanation. The chlorine is evolved in C. A and B contain ammonia; (the quantity of ammonia in A should be more than sufficient by itself to absorb all the chlorine that is likely to be evolved). The flask A is connected with C by means of the tube *a*, the lower end of which does not even reach quite to the surface of the ammonia. The tube *b* conducts the chlorine which may escape absorption in A, into B, and should the chlorine not be retained completely even in B, the last traces of it will be absorbed in the funnel tube *c*; the lower end of this tube is cut obliquely, and is made to reach the surface of the ammonia in B, so as hardly to enter into it; the funnel of this tube contains some loose cotton, which is kept moistened with ammonia. Towards the conclusion of the operation, the last traces of chlorine are expelled, by pouring a solution of bicarbonate of potass into C, through the funnel tube *d*, (which, during the process, was filled with solution of common salt). Several other methods of determining free chlorine will be found § 137. The latter methods must be had recourse to in all cases where hydrochloric acid exists in combination with chlorine.

§ 108.

2. HYDROBROMIC ACID.

I. Determination.

Free hydrobromic acid in solution is precipitated with solution of nitrate of silver, and the further process conducted exactly as directed § 107, for the estimation of chlorine (as chloride of silver). Properties of the bromide of silver, vide § 68, 2. The results are perfectly accurate.

II. Separation of bromine from the bases.

The metallic bromides are analysed exactly like the corresponding metallic chlorides. (§ 107.) In the decomposition of bromides by sulphuric acid, porcelain crucibles ought to be substituted for platinum vessels, since the latter would be affected by the liberated bromine.

Determination of free bromine.

If we have the bromine in aqueous solution, this solution is to be treated exactly as aqueous solution of free chlorine, (vide § 107, Determination of free Chlorine);—if we have bromine mixed with water, the safest way of determining the proportion of bromine, is to introduce the mixture of bromine and water into a capacious flask, to add a tolerably large quantity of water to it, and finally ammonia; the latter is best introduced into the flask through a funnel tube. The nitrogen gas which escapes, is conducted by means of a bent tube into a dilute solution of ammonia; both fluids are finally mixed, and the further operation conducted as directed § 107. This way of proceeding will effectually prevent any loss of bromine.

§ 109.

3. HYDRIODIC ACID.

I. Determination.

Hydriodic acid in solution is precipitated with nitrate of silver, and the further process conducted exactly as directed § 107, (hydrochloric acid). Properties of iodide of silver, vide § 68, 3. The results are perfectly accurate.

The following method is exclusively applied to separate hydriodic acid from hydrochloric acid and hydrobromic acid. The solution of these acids is mixed with solution of protochloride of palladium, as long as a precipitate is formed; the whole mixture is then allowed to stand at rest for twelve hours, and the fluid filtered off from the brown black precipitate, which is then washed with warm water, and dried at a temperature of from 158° to 176°; the process of drying is continued until the weight of the precipitate ceases to vary; but the temperature must not be raised beyond 176°, since this might cause a trifling loss of iodine. The drying may be greatly facilitated by washing the precipitate first with warm water, then with alcohol, and finally with a little ether. The best way, however, is to dry the precipitate in vacuo, by the side of a vessel with sulphuric acid. For the properties of the precipitate, vide § 68, 3. This method, if carefully executed, yields very accurate results.

II. SEPARATION OF IODINE FROM THE METALS.

What we have stated regarding metallic bromides, applies likewise to metallic iodides. In cases where we have to deal with iodides of the alkaline metals, containing free alkali, this alkali must first be nearly neutralized with nitric acid; solution of nitrate of silver in excess is then to be added, and finally nitric acid, until the fluid acquires a strongly acid reaction. Were we to add an excess of nitric acid in the first instance, free iodine might separate, which would subsequently not be completely converted into iodide of silver, upon the addition of the nitrate.

Many iodides, which are insoluble in water, are more advantageously decomposed by boiling in solution of caustic potass, than by solution in dilute nitric acid, since the latter process readily gives rise to the separation of iodine. This applies more particularly to the protiodides of copper, palladium, and mercury. Periodide of mercury is digested with potass to complete decomposition, (hydrated peroxide of mercury separates, whilst soluble periodide of potassium and mercury is formed); hydrosulphuret of ammonia is added, and subsequently sal ammoniac in excess, and the fluid is filtered off from the bisulphuret of mercury, which is then estimated as directed § 89. The iodine in the filtrate is determined according to § 133.

The iodine in the soluble iodides may also be precipitated as protiodide of palladium.

DETERMINATION OF FREE IODINE.

Free iodine in a moist state, or in solution, cannot be converted into iodide of ammonium, like bromine and chlorine, by mixing with ammonia, since the contact of iodide with ammonia gives rise to the formation of iodide of nitrogen, and this compound of iodine is not decomposed by ammonia in excess. We must, therefore, have recourse to the following method:—The free iodine, or the solution of iodine, is mixed with a tolerably large amount of water, and potash ley subsequently added, until the brown color of the solution has completely disappeared. The fluid is then *nearly* neutralized with dilute nitric acid, solution of nitrate of silver added in excess, and finally nitric acid, until the mixture acquires an acid reaction. The precipitate contains five parts of the iodine present, in the form of iodide of silver, and the sixth part iodate of silver. This precipitate is treated exactly as if it did consist wholly of iodide of silver. Upon ignition, the iodate is transformed into the iodide. The results fall a trifle short of theoretical calculation, since iodate of silver is not absolutely insoluble in nitric acid.

§ 110.

4. HYDROCYANIC ACID.

I. DETERMINATION.

Free hydrocyanic acid is best estimated as cyanide of silver.

The cyanides are determined either in the same manner, or the proportion of hydrocyanic acid is inferred from the products of their decomposition; (vide Organic Elementary Analysis). Solution of free hydrocyanic acid is to be tolerably diluted, and solution of nitrate of silver added in excess; the precipitated cyanide of silver is determined as directed § 86.

II. SEPARATION OF CYANOGEN FROM THE METALS.

a. Soluble metallic cyanides, (percyanide of mercury excepted).

The solution of the cyanide is mixed with solution of nitrate of silver in excess; nitric acid is added, until the reaction becomes acid, and the further operation is conducted as directed sub. I. The bases in the filtrate are determined, after the removal of the excess of nitrate of silver; vide section V.

b. Insoluble metallic cyanides, which dissolve readily in dilute nitric acid.

The cyanide is dissolved in highly dilute nitric acid, in a bottle with a ground stopper; the solution is materially promoted by agitating the bottle; nitrate of silver is added in excess, and the further process conducted, as directed sub. II. *a.*

c. Insoluble cyanides without exception.

The cyanide is ignited, and the metallic residue determined, either by direct weighing, or by solution in acid, and subsequent precipitation. The proportion of the cyanide is either inferred from the loss of weight which the analysed substance has undergone, or determined by the method of organic elementary analysis. Many of the metallic cyanides may also be decomposed by evaporation with hydrochloric acid.

d. Percyanide of mercury.

The aqueous solution of percyanide of mercury is precipitated by sulphuretted hydrogen. The cyanogen is determined in another portion of the percyanide by the method for the quantitative estimation of nitrogen described § 147.

III. ANALYSIS OF THE FERROCYANIDES AND OTHER DOUBLE CYANIDES.

a. Compounds free from alkali.

The compound under examination is intensely ignited in a porcelain crucible, small portions of nitrate of potass are projected into it, and the mass is kept in fusion for some time; when cold, it is treated with water. The oxides which remain are separated by methods which will be found described in section V. The cyanogen is determined by ignition with oxide of copper, vide section VI. (This method is inapplicable to compounds containing alkali, since the introduction of nitre into the crucible would give rise to a more or less violent deflagration.)

b. Compounds containing alkali.

The compound under examination is evaporated with concentrated sulphuric acid, fuming nitric acid, or aqua regia; (according as it is more readily decomposed by one or the other of these acids); the free acid is at last completely expelled, the residue ignited, and the further process conducted as directed sub. *a.* Compounds which are not completely decomposed by either of these acids, cobalticyanide of potassium, for instance, are either ignited in the air, and kept in this state for a very considerable time, or they are ignited in contact with oxide of copper; the latter process induces complete decomposition under all circumstances.

c. In cases where we have to deal with ferrocyanides containing a volatile metal, and which consequently lose a constituent upon ignition, this constituent is determined by dissolving another portion of the analysed substance, according to circumstances, either in hydrochloric acid or in potass, and precipitating the metal with sulphuretted hydrogen.

§ 111.

5. HYDROSULPHURIC ACID (sulphuretted hydrogen).

I. DETERMINATION.

Free sulphuretted hydrogen is best determined as SULPHURET OF ARSENIC; the sulphur in metallic sulphurets is determined either as sulphuret of arsenic, or, more frequently, as SULPHATE OF BARYTES.

a. The sulphuretted hydrogen is in aqueous solution.

The solution is mixed, in a closed flask, with an excess of solution of pure arsenious acid in hydrochloric acid; the precipitate which is formed is allowed to subside, the fluid passed through a weighed filter, and the precipitate collected upon the latter, where it is carefully washed with cold water, dried at 212°, and weighed. For properties of the precipitate, vide § 66.

In the chapter on the analysis of mineral waters will be found a method of measuring a certain definite amount of sulphuretted hydrogen water off from a large quantity.

b. The sulphuretted hydrogen is evolved in the gaseous state.

The sulphuretted hydrogen gas is conducted into a solution of arsenious acid in potass ley; after the completion of this operation, hydrochloric acid is added until the reaction becomes acid; the precipitate of sulpharsenious acid which is formed is allowed to subside, and treated as directed sub. I., *a.* The apparatus illustrated by Plate XXXVI. (vide § 107) is likewise well adapted for the evolution of sulphuretted hydrogen gas, and its absorption by arsenious acid. To expel the last traces of sulphuretted hydrogen from C, the same means are had recourse to as for the expulsion of the last trace of chlorine, (vide § 107, determination of free chlorine). In the case of sulphuretted hydrogen, however, the flask C is moderately heated before the solution of bicarbonate of potass is poured into it.

II. SEPARATION OF SULPHUR FROM THE METALS.

1. METHODS IN THE DRY WAY.

a. Sulphurets which lose no sulphur by the action of heat.

The finely levigated sulphuret under examination is mixed with three parts of anhydrous carbonate of soda, and three parts of nitrate of potass, in a porcelain crucible, by means of a rounded glass rod; the particles of the mixture adhering to the rod are carefully wiped off against some carbonate of soda, which is likewise added to the mixture. The crucible is then exposed to a gradually increased heat until its contents are in a state of fusion, in which they are kept for some time. The mass is finally allowed to cool, the residue heated with water, the solution filtered, and the sulphuric acid determined in the filtrate in the manner directed at § 100; the filtrate contains all the sulphur as alkaline sulphate. The residuary metal, metallic oxide, or carbonate, is determined, according to the circumstances of the case, either by direct weighing, or otherwise.

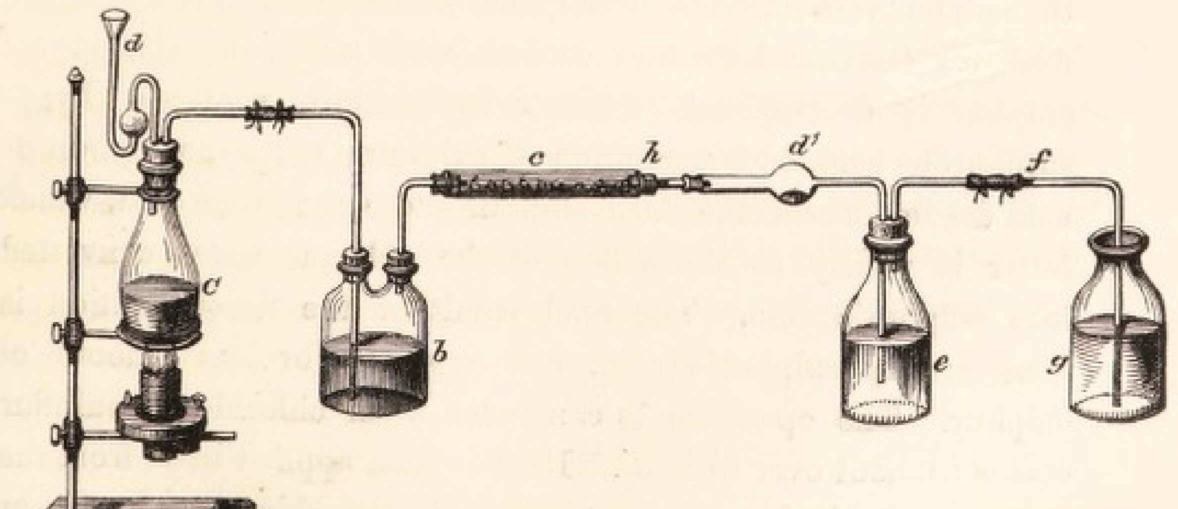
b. Sulphurets which lose sulphur by the action of heat.

The finely levigated sulphuret under examination is mixed with four parts of carbonate of soda, eight parts of nitrate of potass, and sixteen parts of pure and perfectly dry common salt, and the process conducted as directed sub. II. *a.*

c. Sulphurets, the radicals of which form fixed compounds with chlorine.

The apparatus illustrated by Plate XXXVII. is used.

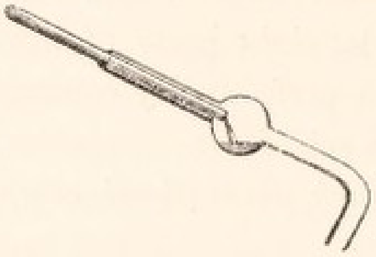
PLATE XXXVII.



C is a flask adapted for the evolution of chlorine gas, *b* contains concentrated sulphuric acid, *c* chloride of calcium; (both these substances serve to dry the evolved chlorine); *d′* is a bulbous-tube, bent at a right angle; the descending limb of this tube passing air-tight through a perforated cork, dips into the flask *e*, which is three-fourths filled with water; *f* conducts the excess of chlorine gas into the flask *g*, which is filled with milk of lime or potass ley, to prevent the operator from being inconvenienced by the smell of chlorine.

When the apparatus is prepared, the sulphuret to be examined is weighed in a narrow glass tube, closed at one end, and subsequently transferred from this tube into the bulb of *d′*, in the manner illustrated by

PLATE XXXVIII.



d′ is then connected with *c* and *e*. The process is commenced by inducing a slow and uniform evolution of chlorine. When the apparatus is completely filled with chlorine,—(which is apparent from the yellow green tint assumed by the empty part of *e*),—a very gentle heat is applied to the bulb of *d′*. The sulphuret is decomposed in this operation, the metal being transformed into chloride, and the sulphur into chloride of sulphur, which latter flows into the flask *e*. Coming here into contact with water, the chloride of sulphur is decomposed, forming hydrochloric acid and hyposulphurous acid, with separation of sulphur; the hyposulphurous acid decomposes further into sulphur and sulphurous acid, which latter is finally, by the action of the chlorine water, converted into sulphuric acid. The final result of the decomposition is consequently sulphuric acid, and a greater or less amount of sulphur. The operation is concluded when chloride of sulphur ceases to distil over from *d′*. Heat is then applied to *d′* from the bulb towards the bend, so as to force all the chloride of sulphur which may remain in this part to pass over into *e*. After allowing the apparatus to stand at rest for some time, the tube *d′* is divided under the bend, and the separated end thrown into *e*.

The flask *e* is gently heated until the free chlorine is completely expelled; it is then permitted to stand at rest until the separated sulphur (which appears as fluid at first) has solidified (this requires generally about twelve hours). The sulphur is then collected upon a tared filter, washed, dried and weighed. The rinsing water is added to the filtrate, and the sulphuric acid in the latter determined as directed § 100. By adding the proportion of the sulphur inferred from the weight of the sulphate of barytes to the amount of the separated sulphur, as ascertained by direct weighing, we obtain the total amount of the sulphur originally present in the analysed compound. The chloride remaining in the bulb *d′* is either weighed directly, (chloride of silver, chloride of lead, &c.,) or, should this not be admissible, (as in the case with copper, for instance, which remains partly as sub-chloride and partly as chloride,) is dissolved in water, aqua regia, or any other appropriate solvent, and the metal determined as directed in the first part of this section.

When we have chloride of silver or chloride of lead to deal with, we weigh the tube *d′* together with its contents, and, as it is necessary to subtract from the weight found, that of the tube, we must clean the latter. If it contains chloride of silver, this may be removed by careful rinsing with water; but if it contains chloride of lead, this is to be fused together with a small portion of sulphuret of potassium and then rinsed with water.

The method *c* is not frequently pursued in the analysis of simple sulphurets, owing to its complexity; but its application is indispensable for the analysis of many compound sulphurets.

2. METHODS IN THE HUMID WAY.

*a. All solid sulphurets, with the exception of sulphuret of lead, of barium, of strontium, and of calcium.**

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* The analysis of sulphuret oflead has been given § 87, 5; the remaining

The sulphuret under examination is finely levigated, and weighed in a small glass tube, closed at one end, which is then thrown into a strong tolerably capacious flask, provided with a glass stopper, and which contains a quantity of red fuming nitric acid, (perfectly free from sulphuric acid,) more than sufficient for the decomposition of the sulphuret in the tube.

The flask is quickly and firmly closed the moment the tube has been thrown into it. The action is very violent at first; when it has relaxed in some measure, the flask is agitated; if this causes no fresh reaction, and the vapors in the flask have condensed, the stopper is removed, and, (after placing a thin glass hook into the mouth of the flask,) loosely replaced, and the flask exposed to a gentle heat.

α. THE WHOLE OF THE SULPHUR IS OXIDIZED, THE FLUID IS PERFECTLY CLEAR. The fluid is diluted with a large portion of water, and the sulphuric acid formed is determined as directed § 100. (Care should be taken to wash the precipitate carefully and *completely* with hot water.) For the methods of separating the bases in the filtrate from the excess of the salt of barytes, we refer to section V.

β. UNDISSOLVED SULPHUR IS FLOATING IN THE FLUID.

aa. No bismuth is present. Chlorate of potass is added in small portions, the mixture digested until all the sulphur is dissolved, and the further process conducted as directed sub. II. 2, *a.*, *a.*

bb. Bismuth is present. The fluid is diluted with water and filtered; the sulphur is collected upon a weighed filter, washed with dilute acetic acid, dried, and weighed. The bismuth in the filtrate is determined as § 91, 1, *c.* directs, and the sulphuric acid in the fluid filtered off from the sulphuret of bismuth, and acidified with hydrochloric acid, estimated as directed sub. II. 2, *a. a.* The amount of sulphur calculated from the sulphate of barytes

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three sulphurets may be treated in a similar manner; it is preferable, however, to decompose them in the dry way.

formed is added to the weight of the undissolved sulphur, (vide supra.)

b. Dissolved sulphurets of the alkalies and alkaline earths.

Sulphurets which contain hyposulphites or sulphates in admixture are analysed as directed § 132.

α. THE SULPHURETS DO NOT CONTAIN AN EXCESS OF SULPHUR.

aa. The sulphuret under examination is decomposed with hydrochloric acid, and the evolved gas conducted into a hydrochloric solution of arsenious acid, supersaturated with ammonia; for the subsequent operations, vide I., *b*. The base remains in the retort as chloride. To be enabled to determine this with facility, solution of carbonate of ammonia is substituted for bicarbonate of potass, in order to expel the last traces of sulphuretted hydrogen from the apparatus.

bb. The solution of the sulphuret under examination is mixed with hydrochloric solution of arsenious acid, supersaturated with ammonia; hydrochloric acid is added, and the further process conducted as directed sub. I., *b*. For the methods of separating the base from the excess of arsenious acid, we refer to section V.

β. THE SULPHURETS CONTAIN SULPHUR IN EXCESS.

The same method is pursued as sub. II., 2, *b*., *α*., *aa*., with this difference, that the sulphur which separates in the retort is collected upon a tared filter, washed, dried, weighed, and its weight added to that calculated from the sulphuret of arsenic (sulpharsenious acid) formed in the process.

THIRD GROUP.

NITRIC ACID—CHLORIC ACID.

§ 112.

1 NITRIC ACID.

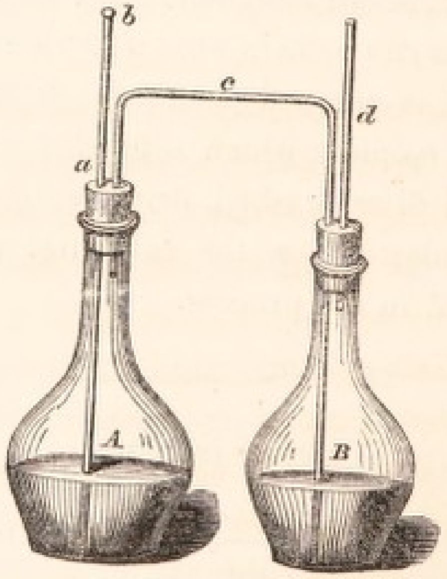
I. DETERMINATION.

Free nitric acid in solution is estimated either from the amount of barytes combining with it, or from the amount of carbonic acid expelled by its action from bicarbonate of soda.

a. The solution is mixed with water of barytes until it begins to acquire an alkaline reaction; the solution is then slowly evaporated in the air, nearly to dryness, the residue again diluted with water, and filtered; the carbonate of barytes formed by the action of the carbonic acid of the air upon the excess of water of barytes is washed, and the rinsing water added to the filtrate, in which the barytes is finally determined as directed § 74;—one equivalent of nitric acid is calculated for every equivalent of barytes. This method, if properly and carefully executed, yields very accurate results. The operator has to take care more especially to avoid adding the water of barytes greatly in excess, and to ascertain whether the evaporated fluid has completely lost its alkaline reaction before he filters it.

b. This method is executed by means of the apparatus illustrated by

PLATE XXXIX.



A portion of the fluid to be examined is weighed into the flask A; a small glass tube is filled with bicarbonate of soda or bicarbonate of potass, (this may contain chloride of sodium, sulphate, &c., in admixture, without interfering with the operation; but it must not contain the slightest trace of simple alkaline carbonate; its quantity should be more than sufficient to saturate the acid in the flask) is suspended with the flask A by means of a thread fixed in between the stopper and the neck of the flask. The apparatus is, in every other respect, arranged exactly like that described § 105.

The apparatus, when fully arranged and prepared, is equipoised upon the balance. The stopper is then slightly lifted, so as to release the thread by which the little glass tube with the bicarbonate is suspended; the operator must take care to refix the stopper air-tight as soon as the glass tube has dropped into the flask. A lively evolution of carbonic acid commences the very instant that the contents of the small glass tube come in contact with the fluid in A, and continues for some time at the same rate of briskness; it grows afterwards gradually slower, and finally ceases altogether, when the flask A is to be placed in a water-bath of from 122° to 131°. The evolution of carbonic acid recommences upon this immersion in hot water; when it has again completely ceased, the little wax stopper *b* is slightly loosened, the flask A removed from the water-bath, and suction applied to *d* (by means of a perforated cork) until the air ceases to taste of carbonic acid. The apparatus, when perfectly cool, is replaced upon the balance, and the original equilibrium restored by additional weights. The sum of the weights required to restore the original equilibrium is equal to the amount of the expelled carbonic acid. Every equivalent of nitric acid yields two equivalents of carbonic acid. ($Na\,O$, $2\,CO_2 + NO_5 = Na\,O, NO\ + 2\,Ca\,O_2$).

The results are very accurate.* That this method will equally serve to determine most other acids, and that it is applicable to the determination of free nitric acid, consequently only in cases where the solution contains no other acid besides this, must be perfectly obvious to every one. The reason which induces me to assign this general method more particularly to nitric acid is, that we posses no other simple and accurate method of determining this acid.

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* Vide New methods of Alkalimetry, &c., by Drs. C. R. Fresenius and H. Will, edited by J. Lloyd Bullock. Taylor and Walton, London.

II. SEPARATION OF NITRIC ACID FROM THE BASES.

a. Anhydrous salts.

α. The base is determined (by the appropriate method) and the proportion of nitric acid present inferred from the difference between the weight of the reduced base and that of the analysed nitrate.

β. The nitrate under examination is finely levigated and intimately mixed with from two to three parts of perfectly anhydrous borax; the mixture is introduced into a platinum crucible, and the latter weighed with its contents. A gentle heat is now applied, which is increased very gradually until the mass in the crucible is in a state of calm fusion, when it is allowed to cool, and finally weighed. The difference between the last and the first weight expresses directly the amount of nitric acid originally present in the analysed nitrate. The results are accurate. This method is inapplicable to nitrate of ammonia. (SCHAFFGOTTSCH, Poggend. Annalen, vol. lvii. p. 260.)

b. Hydrated salts.

A sample of the nitrate under examination is divided into two portions, and the base determined in the one by the appropriate method, the water and acid, (the latter from the volume of nitrogen gas); in the other portion, according to the method of organic elementary analysis, (§ 148,) expelling the air from the combustion tube by means of carbonate of lead, heated to incipient decomposition, instead of using bicarbonate of soda for this purpose, as recommended at § 148. Should the operator not possess the mercury necessary for the latter method, he may confine himself to determine the base and the water, and infer the proportion of nitric acid from the difference between the joint weight of these two constituents and the original weight of the analysed nitrate.

c. Soluble salts, the bases of which are completely precipitated by barytes or sulphuret of barium.

The solution of the nitrate under examination is mixed with water of barytes (or with sulphuret of barium) until it manifests an alkaline reaction, and the base in the precipitate determined by the appropriate method; the filtrate is evaporated to dryness, the residue extracted with water, and the solution of nitrate of barytes thus obtained, treated according to the directions given at I., *a.*, (the solution of nitrate of barytes must not manifest an alkaline reaction). Should sulphuret of barium have been used as precipitant, the extraction of the residue is to be effected according to II. *d.*, (the excess of the sulphuret of barium added, changing, upon evaporation in the air, into insoluble sulphate and hyposulphite of barytes.)

d. Nitrate of barytes, strontia, and lime.

The solution of the salt under examination is mixed with sulphuric acid in very slight excess, and, in the case of the nitrate of strontia and lime, alcohol added to render the precipitation more complete. The fluid is filtered off from the precipitate, and water of barytes dropped into the filtrate until the reaction is feebly alkaline; the mixture is then evaporated to dryness in the water-bath, and the residue heated with water, (which must not ~~lose~~ acquire the slight est alkaline reaction during the process); the resulting solution is subsequently filtered off, and the residue washed with boiling water upon the filter until the last rinsings remain perfectly clear and transparent when tested with sulphuric acid. The solution of nitrate of barytes thus obtained is finally treated according to I. *a.*

e. Soluble salts of the fifth and sixth group.

The highly dilute solution of the salts under examination is introduced into a bottle, provided with a glass stopper, and mixed with strongly saturated sulphuretted hydrogen water in very slight excess, (the exact point may be attained best by adding the sulphuretted hydrogen water in small portions, and agitating the flask after every fresh addition).

The precipitate formed is allowed to subside, the fluid filtered off from it, and the filtrate treated according to the directions of II. *d.* (The sulphuret of barium which forms upon the saturation of the filtrate with water of barytes, changes, upon evaporation in the air, into insoluble sulphate and hyposulphite of barytes.)

f. Insoluble nitrates of metallic oxides may also be decomposed by digestion with sulphuretted hydrogen water or with solution of sulphuret of barium; it is more advisable, however, to analyse them according to II. *a.* or *b.*, which are, moreover, in every respect the most appropriate of all the methods which I have described, and preferable to *c. d.* and *e.*, in all cases admitting of the choice, since the three latter methods are very circuitous, and demand the most careful performance of the several operations.

§ 113.

2. CHLORIC ACID.

I. Determination.

Chloric acid is either converted into hydrochloric acid, for the purpose of its quantitative estimation, or its proportion is determined from the loss of weight which the analysed chlorate suffers in the process of decomposition, or, finally, its amount is calculated from the volume of oxygen which it yields.

Free chloric acid in aqueous solution is determined most simply in the following manner. The solution containing the chloric acid is mixed with an aqueous solution of sulphurous acid until the mixture smells strongly of the latter, even after repeated agitation of the flask which contains it; the flask is then stoppered, and its contents are digested for some time; dilute solution of bichromate of potass is then added until the odour of sulphurous acid has completely disappeared, when nitric acid is added, and subsequently solution of nitrate of silver in excess, the further process being conducted according to § 107. The proportion of chloric acid originally present in the solution is calculated from the amount of chloride of silver obtained.

II. Separation of chloric acid from the bases.

The salt under examination is introduced into a crucible and exposed to a gentle heat, which is gradually increased to intense redness, (the crucible being covered,) and maintained thus until the weight ceases to vary. The residue contains either a metallic chloride (this is the case, for instance, with alkaline chlorates, and with chlorate of lead, chlorate of silver, &c.) or a metallic oxide, in the case of chlorate of alumina, for instance). The proportion of chloric acid originally present in the analysed compound is calculated from the loss of weight which the latter suffers in this process. If the salt under examination contains water, the ignition is to be effected in a small retort, and the escaping gases are to be transmitted through a chloride of calcium tube. The amount of oxygen evolved may be inferred from the difference in the weight of the apparatus *before* and *after* the process; but the oxygen may of course also be collected and measured over mercury.

SECTION V.

SEPARATION OF BODIES.

§ 114.

Having thus disposed of the methods which serve to determine the amount of the basis and acids, present in *simple* compounds, we come now to those methods which are applied to analyse compounds or mixtures containing several or many bases and acids, and to determine the proportional quantity of every individual base, or acid, or, in other words, which serve to effect the separation of bodies from one another.

There are two ways of determining the proportional amount of the individual constituents of complex compounds or mixtures, viz., the way of *direct* analysis, and that of *indirect* analysis.

By *direct* analysis, we understand the *actual* separation of the several individual acids, or bases present in a compound or mixture. Thus we separate potass from soda by means of bichloride of platinum, copper from bismuth by means of cyanide of potassium, arsenic from iron by means of sulphuretted hydrogen, iodine from chlorine by means of protonitrate of palladium, phosphoric acid from sulphuric acid by means of barytes, charcoal from nitrate of potass by means of water, &c. &c. The principle of the methods of direct analysis is accordingly to convert one of the two substances which it is intended to separate into an insoluble state, under circumstances which cause the solution of the other, or *vice versâ*. This mode of analysis is preferable to the *indirect* way, and is accordingly had recourse to wherever the circumstances of the case will permit.

We term an analysis *indirect*, if it does not effect the *actual* separation of the substances which we wish to determine, but causes certain changes enabling us to infer or calculate the proportional amount of the individual bases, or acids, present in the analysed compound or mixture. Thus, for instance, the respective proportional quantity of potass and soda jointly present in a compound or mixture, may be determined by converting these two bases into sulphates, weighing the latter and determining the proportion of sulphuric acid respectively contained in them ; (§ 115 ;) thus the amount of protoxide of iron existing by the side of peroxide may be determined by ascertaining the amount of gold which the former reduces from the perchloride of that metal, &c., &c.

Indirect analysis, though applicable in an exceedingly great number of cases, is generally had recourse to only to supply the deficiency of methods of *actual* separation. It is impossible to point out every *special* case in which indirect analysis may be preferable to direct analysis ; I have, accordingly, confined myself to indicate the more frequently occurring instances of this kind. For the calculations of indirect analyses, I refer to Part II. of this work. (CALCULATION OF ANALYSES.) In certain instances, however, I have deemed it more appropriate to affix the mode of calculation to the description of the method.

For the sake of greater perspicuity and simplicity, I have retained our former subdivision into groups, and, as far as possible, systematically arranged, first, the *general* separation of the substance belonging to one group from those of the preceding group or groups; secondly, the separation of *individual* substances of one group from *all* or from *individual* substances of the preceding group or groups; thirdly, and finally, the separation of substances of one and the same group, from one another. I think I need scarcely observe that the general methods which serve to separate the whole of the substance of one group from those of another group, are equally applicable to the separation of every individual substance of this group from all or from every individual substance of the other group. I beg, moreover, to remark that I do not by any means intend to assert that the *special* methods given subsequently are preferable to the *general* methods, nor that no other methods besides those which I have selected for description in this work, might not be equally advantageously applied. A wide field is left open to individual sagacity in this respect.

In the selection of methods I have been guided entirely by experience, and I have given the preference invariably to those which yield the most accurate results. In cases where two equally accurate methods presented themselves, I have either given both, or selected the more simple of the two. I have, moreover, endeavoured to point out, as far as possible, the particular circumstances under which either the one or the other of several methods deserve the preference.

The methods given in this work are generally based upon the presupposition that the base or acid to be separated exists in a free state, or in the form of a salt soluble in water. Wherever such is not the case, it is specially mentioned.

I have added in some places, for the sake of the connection, certain special analytical methods which serve for the examination of substances employed in arts, manufactures, and trades, such as potass, soda, manganese, chloride of lime, &c., although the *special part* of this work might perhaps be considered a more proper place for their description.

I. SEPARATION OF BASES FROM ONE ANOTHER.

FIRST GROUP.

POTASS—SODA—AMMONIA.

§ 115.

1. SODA FROM POTASS.

a. Direct analysis (by means of bichloride of platinum.)

Of all the methods proposed to effect the actual separation of soda from potass, there is but one that yields accurate results, viz. the separation of the potass by means of bichloride of platinum. This method is based upon the insolubility of the potassio-chloride of platinum in spirits of wine, and the perfect solubility of sodio chloride of platinum in this menstruum.

The application of this method presupposes as an indispensable condition that both alkalies be present in the state of chlorides. Should this, therefore, not be already the case, it is necessary, in the first place, to convert them into chlorides. Simple evaporation with an excess of hydrochloric acid suffices, in most cases, to effect this conversion. But if phosphoric acid, sulphuric acid, and boracic acid are present, this process fails to attain the desired end, and the method described §§ 100, 101, 102, must be resorted to.

The mixed chloride of sodium and potassium is accurately weighed, (§§ 71, 72,) dissolved in a little water, and aqueous solution of bichloride of platinum added in excess; the mixture is then evaporated nearly to dryness, in the water-bath, and the residue treated with spirits of wine of from 76 to 80 per cent. After the lapse of several hours, the solution of the sodio-chloride of platinum is filtered off from the undissolved potassio-chloride of platinum (§ 71). (If the filtrate appear of a deep yellow colour, this may be considered a sure sign that a sufficient amount of bichloride of platinum has been used in the process.) The potassio-chloride of platinum is washed upon the filter with spirits of wine, dried at 212° and weighed The proportion of chloride of potassium present in the potassio-chloride of platinum is found by simple calculation; by subtracting the resulting figure from the total weight of the analysed chloride, we find the proportion in which the chloride of sodium was originally present in the latter. Should it, however, be desirable to determine the proportion of the soda in a *direct* way, the filtrate is to be treated according to § 128.

b. Indirect analysis.

Both alkalies are converted into neutral sulphates (§§ 71 and 72,) and weighed in this form; the proportion of sulphuric acid contained in them is determined according to the directions given at § 100, and the respective quantities of soda and potass calculated from these data. (Vide infra, CALCULATION OF ANALYSES.)

2. AMMONIA FROM SODA AND POTASS.

a. The salts of the alkalies which it is intended to separate, contain the same acid, and this a volatile one, and admit of being freed from water, by drying at 212°, without losing ammonia. (Such, for instance, are the alkaline chlorides.)

The total amount of the mixed salts to be analysed is weighed in a platinum crucible, and a gentle heat applied, which is finally increased to faint redness, and maintained for some time at this point. The loss of weight which the analysed compound undergoes in this process, indicates the amount of the ammoniacal salt originally present in it. Should sulphuric acid be the acid present, the operator must be particularly careful to increase the heat very gradually, since, otherwise, some loss might be incurred by the decrepitation of the sulphate of ammonia; and has, moreover, to bear in mind, that part of the sulphuric acid of the sulphate of ammonia remains in combination with the sulphates of the fixed alkalies, and that the latter must therefore be converted first into neutral sulphates (by ignition in an atmosphere of carbonate of ammonia) before their weight can be determined. (Compare §§ 71, 72.)

This method is also applicable in certain cases where the ammonia exists in combination with a different acid from that combined with the fixed alkalies; thus, for instance, chloride of ammonium or carbonate of ammonia may be most accurately separated in this manner from the sulphates of soda and potass.

b. One or the other of the conditions given at a., is not fulfilled.

Should it be impossible to remedy this by simple means, the mixed compound is to be divided into two portions, the fixed alkalies being subsequently determined in the one, and the ammonia in the other portion. The portion intended for the determination of the soda and potass, is ignited until the ammonia is completely expelled, and the residue treated according to § 115, 1. The ammonia is determined in the other portion as directed § 73, 2, β.

c. The compound under examination contains soda and ammonia, but no potass.

The separation may in such cases be effected also in the same manner as that of soda from potass, by means of bichloride of platinum; (vide § 115. 1. *a.*)

SECOND GROUP.

BARYTES—STRONTIA—LIME—MAGNESIA.

I. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 116.

The application of *one* precipitant is not sufficient to effect the separation of the whole of the alkaline earths from the alkalies; two precipitants are necessary for this purpose. By "*alkalies*," we understand here exclusively potass and soda; should ammonia be present, this is first to be removed by ignition, in the manner described at § 115, 2, *a*.

a. Separation of the whole of the alkaline earths from potass and soda.

The solution of the compound under examination is mixed with chloride of ammonium, and subsequently with an excess of carbonate of ammonia, containing an admixture of caustic ammonia; a gentle heat is then applied, the fluid subsequently filtered off from the precipitate, and the latter thoroughly washed. (§§ 74, 75, 76).

The *precipitate* contains the *barytes*, *strontia*, and *lime*, in the form of carbonates. The *filtrate* is evaporated to dryness, and the residue ignited, to remove the ammoniacal salts. The ignited residue is then extracted with water, (which generally leaves a trifling amount of magnesia undissolved); water of barytes is added in excess, (without previous filtration,) and the mixture heated to boiling, and filtered hot.

The *precipitate* contains the *magnesia* as hydrated oxide; this is finally determined as directed at § 77, 1, *b*. The *filtrate* contains *potass* and *soda*, in conjunction with the excess of barytes used in the process; the latter substance is precipitated with carbonate of ammonia, containing an admixture of caustic ammonia; the fluid is filtered off from the precipitated carbonate of barytes, and evaporated; the alkalies are finally, if necessary, converted into chlorides, (by evaporation with hydrochloric acid,) and weighed in this form. (§§ 71, 72).

For the degree of precision attainable by this method of separating magnesia from the alkalies, I refer to the direct experiment, No. 64.

b. Separation of individual alkaline earths from potass and soda.

1. BARYTES FROM POTASS AND SODA.

The barytes is precipitated by means of dilute sulphuric acid, (§ 74, 1, *a.*) ; the filtrate is evaporated to dryness, and the residue ignited, in conjunction with carbonate of ammonia, (§ 71, 1, § 72, 1). A sufficient amount of sulphuric acid should be added, to convert the alkalies likewise completely into sulphates.

This method is preferable to that described at *a.*, in cases where we have to separate the barytes singly from *either* of the two fixed alkalies, since it yields more accurate results ; in cases, however, where the barytes is to be separated from *both* potass and soda at the same time, the former method is more convenient, since it furnishes the alkalies in the form of chlorides.

2. STRONTIA FROM POTASS AND SODA.

Strontia may, like barytes, be separated from the fixed alkalies, by means of sulphuric acid. The method described at *a.* is preferable, however, in all cases where the choice is permitted. Compare § 75.

3. LIME FROM POTASS AND SODA.

The lime is precipitated with oxalate of ammonia, (§ 76, 2, *b. a.*) the filtrate is evaporated to dryness, and the alkalies determined in the ignited residue. The results are more accurate still than those attained by the application of the method given at *a.*

4. MAGNESIA FROM POTASS AND SODA.

The method which I am about to describe, requires that the bases be present in the form of chlorides.

The concentrated solution of the chlorides under examination, is mixed with finely levigated peroxide of mercury in excess ; the mixture is evaporated, the residue ignited, and the magnesia which is formed in this process, finally separated from the alkaline chlorides, by means of hot water. (§ 77, 3, *b.*) (BERZELIUS.) The results are very accurate.

II. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM ONE ANOTHER.

§ 117.

1. BARYTES FROM STRONTIA.

The neutral or feebly acid solution of the compound under examination, is mixed with *hydrofluosilicic acid* in excess; the mixture is kept standing at rest for twelve hours, and the fluid subsequently passed through a weighed filter, upon which the precipitated *silicofluoride of barium* is to be collected and washed, until the water which runs off ceases to manifest the slightest acid reaction; the precipitate is then finally dried at 212°. For the properties of silicofluoride of barium, vide § 45.

The filtrate is concentrated by evaporation, and the strontia precipitated from it in the form of *sulphate of strontia*. (§ 75, 1, *a.*) The results are pretty accurate. (Compare experiment No. 65.) All other methods that have been recommended to effect the separation of strontia from barytes, are greatly inferior in accuracy to this method. The separation of the chlorides of barium and strontium,* by means of absolute alcohol, yields likewise very indifferent results. (Compare experiment No. 66.)

2. BARYTES FROM LIME.

a. Barytes and lime may be separated in the form of chloride, by means of *absolute alcohol*, in the same manner as the chlorides of barium and strontium. (Vide experiment No. 66.) This method, though yielding somewhat more accurate results than when applied to effect the separation of strontia from barytes, is nevertheless still inferior in point of precision to the method described at *b*. Should its application, notwithstanding, be resorted to, the operator must take care to moisten the mixed chlorides with a few drops of hydrochloric acid, previously to the addition of the alcohol; the lime in the filtrate is precipitated best by means of sulphuric acid. (§ 76, 1, *a.*)

b. The solution of the compound under examination is acidulated with hydrochloric acid, should it no already contain freacid; it is then mixed with *highly dilute* sulphuric acid, (1 part of acid to 300 parts of water,) until the formation of a precipitate ceases; the precipitated *sulphate of barytes* is filtered and determined according to § 74, 1, *a*. The filtrate is concentrated by evaporation, the free acid in it neutralized with ammonia, and the lime finally precipitated in the form of *oxalate of lime*. (§ 76, 2, *b*, *α*.) This method is based simply upon the circumstance that sulphuric acid diluted with 300 parts of water, does not precipitate salts of lime, whilst, on the other hand, it precipitates salts of barytes. The results are accurate.

3. STRONTIA FROM LIME.

The mixed nitrates of strontia and lime are extracted with *absolute alcohol*. The process is conducted in the manner described at experiment No. 66, (separation of strontia from barytes); the undissolved *nitrate of barytes* is collected upon a weighed filter, subsequently dissolved in water, and determined as sulphate of strontia. (§ 75, 1.) The lime is precipitated from the alcoholic solution in the form of *sulphate of lime*. The results are pretty accurate.

4. BARYTES, STRONTIA, LIME, AND MAGNESIA, FROM ONE ANOTHER.

Sal ammoniac is added to the solution of the compound under examination, and the barytes, strontia, and lime, are subsequently precipitated with *carbonate of ammonia*, (§§ 74, 76); the magnesia in the filtrate is precipitated with *phosphate of soda*. (§ 77, 2.)

The precipitated carbonates are converted into chlorides, and the barytes is separated from the strontia and lime, by means of hydrofluosilicic acid. The filtrate is concentrated by evaporation, sulphuric acid added in excess, and subsequently alcohol; the fluid is filtered off from the precipitate of mixed sulphate of strontia and lime, and these two salts are then converted into carbonates, according to § 100, 2, *b*. *α*.; the carbonates are subsequently converted into nitrates, and the latter finally separated as directed at 3.

5. Barytes and strontia from magnesia.

Barytes may also be separated from magnesia by precipitating first the barytes with *sulphuric acid*, (§ 74, 1, *a*.); and subsequently the magnesia in the filtrate with *phosphate of soda* and *ammonia*. (§ 77, 2.) This method yields more accurate results than that described at 4. The separation of strontia from magnesia may likewise be effected in the same manner; this method, moreover, is not preferable to that given at 4.

6. Lime from magnesia.

a. The ammoniacal solution of the compound under examination is mixed with chloride of ammonium, and the lime subsequently precipitated with *oxalate of ammonia*. (§ 76, 2, *b*.) The magnesia in the filtrate is finally precipitated with phosphate of soda. (§ 77, 2.) The results are more accurate than those attainable by the method described at 4.

b. In cases where the lime and magnesia which it is intended to separate exist in combination with phosphoric acid, the solution is acidified with acetic acid, and the lime precipitated in the form of *oxalate of lime*, (§ 76, 2, *b*. *β*.); the magnesia in the filtrate is precipitated as *basic phosphate of magnesia and ammonia*. (§ 77, 2.)

c. Magnesia and lime, when in the state of sulphates, may be separated also in the following manner:—The mixed sulphate of lime and magnesia under examination, is gently ignited, and subsequently weighed; the residue is then digested with a perfectly saturated *solution of gypsum*; the *sulphate of lime*, which of course is absolutely insoluble in this menstruum, is subsequently filtered off, collected upon the filter, and washed with solution of gypsum, until every trace of sulphate of magnesia is removed from the insoluble residue. The moist filter is then placed upon a thick layer of blotting-paper, to remove the fluid as completely as possible; and after this the sulphate of lime is dried, ignited, and weighed. The amount of *sulphate of magnesia* originally present in the analysed compound is ascertained, simply by subtracting the weight of the sulphate of lime from the total weight of the original compound. This method yields pretty accurate results; that obtained for the lime is, however, always a trifle too high, at the expense of the magnesia, since it is impossible to free the sulphate of lime entirely from the solution of gypsum used in the process.

THIRD GROUP.

Alumina ~~STRONTIA~~—OXIDE OF CHROMIUM.

I. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALIES.

§ 118.

a. Alumina and oxide of chromium are separated from AMMONIA by ignition; the process is conducted according to the directions given at § 115, 2. (Separation of ammonia from soda and potass.)

b. The separation of POTASS and SODA from oxide of chromium and alumina, is equally simple. The compound under examination is mixed with a certain amount of sal ammoniac, and *ammonia* added to alkaline reaction; the mixture is then heated, and finally filtered. The precipitate contains the oxide of chromium and the alumina in the form of hydrates. (§ 78, *a.*, and § 79, *a.*)

The filtrate which contains the alkalies is evaporated to dryness, and the residue ignited; every trace of ammoniacal salt present is removed in this manner.

II. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALINE EARTHS.

§ 119.

We have no method of separating oxide of chromium and alumina simultaneously from the alkaline earths; the precipitation of the former two substances may indeed be effected by ammonia in presence of sal ammoniac; but the oxide of chromium combines invariably with small portions of the alkaline earth, at the moment of its precipitation, and the results are therefore too high. We must therefore proceed first to the separation of the alumina from the alkaline earths, and secondly, to the separation of the oxide of chromium from the latter substances.

A. Separation of alumina from the alkaline earths.

a. Separation of alumina from the whole of the alkaline earths.

The solution of the compound under examination is mixed with chloride of ammonium, and pure *ammonia* (free from carbonic acid) added, until it begins to predominate slightly; heat is then applied, and the fluid subsequently filtered off from the precipitate formed, (the funnel must be kept covered carefully with a glass plate, during filtration, to prevent the access of the carbonic acid of the air);—the precipitate is collected upon the filter, and quickly washed with hot water. The filtrate contains the whole of the barytes, strontia, and lime, together with the greater part of the magnesia, the remainder being combined with the precipitated hydrate of alumina. The precipitate is dissolved in dilute hydrochloric acid; and pure *potass ley* added, until the precipitate of hydrate of alumina, which forms at first upon the addition of the potass ley, is completely redissolved; the solution is now heated, and subsequently filtered hot from the precipitated hydrate of magnesia, which is then thoroughly washed with hot water, and subsequently dissolved in some hydrochloric acid; the solution is added to the first filtrate, which contains already the greater part of the magnesia, and likewise the whole of the barytes, strontia, and lime. The alkaline earths are finally separated from one another according to the directions given at § 117. The alumina is precipitated from the potass solution, by strongly acidifying the latter with hydrochloric acid, and adding finally ammonia. (§ 78, *a.*)

b. Separation of individual alkaline earths from alumina.

1. Barytes and strontia from alumina.

The barytes and strontia are precipitated with *sulphuric acid;* (§§ 74, 75;) the alumina in the filtrate is precipitated with ammonia, having previously added sal ammoniac to the filtrate. (§ 78, *a.*) This method is preferable to that given at *a*, for the separation of barytes from alumina, but not for that of strontia from the latter substance.

2. Lime from alumina.

Ammonia is added to the solution of the compound under examination until a permanent precipitate begins to form, which is redissolved by the addition of acetic acid; some acetate of ammonia is now added, and finally oxalate of ammonia in slight excess. (§ 76, 2, *b*, *β.*) The fluid is filtered off from the precipitated oxalate of lime, and the alumina in the filtrate precipitated with ammonia, after the addition of sal ammoniac (§ 78, *a.*)

3. Magnesia from alumina.

Bicarbonate of potass is added to the solution of the compound under examination as long as a precipitate continues to form; (this process should be conducted in a tall flask, to avoid loss by spirting.) The fluid is then filtered off from the precipitate, which consists of hydrate of alumina mixed with potass. The filtrate contains the whole of the magnesia. The precipitate is dissolved in hydrochloric acid, sal ammoniac added to the solution, and the alumina finally precipitated with ammonia. (§ 78, *a.*) The magnesia in the filtrate is precipitated as *basic phosphate of magnesia and ammonia.* (§ 77, 2.) The results are accurate.

This method may be applied also to effect the joint separation of lime and magnesia from alumina; in this case, however, the results are accurate only when the amount of lime present is inconsiderable; since, if a large amount of lime be present, a small portion of bicarbonate of lime will invariably precipitate in conjunction with the hydrate of alumina, (owing to the difficult solubility of bicarbonate of lime in water.) To effect the joint separation of lime and magnesia from ammonia, by means of bicarbonate of potass, it is necessary to dilute the solution considerably before the addition of this reagent.

B. SEPARATION OF OXIDE OF CHROMIUM FROM THE ALKALINE EARTHS.

The most appropriate method of separating the oxide of chromium from the whole of the alkaline earths, is to convert the oxide of chromium into chromic acid. To effect this conversion the finely levigated substance is mixed with two parts of pure *carbonate of soda* and two and a half parts of *nitrate of potass;* the mixture is introduced into a porcelain crucible and heated to fusion. The fused mass is extracted with hot water; the chromium dissolved in the form of an alkaline chromate, and is finally determined according to the directions given at § 99. The residue contains the alkaline earths in the form of carbonates, or in the caustic state (magnesia).

I need hardly mention here that BARYTES and STRONTIA may also be separated from oxide of chromium by means of *sulphuric acid.*

III. SEPARATION OF OXIDE OF CHROMIUM FROM ALUMINA.

§ 120.

The known method of separating alumina from oxide of chromium by protracted boiling of the potass solution of these two substances, (upon which the oxide of chromium precipitates a hydrate, whilst the alumina remains in solution,) yields very indifferent results, since the precipitated hydrate of oxide of chromium contains invariably an admixture of alumina. The separation of oxide of chromium from alumina is effected most completely by the method described at 119, B. (separation of oxide of chromium from the alkaline earths). The residuary alumina which remains upon extracting the fused mass with water, contains alkali; to free it from this admixture it is to be dissolved in hydrochloric acid, sal ammoniac added to the solution, and the alumina finally precipitated with ammonia. (§ 78, *a.*)

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—PEROXIDE OF IRON.

I. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THE ALKALIES.

§ 121.

A. FROM AMMONIA.

The same method is applied which serves to separate oxide of chromium and alumina from ammonia. (§ 118, *a.*) Should this method be inapplicable, in the case of *chloride of iron and ammonium* for instance, the solution is to be divided into two portions, and the metal determined in the one, the ammonia in the other portion, (the latter according to § 73, 2).

B. FROM POTASS AND SODA.

a. Separation of the whole of the oxides of the fourth group from potass and soda.

The solution is mixed with ammonia till neutral, and subsequently with pure colorless hydro-sulphuret of ammonia. The precipitated metallic sulphurets are filtered off from the fluid which contains the alkalies in solution. The filtrate is evaporated and the residue ignited, to remove the ammoniacal salts. The remaining alkalies are finally separated as directed § 115.

b. Separation of individual oxides of the fourth group from potass and soda.

1. OXIDE OF ZINC FROM POTASS AND SODA.

If the bases are combined with acetic acid, and no other acid is present, the zinc may be precipitated from the acid solution as *sulphuret of zinc,* and may thus be separated from the alkalies. (§ 80.)

2. PROTOXIDE OF NICKEL AND PROTOXIDE OF COBALT FROM POTASS AND SODA.

The bases are converted into chlorides, the solution is evaporated to dryness, the residue introduced into a bulbous tube, and heated in a stream of dry hydrogen gas. The chlorides of nickel and cobalt are reduced to the metallic state by this process, whilst the chlorides of the alkalies remain unaltered. The residuary mass is subsequently acted upon by water, when the alkaline chlorides dissolve, leaving the undissolved metals behind.

3. PEROXIDE OF IRON FROM POTASS AND SODA.

The solution is precipitated with ammonia, and the whole process conducted as directed § 118, *b.* (separation of alumina from the alkalies.)

II. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THE ALKALINE EARTHS.

§ 122.

a. Separation of the whole of the oxides of the fourth group from the alkaline earths.

Sal ammoniac is added to the solution, (and ammonia likewise if the solution is acid); the oxides are then precipitated with pure hydrosulphuret of ammonia. The alkaline earths in the filtrate are separated from one another, as directed § 117. Whilst filtering the fluid from off the precipitated sulphurets, the air must be carefully excluded.

b. Separation of the whole of the oxides of the fourth group, or of individual oxides of this group, from the alkaline earths, both collectively and individually.

1. BARYTES AND STRONTIA FROM THE WHOLE OF THE OXIDES OF THE FOURTH GROUP.

Barytes and strontia are precipitated from the acid solution by means of sulphuric acid, vide § 74, 1, and § 75, 1. (For the separation of barytes, this method is invariably preferable to that described sub. *a.*; and, in some instances, it is equally preferable for the separation of strontia.

2. LIME FROM THE WHOLE OF THE OXIDES OF THE FOURTH GROUP.

a. Sal ammoniac and tartaric acid are added to the solution, and subsequently ammonia, till the reaction becomes alkaline; the clear fluid is precipitated with oxalate of ammonia in excess. The precipitated oxalate of lime is determined as directed at § 76, 2, *b.* *a.*

b. The neutral or feebly acid solution is mixed with acetate of ammonia, and finally with oxalate of ammonia in excess. (Vide § 76, 2, *b.*, *β.*)

c. In cases where the lime is to be separated simply from zinc, nickel, and cobalt, or from small quantities of manganese, the method *a.* is pursued, with this exception, that no tartaric acid is added to the solution.

3. OXIDE OF ZINC FROM THE ALKALINE EARTHS.

This separation is accomplished in exactly the same way as that of oxide of zinc from the alkalies. (§ 121, B., *b.*, 1.)

4. IRON FROM BARYTES, STRONTIA, AND LIME.

The solution is precipitated with ammonia free from carbonic acid, and the precipitated hydrated peroxide of iron, filtered off. The filtrate contains the alkaline earths (§ 85). The access of air is to be precluded during the filtration.

5. COBALT, NICKEL, AND ZINC FROM BARYTES, STRONTIA, AND LIME.

The solution is mixed with carbonate of potass in excess, cyanide of potassium added, and a very gentle heat applied until the carbonates of cobalt, nickel, and of zinc, which precipitate at first, are redissolved; the solution of the metallic cyanides is then filtered off from the precipitated carbonates of the alkaline earths; these are dissolved in dilute hydrochloric acid, and separated from one another as directed § 117. The cyanides in the filtrate are separated according to the directions given in § 124, 6 and 7.

6. THE PROTOXIDES OF COBALT AND NICKEL FROM MAGNESIA.

The solution is precipitated with a mixture of solution of hypochlorite of potass and caustic potass. The precipitate formed, which consists of peroxide of nickel, peroxide of cobalt, and hydrated magnesia, is washed, and while still moist, digested at from 86° to 104°, with solution of perchloride of mercury in excess. In this process, a double salt is formed,

$$MgCl + 3\,HgCl,$$

and the magnesia dissolves, whilst a corresponding amount of basic perchloride of mercury precipitates. (Ullgren, Berzelius, Jahresbericht, 21, 146). The solution and the rinsing water are evaporated, with addition of pure peroxide of mercury, and the magnesia is determined as directed § 77, 3, *b*. The mercury is separated by ignition from the oxides of nickel and cobalt, and the latter are finally separated from one another, as will be found directed § 124, 6.

III. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THOSE OF THE THIRD.

§ 123.

A. FROM ALUMINA.

a. Separation of the whole of the oxides of the fourth group from alumina.

The solution is mixed with potass ley in excess, and boiled. Iron, nickel, cobalt, and manganese separate as hydrated peroxides or hydrated protoxides, whilst alumina and oxide of zinc remain in solution, (the latter, with the exception of a minute fraction, which is carried down with the precipitate). The solution is diluted and filtered, and the precipitate washed; the oxides of which it consists are separated from one another, as will be found directed § 124. The zinc in the filtrate is precipitated by means of sulphuretted hydrogen; the fluid is filtered off from the precipitated sulphuret of zinc, and the alumina in the filtrate determined as directed § 78.

b. Separation of individual oxides of the fourth group from alumina.

1. OXIDE OF ZINC FROM ALUMINA.

The separation of oxide of zinc from alumina is effected by the same means as that of oxide of zinc from the alkalies, (§ 121, B. *b*., 1), viz., by precipitating the acetic solution with sulphuretted hydrogen, (§ 80). Alumina and oxide of zinc are, in many instances, most readily brought into acetic solution, by mixing their solution in sulphuric acid with acetate of barytes in exceses.

Sulphuretted hydrogen is then conducted into the solution, without applying heat; the fluid is filtered off from the mixed precipitate of sulphuret of zinc and sulphate of barytes; this precipitate is washed, and the sulphuret of zinc dissolved out with hydrochloric acid; the zinc is finally precipitated from this solution as directed § 80. The alumina in the filtrate is determined as directed § 78, after removing previously the barytes by means of sulphuric acid.

2. COBALT, NICKEL, AND ZINC FROM ALUMINA.

The separation is effected by means of cyanide of potassium in the same manner in which cobalt, nickel, and zinc are separated from lime, barytes, and strontia, § 122, 5, with this difference, however, that no heat is to be applied in the process of separation of which we are treating at present. The alumina which separates contains alkali, and must therefore be dissolved in hydrochloric acid, and re-precipitated from this solution by means of ammonia, (§ 78).

B. FROM OXIDE OF CHROMIUM.

a. Separation of all the oxides of the fourth group from oxide of chromium.

The whole of the oxides are fused with nitrate of potass and carbonate of soda, (compare § 119, B.), the residue is boiled with water, a tolerable amount of spirits of wine added, and a gentle heat applied for the space of several hours. The solution is then filtered, and the chromium in the filtrate determined as directed § 67; the bases in the residue are separated from one another, as will be found directed § 124. The following is the theory of the process: — the oxides of zinc, cobalt, nickel, iron, and partly that of manganese, separate upon fusion with nitre and soda, whilst, on the other hand, manganate and chromate of potass are formed, (perhaps also some ferrate of potass). Upon boiling with water, the chromate of potass dissolves, together with hypermanganate of potass, the formation of the latter causing peroxide of manganese to separate in addition to the already separated oxides. Upon the addition of alcohol, combined with the application of a gentle heat, the hypermanganate of potass is decomposed, the last portion of the manganese separating as peroxide. Thus, upon filtering the mixture, we have all the chromium in the filtrate as an alkaline chromate, and in the residue we have all the metals of the fourth group.

The analysis of the natural compound of oxide of chromium with protoxide of iron, which is known as chrome-iron, requires the most careful levigation and elutriation of the mineral, and long protracted fusion with the appropriate flux. In most instances, even the strictest attention to these points will not prevent part of the mineral remaining undecomposed; whether such be the case, may be readily known from the circumstance that the residue is not completely dissolved by the action of hydrochloric acid. In such cases the weight of the undecomposed portion of the mineral is determined and subtracted from the total weight analysed.

b. Separation of individual oxides of the fourth group from oxide of chromium.

1. ZINC, MANGANESE, COBALT, AND IRON FROM OXIDE OF CHROMIUM.

The solution is mixed with tartaric acid, potass added in excess, and the perfectly clear solution precipitated with colorless sulphuret of potassium. The precipitated sulphurets of the fourth group are separated from one another, in the way described § 124. The filtrate which contains the oxide of chromium is evaporated, the residue ignited, and subsequently fused with carbonate of soda and nitrate of potass, (§ 119 *B.*); the chromium in the thus obtained alkaline chromate is determined as § 99 directs. (It is a wrong notion to suppose that ammonia fails to precipitate solutions of oxide of chromium, in presence of tartaric acid; the contrary is the case, and for this reason ammonia cannot be substituted for potass in the process described above, nor hydrosulphuret of ammonia for sulphuret of potassium.)

If the solution contains but a slight amount of nickel, this method may be advantageously resorted to; but if the solution, on the contrary, contains a large proportion of that metal, the exceedingly large amount of tartaric acid required to prevent the precipitation of the nickel by potass, renders its application far less advantageous.

2. OXIDE OF ZINC, PROTOXIDE OF NICKEL, AND PROTOXIDE OF MANGANESE, may also be separated from oxide of chromium, by means of carbonate of barytes, as will be found explained in § 124, 1, *β*. The digestion with the carbonate of barytes in excess should be continued for several hours, otherwise some chromium might remain in solution.

IV. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM ONE ANOTHER.

§ 124.

1. PEROXIDE OF IRON FROM ZINC, MANGANESE, AND NICKEL.

Of the two methods which I shall describe here, the first is to be preferred when the relative quantity of peroxide of iron present is considerable, the second when this quantity is small.

a. Separation by means of succinate of ammonia.

The acid solution is mixed with sal ammoniac, and subsequently neutralized with ammonia, so as to precipitate a very trifling portion of the peroxide of iron; solution of neutral succinate of ammonia (benzoate of ammonia will answer equally well) is then added, and the precipitated persuccinate of iron filtered off; the filtrate contains the other metals in solution. For the details of this process, vide § 85. The separation achieved by this method is complete, provided the process be properly and carefully performed.

β. Separation by means of carbonate of barytes.

This method is applicable only in cases where the metallic oxides present are combined with acids which form soluble compounds with barytes; those acids should not be present in too great excess.

The acid solution is very gently heated, (to from 86° to 104°,) and mixed with artificially produced carbonate of barytes (still moist) (vide § 37. 6) until this reagent manifestly predominates, even after protracted digestion of the mixture; (this point is marked by the cessation of disengagement of gas and its non-renewal upon addition of a fresh portion of the carbonate). The precipitate which forms is allowed to subside, the fluid is filtered off, and the precipitate carefully washed. It consists of basic carbonate of the peroxide of iron, mixed with the excess of the carbonate of barytes added; it is dissolved in dilute hydrochloric acid, the barytes precipitated with sulphuric acid, the fluid filtered off from the precipitated sulphate of barytes, and the peroxide of iron in the filtrate finally precipitated with ammonia, (§ 85). The first filtrate contains, besides the salts of manganese, nickel, &c., the newly-formed salt of barytes; the barytes here is likewise removed by means of sulphuric acid, and the remaining metals are separated from one another by methods which we shall shortly have occasion to describe. The results afforded by this method are satisfactory. The digestion heat must not be carried beyond 104°, otherwise traces of manganese, &c., may be precipitated in conjunction with the basic persalt of iron. However, we obtain always rather a little too much of the iron at the expense of the other metals, than the reverse, since there is invariably a tendency for traces of the latter to precipitate with the basic persalt of iron. Artificially prepared carbonate of lime may be substituted for the carbonate of barytes, which latter is however to be preferred in most instances, since barytes is more readily removed both from the precipitated peroxide of iron and from the filtrate, than is the case with lime.

2. PEROXIDE OF IRON FROM COBALT.

The separation is effected by means of succinate of ammonia in exactly the same manner as § 124, 1, *a*. Complete separation of these two metals is not to be attained by carbonate of lime or of barytes.

3. PEROXIDE OF IRON FROM OXIDE OF ZINC.

The acetic solution, to which free acetic acid is to be added, and which must contain no other acid, is acted upon by sulphuretted hydrogen, (compare separation of alumina from oxide of zinc, § 123, *A.*, *b.*, 1). Should the precipitated sulphuret of zinc not be of a pure white color—a sign that it contains some sulphuret of iron in admixture—the precipitated fluid is to be digested at a gentle heat until the precipitate acquires a pure white tint, and after cooling, a fresh amount of sulphuretted hydrogen is to be transmitted through it.

4. PROTOXIDE OF IRON FROM ZINC, COBALT, MANGANESE, AND NICKEL

The protoxide of iron is converted into peroxide, (§ 84), and the separation effected as directed § 124, 1.

5. PEROXIDE OF IRON FROM PROTOXIDE OF IRON.

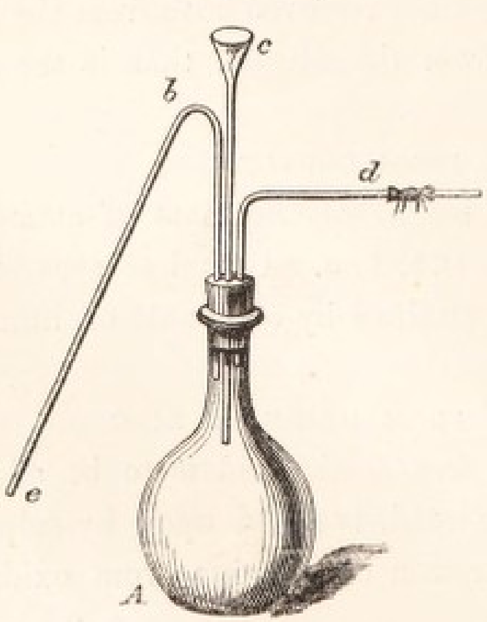
The separation of the peroxide from the protoxide of iron is a difficult task, and requires the strictest attention in the performance of the requisite process.

The proportion of these two substances may, however, be likewise determined in an *indirect* manner, and this proceeding is, in general, preferable to *direct* separation.

a. Analysis by direct separation.

This method is applicable only when both oxides exist in a form in which they are soluble by hydrochloric acid, or when we have them in a solution which contains no acids, forming insoluble salts with barytes. The apparatus illustrated by Plate XL. serves for its execution.

PLATE XL.



The finely levigated substance is introduced into the flask A, and carbonic acid gas conducted into the flask through the tube *d*. As soon as the air is completely expelled, hydrochloric acid is poured into the flask through the funnel-tube *c*, a slow stream of carbonic acid gas being maintained all the while. The action of the hydrochloric acid is assisted by the application of heat. The acid must not be added too greatly in excess. The solution obtained by this operation is diluted with boiled and still hot water, and, after cooling, pure recently precipitated carbonate of barytes, mixed with boiled water to a milky fluid, is added through the funnel tube until it predominates; the whole mixture is then digested for some time a little above the common temperature. The flask is then filled with boiled water nearly up to the end of the tube *b*, which is afterwards slowly and cautiously depressed (by turning) and immersed into the clear fluid as far as necessary. The clear fluid is then drawn off through this tube, which is subsequently raised again. The flask is once more filled with boiled water, and the fluid again drawn off through the tube *b*; the remaining contents of the flask are rinsed out with boiled water and placed upon a filter, where they are subsequently washed with boiled water, avoiding as much as possible the contact of air; the peroxide of iron in the washed precipitate is then finally determined. (Compare § 124, 1, *β*.) The whole of the dissolved protoxide of iron is contained in the liquid drawn off, and in the fluid filtered off from the precipitated peroxide. This solution is concentrated by evaporation, the protoxide is peroxidized, (§ 84,) and the peroxide of iron formed, precipitated, after previously removing the barytes, (§ 85). Should the analysed compound contain a constituent insoluble in hydrochloric acid, this is regained upon the subsequent solution in hydrochloric acid of the precipitate containing the basic persalt of iron; its weight is ascertained, and subtracted from the total weight of the analysed substance.

β. Indirect analysis.

This may be achieved in various ways; I will, however, content myself with giving the two following methods, which will be found sufficient under all circumstances. The process in both commences with the solution of the substance in hydrochloric acid, which may be effected either as directed sub. *α*., or in some other appropriate manner.

aa. The solution is effected in a weighed flask, (which we will designate *a*); the flask is then weighed with its contents, and about one-half of the latter poured into another flask (*b*), filled previously with carbonic acid, and provided with a ground-glass stopper; the quantity of the solution poured into this flask is ascertained from the loss of weight of *a*. The solution in *b* is then strongly acidified with hydrochloric acid, the flask filled nearly to the brim with boiled water, a weighed slip of clean sheet copper § 37, (16) is introduced into it, the flask stoppered, a piece of bladder tied over it, and the mixture digested in boiling water until the fluid grows colorless, or acquires a greenish hue,—a sign that the perchloride of iron is completely converted into protochloride. The slip of sheet copper is then taken out of the flask, dried and weighed. The total amount of peroxide of iron in *a* is determined after previous oxidation of the protoxide, (§ 84). The calculation is very simple. The quantity of peroxide of iron obtained in the last process, calculated upon the total amount of the solution, shows the total amount of iron operated upon. The diminution in the weight of the copper slip, calculated from the part to the whole, indicates the amount of chlorine consumed to convert the original protochloride of iron into perchloride, since every one equivalent of dissolved copper corresponds to one equivalent of chlorine; every one equivalent of chlorine converting two equivalents of protochloride of iron into perchloride, ($2\ \mathrm{Fe\ Cl} + \mathrm{Cl} = \mathrm{Fe_2\ Cl_3}$); it follows that every one 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 analysed substance. (Fuchs.) This method is not applicable in presence of arsenic acid.

bb. The solution is effected in a flask, solution of chloride of gold and sodium is added in excess, the flask stoppered, and the precipitated metallic gold allowed to subside. The fluid is filtered off from the precipitated gold, and the amount of the latter determined as directed § 93. The total amount of iron present is then determined in the filtrate, or in a fresh portion of the original solution. The calculation is very simple; the operator need only remember that one equivalent of precipitated gold corresponds to six equivalents of protochloride or protoxide of iron. ($6\,Fe\,Cl + Au\,Cl_3 = 3\,Fe_2\,Cl_3 + Au$). (H. Rose).

6. COBALT FROM NICKEL.

Although these metals may be separated from one another in various ways, yet there is but one method which affords truly accurate results, viz. separation with cyanide of potassium. We will, however, besides this, describe Phillip's method, which is very convenient, although not quite accurate in its results.

a. Separation with cyanide of potassium.—(LIEBIG.)

aa. The solution is strongly acidified with hydrochloric acid, and cyanide of potassium added, until the precipitate which forms at first is redissolved; a fresh amount of cyanide of potassium is then added, and the solution boiled for a while, adding from time to time one or two drops of hydrochloric acid, but not sufficient to render the reaction acid.

bb. The solution is then mixed with hydrochloric acid, in an obliquely-placed flask, and boiled until the odor of hydrocyanic acid ceases to be perceptible upon a fresh addition of hydrochloric acid.

cc. Potass ley in excess is now added, the mixture boiled for the space of ten minutes, and the fluid filtered off from the precipitated hydrated protoxide of nickel, (the weight of which is determined as directed § 82). The filtrate contains the whole of the cobalt as cobalticyanide of potassium.

dd. The filtrate is evaporated with an excess of nitric acid, and the residue fused for some time, and subsequently treated with hot water; the precipitated peroxide of cobalt is filtered off, washed, dissolved in hydrochloric acid, and its weight determined as directed § 83.

To understand the rationale of this process, it is necessary to bear in mind that the relative proportion which the protoxide of cobalt bears to that of nickel may be threefold, viz.

1) $Co : Ni = 2 : 3$
2) $Co : Ni = (2 + x) : 3$

$$3)\ \mathrm{Co} : \mathrm{Ni} = 2 : (3+x)$$

In *aa.* we have consequently in solution :

in case 1 (—3 (Ni Cy, K Cy)+Co_2 Cy_6, 3 K*)
in case 2 (—3 (Ni Cy, K Cy)+x (Co_2 Cy_6, 3 K)
in case 3 (—3 (Ni Cy, K Cy)+x (Ni Cy, K Cy).

} See Errata

Cobalticyanide of nickel and cobalticyanide of potassium are not decomposed by hydrochloric acid, but the double cyanide of nickel and potassium is decomposed—the cyanide of nickel precipitates, whilst its solvent, the cyanide of potassium, transposes with the hydrochloric acid into hydrocyanic acid and chloride of potassium. Cyanide of nickel, when long boiled with hydrochloric acid, undergoes finally the same decomposition. When cyanide of nickel, cobalticyanide of potassium, and hydrochloric acid, act upon one another, cobalticyanide of nickel, chloride of potassium, and hydrocyanic acid are found. (3 Ni Cy+Co_2 Cy_6, 3 K+3 Cl H=Co_2 Cy_6, 3 Ni+3 K Cl+3 Cy H.)—In *bb.* we have consequently,

in case 1, as precipitate: Co_2 Cy_6, 3 Ni—
in solution neither nickel nor cobalt, but simply K Cl; Cy H has escaped as gas.

in case 2, as precipitate likewise: Co_2 Cy_6, 3 Ni—
in solution the unaltered x (Co_2 Cy_6, 3 K) in conjunction with K Cl.

in case 3, at first as precipitate: Co_2 Cy_6, 3 Ni+x Ni Cy, (in solution neither nickel nor cobalt;)
finally, as precipitate Co_2 Cy_6, 3 Ni,—in solution Ni Cl in conjunction with K Cl.

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* That is, three equivalents of double cyanide of nickel and potassium, and one equivalent of cobalticyanide of potassium. The formation of cobalticyanide of potassium from the protocyanide of cobalt which is precipitated at the commencement of the process, and which redissolves at first as *cyanide of cobalt and potassium*, may be illustrated as follows: [2 (Co Cy, K Cy) K Cy+Cy H]=(Co_2 Cy_6, 3 K+H). It is evident from these figures, that the presence of free hydrocyanic acid, and of an excess of cyanide of potassium, is necessary for the transformation of the protocyanide of cobalt into cobalticyanide of potassium, and that hydrogen gas is liberated in this process.

Cobalticyanide of nickel, when boiled with potass, transposes with the latter into protoxide of nickel and cobalticyanide of potassium $(Co_2\,Cy_6,\ 3\,Ni + 3\,KO) = (Co_2\,Cy_6,\ 3\,K + 3\,Ni\,O)$. Cobalticyanide of potassium remains unaltered upon boiling with potass. Chloride of nickel, when boiled with potass, transposes with the latter into protoxide of nickel and chloride of potassium. In *cc.* we have therefore,

in case 1, $Co_2\,Cy_6,\ 3\,K +$ . . . . $3\,Ni\,O$
in case 2, $Co_2\,Cy_6,\ 3\,K + x\,(Co_2\,Cy_6,\ 3\,KO) +$ $3\,Ni\,O$
in case 3, $Co_2\,Cy_6,\ 3\,K +$ . . . $x\,Ni\,O$ $+ 3\,Ni\,O$

and consequently, in all three cases, cobalticyanide of potassium and protoxide of nickel.

β. Phillips' method.

The solution is mixed with sal ammoniac, and ammonia in excess added. The clear blue solution is introduced into a flask provided with a stopper; it is greatly diluted with boiled water, still hot, and potass added until the formation of a precipitate ceases, and the blue color of the fluid changes to a brownish red. The flask is then closed, the precipitate allowed to subside, and the precipitated protoxide of nickel filtered off; the cobalt is contained in the filtrate. Complete separation is not to be achieved by this method; the cobalt contains invariably traces of nickel, and the precipitated nickel frequently traces of cobalt.

7. COBALT FROM ZINC.

α. The separation of cobalt from zinc may be effected in the same manner as that of cobalt from nickel—vide 6, *α.*, operations *aa.* and *bb.*—According to the relative proportion which the zinc bears to cobalt, (compare the three cases in 6 *α.*,) we obtain at first, upon the addition of the hydrochloric acid, either simply cobalticyanide of zinc, (case 1,) as a white and insoluble precipitate, or we get, besides their precipitate, in solution cobalticyanide of potassium, (case 2,) or chloride of zinc, (case 3). However, upon continued boiling in hydrochloric acid, we obtain a clear solution, the cobalticyanide of zinc dissolving gradually in the menstruum present, (without decomposition, we may assume).

Potass ley in excess is now added, and the mixture boiled till a clear solution results, (it may be assumed that the whole of the cobalt is contained in this solution, as cobalticyanide of potassium, and the whole of the zinc as a compound of oxide of zinc with potass). The zinc is precipitated from this solution by means of sulphuretted hydrogen. The cobalt in the filtrate is determined as directed 6 *a.*, *dd.* This process is simple, and the separation complete.

β. This separation may likewise be effected in the same manner as that of zinc from iron—vide 3, (by precipitating the zinc with sulphuretted hydrogen, from acid solution in acetic acid).

γ. BERZELIUS (Jahresbericht 21, 144) recommends the following method for the absolute separation of cobalt from zinc :

The solution is precipitated with potass ley in excess, and boiled ; the precipitated hydrate of protoxide of cobalt is filtered off, and carefully washed with boiling water. The zinc in the filtrate is determined as directed § 80. The washed precipitate is dried, ignited, weighed, reduced to powder in an agate mortar, and mixed, in a porcelain crucible, with pure sugar in powder, (the sugar intended for this purpose is purified best by recrystallization from alcoholic solution). The mixed mass is slowly heated until the sugar is completely carbonized ; the porcelain crucible, covered with its lid, is then placed into a bath of magnesia, contained in a large-sized crucible of clay, and the latter exposed, for the space of one hour, to the very highest degree of heat attainable by a wind furnace. This process causes the reduction of the metals, the whole of the zinc present rises in vapor, whilst the cobalt remains mixed with charcoal. This residue is acted upon with nitric acid, the solution of cobalt obtained evaporated in the water bath, the residue ignited, and the peroxide of cobalt produced by this method finally weighed. By subtracting the weight of the peroxide of cobalt from the total weight of the original precipitate, we find the proportion of oxide of zinc which precipitated in conjunction with the peroxide of cobalt. This method is defective, inasmuch as the cobalt is weighed as peroxide. (Compare

§ 54, *b.*) This may be remedied, however, by heating a portion of the mixed oxides precipitated by the potass, to incipient redness, in a stream of hydrogen gas, (§ 83);—in this process the protoxide of cobalt alone is reduced, not the oxide of zinc;—another portion is ignited with sugar, as directed above. The peroxide of cobalt, which is finally produced, is to be weighed as metal, and not as peroxide. (§ 83.)

δ. Ullgren (Berzelius' Jahresbericht, 21, 145) recommends to precipitate the solution with carbonate of soda, in the manner described § 80, *a.* The precipitates are carefully washed with boiling water, dried, ignited, and weighed They are then finely levigated, and a weighed portion of the powder is introduced into the bulb of a bulbous tube; the bulb is then heated to incipient redness, and a slow and continuous stream of hydrogen gas transmitted through the tube. When the formation of water has completely ceased, the mass is allowed to cool, the transmission of hydrogen being continued all the while. The residuary mass contains the whole of the cobalt as metal, and the whole of the zinc as oxide. The tube is then closed by fusion at one end, filled with a concentrated solution of carbonate of ammonia, corked at the other end, and exposed for the space of twenty-four hours to a gentle heat, not exceeding from 100 to 105 degrees. The oxide of zinc dissolves completely in this process; the cobalt remains undissolved; this is repeatedly washed with solution of carbonate of ammonia, dried and weighed. The proportion of the oxide of zinc is determined by careful evaporation of the ammoniacal solution, and ignition of the residue.

8. Cobalt from manganese.

a. The acid solution is mixed with cyanide of potassium, precipitates of protocyanide of cobalt and protocyanide of manganese are formed; cyanide of potassium is then added in excess, which causes the re-solution of the protocyanide of cobalt, and of part of the protocyanide of manganese, whilst another portion of the latter remains undissolved. The fluid is filtered off, and the remaining precipitate washed. The filtrate is heated to boiling, adding from time to time a drop of hydrochloric acid, (yet not sufficient to acidify the solution,) and the manganese and cobalt which it contains in solution are separated from one another in the same manner as nickel is separated from cobalt. The first precipitate of protocyanide of manganese is dissolved in hydrochloric acid, and the solution boiled until the hydrocyanic acid is completely expelled. The solution is then precipitated with carbonate of soda, and the weight of the manganese obtained added to that of the manganese produced from the first filtrate.

β. Both metals are first converted into oxides. In solution, free from ammoniacal salts, this is effected simply by precipitation with potass. In the presence of a considerable proportion of ammoniacal salts the solution is more advantageously precipitated with sulphuret of ammonium; the washed metallic sulphurets are dissolved in aqua regia, and the solution is finally precipitated with potass. The mixed peroxides are weighed, and the whole, or a weighed portion, is introduced into the bulb of a bulbous tube; heat is applied to the bulb, and a continuous stream of hydrochloric acid gas transmitted through the tube until the oxides are completely converted into chlorides. The attainment of the desired end (which requires a long time) is indicated by the cessation of the formation of water. A strong heat is then applied to the bulb, and dry hydrogen gas transmitted over the chloride until only very faint vapours are perceptible upon approaching a glass rod moistened with ammonia to the mouth of the tube. The protochloride of cobalt is reduced to metal, in this process, whilst the protochloride of manganese remains unaltered. The contents of the tube are allowed to cool, the transmission of hydrogen being continued all the while, and the tube is finally placed into a cylinder filled with water. The greater part of the protochloride of manganese is dissolved, a smaller portion of it floats about in the fluid in the shape of brown flakes, and the cobalt subsides quickly. The fluid with the suspended brown flakes is decanted from off the cobalt, and the latter washed upon a weighed filter, first with some highly dilute hydrochloric acid, and finally with water, dried and weighed. The decanted fluid to which the rinsing water of the cobalt is added is concentrated by evaporation, adding at the same time some hydrochloric acid to it, and the manganese finally precipitated with carbonate of soda, § 81. The results are very accurate. (H. Rose.)

9. Nickel from manganese.

The separation is effected in the same manner as that of cobalt from manganese, method β.

10. Nickel from zinc.

Like cobalt from zinc, methods β. γ. and δ.

11. Manganese from zinc.

Like cobalt from zinc, method β.

12. Separation of the whole of the oxides of the fourth group from one another.

The iron is separated from the other metals as directed at 1, α. The filtrate is precipitated with ammonia and sulphuret of ammonium, and the precipitated sulphurets of cobalt, nickel, manganese, and zinc are dissolved in aqua regia, (the filter upon which the precipitated sulphurets were collected is to be incinerated and the ashes added to the precipitate, vide § 82, *b*.) The metals are then separated from one another by means of cyanide of potassium in the following manner: The process is first conducted exactly like that adapted for the separation of manganese from cobalt. This process yields a precipitate of part of the manganese as protocyanide of manganese, whilst another part of this metal remains in solution in conjunction with the whole of the cobalt, nickel and zinc. This solution is filtered off from the precipitated protocyanide of manganese, and boiled with hydrochloric acid in excess until the smell of hydrocyanic acid is no longer perceptible. Potass ley is then added in excess, and the mixture boiled until the ammonia (formed in consequence of the decomposition of the cyanate of potass contained in Liebig's cyanide of potassium) is completely expelled. The precipitate which forms consists of a mixture of the protoxides of manganese and nickel, and contains moreover some oxide of zinc; the greater portion of the zinc is in solution as oxide of zinc and potassium, and in conjunction with the whole of the cobalt in the form or cobalticyanide of potassium. The zinc is precipitated from this solution by means of sulphuretted hydrogen, and the cobalt in the filtrate determined as directed 6, *a, dd.* The precipitate of the protoxide of manganese and nickel, mixed with oxide of zinc, is dissolved in acetic acid, the zinc precipitated by means of sulphuretted hydrogen, and the fluid filtered off from the precipitated sulphuret of zinc which is added to the first precipitate of sulphuret of zinc. The nickel and manganese in the filtrate are separated as directed 9. The weight of the manganese obtained is added to that of the manganese produced from the undissolved portion of the protocyanide of that metal. The results are perfectly accurate.

APPENDIX.

§ 125.

METHOD OF DETERMINING THE PROPORTIONAL AMOUNT OF PEROXIDE CONTAINED IN MANGANESE ORES.

The natural manganese ores are compounds or mixtures of peroxide of manganese with the lower oxides of this metal, and moreover peroxide of iron, alumina, sulphate of barytes, &c., &c. It is a matter of the greatest importance for merchants and manufacturers to know the exact proportion of peroxide of manganese present in any of the manganese ores, since the commercial value of these ores depends entirely upon the relative amount of peroxide which they contain. The following method of determining this amount, is the most simple in its execution, and at the same time the most accurate in its results.

The following remarks will show and explain the principle upon which it is based.

a. When oxalic acid or an oxalate is brought into contact with peroxide of manganese, in presence of sulphuric acid in excess, protosulphate of manganese is formed, and carbonic acid evolved, owing to the oxygen which we may assume to exist in the peroxide of manganese in combination with the protoxide of the metal, combining with the oxalic acid, and consequently converting this acid into carbonic acid.

$$\text{Mn O}_2 + \text{SO}_3 + \text{C}_2\ \text{O}_3 = \text{Mn O, SO}_3 + 2\ (\text{CO}_2)$$

For every equivalent of available oxygen or, what amounts to the same, for every equivalent of peroxide of manganese present, we obtain consequently two equivalents of carbonic acid.

b. If this process is performed in a weighed apparatus, from which nothing except the evolved carbonic acid can escape, and which, at the same time, permits the complete expulsion of this acid, the diminution in the weight of the apparatus will at once indicate the amount of carbonic acid which has escaped, and consequently, by a very simple calculation, the proportion of peroxide present in the analysed manganese ore.

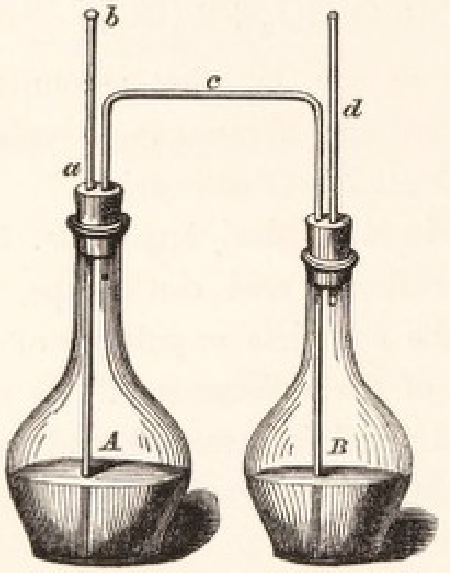
c. This calculation may, however, be altogether avoided; for this purpose it is necessary simply to use a certain definite proportion of the manganese ore to be examined, which, if the ore consisted of pure peroxide of manganese, would yield one hundred parts of carbonic acid. This proportion is found by the following equation :—

$$\begin{array}{ccccc} \text{2 eq. of CO}_2 & & \text{1 eq. of Mn O}_2 & & \\ 550.00 & : & 544.44 & :: & 100 : x = 98.989 \end{array}$$

The figure expressive of the amount of carbonic acid evolved indicates directly the proportional amount of peroxide contained in the analysed manganese ore: thus, if we make our experiment upon 0.98989 gramme of manganese, the number of centigrammes of the carbonic acid evolved in the process, expresses directly the percentage amount of peroxide contained in the analysed manganese ore. The amount of carbonic acid evolved from so small a weight as 0.98989 grammes of manganese, would be too small for accurate weighing; it is advisable therefore to take a multiple of this weight, say the triple = 2.96967, or, for shortness sake, 2.97 grammes, and to divide by three the number of centigrammes of carbonic acid evolved from this multiple weight.

The analytical process is performed in the apparatus illustrated by plate XLI. (Compare § 105.)

PLATE XLI.



The flask A should have a capacity of about two and a half ounces; B should hold two ounces. The latter is filled to one half with sulphuric acid; the tube *a* is closed at *b* with a small wax stopper.

The manganese ore to be examined is very finely levigated, (best in an agate mortar,) and 2.97 grammes of the powder are introduced into A; 2.5 grammes or more of neutral oxalate of potass* in powder, or about 2 grammes of neutral oxalate of soda, are then added, and as much water as will fill the flask to about one-third. The flask A is then corked, and the apparatus accurately equipoised upon the balance. Some sulphuric acid is made to flow from B into A, by applying suction to the tube *d*. The evolution of carbonic acid commences immediately in a steady and uniform manner.†) When the evolution begins to

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* This may be readily produced by saturating the common oxalate of potass with carbonate of potass, and evaporating to crystallization.

† If the carbonic acid be disengaged slowly, the contents of A will acquire an intensely red tint; this is not owing, as might be supposed, to the formation of hypermanganic acid, but to that of sulphate of sesquioxide of

flag, a fresh portion of sulphuric acid is sucked over into A, and the same process is repeated until the manganese ore is completely decomposed. This requires at the utmost about ten minutes if the ore is very finely levigated. The complete decomposition of the analysed ore is indicated, on the one hand, by the cessation of the disengagement of carbonic acid, and its non-renewal, upon the influx of a fresh portion of sulphuric acid into A; and, on the other hand, by the total disappearance of every trace of black powder from the bottom of A.*)

A more considerable portion of sulphuric acid than usual is finally sucked into A, so as to heat strongly the fluid contained in this flask, and consequently to expel the last traces of carbonic acid from it; the little wax stopper *b* is then slightly lifted, and a gentle suction applied to *d* until the air tastes no longer of carbonic acid. The apparatus is then allowed to cool, replaced upon the balance, and the original equilibrium restored; the number of centigramme weights required to effect this end, divided by three, expresses the per centage of peroxide contained in the analysed ore.

Some ores of manganese contain carbonates of the alkaline earths in admixture. To analyse ores of this description, the foregoing process is to be modified as follows: 2.97 grammes of the ore to be analysed are introduced into A, and drenched with very dilute sulphuric acid, so as to fill the flask to about one-third; the flask is then allowed to stand at rest, with occasional agitation, until all effervescence has completely ceased; a gentle heat is then applied to expel the last traces of carbonic acid from the fluid. About 3 grammes of powdered oxalic acid of commerce are introduced into a small tube, (compare § 112,

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manganese, since the peroxide yields at first only one-fourth of its oxygen to the oxalic acid. $2\ Mn\ O_2+3\ SO_3+C_2\ O_3=Mn_2\ O_3,\ 3\ SO_3+2\ CO_2$.

* If the manganese ore has been pounded or levigated in an iron mortar, few black spots will invariably remain perceptible; these consist of minute particles of iron which have got detached from the mortar during the pounding or levigation of the ore.

I., *b.*,) and the latter suspended into A by a thread. The apparatus thus prepared is equipoised upon the balance, and the small tube with the oxalic acid subsequently dropt into the fluid; the evolution of carbonic acid commences immediately. The process is then continued and concluded as usual. (Vide supra.)

This method yields exceedingly accurate results.

FIFTH GROUP.

OXIDE OF SILVER—PROTOXIDE OF MERCURY—PEROXIDE OF MERCURY—OXIDE OF LEAD—OXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

I. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM THOSE OF THE PRECEDING FOUR GROUPS.

§ 126.

a. Separation of the whole of the oxides of the fifth group from those of the preceding four groups.

The oxides of the fifth group are precipitated from acid solution by means of sulphuretted hydrogen, whilst those of the first four groups are not precipitated by this reagent. The separation of the oxides of this group from those of the four preceding groups is based upon this different deportment with sulphuretted hydrogen.

The following points are to be especially attended to in the process of separation.

α. To effect the complete separation of the oxides of the fifth group from those of the first, second, and third groups, by means of sulphuretted hydrogen, it is necessary simply that the reaction of the solution be acid, no matter whether owing to the presence of free nitric acid or to that of any other acid. But to achieve the separation of the oxides of the fifth from those of the fourth group, it is necessary that a free mineral acid be present in the solution, otherwise zinc, and, under certain circumstances, cobalt and nickel may be precipitated in conjunction with the oxides of the fifth group.

β. Hydrochloric acid is preferred to nitric acid for the acidification of the solution; in all cases, however, where the use of hydrochloric acid would create a precipitate in the solution, nitric acid is substituted instead, and the solution is considerably diluted.

γ. To achieve the *complete* precipitation of the sulphurets corresponding to the oxides of the fifth group, it is absolutely necessary that the solution be diluted to a certain degree, even though no other except hydrochloric acid be present.

b. Separation of individual oxides belonging to the fifth group from those of the first four groups.

1. SILVER is most simply and completely separated from the oxides of the four first groups, by means of hydrochloric acid. The solution should be sufficiently diluted, and the acid should not be added too greatly in excess. The separation of the chloride of silver is to be promoted by the addition of nitric acid; the precipitate is to be collected upon a filter (§ 86, 1, *a.*, *β.*)

2. The separation of MERCURY from the metals which we have treated of in the preceding paragraphs, may also be effected by ignition, since this will cause the mercury or mercurial compounds to volatilize, whilst the non-volatile substance will remain behind. This method is applicable to alloys as well as to oxides, chlorides, and sulphurets. Whether the one or the other of these forms is the most appropriate depends upon the nature of the metals from which the mercury is to be separated. The proportion of the mercury is determined in this method, either from the loss of weight which the ignited substance suffers—in which case the operation is conducted in a crucible—or the subliming mercury is collected and weighed in the manner described § 89. The best way of conducting the process of sublimation will be

found described § 127, 1, γ, (separation of silver from mercury).

3. From those oxides, of which the corresponding chlorides are soluble in alcohol, LEAD may be separated also by converting the mixed oxides into chlorides, and treating the mass with strong alcohol when the chloride of lead, being insoluble in alcohol, will remain behind. This method, besides yielding no absolutely accurate results, is, moreover, applicable only if the compounds to be analysed admit of ready transformation into chlorides. The method of precipitating lead by means of sulphuric acid, and thus separating it from the other oxides, yields likewise no absolutely accurate results, since sulphate of lead is not altogether insoluble in water. (Compare § 87.)

II. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM ONE ANOTHER.

§ 127.

1. SILVER FROM MERCURY.

Silver may be separated from mercury either by means of hydrochloric acid,—chloride of silver being insoluble whilst perchloride of mercury is soluble,—or by means of cyanide of potassium. Cyanide of silver being insoluble whilst cyanide of mercury is soluble, or, finally, by heat, silver and chloride of silver being non-volatile, whilst mercury and perchloride of mercury are volatile.

The application of the two first methods requires that the mercury be present in the form of peroxide; should it therefore exist, in the solution to be analysed, in the form of protoxide, this must first be peroxidized by heating with nitric acid. The first method is generally preferable to the two latter, which can be advantageously applied only under particular circumstances.

a. Separation by means of hydrochloric acid.

Some nitric acid is added to the dilute solution, and subsequently hydrochloric acid until the formation of a precipitate ceases; the operator should avoid adding the acid greatly in excess. All the silver is precipitated in this manner, whilst all the mercury remains in solution. The precipitated chloride of silver is separated from the fluid by filtration, and the subsequent operations are conducted as directed § 86 and § 89.

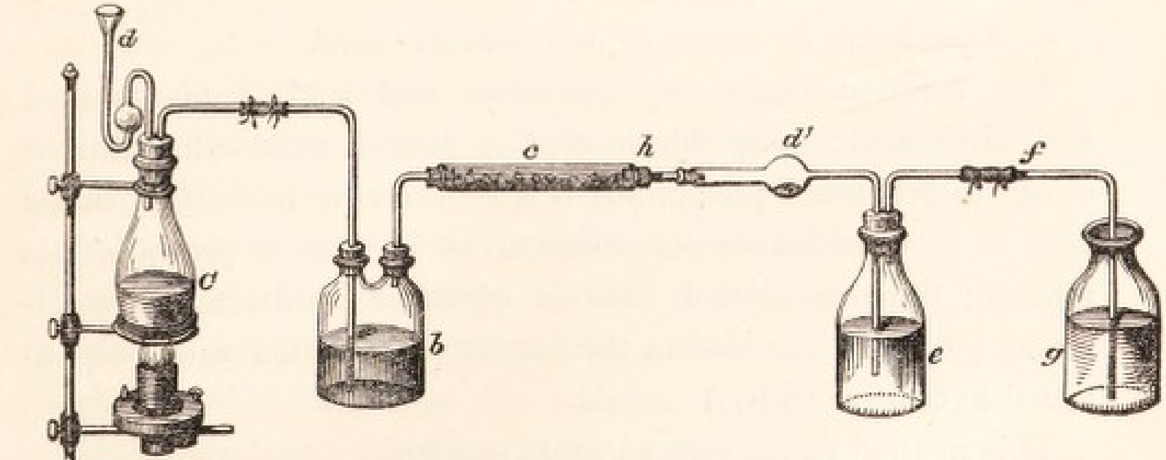
β. Separation by means of cyanide of potassium.

Cyanide of potassium is added to the solution until the precipitate which is formed at first is completely redissolved. If the solution contains much free acid, this must first be nearly neutralized with potass before the cyanide of potassium is added.) The solution contains now a double cyanide of silver and potassium, and a double cyanide of mercury and potassium. Nitric acid is then added in excess; this causes the decomposition of both double cyanides, and transformation of the whole of the cyanide of potassium present into nitrate of potass; the insoluble cyanide of silver separates, and is treated as directed § 86; the soluble cyanide of mercury remains in the filtrate, from which the mercury is finally precipitated with sulphuretted hydrogen, (§ 89).

γ. Separation by heat.

This is best effected by means of the apparatus illustrated by

PLATE XLII.



The solution of the two metals is precipitated with sulphuretted hydrogen, the precipitated sulphurets are collected upon a tared filter, dried at 212°, and weighed; a portion of the dry precipitate is then weighed off, and introduced into the bulb *d′*, which is then heated, gently at first, but increasing gradually to feeble redness, transmitting all the while a slow stream of chlorine gas through it. Chloride of sulphur distils over at first; this decomposes with the water in *e*, (vide § 111, II., 1, *c.*;) the perchloride of mercury formed sublimes subsequently, and condenses partly in the flask *e*, and partly in the posterior part of the tube *d′*. This part of the tube is then cut off, and the sublimate which it contains rinsed into the flask *e*; the water in *g* is finally likewise added to the contents of *e*. The contents of *e* are then heated until all smell of chlorine ceases to be perceptible; the mercury in *e* is then finally determined, as directed § 89. Should there remain some undissolved sulphur in *e*, the fluid part of the contents of this flask must be filtered off from this before the operator proceeds to determine the proportion of mercury present. The proportion of chloride of silver in the bulb of *d′* is determined by weighing the tube with its contents, reducing the fused chloride of silver which adheres firmly to the interior of the bulb by means of zinc, (§ 86,) and finally re-weighing the tube after having thus perfectly cleansed it.

2. Silver from lead.

a. Separation by means of hydrochloric acid.

The solution containing the silver and lead is first mixed with nitric acid; hydrochloric acid is diluted with water until it ceases to produce a precipitate in a solution of lead; this dilute acid is then added to the solution as long as a precipitate is formed; the precipitated chloride of silver is filtered off as directed § 86, and the lead in the filtrate precipitated with sulphuretted hydrogen. (§ 87.)

This method yields very accurate results.

β. Separation by means of cyanide of potassium.

The solution is first diluted to a certain extent, and mixed with carbonate of soda slightly in excess; cyanide of potassium is subsequently added, and heat applied. The carbonate of lead which forms upon the addition of the carbonate of soda remains undissolved, whilst the silver is obtained in solution in the form of double cyanide of silver and potassium. The fluid is filtered off from the carbonate of lead; the filtrate is precipitated with nitric acid, and the cyanide of silver produced treated as directed § 86. The carbonate of lead which contains traces of alkali is dissolved in dilute nitric acid, and its proportion determined as directed § 87. This method yields pretty accurate results, although a trifling loss of carbonate of lead occurs generally, since this substance is not absolutely insoluble in water, (§ 57). The operator must take care to dilute the solution properly, and to add the carbonate of soda only *slightly* in excess, or otherwise a perceptible amount of lead may dissolve in the menstruum. Cyanide of potassium containing the slightest trace of sulphuret of potassium is wholly unfit for use in this process.

3. SILVER FROM BISMUTH.

α. Separation by means of hydrochloric acid.

The same method as described § 127, 1, *α.*, (separation of silver from mercury).

β. Separation by means of cyanide of potassium.

The same method as described § 127, 2, *β.*, (separation of silver from lead).

4. SILVER FROM COPPER.

α. Separation by means of hydrochloric acid.

Vide § 127, 1, *α.*, (separation of silver from mercury.)

β. Separation by means of cyanide of potassium.

The solution, if necessary, is first neutralized with potass; cyanide of potassium is subsequently added until the precipitate which forms at first, upon the addition of this reagent, is completely redissolved; the silver is then either

aa. Precipitated from this solution with sulphuretted hydrogen; the excess of sulphuretted hydrogen is expelled by heat, and a fresh portion of cyanide of potassium added; by this means the copper is completely retained in solution. Or,

bb. The solution is mixed with nitric acid in excess; the cyanide of silver separates completely, (§ 86,) whilst the cyanide of copper redissolves in the excess of nitric acid. The solution is in either case filtered off from the precipitate, and evaporated with sulphuric acid (in case *aa.*, with addition of nitric acid) until all smell of hydrocyanic acid disappears; the solution of sulphate of copper, which is thus produced, is precipitated with potass. (§ 90.)

This method yields very accurate results.

5. Silver from cadmium.

Like silver from copper, methods *α.* and *β.*, *bb.*

6. Mercury from all those metals of which the chlorides are non-volatile.

Like mercury from silver, § 127, 1, *γ.* The operator must bear in mind

α. that a gentle heat only should be applied in presence of lead, or part of the chloride of lead formed will volatilize; and *β.*, that the chloride of copper formed cannot be weighed directly, since it remains partly as chloride and partly as subchloride.

The method described § 126, *b.*, 2, may also frequently be resorted to.

7. Peroxide of mercury from oxide of lead.

α. Separation by means of cyanide of potassium.

Vide § 127, 2, *β.* (Separation of silver from lead.) The mercury is precipitated from the filtrate as sulphuret of mercury. (§ 89.) The results are accurate.

β. Separation by converting the oxides of lead and mercury into chlorides, and treating the latter with alcohol.

Both the peroxide of mercury and oxide of lead are converted into dry chlorides in the proper way; the chlorides formed are digested with strong alcohol, mixed with ether, and the solution, which contains the whole of the perchloride of mercury, is filtered off from the undissolved chloride of lead; the latter is then determined as directed § 87. The filtrate is diluted with water, the ether and alcohol evaporated at a very gentle heat, and the mercury finally determined as directed § 89.

γ. *Separation by means of sulphuric acid.*

The somewhat concentrated solution is mixed with dilute sulphuric acid in excess, allowed to stand at rest for the space of twelve hours, filtered, and the precipitate completely washed with water mixed with sulphuric acid; this is finally replaced by alcohol, and the washed precipitate is then dried and weighed. (§ 87.) The mercury in the filtrate is determined as directed § 89. With regard to the degree of accuracy of the results, we refer to § 87, 2, *a*.

8. Peroxide of mercury from oxide of bismuth.

The separation is effected by means of cyanide of potassium, like that of mercury from lead, § 127, 7, α. The results are accurate.

9. Peroxide of mercury from oxide of copper.

α. *Separation by means of cyanide of potassium.*

Like that of silver from copper, § 127, 4, β., method *aa*.

β. *Separation by means of formiate of soda.*

The solution is mixed with hydrochloric acid, (should it not already contain this acid,) nearly saturated with potass, and the mercury precipitated with formiate of soda. (§ 89, 2.) The copper in the fluid, filtered off from the protochloride of mercury, is determined as directed § 90.

10. Peroxide of mercury from oxide of cadmium.

Like peroxide of mercury from oxide of copper, § 127, 9, β.

11. Protoxide of mercury from the oxides of lead, copper, bismuth, and cadmium.

a. The protoxide of mercury is peroxidized, (§ 88,) and the further operations conducted as directed § 127, 7, 8, 9, and 10.

b. Hydrochloric acid is added to the dilute solution as long as a precipitate is formed. The mercury in the precipitate is determined as directed § 89, 2. The other metals are contained in the filtrate. If lead is present, the separation is to be effected as directed § 127, 2, *a*. If the compounds are insoluble in water, they are to be dissolved in cold and very dilute nitric acid.

12. Protoxide of mercury from peroxide of mercury.

a. In Solution.

The solution is strongly diluted, and hydrochloric acid added as long as a precipitate is formed, (protochloride of mercury). The precipitate is allowed to subside, collected upon a tared filter, dried at 212°, and weighed. The peroxide of mercury in the filtrate is determined as directed § 89.

β. As an insoluble compound.

The insoluble compound containing the protoxide and peroxide of mercury, is acted upon with highly dilute nitric acid, at a low temperature, until it is completely dissolved, and the further operation is then conducted as directed sub. *a*.

The results are accurate: there is, however, invariably rather a tendency to a surplus of peroxide and loss of protoxide than the reverse.

13. Oxide of lead from oxide of bismuth.

a. Separation by means of sulphuric acid.

The solution is mixed with pure sulphuric acid in excess, evaporated until the sulphuric acid begins to volatilize, allowed to cool, water added, and the solution of sulphate of bismuth filtered off without delay from the undissolved sulphate of lead. The lead is determined as directed § 87, 2, *a*., the bismuth according to § 91, 1, *c*. Concerning the degree of accuracy of the results, we refer to § 87, 2, *a*.

β. Separation by heat.

Vide § 127, 1, *γ*. (Separation of silver from mercury.) This method is particularly convenient for the analysis of alloys of the two metals. The heat must not be carried to a very high degree, since this would give rise to the volatilization of the chloride of lead; but its application should be protracted sufficiently long, since otherwise bismuth may remain in the residue. The proportion of the bismuth is either determined from the loss of weight which the analysed substance suffers, or the volatilized chloride of bismuth is conducted into water impregnated with hydrochloric acid, and subsequently determined according to § 91.

γ. *Separation by means of metallic lead.*

The solution is precipitated with carbonate of ammonia; the precipitated carbonates are washed, and subsequently dissolved in acetic acid. The solution is introduced into a flask provided with a ground stopper, a weighed rod of pure lead is placed upright into the solution, and the flask nearly filled with water, so that the upper end of the lead does not project beyond the surface of the fluid; the flask is then closed, and allowed to stand at rest for the space of twelve hours, with occasional agitation. The bismuth which precipitates upon the metallic lead, is rinsed off from the rod, and collected upon the filter; it is then washed, and dissolved in nitric acid; the solution is evaporated, and the bismuth determined as directed § 91. The lead in the filtrate is determined according to § 87; the lead-rod is dried, and re-weighed; the loss of weight which it has suffered in the process, is subtracted from the amount of lead produced from the filtrate. (Ullgren.)

14. OXIDE OF LEAD FROM THE OXIDES OF COPPER AND CADMIUM.

α. *Separation by means of cyanide of potassium.*

Like oxide of lead from oxide of silver. (§ 127, 2, β.)

β. *Separation by means of sulphuric acid.*

Like oxide of lead from peroxide of mercury. (§ 127, 7, γ.)

15. OXIDE OF BISMUTH FROM OXIDE OF COPPER.

α. *Separation by means of cyanide of potassium.*

Like oxide of lead from oxide of copper. (§ 127, 14.)

β. *Separation by heat.*

Like mercury from copper, § 127, 6; compare likewise § 127, 13, β. This method is especially applicable in the case of alloys.

γ. *Separation by means of ammonia.*

The solution is mixed with sal ammoniac, and then gradually dropped into dilute ammonia. This causes the bismuth to precipitate as a basic salt, whilst the oxide of copper remains in solution as an ammoniacal double salt. (BERZELIUS.) The precipitate is washed with dilute ammonia, dissolved in dilute nitric acid, and the bismuth in the solution determined according to the directions given § 91. The copper in the ammoniacal solution is determined as directed § 90, 1, *a.*, *β*.

16. OXIDE OF BISMUTH FROM OXIDE OF CADMIUM.

The separation is effected by means of cyanide of potassium, like that of oxide of lead from oxide of cadmium; vide § 127, 14, *a.*

17. OXIDE OF COPPER FROM OXIDE OF CADMIUM.

The separation is effected by means of cyanide of potassium, in the same manner as that of oxide of silver from oxide of copper; vide § 127, 4, *β*, *aa.*

18. ALL THE METALS OF THE FIFTH GROUP FROM ONE ANOTHER.

The dilute solution is mixed with carbonate of potass, and subsequently with cyanide of potassium in excess; the mixture is digested for some time, at a gentle heat, and filtered. The carbonates of lead and of bismuth (mixed with alkali) remain upon the filter; the lead is separated from the bismuth as directed § 127, 13. The filtrate is mixed with dilute nitric acid in excess, and the fluid filtered off from the precipitated cyanide of silver, which is to be determined according to § 86, 3. The filtrate is again neutralized with carbonate of potass; cyanide of potassium is then added, and sulphuretted hydrogen in excess transmitted through the solution; a fresh portion of cyanide of potassium is then added—(to re-dissolve every trace of sulphuret of copper which may perchance have been precipitated)—and the solution which contains all the copper, filtered off from the precipitated bisulphuret of mercury and sulphuret of cadmium, which are finally separated from one another, as directed § 127, 10. The copper in the filtrate is determined according to § 127, 4.

SIXTH GROUP.

PEROXIDE OF GOLD—PEROXIDE OF PLATINUM—PROTOXIDE OF TIN—PEROXIDE OF TIN—OXIDE OF ANTIMONY—ARSENIOUS ACID—ARSENIC ACID.

I. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

§ 128.

a. Separation of all the oxides of the sixth group from those of the first four groups.

α Sulphuretted hydrogen in excess is conducted into the acid solution, and the precipitated sulphurets (corresponding to the oxides of the sixth group) are filtered off.

The points mentioned § 126, *a.*, *α* and *γ* are here to be likewise attended to. With regard to the particular conditions requisite to effect the complete precipitation of the individual metals of the sixth group, I refer to section IV. Wöhler has found that sulphuretted hydrogen fails to separate arsenic acid from oxide of zinc, even though a considerable excess of mineral acid be present, since the whole, or a portion of the zinc, will invariably precipitate in conjunction with arsenic: $Zn\,S, As\,S_5$. In cases, therefore, where we have oxide of zinc and arsenic acid together in solution, the arsenic acid must first be converted into arsenious acid, by heating with sulphurous acid, before the sulphuretted hydrogen is transmitted through the solution.

β. It is more convenient in some cases to base the separation of the metals of the sixth group from those of the third and fourth groups, upon the solubility of the sulphurets of the former in alkaline sulphurets, since neither the hydrates of alumina and oxide of chromium, nor the sulphurets of the metals of the fourth group, are dissolved by alkaline sulphurets. The process is, in such cases, conducted as directed § 129, *a*, *β*. This method is not applicable in cases where the compound to be analysed contains nickel.

b. Separation of individual oxides of the sixth group from those of the first four groups.

1. GOLD.

a. Metallic gold may be readily separated from the metals of the fourth group, by means of nitric acid or hydrochloric acid, since these acids dissolve the other metals, and leave the gold intact.

β. If we have peroxide of gold in acid solution, together with the oxides of the four first groups, the gold may be readily precipitated with oxalic acid, (§ 93,) and thus separated from the other oxides. Care must be taken to add a sufficient amount of hydrochloric acid to the solution, lest oxalates insoluble in water should precipitate in conjunction with the gold, owing to a deficiency of their proper solvent.

2. PLATINUM may be separated from all those metals of the four first groups, of which the chlorides dissolve in alcohol, by precipitating it with sal ammoniac, according to § 94. Compare likewise the separation of platinum from the metals of the fifth group, § 129, 5.

3. TIN AND ANTIMONY.

a. These metals may be separated from their alloys with metals of the fourth group, by means of nitric acid, since this leaves the oxides of tin and antimony which are formed, undissolved, whilst it dissolves the other oxides. (The results are not perfectly accurate, especially in the case of antimony, of which a small portion is dissolved in the process.)

β. Tin and antimony may be readily separated from those metals of which the chlorides are fixed, by heating the mixed metals in a stream of chlorine gas; compare § 127, 1, *γ*. The volatilizing chloride of antimony and chloride of tin are to be conducted into water impregnated with hydrochloric acid.

4. ARSENIC may, under certain circumstances, be advantageously separated from the oxides of the fourth group, &c., by the method which will be found described § 129, 7, *a*. This method is not applicable, however, for the separation of the acids

of arsenic from alumina. From barytes, strontia, and lime, arsenic acid may be readily separated by means of sulphuric acid. In the case of strontia and lime, alcohol is added, to separate the precipitates completely from the fluid. The best way is, to dissolve the compound to be analysed in hydrochloric acid before adding the sulphuric acid; should the compound be insoluble in hydrochloric acid, it is to be reduced to a very fine powder, boiled for some time with concentrated sulphuric acid, and the further process conducted as stated above. The proportion of the arsenic acid may be calculated from the loss of weight which the analysed compound undergoes, or it may be determined in the filtrate by means of sulphuretted hydrogen.

Arsenite of barytes may be decomposed *immediately* by sulphuric acid, but the arsenites of strontia and lime must first be converted into arseniates by repeated evaporation with nitric acid and cautious ignition.

II. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIFTH.

§ 129.

a. Separation of all the oxides of the sixth group from those of the fifth.

The sulphurets of the sixth group are soluble in alkaline sulphurets, whilst those of the fifth group are insoluble in these reagents. This furnishes us with a ready means of separating the metals of the fifth from those of the sixth group. Sulphuret of ammonium is generally used as the solvent; if protosulphuret of tin is present, the sulphuret of ammonium must contain sulphur in excess, or a certain amount of sulphur must be added to it. If copper is present, sulphuret of potassium is to be substituted for ammonium, since sulphuret of copper is slightly soluble in the latter; this substitution, however, is admissible only if no mercury is present, since the sulphurets of mercury are soluble in sulphuret of potassium. The separation may be effected in two ways, viz.,

α. The oxides of both groups are precipitated from their acid solution with sulphuretted hydrogen, and the precipitate digested some time with sulphuret of ammonium, (or sulphuret of potassium instead, in presence of copper and absence of mercury ;) the fluid which contains the sulphurets of the sixth group in solution is then filtered off from the undissolved sulphurets of the fifth group.

β. The solution is neutralized with ammonia, (or with potass instead, under certain circumstances,) and sulphuret of ammonium (or sulphuret of potassium instead) added in excess. The mixture digested some time; the fluid which contains the sulphurets of the sixth group in solution is then filtered off from the undissolved sulphurets of the fifth group.

If the compound to be analysed is in a solid and dry state, the object in view may frequently be attained most readily by fusing it together with sulphuret of potassium, and treating the fused mass with water, when the sulphurets of the sixth group will dissolve, whilst those of the fifth group will remain undissolved.

Brunner has shown that these methods fail to separate copper completely from arsenic ; for the separation of these two metals, therefore, the method described here below (*b.*, 7, *a.*) is to be preferred.

b. Separation of individual oxides of the sixth group from those of the fifth.

1. GOLD FROM SILVER (in alloys).

Before we proceed to treat of the separation of these two metals, we have to consider the deportment of differently composed alloys of gold and silver.

aa. When an alloy containing less than fifteen per cent. of silver, is treated with aqua regia, all the gold is obtained in solution, whilst all the silver remains undissolved as chloride of silver.

bb. If the alloy contains more than fifteen per cent. of silver, the chloride of silver formed protects the yet undecomposed portion of the alloy so as to prevent the complete solution of the gold.

cc. If an alloy containing eighty per cent. or more of silver, is acted upon by nitric acid, all the silver is dissolved, whilst the gold remains undissolved.

dd. If the alloy contains less than eighty per cent. of silver, nitric acid fails to dissolve the silver completely.

From a due consideration of these points result the following methods of separation.

α. Alloys containing less than fifteen per cent. of silver are to be treated with aqua regia.

β. Alloys containing more than eighty per cent. of silver are to be treated with nitric acid.

γ. Alloys containing between fifteen and eighty per cent. of silver, are to be fused in a porcelain crucible, together with three parts of pure lead; the fused mass is to be treated with nitric acid. All the gold remains undissolved, whilst the whole of the silver and lead dissolve; the lead is finally separated from the silver as directed § 127, 2.

2. GOLD FROM COPPER, BISMUTH, AND CADMIUM.

The gold is precipitated by means of oxalic acid (vide § 93, *b*, γ.) and the other metals are determined in the filtrate.

3. GOLD FROM MERCURY.

These metals may be readily separated from one another by ignition, no matter whether we have to operate upon them in alloys or in chemical compounds. The proportion of the mercury is either calculated from the loss of weight which the ignited alloy or compound has suffered in the process, or the sublimed mercury is collected and weighed directly. Compare § 89.

4. GOLD FROM LEAD AND BISMUTH.

If we have these metals in solution, they may be readily separated from one another by means of cyanide of potassium, in the same manner in which mercury is separated from lead and bismuth, § 127, 7, *a*. The solution of the double cyanide of gold and potassium is decomposed by boiling with hydrochloric acid, and after the expulsion of the hydrocyanic acid, the gold is determined by one of the methods described § 93.

N.B. to 2, 3, and 4. From alloys with copper, bismuth, cadmium, mercury, and lead, containing no very large proportion of gold, the latter metal may also be separated in a very simple manner—by treating the alloy with nitric acid.

5. PLATINUM FROM THE METALS OF THE FIFTH GROUP.

α. The separation of platinum from alloys may, in most instances, be effected by treating the alloys under examination with nitric acid. The presence of some metals, however, (silver for instance,) imparts to the nitric acid the property of dissolving platinum likewise. Metals of this description may generally be separated from platinum by means of boiling concentrated sulphuric acid, provided, of course, they be soluble in this acid.

β. From those metals the chlorides of which are soluble in spirits of wine, platinum may be separated by means of sal ammoniac. Compare § 94.

6. TIN AND ANTIMONY FROM THE METALS OF THE FIFTH GROUP, (in alloys).

α. The separation of tin and antimony from the whole of the metals of the fifth group, may be effected by means of nitric acid. Compare § 128, *b*. 3, *α*. In the analysis of alloys of copper and tin, this method does not yield absolutely accurate results, since the insoluble peroxide of tin formed retains invariably an admixture of oxide of copper ; nor are the results more accurate in the analysis of alloys of antimony. (Compare § 128, *b*. 3, *α*.) The application of this method should accordingly be more exclusively confined to the analysis of alloys containing but a small proportional amount of tin or antimony.

β. From those metals the chlorides of which are fixed, tin and antimony may be separated by means of chlorine. Compare § 128, *b*. 3, *β*. This method is preferable for alloys containing a large proportion of tin or antimony.

7. ARSENIC FROM THE METALS OF THE FIFTH GROUP.

α. The compound under examination is fused with 2 parts of carbonate of soda, and 2½ parts of nitrate of potass; the fused mass is subsequently treated with water. Arseniated alkali is dissolved out in this manner, whilst the metallic oxides remain undissolved; the latter are not to be weighed directly, since they retain, in most instances, an admixture of alkali.

β. From those metals the chlorides of which are fixed, arsenic may be separated by means of chlorine, in the same manner as tin and antimony. (Compare § 128, *b.* 3, *β,* and also § 127, 1. *γ.*) This method is not often resorted to, however, since it effects the complete decomposition of alloys of arsenic only with the very greatest difficulty.

γ. Arsenic acid may be separated from lead by means of sulphuric acid in a very simple and precise manner. The separation is effected either by boiling the very finely levigated compound under examination with hydrated sulphuric acid, and maintaining the mixture for some time in a state of ebullition; or by dissolving the compound in nitric acid, and precipitating the solution subsequently with sulphuric acid and alcohol. (§ 87.) The arsenic is either to be determined in the filtrate by means of sulphuretted hydrogen, or its proportion may be inferred from the amount of lead obtained in the form of sulphate.

III. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM ONE ANOTHER.

§ 130.

1. GOLD FROM PLATINUM.

The platinum is precipitated from the acid hydrochloric solution of the two metals by means of chloride of potassium; (vide § 94;) the gold in the filtrate is subsequently precipitated with protosulphate of iron. (Vide § 93.)

2. GOLD AND PLATINUM FROM TIN, ANTIMONY, AND ARSENIC.

The alloys or sulphurets of the metals in question are to be heated in a stream of chlorine gas; the gold and platinum remain, whilst the chlorides of tin, antimony, and arsenic distil over into the water of the receiver. Compare § 127, 1, γ.

3. TIN FROM ANTIMONY.

a. In alloys.

α. Separation by means of hydrochloric acid.

A weighed portion of the very finely levigated alloy under examination is heated with hydrochloric acid, and solution of chlorate of potass added until the alloy is completely dissolved.

The solution is introduced into a flask, and a clean slip of zinc placed into the latter. The disengaged hydrogen gas is transmitted, first through a small washing bottle half filled with water, and subsequently through a LIEBIG's potass apparatus (compare § 141) filled with a solution of neutral nitrate of silver. When the evolution of gas has completely ceased, the apparatus is taken asunder, and the slip of zinc withdrawn from the flask, and freed by repeated rinsing in a porcelain dish, from the adhering tin and antimony. The rinsing water is then added to the contents of the flask, the precipitated metals are allowed to subside, and the clear supernatant fluid is cautiously decanted.

The flask contains now the whole of the tin, nearly the whole of the antimony, and a small portion of solution of zinc, whilst in the potass apparatus, we have a black powder which consists of antimonuret of silver.

Hydrochloric acid is now poured into the flask, and the latter again connected with the washing bottle, and the same potass apparatus; heat is then applied until the tin is completely dissolved. After cooling, the solution of protochloride of tin is filtered off from the undissolved powder of antimony, and the latter collected upon the filter, washed, first with dilute hydrochloric acid, finally with water, dried and weighed. For the properties of antimony, vide § 64, *c.* The tin in the filtrate is precipitated with sulphuretted hydrogen. (§ 128.)

The contents of the potass apparatus are filtered, the antimonuret of silver is collected upon the filter, washed, and the antimony finally determined according to § 129; the resulting quantity is added to the weight of the first precipitate of antimony.

β. SEPARATION BY MEANS OF METALLIC TIN.

The solution of the compound under examination is effected in the same manner as at α; a considerable amount of hydrochloric acid is subsequently added, and the mixture heated for some time with a clean slip of tin. Upon this, the whole of the antimony will separate in the form of a black powder, the perchloride of tin being reduced, at the same time, to the state of protochloride. The slip of tin is now withdrawn, thoroughly freed from the adhering particles of antimony, by washing with water impregnated with hydrochloric acid; the whole of the antimony is finally collected upon a tared filter, dried and weighed. The difference between the weight of the antimony and that of the analysed alloy, indicates directly the amount of tin originally present in the latter.

b. In solution.

α. Should the solution contain free nitric acid, this is to be removed completely by adding hydrochloric acid, and evaporating to dryness at a *very gentle* heat; the residue is to be heated as directed at *a*, α.

β. The two metals are precipitated as sulphurets; the precipitate is weighed, and subsequently dissolved in hydrochloric acid by digestion at a gentle heat, with addition of chlorate of potass; the solution is treated according to *a*, β.

The latter method is applicable only in cases where the degree of sulphuration in which the two metals exist in the precipitate is accurately known; moreover, the precipitate must contain no free sulphur in admixture.

4. TIN FROM ARSENIC.

a. In alloys.

The alloy under examination is treated according to 3, *a*. α. (Separation of tin from antimony.) Finally, upon treating the precipitated metals with hydrochloric acid, two cases may present themselves.

α. *The fluid in the flask is perfectly clear.* This is a sure sign that all the arsenic originally present in the precipitate is volatilized in the form of arseniuretted hydrogen.

The contents of the potass apparatus are filtered, and the silver, which contains only a trace of arsenic, is dissolved in nitric acid, the solution being subsequently added to the filtrate which contains nearly the whole of the arsenic in the form of arsenious acid. The arsenic is finally separated from the silver by means of hydrochloric acid.

The proportion of tin present in the analysed alloy is either determined by treating the solution in the flask according to 3, *a.*, α., or inferred from the weight of the arsenic obtained.

β. A black powder remains in the flask.

This consists of metallic arsenic. The fluid is filtered off from the arsenic, and the latter collected upon the filter, washed, dried, and weighed; the weight is added to that of the arsenic contained in the potass apparatus, which is to be determined according to α. The proportion of tin present in the analysed alloy is either determined by treating the filtrate according to 3, *a.*, α., or inferred from the weight of the arsenic obtained.

b. In solution.

Should the solution contain free nitric acid, it is to be perfectly freed from this by adding hydrochloric acid, and evaporating to dryness at a gentle heat. The residue is to be treated according to the directions of *a.*

5. Protoxide of tin from peroxide of tin.

It is impossible to effect a direct separation of the two oxides of tin; recourse must be had, therefore, to the methods of indirect analysis.

The desired end may be attained best in the following manner. The solution containing the two oxides, or corresponding chlorides, is divided into two portions, and the amount of tin determined in the one portion, according to § 96; the other portion is dropped into a considerable excess of dilute hot solution of perchloride of mercury, acidified with hydrochloric acid; this causes the precipitation of a certain amount of protochloride of mercury exactly corresponding to the proportion of protoxide of tin present in the analysed solution. The precipitated protochloride of mercury is collected upon a filter, washed, dried, and weighed as directed § 89.

The proportions of protoxide and peroxide of tin, present in the whole of the analysed solution, may now be readily calculated from the results of these two experiments. (H. Rose.)

6. ANTIMONY FROM ARSENIC.

The separation of these two metals is a problem for which Chemistry has not yet found a perfectly satisfactory solution. The following methods may be recommended as the most suitable.

a. In alloys.

The alloy under examination is introduced into a bulbous tube, and covered with a mixture of common salt and carbonate of soda; the tube is connected with an apparatus evolving dry carbonic acid gas, and a gentle heat applied to the bulb; this is gradually increased to the very highest degree of intensity, and maintained thus until the characteristic odor of arsenic has completely disappeared. (The operator must take care not to inhale the escaping fumes. The most judicious way is to introduce the end of the bulbous tube into a flask, so as to permit the arsenic to sublime in the latter.) After cooling, the tube is filled with water, in order to dissolve the saline mass which it contains in conjunction with the residuary antimony; the latter is finally washed, dried, and weighed. The difference between the weight of the antimony and that of the analysed alloy, indicates directly the proportion of arsenic originally present in the latter. The results obtained by this method are not quite accurate, being always somewhat too low.

The layer of common salt and carbonate of soda serves to prevent the volatilizing of the antimony, which would take place to a very considerable extent were the alloy to be fused in a stream of carbonic acid or hydrogen gas, without being thus protected.

b. In solution.

The two metals are precipitated in the form of protosulphurets;

the precipitate is collected upon a filter and washed; and, while still moist, introduced (together with the filter) into a porcelain dish, when it is mixed with an equal volume of neutral nitrate of lead in powder, and with about the same amount of water; the contents of the dish are then heated to boiling, and kept in a state of ebullition, with constant stirring and renewal of the evaporating water, until the mass acquires a dark brown tint. The fluid is then filtered off from the undissolved residue, which latter contains the whole of the antimony (partly in the form of oxide, and partly as a double sulphuret of antimony and lead) in conjunction with part of the arsenic in the form of a double sulphuret of arsenic and lead. The filtrate contains the rest of the arsenic in conjunction with the excess of the nitrate of lead used in the process. The arsenic in the filtrate is determined according to § 129, *a.*, or 129, *b.*, 7. The residue is digested with ammonia, which decomposes the double sulphuret of arsenic and lead, and dissolves the sulphuret of arsenic; the solution thus obtained is precipitated with hydrochloric acid, and the precipitated sulpharsenious acid filtered, washed, dried, and weighed, and its proportional amount of arsenic added to the weight of the principal portion of the arsenic which has been determined in the filtrate. The antimony and lead in the residue are separated according to § 129, *a.* This method was recommended by BEHRENS. (Journal de Pharmacie, 1843. Juillet, p. 17.) The results, though not absolutely precise, may be considered pretty accurate. Behrens proposes to precipitate the lead in the first filtrate, by means of carbonate of ammonia, to filter the fluid off from the precipitated carbonate of lead, and finally to precipitate the arsenic from the filtrate by means of sulphuretted hydrogen. I think it impossible, however, that *this* method can under all circumstances, yield accurate results.

7. ARSENIOUS ACID FROM ARSENIC ACID.

The following method of indirect analysis yields very satisfactory results.

a. The solution of the two acids is divided into two accurately weighed portions; the arsenic acid in the one portion is reduced to arsenious acid by means of sulphurous acid, (§ 97, *b.*, 2, *b.*,) and the whole of the arsenious acid subsequently converted into sulpharsenious acid, which is finally washed, dried at 212°, and accurately weighed.

b. In the other portion the arsenious acid is converted into arsenic acid by means of chlorine. The solution is, for this purpose, mixed with some hydrochloric acid, and solution of indigo subsequently added until the fluid appears distinctly blue. Part of a weighed or measured solution of chloride of lime (of which the proportion of chlorine is accurately known) is then added to the fluid until the blue color has disappeared again; the amount of solution of chloride of lime added is found by weighing or measuring the remainder. For further details, I refer to § 137, B. (Chlorimetry.)

The proportion of arsenious acid originally present in the analysed solution may now be readily calculated from the amount of chlorine that has been required in the process; two equivalents of chlorine correspond to one equivalent of arsenious acid.

$$(2\ Cl + 2\ H\ O + As\ O_3 = As\ O_5 + 2\ Cl\ H.)$$

By calculating the resulting quantity of arsenious acid upon sulpharsenious acid, and subtracting the weight of this from the total weight of sulpharsenious acid obtained from the first portion of the analysed solution, we find the amount of arsenic acid originally contained in the latter.

8. ANTIMONY, ARSENIC, AND TIN FROM ONE ANOTHER.

The same method is pursued as in the separation of tin from antimony, vide § 130, 3, *a.*, *α*.

Upon boiling the precipitated metals with hydrochloric acid, the whole of the tin is dissolved, whilst the undissolved residue contains part of the antimony and arsenic, (such we must, at least, assume to be the case). The fluid is filtered off from the residuary mass, and the latter washed, first with water containing hydrochloric acid, and subsequently with pure water, dried, and weighed. The final separation of the arsenic from the antimony is effected in the manner described at 6, *a.* The tin in the filtrate is determined by means of sulphuretted hydrogen, vide § 128.

The contents of the potass apparatus are filtered; the insoluble antimonuret of silver is collected upon the filter, washed, and the antimony finally determined according to § 130; the resulting amount is added to the weight of the first precipitate of antimony. The arsenic in the filtrate is determined by the appropriate method, and the resulting amount added to the weight of the first precipitate of arsenic. The results are not quite accurate, since the antimonuret of silver contains invariably traces of arsenic; this defect, however, is of no great consequence.

The following formula will serve to illustrate the decompositions and transpositions which antimonuretted and arseniuretted hydrogen undergo when coming into contact with nitrate of silver.

$$6\,(Ag\,O,\,N\,O_5)+As\,H_3=6\,Ag+As\,O_3+3\,H\,O+6\,N\,O_5,$$
$$3\,(Ag\,O,\,N\,O_5)+Sb\,H_3=Ag_3\,Sb+3\,H\,O+3\,N\,O_5.$$

II. SEPARATION OF THE ACIDS FROM ONE ANOTHER.

I have here to remark once more, that the methods of separation which I am about to describe, are generally based upon the presupposition that the acids exist either in the free state or in combination with alkaline bases.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—SILICIC ACID—CARBONIC ACID.

§ 131.

1. ARSENIOUS AND ARSENIC ACID FROM THE OTHER ACIDS.

The whole of the arsenic is precipitated by means of sulphuretted hydrogen. (§ 97.) The filtrate contains the other acids, which are finally determined by the appropriate methods. Should chromic acid be present, this must first be reduced to the state of oxide, (§ 99,) to prevent the precipitation of sulphur in conjunction with the sulphuret of arsenic.

2. SULPHURIC ACID FROM THE OTHER ACIDS.

The solution under examination (which should be dilute) is strongly acidified with hydrochloric acid, and subsequently mixed with chloride of barium. The precipitated sulphate of barytes is filtered, and subsequently determined according to the directions of § 100. The filtrate contains the whole of the other acids, which are finally determined by the proper methods.

3. CHROMIC ACID FROM PHOSPHORIC ACID.

The phosphoric acid is precipitated with sulphate of magnesia, (§ 101,) and the chromic acid in the filtrate determined as directed § 99.

4. CHROMIC ACID FROM BORACIC ACID.

The chromic acid is first reduced to the state of oxide, (§ 99,) and the oxide of chromium subsequently separated from the boracic acid, as directed at § 102.

5. PHOSPHORIC ACID FROM BORACIC ACID.

The phosphoric acid is precipitated by means of sulphate of magnesia, (§ 101, I., *b.*,) and the boracic acid in the filtrate subsequently determined by one of the methods described at § 102.

6. PHOSPHORIC ACID OR BORACIC ACID FROM OXALIC ACID.

The alkaline salts of these acids are ignited, and the phosphoric or boracic acid in the residue is determined by the appropriate method; the amount of oxalic acid is determined in another portion of the compound under examination, according to the directions given at § 103, I., *b*.

7. FLUORINE FROM SILICIC ACID AND THE SILICATES.

a. Wöhler's method.

The compound under examination, very finely levigated, is introduced into a small flask, and pure hydrated sulphuric acid poured over it; the flask is quickly closed with a perforated cork, into which a small chloride of calcium tube is tightly fitted; the apparatus thus prepared is weighed with the greatest possible expedition, and subsequently exposed to the action of heat until the evolution of fumes of fluoride of silicon ceases; the last traces of gas are finally removed from the flask, by means of an exhausting syringe. The apparatus is then allowed to cool, and subsequently weighed; the loss of weight which it has undergone, indicates the amount of fluoride of silicon expelled in the process; the proportion of the fluorine and that of the silicon are calculated from this, and the amount of the latter is then calculated upon silicic acid, the resulting amount being finally added to the weight of the silicic acid in the residue. The apparatus may be modified by adding a second tube, closed with a wax stopper at the top, and the lower end of which is made to reach nearly to the bottom of the flask. This modification of the apparatus renders the use of an exhausting syringe unnecessary, since the last traces of gas may now 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. Should the proportion of fluorine be very considerable, and that of silicon comparatively small, the compound under examination is to be mixed with a weighed amount of chemically pure silicic acid, which is finally to be deducted from the results.

β. *Berzelius' method.*

aa. The compound under examination is levigated and elutriated to the highest degree of fineness, and the powder thus prepared is subsequently fused with four parts of carbonate of soda; the fused mass is kept for some time at an intense red heat, and subsequently extracted by boiling with water; the solution thus obtained is saturated with carbonic acid, filtered, and the residue washed with water, until the rinsings cease to manifest an alkaline reaction. The washed residue contains the whole of the silicic acid,—(provided this acid be not present in superabundance, in which case the modified method *bb.* must be resorted to,)—

alumina, &c. &c.; the solution, which contains the whole of the fluorine in the form of fluoride of sodium, in conjunction with carbonate of soda, is to be cautiously neutralized with hydrochloric acid, and subsequently kept exposed to the air for twenty-four hours in an open basin, in order to remove the carbonic acid—(this may be more safely attained by placing the basin under a bell-jar, by the side of a vessel filled with potass ley.)—The hydrofluoric acid is then finally precipitated by means of chloride of calcium, in conjunction with ammonia, free from carbonic acid. (§ 104.)

bb. Should the compound under examination contain a very abundant proportion of silicic acid, the method described sub. *aa.* will fail to separate the whole of this acid. REGNAULT recommends in such cases to mix the filtered solution of *aa.* with a solution of carbonate of zinc in ammonia, and to evaporate the mixture to dryness. The solution of fluoride of sodium, which is now obtained upon extracting the residue with water, is perfectly free from silicic acid, and is to be treated according to *aa.*; the silicic which the residue contains, in conjunction with carbonate of zinc, is best determined *per se*, and the resulting weight added to that found in the principal residue.

If the compound under examination contain a large proportion of lime, fluxing it with carbonate of soda will not effect its complete decomposition; so much is certain, at least, that fluoride of calcium is not completely resolved by fusion with carbonate of soda.

8. METALLIC FLUORIDES, SILICATES, AND PHOSPHATES FROM ONE ANOTHER.

Compounds of metallic fluorides, silicates, and phosphates, are of rather frequent occurrence in nature; their analysis may be effected according to 7, *α.*, or *β. aa.*, although the latter method must not be expected to effect invariably complete decomposition; at any rate, fluxing with carbonate of soda fails to effect the complete decomposition of phosphate of lime. The solution which is obtained upon treating the fused mass by boiling with water, (7, *β.*, *aa.*,) contains, in presence of phosphates, besides fluoride of sodium and carbonate of soda, also phosphate of soda, and the precipitate which this solution yields subsequently with chloride of calcium, consists therefore of fluoride of calcium mixed with phosphate of lime. This precipitate is washed, dried, ignited, and weighed, and subsequently heated with pure sulphuric acid in moderate excess, until the whole of the hydrofluoric acid present is expelled; the residue is then treated with alcohol, and the solution filtered off from the insoluble sulphate of lime, which latter is to be determined according to § 76;—the phosphoric acid in the filtrate is determined as directed at § 101, I., *b*. The amount of fluorine originally present in the mixed precipitate of fluoride of calcium and phosphate of lime, is inferred from the loss of weight suffered by the precipitate in the process of heating with sulphuric acid.

9. SILICIC ACID FROM ALL OTHER ACIDS (hydrofluoric acid excepted).

a. In compounds decomposed by hydrochloric acid.

The compound under examination is decomposed by more or less protracted digestion with hydrochloric acid, and the mixture finally evaporated to dryness, (§ 106, 2, *b*.); the residue is treated, according to circumstances, either with water, hydrochloric acid, or nitric acid, and the solution filtered off from the residuary silicic acid; the filtrate contains the whole of the other acids. Should boracic acid be present, the evaporation is to be conducted in a flask, and the disengaged vapor received in water, so as to avoid any loss of substance. Should carbonates be present, the carbonic acid is to be determined in a fresh portion of the analysed compound.

β. In compounds which hydrochloric acid fails to decompose.

The substance under examination is fused with alkalies, (compare § 20); the mass may either at once be acted upon with dilute hydrochloric or nitric acid, and the solution treated according to *a.*; or the fused mass may be extracted with water; part of the silicic acid dissolves, however, in this process, in conjunction with the other acids; this is precipitated again by heating with bicarbonate of ammonia. The fluid is filtered off from the precipitate, and the latter washed, and subsequently added to the residue, which is then treated with hydrochloric acid in the manner described at § 106, in order to determine the amount of silicic acid originally present in the analysed compound. The filtrate contains the whole of the other acids. Which of these methods is preferable in particular cases depends upon the nature of the bases and the relative proportion of silicic acid present.

10. Carbonic acid from all other acids.

As carbonic acid is expelled and removed upon heating its salts with stronger acids, the presence of carbonates does not interfere with the determination of most other acids; and since, on the other hand, the proportion of carbonic acid present in a compound is most simply inferred from the loss of weight suffered by the latter, the presence of salts of non-volatile acids does not interfere with the determination of the carbonic acid. Accordingly, when we have to analyse compounds consisting of carbonates, sulphates, phosphates, &c., &c., we determine the carbonic acid in one portion, and the other acids in another portion of the substances under examination. Should the compound contain fluorides, the carbonic acid must be expelled by one of the weak non-volatile acids, (e. g. tartaric acid, citric acid,) since, were we to use sulphuric acid or hydrochloric acid, part of the liberated hydrofluoric acid would escape in conjunction with the carbonic acid. It happens sometimes in the course of analysis, that we obtain a mixed precipitate of fluoride of calcium and carbonate of lime; these two substances may, in such cases, be separated by pouring acetic acid over the mixed precipitate, adding alcohol, filtering, and finally washing the residue with alcohol.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID (SULPHURETTED HYDROGEN).

I. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 132.

a. Separation of the whole of the acids of the second group from those of the first.

The dilute solution of the compound under examination is mixed with nitric acid, solution of nitrate of silver added in excess, and the fluid filtered off from the insoluble silver compounds of chlorine, bromine, iodine, &c., &c. The filtrate contains the whole of the acids of the first group, the silver salts of these acids being soluble in water or in nitric acid. Carbonic acid requires, under all circumstances, a separate determination.

b. Separation of individual acids of the second group from individual acids of the first group.

Since it is inconvenient for the further separation of the acids of the second group, to have them all in the form of insoluble silver compounds, the following methods are preferred to that described at *a.*, in cases where we have to separate *several* acids of the second group from individual acids of the first group.

1. SULPHURIC ACID may be separated from the acids of the second group, by the method described at § 131, 2, with this difference, that nitrate of barytes is substituted for chloride of barium.

2. PHOSPHORIC ACID may be precipitated by means of nitrate of magnesia in conjunction with ammonia, in presence of nitrate of ammonia, (compare § 101, I., *b.*) The filtrate contains the whole of the acids of the second group.

3. Oxalic acid may be readily removed by means of nitrate of lime.

4. Sulphuretted hydrogen may be separated from the acids of the first group by means of nitrate of copper, or by means of a solution of arsenious acid in water.

APPENDIX.

The various sorts of *hepar sulphuris*—which, when prepared in the humid way, or at a feeble heat in the dry way, contain, besides the alkaline sulphurets, an admixture of hyposulphites and frequently of sulphates,—may be analysed in the following manner. The solution of the hepar sulphuris under examination is introduced into a flask, provided with a ground stopper, and solution of neutral nitrate of zinc added in excess; the precipitate which forms is allowed to subside, and the fluid subsequently filtered off; (the operator must take care to prevent the access of air as much as possible during the filtration); the precipitate is collected upon the filter, and quickly washed with cold water which has previously been freed from air by ebullition; the proportion of sulphur in the washed precipitate is finally determined according to § 111. The filtrate is mixed with an excess of highly dilute solution of nitrate of silver, and the mixture subsequently heated for some time. The hyposulphurous acid undergoes decomposition in this process, the one half of it being converted into sulphuric acid, at the expense of the oxygen of the other half, and moreover of the oxygen of one equivalent of oxide of silver, whilst the reduced sulphur combines with the reduced silver to sulphuret of silver, which precipitates

$$(KO, S_2O_2 + AgO, NO_5) = (KO, SO_3 + AgS + NO_5).$$

The fluid is filtered off from the precipitated sulphuret of silver, and the weight of the latter determined as directed at § 86; the proportion of sulphur contained in this is finally calculated; the resulting figure doubled indicates the amount of sulphur originally present in the analysed hepar sulphuris, in the form of hyposulphurous acid. The fluid filtered off from the sulphuret of silver is acted upon with nitrate of barytes, and the precipitated sulphuret of barytes determined as directed at § 100. If the calculated amount of sulphur present in this precipitate is equal to that contained in the first precipitated sulphuret of silver, this is a proof that the analysed hepar sulphuris contains no sulphuric acid. If, on the other hand, the calculated amount of sulphur in the sulphate of barytes exceeds the proportion of sulphur present in the sulphuret of silver, this is a proof that the analysed substance contains sulphuric acid; the proportion of the latter is found, in such cases, by calculating the difference upon sulphuric acid. The amount of the alkali is determined in a separate portion of the solution by evaporating this in conjunction with sulphuric acid.

II. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM ONE ANOTHER.

§ 133.

1. CHLORINE FROM BROMINE.

a. Direct analysis.

The solution under examination is precipitated with nitrate of silver, (§§ 107 and 108.) The precipitate is collected upon the filter, washed, dried, and heated to a state of semifusion, and subsequently reduced by means of zinc, in conjunction with a little dilute sulphuric acid; the solution of bromide and chloride of zinc which is thus produced (and which contains free sulphuric acid) is precipitated with water of barytes in excess, and the fluid filtered off from the mixed precipitate of hydrated oxide of zinc and sulphate of barytes, which is then thoroughly washed upon the filter. The filtrate is evaporated to dryness, and the residue subsequently treated with absolute alcohol, which dissolves the bromide of barium, leaving the chloride of barium intact. The chlorine and bromine are now respectively determined in the thus separated barium compounds, according to the directions given at §§ 107 and 108. (Henry.) The results are approximate.

β. Indirect analysis.

Solution of nitrate of silver is added to the solution under examination, and the mixed precipitate of chloride and bromide of silver which is thus obtained, is thoroughly washed, dried, fused, and most accurately weighed. A weighed portion of it is introduced into a tared bulbous tube,* and heated to fusion; the tube is then allowed to cool, and weighed when perfectly cold. A slow stream of pure and dry chlorine gas is now transmitted through the tube, and the contents of the bulb are again heated to fusion; the fused mass is agitated from time to time. After the lapse of about twenty minutes, the tube is removed from the chlorine apparatus, allowed to cool, held obliquely for some time, to replace the chlorine gas by atmospheric air, and finally weighed; the contents of the tube are then again heated in a stream of chlorine gas, for the space of about ten minutes, and subsequently reweighed. If the results of the two last weighings agree, the process may be considered concluded; if not, the operation must be repeated. The amount of bromine originally present in the mixed precipitate of chloride and bromide of silver, is inferred from the diminution of weight which the tube exhibits at the conclusion of the process. For the mode of calculating the results, vide infra.

2. CHLORINE FROM IODINE.

None of the methods which were formerly pursued to effect the separation of these two salt-radicals, (separation of chloride from iodide of silver, by means of ammonia, or precipitation of the iodine by means of solution of subchloride of copper in hydrochloric acid, or by means of a mixed solution of protosulphate o iron and sulphate of copper,) yield accurate results. The following methods have completely superseded them.

α. Direct analysis.

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* The best way of effecting the transfer of this portion from the crucible to the tube, is to fuse the mass again.

aa. The iodine is precipitated by means of protonitrate of palladium, (§ 109); the chlorine in the filtrate is precipitated with nitrate of silver, (§ 107). The results are very accurate. This method deserves particular commendation.

bb. The solution under examination is mixed with a solution of sulphate of copper in sulphurous acid; this re-agent precipitates the whole of the iodine, (present in the form of hydriodic acid, or in that of metallic iodide,) whilst the whole of the hydrochloric acid remains in solution. The fluid is filtered off from the precipitate, and the latter collected upon the filter, and washed. The washed precipitate is now to be dried at 248°, and subsequently weighed at once. (DUFLOS.) A still more simple and accurate way is, to dissolve the precipitate in very dilute nitric acid, and to precipitate the solution subsequently with nitrate of silver. (§ 109.)

β. Indirect analysis.

The method described at 1, *β.* (Separation of chlorine from bromine, is pursued). The results are still more accurate here, since the difference between the atomic weight of chlorine and that of iodine is far more considerable than that between the respective atomic weights of chlorine and bromine.

3. CHLORINE, BROMINE, AND IODINE FROM ONE ANOTHER.

The iodine is precipitated from the mixed solution by means of protonitrate of palladium. (§ 109.) The chlorine and bromine in the filtrate are subsequently precipitated with nitrate of silver, and their relative proportions determined as directed at 1, *β.* (Separation of chlorine from bromine.)

4. CYANOGEN FROM CHLORINE, BROMINE, OR IODINE.

a. The mixed solution under examination is precipitated with nitrate of silver; the precipitate is collected upon a tared filter, washed, and subsequently dried in the water-bath until its weight remains constant; the proportion of cyanogen contained in it, is then determined by the method of organic elementary analysis. The proportion of the chlorine, bromine, or iodine is inferred from the difference.

β. The relative proportions of hydrocyanic and hydrochloric acid present in one and the same solution, may be determined also in the following manner. The solution is divided into two perfectly equal portions. The one portion is precipitated with nitrate of silver, and the mixed precipitate of cyanide and chloride 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 of the first portion. This method is based upon the circumstance, that percyanide of mercury is not decomposed by nitrate of silver.

5. SULPHURETTED HYDROGEN FROM THE SALT-RADICALS.

α. *The solution under examination contains free sulphuretted hydrogen either with free hydriodic, hydrobromic, or hydrochloric acid, or a metallic iodide, chloride, or bromide.*

The solution is mixed with an aqueous solution of arsenious acid, and the sulphur in the precipitate which forms, is determined as directed at § 111. The filtrate contains the salt radicals.

β. *The solution contains an alkaline sulphuret in conjunction with metallic bromides, iodides, or chlorides.*

The solution under examination is mixed with a sufficient amount of solution of arsenite of potass, and dilute nitric acid subsequently added in moderate excess; the further process is conducted as directed at α. I need hardly remark that the precipitate of sulpharsenious acid cannot be weighed *directly* in cases where the sulphuret originally present in the analysed compound is of a higher degree of sulphuration than the sulpharsenious acid. In such cases a separate determination of the amount of sulphur contained in the precipitate is indispensable.

THIRD GROUP.

NITRIC ACID—CHLORIC ACID.

I. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM THOSE OF THE TWO FIRST GROUPS.

§ 134.

A general method to effect the separation of nitric and chloric acid from other acids can hardly be attempted, since even the simple direct determination of these acids is attended with so many difficulties; every individual case may in fact require the application of a different and particular method. In many cases, for instance, where we have nitric acid mixed with another acid, it will be necessary in the first place to determine the joint amount of the two acids, and subsequently the separate amount of the admixed acid, when the difference between the latter and the former will express the proportion of the nitric acid; thus, for instance, to analyze a mixture of sulphuric acid and nitric acid, the joint amount of the two acids may be determined by evaporating the fluid in conjunction with a weighed amount of oxide of lead, or according to the acidimetrical method described at § 112, and the amount of sulphuric acid may then be separately determined in a fresh portion of the mixture, by means of barytes. In other cases, the removal of the admixed acid may be effected by means of a weighed amount of a nitrate, and the nitric acid subsequently determined according to one of the methods described at § 112; thus, for instance, from a mixture of a nitrate with a metallic chloride, the hydrochloric acid may be precipitated and removed by means of a weighed amount of nitrate of silver, &c. &c. The property of chlorates to be converted into chlorides by ignition, furnishes us usually with a means to effect the determination of the amount of chloric acid present in a compound which contains several acids; and since chloric acid forms no insoluble salts, the presence of chlorates does not interfere with the quantitative determination of the other acids. The estimation of the chloric acid present in a mixed compound of a chlorate and chloride, is to be effected in the following manner:—A weighed portion of the compound under examination is precipitated with nitrate of silver, and the precipitated chloride of silver accurately weighed; an equal portion of the substance is ignited, the residue redissolved, and the solution precipitated with nitrate of silver; this precipitate is likewise accurately weighed, and the amount of chloric acid is finally calculated from the difference between the respective weight of the two precipitates.

II. Separation of the acids of the third group from one another.

We have as yet no method to effect the direct separation of nitric acid from chloric acid; these two acids must accordingly be determined indirectly. It is impossible to lay down any general instruction or rules as to the selection of the most appropriate method in every individual case.

APPENDIX TO THE SECOND PART OF THE FIFTH SECTION.

I.

ALKALIMETRY.

It is well known that the potash and soda of commerce consist of a mixture of alkaline carbonate with a number of other salts. The commercial value of potash and soda depends entirely upon the proportional amount of carbonated (or caustic) alkali which they contain, the admixed salts being of no value to the purchaser. Now, as the proportion of these admixed salts is exceedingly variable, it will be readily conceived that, to estimate the value of any of the samples of potash or soda which may occur in commerce, it is necessary to ascertain the proportional amount of carbonated (or caustic) alkali whlch they respectively contain. The methods which serve to determine the value of potash and soda in this respect, are called individually *alkalimetrical methods*, and collectively "*alkalimetry*." I will describe here two methods of alkalimetry, which are respectively based upon essentially different principles; the one of these methods is of more expeditious execution, the other yields more accurate results. (Compare experiments, sub. No. 67.)

§ 135.

A. ALKALIMETRICAL METHOD OF DESCROIZILLES AND GAY-LUSSAC.

1. The following is the principle of this method: 1 equivalent of potass or soda requires one equivalent of sulphuric acid to form a neutral salt; that is, in other terms, 588.94 parts of potass, or 390.9 parts of soda require 500.00 parts of anhydrous, or 612.50 parts of hydrated sulphuric acid.

Accordingly, if the quantity of sulphuric acid required to saturate an unknown amount of caustic or carbonated potass or soda, be known, the quantity of the alkalies may be readily ascertained by simple calculation; and, on the other hand, if the quantity of caustic or carbonated alkali required to saturate an unknown amount of sulphuric acid be known, the amount of the acid may be readily calculated from this.

2. The sulphuric acid cannot be used in the anhydrous state, nor as pure hydrate, but must be diluted with water. Dilute sulphuric acid of determinate strength may be procured in two ways; viz.

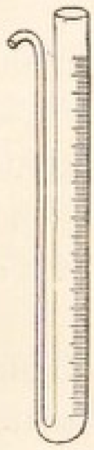
a. A weighed amount of pure hydrated sulphuric acid is mixed with a weighed amount of water.

b. The saturating capacity of a given dilute sulphuric acid is determined by ascertaining how much of the acid is required to neutralize a definite amount of potass or soda.

To the method *a.* (GAY-LUSSAC's) there is this objection, that it is difficult to prepare perfectly pure hydrated sulphuric acid.—The method *b.* (OTTO's) yields at the least equally accurate results, and has moreover this advantage over *a.*, that the sulphuric acid of commerce may be used at once, without any further preparation. I prefer Otto's method decidedly to that of Gay-Lussac.

3. The amount of sulphuric acid used in this process may be ascertained either by weighing, or by measuring. The latter way is universally adopted, since it admits of a more expeditious execution than the former. The graduated glass measure illustrated by Fig. 44 is the most appropriate instrument to effect this purpose.

PLATE 44



To make this ingenious instrument less fragile, the interval between the graduated tube and the effusion tube may be filled with wax, somewhat below the upper bend of the latter, and a piece of fine wire subsequently tied round this part of the instrument.—The measure glasses, which are manufactured at Paris or upon the Paris model, are graduated in such a manner that every degree, i. e. the interval between every two divisional lines, corresponds to $\frac{1}{2}$ cubic centimeter ;—8 drops form the average amount of every degree.

Were it intended to draw up a calculation after every experiment, it would simply be necessary to know the exact proportion which the dilute acid bears to the alkalies, and thus, for instance, to know that 97 cubic centimeters of the acid saturate 4.5 grammes of carbonate of soda ;—if it were now found that 6.7 grammes of a given sort of soda require 85 cubic centimeters of the acid for their saturation, the proportion of the carbonate of soda contained in the analyzed article, would at once result from the following equation :

$$97 : 4.5 :: 85 : x = 3.94$$

The 6.7 grammes of the analyzed soda would accordingly contain 3.94 grammes of pure carbonate of soda, that is, 58.8 in every 100 parts. But even this simple calculation may be saved by preparing at once a stock of test acid of a definite saturating capacity.

4. For instance, let us prepare an acid of which 100 volumes are required to saturate a certain definite amount, say 5 grammes of potass; now it is evident that, if we mix the potass with an equal weight of a neutral substance, e. g. chloride of sodium, and weigh off 5 grammes of the mixture, the saturation of these 5 grammes will require only 50 volumes of our test acid, and accordingly that the number of volumes required will directly indicate the percental proportion of potass contained in the mixture.

5. A test acid of this kind is prepared most simply in the following way:

a. About 70 grammes of sulphuric acid are mixed with 600 grammes of water, and the mixture is allowed to cool.

b. 5 grammes of anhydrous pure carbonate of soda are accurately weighed off, introduced into a beaker-glass, and dissolved in hot water; the solution is colored blue, with a little tincture of litmus.

c. The graduated tube is filled up to 0. with the cold dilute acid, and this is subsequently dropped from the measure into the solution of soda, until the latter is saturated. (Vide infra.) The number of volumes required to effect this object is accurately noted.

d. The rest of the acid is now mixed with an amount of water exactly sufficient to raise the number of volumes found in *c.* to 100. Thus, for instance, suppose you find that 75 volumes of your acid are required to saturate 5 grammes of carbonate of soda, you will have to add 25 volumes of water to every 75 volumes of the acid. The best way of effecting this object, is to measure the whole of the remaining acid in a larger measure-glass, to calculate from the measured quantity of the acid, the amount of water required, to measure off the required portion of the latter fluid, and to add this finally to the acid.

The so prepared test-acid is kept in well-closed vessels. It serves for the examination of all alkaline fluids, and indicates the proportional amount of caustic or carbonated alkali which they contain, directly in percents, provided the experiment be made upon a weighed amount of the fluid equivalent to 5 grammes of carbonate of soda.

6. These equivalent proportions may be seen from the following table:

100	volumes of test-acid	saturate	5.000	grammes of	carbonate of soda.
100	,,	,,	2.935	,,	soda.
100	,,	,,	6.487	,,	carbonate of potass.
100	,,	,,	4.421	,,	potass.

Accordingly, if we take 6.487 grammes of a given sample of potash which we wish to analyze, the number of volumes of the test-acid required for the saturation of these 6.487 grammes, is directly indicative of the proportional amount of carbonate of potass present—if we take 4.421 grammes, the number of volumes of our test-acid required for the saturation of these 4.421 grammes, indicates at once, and without any further calculation, the proportion of anhydrous caustic potass contained in the analyzed sample, &c. &c.

When we have to examine substances poor in caustic or carbonated alkalies, it is preferable to take a multiple of the above figures; for instance, the double, triple, &c.; and to divide subsequently the number of volumes of the test-acid required in the process, by the corresponding figures, (2, 3, 10, &c.)

7. The following points require particular attention in the execution of the process:

a. The measure-tube must be correctly and accurately graduated. (§ 11.)

b. The operator must take care to read the volume of the test-acid used, correctly off. (§ 12.)

c. The tincture of litmus must not in itself contain a large portion of free alkali; should this be the case, the free alkali is to be neutralized first in a great measure, by means of highly dilute sulphuric acid.

d. The point of saturation, or rather of commencing supersaturation, must be noted with the greatest accuracy.—Caustic alkalies offer no difficulty in this respect, but when we have to deal with alkaline carbonates, the liberated carbonic acid renders the attainment of this object a matter of some difficulty, and diminishes the accuracy of the results. — To promote the evolution of the carbonic acid, the potash or soda are dissolved in hot water, and the test-acid is added until the color of the solution appears wine-red; the test-acid is then added more cautiously, and finally by 2 and 2 drops, (about $\frac{1}{4}$ of a volume.) To decide whether the red coloration proceeds from the sulphuric acid, or from the liberated carbonic acid, a glass rod is dipped into the fluid, and subsequently drawn across a slip of litmus paper; and the same process is repeated while the addition of the test acid by 2 and 2 drops is continued. If the red coloration proceeds from the *sulphuric acid*, the red streaks will remain visible upon the paper when dry, whilst they will completely disappear upon drying, if arising from the action of *carbonic acid* upon the test-paper. The number of red streaks which are counted upon the litmus paper after drying, indicate the numbers of quarters of a volume added in excess;—to this number is to be added one quarter of a volume for the free alkali calculated to exist in the litmus tincture; and the sum total is finally to be subtracted from the number of volumes of the test-acid used in the process.

8. PRACTICAL APPLICATION OF THE METHOD FOR THE EXAMINATION OF COMMERCIAL POTASH.

The various sorts of potash of commerce contain, besides carbonate of potass,

a. Neutral salts (e. g. sulphate of potass, chloride of potassium).

b. Salts with alkaline reaction (e. g. silicate of potass, phosphate of potass).

c. Constituents insoluble in water, viz., carbonate, phosphate, and silicate of lime, &c.

The salts mentioned sub. *a.* are without influence upon the results of the examination, but not so those enumerated sub. *b.* and *c.*; the latter may be removed, however, by simple solution and subsequent filtration. But the admixture of salts with alkaline reaction forms an irremediable source of error.

The process is conducted as follows: 6.487 grammes of the potash under examination are weighed off, and dissolved in hot water; the solution is subsequently filtered, if necessary; the *alkalimeter* is then filled up to 0. with the test acid, and the further operation conducted as directed above. Should the operator be desirous to ascertain whether the potash contains, besides extraneous salts, an admixture of water, he must determine this point before he proceeds to the alkalimetrical examination.

9. PRACTICAL APPLICATION OF THE METHOD FOR THE EXAMINATION OF COMMERCIAL SODA.

The soda of commerce, prepared according to LEBLANC'S method, contains, besides carbonate of soda, invariably, or at least generally,

Sulphate of soda.
Chloride of sodium.
Sulphuret of sodium.
Basic silicate of soda.
Hydrate of soda.
Hyposulphite of soda,
and sometimes
Sulphite of soda.

Of these admixtures, the sulphuret of sodium, silicate, sulphite, and hyposulphite of soda, impede the examination considerably, and interfere more or less with the accuracy of the results.

This source of error may be in some measure remedied by igniting the soda under examination in conjunction with chlorate of potass; since this process effects the transformation of the sulphuret of sodium and of the hyposulphite and sulphite of soda into sulphate of soda. If hyposulphite of soda be present, however, this process will create a fresh source of error, since this salt, upon its conversion into sulphate, decomposes one equivalent of carbonate of soda, and expels its carbonic acid.

$$[\mathrm{Na\ O, S_2\ O_2} + 4\ \mathrm{O}\ \text{(from the chlorate of potass)}$$
$$+ \mathrm{Na\ O, C\ O_2} = 2\ (\mathrm{Na\ O, S\ O_3}) + \mathrm{C\ O_2}.]$$

Accordingly, before proceeding to the application of Gay Lussac's test method, it is necessary, in the first place, to ascertain by a preliminary examination, whether the soda which it is intended to examine does or does not contain an admixture of the above enumerated salts which may interfere with the accuracy of the results. This object may be effected most simply as follows.

a. The sample under examination is mixed with sulphuric acid. The odor of sulphuretted hydrogen indicates the presence of *sulphuret of sodium*.

b. Dilute sulphuric acid is colored with a drop of solution of chromate of potass, and a portion of the sample under examination added, but not sufficient to saturate the acid. If the solution remains of a red yellow, this may be considered a proof of the absence of sulphite or hyposulphite of soda. Should it turn green, on the contrary, this is a sure sign of the presence of either of these salts.

c. Whether the green coloration of the solution in *b*. proceeds from sulphite or hyposulphite of soda, is ascertained by supersaturating a clear solution of the sample under examination, with hydrochloric acid. If the solution, after the lapse of some time, becomes turbid, owing to the separation of sulphur, (exhaling at the same time the odor of sulphurous acid,) this may be looked upon as a certain proof of the presence of hyposulphite of soda; the solution may however, besides the hyposulphite, contain also sulphite of soda.

B. Alkalimetry according to Fresenius and Will.*

§ 136.

The principle of this method is to calculate the proportion of carbonated alkali contained in the various sorts of potash and soda of commerce from the amount of carbonic acid which they contain. It is necessary for the application of this method that the whole of the alkali, in which the commercial value of the articles in question consists, be present in the form of a neutral carbonate; and, moreover, that besides this no other carbonate be present. Should the potash or soda under examination fail to satisfy these conditions, their accomplishment must be effected in the appropriate manner.

The determination of the carbonic acid is effected according to § 105, II., *b.*, *β.*, *aa.* The flasks of the apparatus illustrated by Plate XXXIV. should not be selected of too small a size; A should have a capacity of from two to two ounces and a half; B should hold from one ounce and a half to two ounces. It is always advisable, although not absolutely necessary to determine in the first place, the amount of water contained in the sample under examination before proceeding to effect the determination of the carbonic acid.

1. Examination of potash.

a. Determination of the water.

A small sheet iron basin of about two inches in diameter, and provided with a somewhat loosely fitting cover, is placed upon the one scale of a balance, and a ten grammes weight put upon the same scale; the balance is then accurately equipoised by means of small shot, &c.; samples of the potash under examination are then taken from different parts of the mass, and quickly

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* New Methods of Alkalimetry, &c., by Drs. C. R. Fresenius and H. Will, edited by Lloyd Bullock. 12mo. London: Taylor and Walton.

levigated in a dry mortar; the ten grammes weight is now removed from the scale, and the potash powder projected into the basin until the original equilibrium is perfectly restored.

We have now in the basin exactly ten grammes of the potash sample. A gentle heat is then applied to the basin until the whole of the water present is expelled, which may be ascertained by holding a glass plate over the open basin and observing whether any aqueous vapor condenses upon it or not. The basin is then covered, allowed to cool, and, when cold, replaced upon the balance; the equilibrium is restored by additional weights. The number of decigrammes required to restore the equilibrium indicates directly the amount of water present in every one hundred parts of the examined potash. (A porcelain crucible provided with a lid may be substituted for the iron basin).

b. Determination of the carbonic acid.

6.283 grammes of the anhydrous residue of *a.* are weighed off, and the amount of carbonic acid contained in them is determined according to § 105, II., *b.*, *β.*, *aa.* The amount of carbonate of potass contained in the analysed potash is found directly by simply dividing by 2 the number of centigrammes of carbonic acid evolved. Thus, let us suppose, that 6.283 grammes of potash yield 1.80 grammes of carbonic acid, the examined potash will contain $\frac{180}{2}=90$ per cent. of carbonate of potass.

Should the potash contain an admixture of carbonate of lime—(which is but very rarely the case)—the sample is to be dissolved in water, the solution filtered, and the filtrate concentrated by evaporation, and finally treated according to the directions of *b.* Potash which contains admixtures of sulphuret of potassium and caustic potass is treated like soda under analogous circumstances. (Vide 2.)

2. Examination of soda.

The general method is the same with that applied for the examination of potash. 4.84 grammes of the anhydrous residue are to be weighed off, if the operator wishes to find the percentage amount of carbonate of soda contained in the analysed substance, by simply dividing by 2 the number of centigrammes of carbonic acid evolved.

Should the soda under examination contain an admixture of sulphuret of sodium, sulphite or hyposulphite of soda, the common process of determining the carbonic acid would give rise to the disengagement of sulphuretted hydrogen or sulphurous acid, which would of course add to the amount of the carbonic acid. This may be readily remedied by adding to the solution of the soda in A a small amount of solution of neutral chromate of potass, since this will effect the decomposition of the sulphuretted hydrogen or sulphurous acid, and the products of this decomposition being non-volatile, the carbonic acid will now escape without the slightest admixture. Since most sorts of soda of commerce contain admixtures of sulphuret of sodium, sulphite or hyposulphite of soda, and since it is far more simple to add at once some chromate of potass to the soda solution than to ascertain first whether either of the three salts be present or not, it is advisable to make the addition of some chromate of potass an invariable rule in the examination of soda.

Should the soda under examination contain an admixture of caustic soda, which may be detected by the alkaline reaction which the solution of the sample manifests, after the addition of chloride of barium in excess, the following modification of the common method is to be adopted.

a. DETERMINATION OF THE WATER.

This is effected in the usual manner. (Vide 1, *a.* Examination of potash.)

b. DETERMINATION OF THE CARBONIC ACID.

4.84 grammes of the anhydrous residue of *a* are weighed off and triturated in a mortar with from three to four parts of pure quartz sand, and about one-third part of carbonate of ammonia in powder; the mixture is transferred to a small iron basin, and the mortar rinsed with sand, which is also transferred to the basin. The whole mass is then moistened with as much water as it can imbibe, allowed to stand for a little while, and subsequently gently heated until the whole of the water is expelled again. The residue will contain no longer the slightest trace of carbonate of ammonia. Should the soda under examination contain sulphuret of sodium besides caustic soda, solution of caustic ammonia is to be substituted for the water, to effect the reduction of the sesqui-carbonate of ammonia to neutral carbonate; otherwise sulphuret of ammonium would be evolved, and part of the sulphuret of sodium would be transformed into carbonate of soda.

The mass, when cold, is transferred from the basin to the flask A—(this may be readily effected by the aid of a blunt knife)—the basin is rinsed with a little water, which is then likewise poured into A. The rest of the process is conducted in the usual way. The admixture of sand in this process is intended to prevent the lumping of the mass, and also the spitting and spirting which would otherwise attend the expulsion of the water, unless the greatest caution were used in the process of heating; moreover, the perfect removal of the dried mass would be rather a difficult task without the sand.

The latter operation may be still more facilitated by coating the inside of the basin with sand, previously to the introduction of the mixture; this is effected most simply by moistening the inner walls and bottom of the basin with water, throwing a handful of sand into it, and shaking the superfluous quantity out again.

3. DETERMINATION OF THE CAUSTIC ALKALI WHICH COMMERCIAL POTASH AND SODA MAY CONTAIN IN ADMIXTURE WITH THE CARBONATE.

Two portions, of 6.283 grammes each, of the anhydrous residue of the potash sample or, of 4.84 grammes each, of the anhydrous residue of the soda sample are weighed off, and the carbonic acid is determined in the one portion directly, and in the other after previous treatment with carbonate of ammonia, (vide 2, *b*.) The number of centigrammes of the carbonic acid evolved from the latter portion, divided by 2, gives the joint per centage amount of carbonated and pure alkali (expressed as carbonate). The number of centigrammes of the carbonic acid evolved from the first portion, divided by 2, gives the per centage amount of the carbonated alkali. The difference between the two figures indicates accordingly the quantity of carbonated alkali which was originally present in the examined potash or soda, in the form of caustic alkali. The corresponding quantities of potass or soda are found most readily by multiplying this difference with 0.6817 in the case of potass, and with 0.5886 in the case of soda.

II. CHLORIMETRY.

§ 137.

The chloride of lime, or bleaching powder of commerce, is a mixture of hydrate of lime with hypochlorite of lime and chloride of calcium; the normal chloride of lime contains the two latter constituents in equal proportions. The action of an acid upon chloride of lime effects the liberation of the whole of the chlorine present.

$$\mathrm{Ca\,O,\,Cl\,O + Ca\,Cl + 2\,S\,O_3 = 2\,Ca\,O,\,S\,O_3 + 2\,Cl.}$$

The bleaching powder of commerce varies exceedingly in the proportional amount of chlorine which it yields when treated with acids. Now, as the commercial value of this article, which is manufactured on an immense scale, depends entirely upon the proportional amount of chlorine which it contains, it was very natural that chemists should endeavour to devise some simple method to determine the available amount of chlorine present in any given sample of bleaching powder. The various methods proposed with the view of effecting their object have collectively received the name of "*Chlorimetry*."

I will here describe three different methods which yield equally satisfactory results. These methods are valuable not simply in a commercial, but also in a purely scientific point of view, since they will serve to determine with great accuracy the amount of free chlorine present in a given fluid.

A. METHOD OF DETERMINING THE AMOUNT OF AVAILABLE CHLORINE BY MEANS OF PROTOCHLORIDE OF MERCURY. (After MAROZEAU and GAY-LUSSAC, slightly modified.)

1. This method is based upon the circumstance that one equivalent of chlorine converts one equivalent of protochloride of mercury into perchloride.

$$Hg_2\,Cl + Cl = 2\,Hg\,Cl.$$

2. It follows accordingly that the amount of protochloride of mercury converted into perchloride indicates at once the amount of chlorine which has served to effect this conversion. If we take, therefore, a fluid which holds a known quantity of protochloride of mercury in suspension, and add to it solution of chlorine until the whole of the protochloride of mercury is dissolved as perchloride, we know at once the proportion of chlorine contained in the solution which has served to effect this conversion.

3. The most simple and accurate method of preparing a fluid holding in suspension a definite and known amount of protochloride of mercury, is based upon the following principle.

a. 2945 parts of protochloride of mercury require 443 parts of chlorine to be converted into perchloride.

b. 734 parts of chloride of sodium are required to form 2945 parts of protochloride of mercury.

c. 734 parts of chloride of sodium (the chlorine being transferred to protoxide of mercury) correspond accordingly to 443 parts of chlorine, or, what comes to the same point, 165.7 parts of chloride of sodium correspond to 100 parts of chlorine.

d. Now if 1.657 grammes of chloride of sodium be weighed off and dissolved, and solution of protonitrate of mercury be carefully added until the formation of a precipitate ceases, the quantity of the solution of protoxide of mercury will exactly correspond to 1.657 gramme of common salt, or 1.00 gramme of chlorine; if another quantity of the solution of protonitrate of mercury, of exactly the same volume as the amount used in the process, be now mixed with water until the whole volume corresponds to 100 volumes of any accurately graduated glass measure, a fluid will be produced of which every volume contains exactly as much protoxide, or, if the solution be previously precipitated with common salt, protochloride of mercury, as will be converted respectively into peroxide and perchloride, by 0.01 gramme of chlorine.

4. *Preparation of a solution of protoxide of mercury of known and definite amount.*

According to the principle developed in 3, a solution of this kind is best prepared as follows:

a. 5 grammes of chemically pure ignited chloride of sodium are weighed off, and dissolved in water; the solution is poured into a measure-glass, and as much water added as will make the volume of the whole fluid correspond to 400 volumes of the graduated dropping-tube, illustrated by Plate XLIV.

b. 50 volumes (or less or more according to the degree of concentration of the fluid) of a solution of protonitrate of mercury, are measured off by means of a graduated syphon, of which the scale corresponds exactly with that of the dropping-tube; this measured portion of the solution is poured into an eight-ounce bottle, provided with a glass stopper, and is then finally diluted with water until the weight of the whole liquid is about five ounces.

c. The graduated dropping-glass is now filled with the solution of chloride of sodium of *a.*, and the latter is then cautiously added to the solution of the protonitrate of mercury (*b.*) until the last drop added ceases to produce a precipitate. The bottle is to be placed in hot water during this operation, and agitated after every fresh addition of solution of chloride of sodium, in order to promote the subsidence of the precipitate. Should the operator happen to add an excess of chloride of sodium, which will sometimes occur, he need simply add a few more volumes of the solution of protonitrate of mercury, and be more careful in the renewed addition of the chloride of sodium solution.

d. The measures of the chloride of sodium solution which have been used in this process, are accurately read off, and the amount of solution of mercury which corresponds to 1.657 gramme of common salt, is calculated from the resulting figure. Thus, for instance, let us suppose that 80 volumes of the solution of chloride of sodium have been required for the precipitation of 50 volumes of the solution of protonitrate of mercury: the calculation would proceed as follows:

α. 400 volumes of solution of Na Cl : 5 grammes of Na Cl : : 80 volumes : x—x=1 gramme;

β. 1 gramme of Na Cl : 50 volumes of solution of protonitrate of mercury : : 1.657 of common salt : x—x=82.85; which means that 82.85 volumes of the solution of protonitrate of mercury correspond to 1.657 gramme of chloride of sodium or to 1.00 gramme of chlorine. We have accordingly to add 17.15 volumes of water to every 82.85 volumes of the solution of protonitrate of mercury

$$\begin{array}{r} 82.85 \\ 17.15 \\ \hline 100.00 \end{array}$$

to produce a test fluid of the desired strength, i. e. of which every one volume corresponds to 0.01 gramme of chlorine. It is more advantageous still, to mix this fluid now with an equal volume of water, when every one volume will correspond simply to 0.005 gramme, and every 100 volumes to 0.5 gramme of chlorine.

In the following instructions for the performance of the analysis, I shall assume the test solution to possess the latter degree of concentration.

5. *Performance of the analytical process.*

a. 5 grammes of the sample of chloride of lime under examination are weighed off, finely triturated with a little water, and subsequently rinsed into a cylinder, which has been previously prepared for the purpose for which it is intended, by measuring into it 200 volumes of water from the graduated dropping-tube, and scratching a mark into the glass at the exact spot to which these 200 volumes of water reach. The cylinder is then filled with water up to the mark, and the mixture agitated.

b. 100 volumes of the solution of protonitrate of mercury (corresponding to 0.5 gramme of chlorine) are measured off by means of a graduated syphon; they are then poured into a beaker-glass, and diluted with water; an excess of solution of common salt is added, and finally a small portion of hydrochloric acid, which must be perfectly free from admixture of chlorine or sulphurous acid.

c. The graduated dropping-tube is now filled up to the 0 point with the well-shaken solution of chloride of lime, (*a.*), which latter is then dropped cautiously and with constant stirring into the fluid of *b.* (which must invariably remain acid) until the mixture appears perfectly clear.

The per centage amount of chlorine contained in the examined sample of bleaching powder may now be at once found, simply by dividing 2000 by the number of volumes of the solution of the latter which have been used in the process. The calculation proceeds as follows:

The amount used of the chloride of lime solution corresponds to 0.5 grammes of chlorine; how much chlorine do the whole 200 volumes of this solution contain? Let us suppose we have used 90 volumes of the chloride of lime solution.

$$90 : 0.5 : : 200 : x$$

$$x = \frac{200 : 0.5}{90} = \frac{100}{90} = 1.111 \ldots$$

$$5 \text{ grammes} : 1.1111 : : 100 : x$$

$$x = 22.22.$$

B. Method of determining the amount of available chlorine by means of arsenious acid (after Gay-Lussac, slightly modified).

1. This method is based upon the circumstance that the con-

tact of chlorine with arsenious acid, in presence of water, gives rise to the formation of arsenic acid and hydrochloric acid.

$$As\,O_3 + 2\,Cl + 2\,H\,O = As\,O_5 + 2\,Cl\,H.$$

1 equivalent of arsenious acid=1240, requires accordingly 2 equivalents of chlorine=886 for its conversion into arsenic acid, or, in other terms, 140 parts of arsenious acid require 100 parts of chlorine. Consequently the amount of a solution of chlorine required to convert a definite quantity of arsenious acid into arsenic acid indicates at once the proportional amount of chlorine present in the solution in question. The arsenious acid is best used in solution. A solution of arsenious acid of definite strength is to be prepared as follows:

2. Preparation of the test solution.

14 grammes of pure arsenious acid are dissolved in potass ley, and as much water added as will raise the whole amount of the fluid to exactly 2000 volumes of the graduated dropping-tube. 100 volumes of this solution will thus contain $\frac{1.4}{2}=0.7$ gramme of arsenious acid, and the solution of chlorine required to convert this into arsenic acid will accordingly contain 0.5 gramme of chlorine.

3. Performance of the analytical process.

a. The solution of the chloride of lime under examination is prepared as directed at *A.*, 5, *a.*, so that 5 grammes yield 200 volumes.

b. 100 volumes of the solution of arsenite of potass (2) (corresponding to 0.5 gramme of chlorine) are measured off by means of a graduated syphon, transferred to a beaker-glass, and diluted with water; hydrochloric acid is then added until it commences to predominate strongly, and the fluid is finally colored with one or two drops of solution of indigo.

c. The graduated dropping-tube is now filled up to the 0 point with the well-shaken solution of the chloride of lime, (*a.*) which latter is then dropped into the colored solution of arsenious acid (*b.*) until the blue tint of the fluid disappears; (should this tint become indistinct towards the conclusion of the process, a fresh drop of solution of indigo may be added). The amount used of the chloride of lime solution contained 0.5 gramme of chlorine. The calculation proceeds as directed at A.

C. METHOD OF DETERMINING THE AMOUNT OF AVAILABLE CHLORINE BY MEANS OF PROTOSULPHATE OF IRON. (OTTO.)

The principle of this method is as follows:

Two equivalents of protosulphate of iron, when brought into contact with chlorine, in the presence of water and of free sulphuric acid, transpose with one equivalent of chlorine, one equivalent of water, and two equivalents of sulphuric acid, to one equivalent of persulphate of iron, and one equivalent of hydrochloric acid.

$$2\,Fe\,O, S\,O_3 + 2\,S\,O_3 + H\,O + Cl = Fe_2\,O_3, 3\,S\,O_3 + Cl\,H.$$

Two equivalents of $Fe\,O, S\,O_3 = 1900$, or, calculated upon crystallized protosulphate of iron,

$$2\,(Fe\,O, S\,O_3\,H\,O + 6\ aq.) = 3475.0$$

correspond to 443.2 of chlorine, or, in other terms, 3.924 grammes of crystallized protosulphate of iron correspond to 0.5 gramme of chlorine.

The protosulphate of iron required for these experiments is best prepared as follows:

Iron nails, free from rust, are dissolved in dilute sulphuric acid, finally with the application of heat; the solution is filtered, whilst still warm, into about twice its own volume of spirits of wine. The precipitate which is produced consists of

$$Fe\,O, S\,O_3 + H\,O + 6\ aq.$$

This precipitate is collected upon 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 protosulphate of iron is kept in well-closed bottles.

PERFORMANCE OF THE ANALYTICAL PROCESS.

3.924 grammes of the precipitated protosulphate of iron are dissolved in a few ounces of water, and the solution is strongly acidified with pure sulphuric acid. The graduated dropping-tube is now filled up to 0 with the well-shaken solution of the sample under examination, (vide *A., 5, a.,*) and the latter is then dropped into the solution of the protosulphate of iron until the whole of the protosulphate is converted into persulphate. To hit the exact point at which the peroxidation is completed, a clean plate is sprinkled over with a solution of ferricyanide of potassium, and when the operation draws towards the end, a minute quantity of the mixture is conveyed, by means of a small stirring rod to one of the drops of ferricyanide of potassium solution upon the plate, in order to ascertain whether this continues to produce a blue precipitate or coloration in the latter. The same test is repeated upon every fresh addition of two drops of chloride of lime solution. When the object in view is attained, the measure used of the chloride of lime solution is accurately read off. The amount used contained 0.5 gramme of chlorine. The calculation proceeds exactly as directed at A.

SUPPLEMENTARY REMARKS.

a. The three methods of chlorimetry which I have just now described yield equally accurate, corresponding, and constant results, provided, of course, the test solutions required in A. and B. be correctly prepared, and the protosulphate of iron used in C. be perfectly pure and dry. Any superiority which may be considered to exist with respect to the relative degree of accuracy attainable by either of these three methods, must be accorded to B. and C., since the test-solution of arsenious acid and the protosulphate of iron (when prepared and kept according to the directions given at C.) may be preserved unaltered, or are, at all events, less liable to suffer any modification than a solution of protonitrate of mercury.

b. It is usually recommended to allow the solution of chloride of lime to clear by subsidence, and to test simply the clear decanted fluid. My own experience has taught me, however, that it is preferable to test the uniform turbid mixture, which is, of course, to be sufficiently diluted to permit its ready effusion and transfer from one vessel to another. Any one may readily convince himself that the results obtained in the latter case are more accurate and constant than those obtained in the former; he need, for this purpose, simply make two distinct experiments with the same solution of chloride of lime, viz., one with the clear decanted portion of the solution, and the other with the remaining turbid mixture. Thus, for instance, direct experiments, made according to method A, yielded,

1. The clear decanted solutions from 22.99 to 23.22 of chlorine.
2. The remaining turbid mixture 25.0 of chlorine.
3. The uniformly mixed solutions from 24.2 to 24.8 of chlorine.

SECTION VI.

ORGANIC ELEMENTARY ANALYSIS.

§ 138.

Organic compounds contain only comparatively few of the elements which constitute the material world. A small number of organic compounds consist simply of two elements, viz.,

C and H;

The greater number contain three elements, viz., usually,

C, H, and O.

Most of the rest contain four elements, viz., generally,

C, H, O, and N;

A small number contain five elements, viz.

C, H, O, N, and S,

And a few contain six elements, viz.,

C, H, O, N, S, and P.

This applies to all the natural organic compounds which have as yet come under our notice. But we may *artificially* prepare organic compounds which contain other elements besides those enumerated; thus we know many organic substances, the radicals of which contain chlorine, iodine, or bromine; or arsenic, platinum, iron, cobalt, &c., &c.; and it is quite impossible to say which of the other elements may not be similarly capable of forming constituents of organic compounds, (constituents of organic radicals).

With these compounds we must not confound those which are to be looked upon as binary compounds of the first, or of a higher order, such as tartrate of lead, for instance, silicate of oxide of ethyle, borate of morphia, &c.; since in the latter class of compounds, of course, all and every one of the elements may happen to be present.

Organic compounds may be analysed either with a view simply to resolve them into their proximate constituents, thus, for instance, a gum resin is resolved into resin, gum, and ethereal oil;—or the analysis may have for its object the respective determination of the absolute and relative weight of the ultimate constituents (the elements) which constitute the analysed compound. The simple resolution of analysed compounds into their proximate constituents, is effected by methods perfectly similar to those applied for the analysis of inorganic compounds; that is, the operator endeavours to separate (by solvents, application of heat, &c. &c.) the individual constituents from one another, either *directly*, or after having previously converted them into appropriate forms. We disregard here altogether this branch of organic analysis—of which the methods must be nearly as numerous and varied as the cases which require their application—and proceed at once to treat of the second branch, which, to distinguish it from the other, is called ORGANIC ELEMENTARY ANALYSIS.

Organic elementary analysis, as I have already stated, has for its object the determination of the absolute and proportional weight of the individual elements of organic compounds. It attains this object by teaching us how to convert these elements into compounds of known constitution, to separate the new compounds subsequently from one another, to weigh them individually, and finally to infer from their respective weight that of the original elements in question.—Organic elementary analysis, therefore, is based upon the same principle upon which rest most of the methods of separating and determining inorganic compounds.

The decomposition of most organic substances into distinctly characterized and readily separable products, which will permit an accurate determination of their weight, offers no great difficulties, and organic elementary analysis is therefore usually one of the more easy tasks of analytical chemistry;—and as the limited number of the elements which constitute organic bodies induces a great sameness in the products of their decomposition, the mode of performing the analysis is always very similar, and a few methods suffice for all cases.—It is principally ascribable to this latter circumstance that organic elementary analysis has so speedily attained its present high degree of perfection:—the constant examination and improvement of a *few* methods by a *great number* of chemists, could not fail to produce this result.

Organic elementary analysis may have for its object either simply to ascertain the *relative* number of the elements which constitute the analysed substance, as when woods are analysed to ascertain their value as fuel, or fats to ascertain their capacity of furnishing light—or to determine not only the *relative proportions* of the constituent elementary atoms, but likewise their *absolute quantity*, that is, to determine the exact number of atoms of carbon, hydrogen, oxygen, &c. &c, which constitute one atom of the analysed compound. In scientific investigations we have invariably the latter object in view, although we are not yet able, in all cases, to attain it. The respective attainment of these two distinct purposes, requires of course the application of different and distinct methods. Those methods which enable us to ascertain the relative proportions of the constituent elements of organic compounds, may be collectively called, " *organic elemen-*

tary analysis in a more restricted sense;" whilst those methods which reveal to us the *absolute number* of elementary atoms constituting the complex atom of the analysed compound, may be styled "*determination of the atomic weight of organic bodies.*"

The success of an elementary analysis depends upon two conditions; viz. 1, upon the selection of the appropriate method; and 2, upon the correct performance of the necessary operations and processes: the latter may be readily acquired by any one endowed with some patience, clearness of perception, and skill in chemical manipulation. The selection of the method depends upon the knowledge of the constituents of the compound under examination, and the method selected will always require certain modifications, according to the different properties and state of aggregation of these constituents. Before we can proceed, therefore, to describe the various methods applicable in the different cases which may occur, we must, in the first place, study the manner of ascertaining the nature of these constituents.

I. QUALITATIVE EXAMINATION OF ORGANIC BODIES.

§ 139.

It is not necessary for the correct selection of the appropriate method, to know all and every one of the elements of an organic compound, since the presence or absence of some of them—of oxygen, for instance—has not the slightest modifying influence upon the manner of proceeding with the analysis. But with regard to other elements, such as nitrogen, sulphur, phosphorus, chlorine, iodine, bromine, &c. &c., and also the various metals, it is absolutely indispensable that the operator should know positively whether either of them are present. This may be ascertained in the following manner.

1. *Testing for nitrogen.*

Substances which contain a tolerably large amount of nitrogen, exhale upon combustion, or when intensely heated, the well-known smell of singed hair or feathers. No further test is required, if this smell is distinctly perceptible upon burning or heating a sample of the substance under examination; otherwise the following experiments are to be resorted to.

a. The substance under examination is mixed with caustic potass in powder, or with *soda-lime,* (§ 40. 4,) and the mixture heated in a test-tube. Should the examined substance contain nitrogen, ammonia will be evolved, which may be readily detected by its peculiar odor, reaction upon vegetable colors, and formation of white fumes when brought into contact with volatile acids. Should these reactions fail to afford positive proof of the presence of nitrogen, every doubt as to the presence or absence of this element may be removed by the following experiment:—A somewhat larger portion of the substance under examination is heated, in a short tube, in conjunction with an excess of *soda-lime,* and the products of the combustion are conducted into dilute hydrochloric acid; the acid is subsequently evaporated in the water-bath, the residue re-dissolved in a little water, and the solution finally mixed with bichloride of platinum and alcohol. Should no precipitate form, even after the lapse of some time, the examined substance may be considered free from nitrogen.

b. LASSAIGNE has recently proposed another method, which is based upon the property of potassium to form cyanide of potassium when ignited with a nitrogenous organic substance. The following is the best mode of performing the experiment:—

The substance under examination is heated in a small test-tube, with a fragment of potassium, and, after the complete combustion of the whole of the potassium, the residue is treated with a little water, (cautiously); the solution is filtered, and the filtrate mixed with solution of ferroso-ferric oxide; the mixture is slightly digested, and hydrochloric acid in excess is subsequently added. The formation of a blue precipitate or coloration proves the presence of nitrogen.

Both methods are delicate; the latter admits less readily of mistakes than the former.

2. *Testing for sulphur.*

a. Solid substances are intimately mixed with some pure carbonate of soda and nitrate of potass; nitrate of potass is then heated to fusion in a porcelain crucible, and the mixture gradually projected into the fusing mass. The mass is subsequently allowed to cool, and, when cold, dissolved in water, and the solution, after previous acidulation with hydrochloric acid, is finally tested with barytes.

b. Fluids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potass, at first in the cold, and finally with application of heat; – the solutions are subsequently treated as directed at *a.*

c. Instead of the methods described at *a.* and *b.*, the following process may likewise be resorted to:—

The substance under examination is kept boiling with a concentrated solution of potass, so as to evaporate the mixture nearly to dryness. The residue is dissolved in a small portion of water, and the solution poured into the flask A. (Plate 45.); dilute hydrochloric acid is then slowly added through the funnel-tube *c*; should sulphur be present, the paper-slip *b*, which is thoroughly moistened with solution of acetate of lead, and subsequently touched with a few drops of solution of carbonate of ammonia, will turn brown. I need hardly mention that the cork must not fit air-tight into the mouth of A. This method yields often more satisfactory results than *a.* and *b.*

Plate 45.

3. *Testing for phosphorus.*

The methods described at 2. *a.* and *b.* may likewise serve for phosphorus. The solutions obtained are tested for phosphoric acid with sulphate of magnesia, or with perchloride of iron in conjunction with acetate of soda. (Compare qualit. analysis.) In method *b.* the greater portion of the excess of nitric acid must first be removed, is mostly effected by evaporation.

4. *Testing for inorganic substances.*

A portion of the substance under examination is heated upon a platinum plate, to see whether a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum plate to the most intense redness, directing the flame of the blow-pipe upon the corresponding point of the lower surface of the plate. The nature of the residue is subsequently examined by the usual methods.

These preliminary experiments should never be neglected, since neglect in this respect may give rise to the very grossest errors. Thus, for instance, *taurine,* a substance in which a considerable proportion of sulphur has recently been found to exist, had originally the formula $C_4 \, N \, H_7 \, O_{10}$ assigned for its composition. The preliminary examination of organic substances for chlorine, bromine, and iodine, is generally unnecessary, since these elements do not occur in natural organic compounds, and since their presence in compounds artificially produced by the action of the salt-radicals, require generally no further proof or examination.—Should it, however, be desirable to ascertain positively whether a substance does or does not contain chlorine, iodine, or bromine, the same methods are to be resorted to which we shall have occasion to describe in the quantitative determination of organic compounds.

II. ORGANIC ELEMENTARY ANALYSIS IN A MORE RESTRICTED SENSE.

It is not my intention here to give an account of the rise and progress of organic elementary analysis; I shall therefore confine myself to the description of the most simple, precise, and universally applicable methods, omitting all the rest.

The accuracy of the results depends both upon the appropriate construction and arrangement of the apparatus necessary for the various analytical processes, and upon the execution of these processes. I am anxious, therefore, to impress upon the student the necessity of bestowing equal attention and diligence upon both; the rules which I have laid down are the fruits of long experience and of innumerable experiments.

A. ANALYSIS OF COMPOUNDS WHICH CONSIST SIMPLY OF CARBON AND HYDROGEN, OR OF CARBON, HYDROGEN, AND OXYGEN.

§ 140.

The principle of the method which serves to effect the quantitative analysis of these compounds, and which owes its present perfection to Professor LIEBIG, is exceedingly simple. The substance under examination is burned into carbonic acid and water; these products are separated from one another, weighed, and the carbon of the analyzed substance calculated from the weight of the carbonic acid, the hydrogen from that of the water. If the sum of the calculated weight of the carbon and hydrogen is equal to the original weight of the substance, the absence of oxygen is at once satisfactorily proved; should the sum on the other hand be less than the original weight of the substance, the difference will at once indicate the amount of oxygen originally present in the analyzed compound.

The combustion is effected either by igniting the organic substances in conjunction with oxygenized bodies which readily yield up their oxygen, (oxide of copper, chromate of lead, &c. &c.,) or directly, by means of free oxygen gas, or, finally, at the expense both of free and combined oxygen.

a. SOLID BODIES.*

a. Readily combustible, non-volatile substances. (Ex. gr. sugar, starch, tartaric acid, in short, most solid organic substances.)

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* For the analysis of waxy, fatty and other similar bodies, which cannot be reduced to powder, I refer to § 145.

§ 141.

I. APPARATUS AND PREPARATIONS NECESSARY FOR ORGANIC ELEMENTARY ANALYSIS.

The following is a complete list of every thing required for the performance of organic elementary analysis :

1. THE SUBSTANCE INTENDED FOR ANALYSIS.—This must be very finely levigated, and perfectly pure and dry ;—for the method of effecting the exsiccation of organic substances, I refer to § 14.

2. A TUBE IN WHICH TO WEIGH THE SUBSTANCE.—A small and perfectly dry glass tube, about $1\frac{1}{2}$ to 2 inches long, and a few lines in diameter, is selected for this purpose ; the weight of this tube is to be accurately determined. It is advisable to place the tube in the drying apparatus together with the substance intended for analysis.

3. THE COMBUSTION TUBE.—A tube of difficultly fusible glass, (potass glass,) about one half line in thickness, three feet in length, and from 0.4 to 0.5 inches in diameter, is softened in the middle before a glassblower's lamp, drawn out as represented in and finally rent asunder at *a*. The fine points of the two pieces are then slightly thickened in the flame, and the sharp edges of the open ends slightly rounded by fusion, care being taken to leave the aperture perfectly round ; it is necessary for this purpose to select in the first place a tube, of which the apertures represent the appearances illustrated by Plate XLVII, but not that exhibited in Plate XLVIII.

PLATE XLVI.

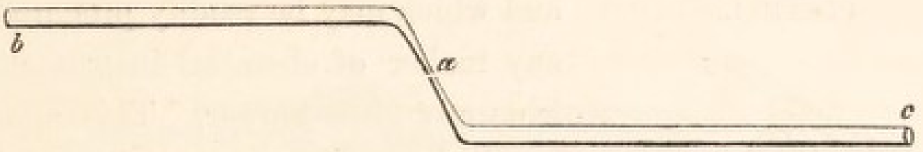


PLATE XLVII.

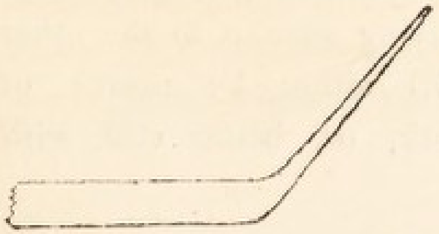
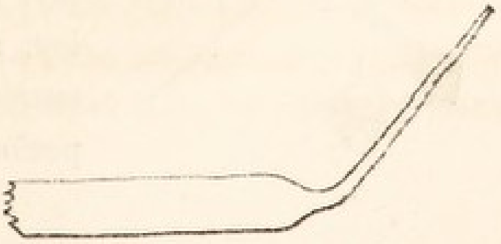


PLATE XLVIII.



Two perfect combustion tubes are thus produced. The combustion tube intended for use, is cleaned with a linen or paper-wiper attached to a piece of wire, and is subsequently thoroughly dried. This is effected either by placing the tube, with a piece of paper twisted over its mouth, upon the plate of a common stove, or into a sand-bath, and keeping it there for some time; or, in cases where it is desirable to accomplish the exsiccation in a more expeditious manner, by thrusting a small glass tube into the combustion tube, heating the latter in its whole length, by moving it backwards and forwards over the flame of a spirit-lamp, and continually removing the hot air by suction.

PLATE XLIX.

The tube, when perfectly dry, is closed air-tight with a cork, and kept in a warm place until required for use.

4. A Liebig's apparatus, as illustrated by

PLATE L.

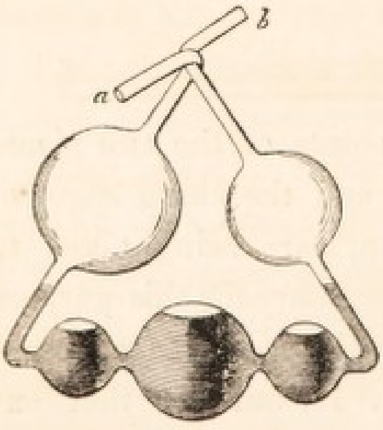
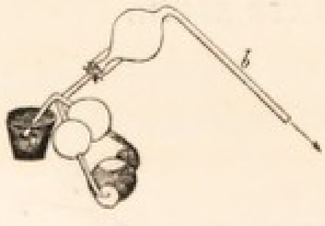


PLATE LI.



and which may be readily procured from any maker of chemical instruments, or from any glass-blower. This apparatus is filled to the extent indicated in the engraving, with a clear solution of caustic potass of 1.27 sp. gr., and which must be free from admixture of carbonate of potass, (§ 40. 7.) The introduction of the potass solution into the apparatus, is effected by plunging the extremity *a* (but *never* the other) into the vessel which contains the potass ley, and applying suction to the other extremity (*b*,) either by means of perforated cork, or, better still, with the aid of a syphon,"(Plate LI.) The two extremities are then wiped perfectly dry with twisted paper slips, and the apparatus is finally wiped dry with a clean cloth.

5. THE CHLORIDE OF CALCIUM TUBE (Plate LII.) may also be purchased. This tube is prepared for use in the following manner:—

PLATE LII.

In the first place, the end *a* of the tube *b a* is loosely stopped with a cotton plug, which is made to protrude from ¼ to ½ inch into *b a*; this is effected by introducing a very loose cotton plug into *c*, and applying a sudden and energetic suction to *b*. The bulb of the tube is then filled with small lumps of chloride of calcium, (§ 40. 8. *b*.), and the tube *d c* is filled up to *e* with smaller fragments, intermixed with coarse powder of the same substance; a loose cotton plug is placed over the chloride of calcium, and the tube is finally closed with a perforated cork, into which a small glass tube is fitted; the protruding part of the cork is cut off, and the cut surface covered over with sealing-wax; the edge of the little tube *f g* is slightly rounded at *g* by fusion, (vide Plate LIII.)

PLATE LIII.

6. A SMALL CAOUTCHOUC TUBE. This is made in the following manner: a piece of sheet india-rubber is slightly warmed by gentle stretching, and subsequently bent round a moistened glass rod; the superfluous portion is removed, with sharp and *perfectly clean* scissors, at one cut, when the fresh cut edges of the caoutchouc, pressed closely together, will completely cohere, provided they have not been soiled by contact with the fingers.—Another piece of india rubber is then stretched round the first piece, and cut in the same manner, taking care to place the cut edges of the inner and outer tube on opposite sides

This kind of double cautchouc tube will stand the wear and tear of fifty and more analyses. It is carefully drawn off the glass rod, and dried at a very gentle heat, (the temperature of the water-bath is far too high for this purpose.) The diameter of this little connecting tube must be sufficiently wide to permit the ready introduction of the extremity *a* of the potass apparatus, and of the tube *f g* of the chloride of calcium tube. (Plate LIII.)

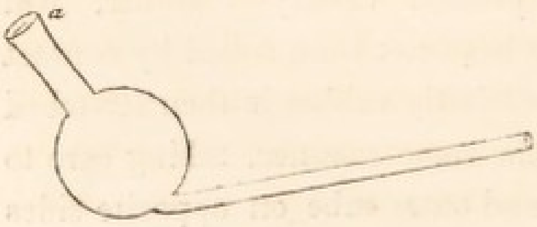
7. Silk cord.—A strong twisted silk cord is selected; this is cut into pieces of from two to ten inches long, and each of them tied into a knot at both ends.

8. Cork stoppers. — Soft and smooth corks, as much as possible free from visible pores, are best adapted for this purpose; a cork should be selected which fits perfectly tight, and enters into the mouth of the combustion tube only one-third of its length; a perfectly smooth and round hole, of the same diameter with the end *b a* of the chloride of calcium tube, is then patiently and carefully bored through the axis of the cork by means of a fine round file; into this perforation the end *b a* of the chloride of calcium tube must fit perfectly air-tight. The cork, thus prepared, is finally dried in the water-bath. It is necessary always to have two corks of this description ready.

9. A mortar.—A porcelain mortar, of greater width than depth, should be selected; it must be provided with a lip, and free from indentations and fissures, and should not be glazed inside. The mortar is washed with water previously to use, and kept in a warm place, until required.

10. A suction tube.—Plate LIV. illustrates the most appropriate form of a suction tube.

PLATE LIV.



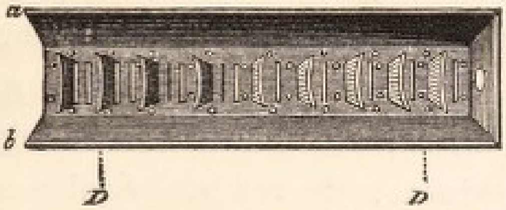
The aperture *a* is closed with a perforated cork, into which the tube *b* of the potass apparatus is fitted.

11. A GLASS TUBE open at both ends, about two feet in length, and of sufficient width to admit being drawn over the beak of the combustion tube when in use; this tube is leaned against a filtering stand. (Vide Plate XX.)

12. A sheet of GLAZED PAPER, with cut edges.

13. A LIEBIG'S COMBUSTION FURNACE of sheet iron, with a single and a double screen. The furnace has the form of a long box open at the top and behind. Plate LV. represents the furnace as seen from the top.

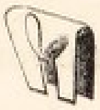
PLATE LV.



It is about twenty-four inches long and four inches deep, and the bottom which, by the excision of small slips of the iron sheet, is converted into a grating, has a width of about three inches. The side walls are inclined slightly outward, so that at the top they are about five inches from one another. The furnace is provided with a series of straight and upright pieces of strong sheet iron of the form illustrated in Plate LVI. B, and which are fastened upon the bottom of the furnace, at intervals of about two inches between each other. These pieces serve to support the combustion tube. They must be of exactly corresponding height, with the round aperture in the front piece of the furnace.

PLATE LVI.

PLATE LVII.



This aperture must be sufficiently large to permit the easy introduction of the combustion tube. Of the two screens, the one has the form represented by Plate LVII., the other that is represented by Plate LVI. A, with the border turned down at the upper edges. The openings cut into the screens must be sufficiently large to receive the combustion tube without difficulty. The furnace is placed upon two flat bricks resting upon wood, and is slightly raised at the posterior end, by introducing a piece of wood between the supports, (vide Plate LX.) The apertures of the grating at the anterior extremity of the furnace, must not be blocked up by the supporting brick. In cases where the combustion tubes are of a good quality, the furnace may be raised more advantageously by introducing a little iron staff or a piece of a tile between the furnace and the supporting brick; this arrangement will give the air free access to all the holes of the grating; or the furnace may also be directly placed upon a tripod.

14. OXIDE OF COPPER. A Hessian crucible, capable of holding about three ounces of water, is to be nearly filled with oxide of copper prepared according to § 40, 1; the crucible is then closely covered and heated to very gentle redness; the red-hot crucible is subsequently allowed to cool in some measure, so that the hand can just, but hardly, bear its contact by the time that the oxide of copper is required for use.

15. AN EXHAUSTING SYRINGE WITH CHLORIDE OF CALCIUM TUBE. Vide Plate LIX. For the manner of performing organic elementary analysis without the aid of this apparatus, I refer to § 143.

16. HOT SAND, the temperature of this should exceed 212°, but must not be sufficiently high to singe paper.

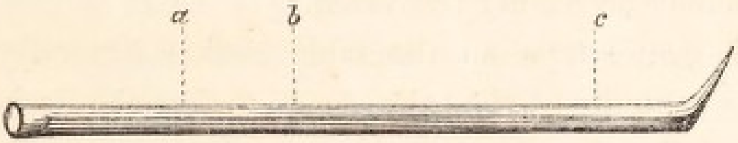
17. A wooden trough for the sand. Vide Plate LIX.

II. PERFORMANCE OF THE ANALYTICAL PROCESS.

a. Both the potass apparatus and the chloride of calcium tube must be accurately weighed. From 0.350 to 0.600 grammes (more or less according as the substance under examination is rich or poor in oxygen) are introduced into the little tube (I., 2,) and the latter is then accurately weighed with its contents. The weight of the empty tube being known, it is easy to hit the right quantity required for the analysis of the substance. The tube is then closed with a smooth cork, under which may be placed a little piece of tinfoil.

b. The sheet of glazed paper (I., 12) is spread upon a clean table, and moderately warm mortar (I., 9) placed upon it. Both the combustion tube—(which is likewise still warm)—and the mortar are then rinsed with a little of the hot oxide of copper, (the oxide which has served for this purpose is put by for the moment). The combustion tube (vide Plate LVIII.) is now filled up to *b* with oxide of copper, which is transferred *directly* from the crucible to the tube. A portion of the oxide of copper is now projected from the tube into the mortar, and the whole of the substance intended for analysis is added to it from the small tube in which it has been weighed; this small tube is put by in a secure place, since it is necessary to reweigh it.

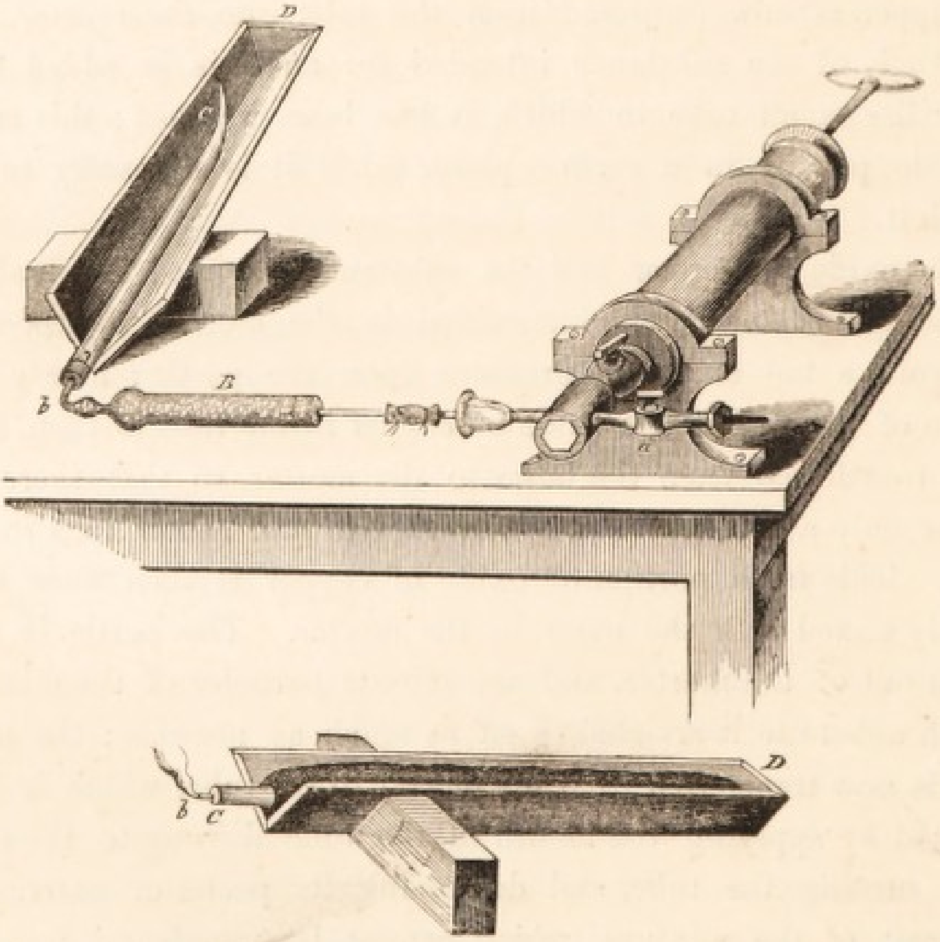
PLATE LVIII.



The oxide of copper and the substance intended for analysis are now most intimately intermixed in the mortar, taking care to avoid a too energetic pressure upon the pestle; nearly the whole of the rest of the oxide of copper in the tube is then likewise transferred from the latter to the mortar, so that there remains only a layer of about one to one and a half inch in the tube. This fresh portion of oxide of copper is then most intimately mixed with the mass in the mortar. The pestle is now taken out of the mortar, and the minute particles of the mixture which adhere to it are shaken off as much as possible; the mixture is now transferred from the mortar to the tube, which is best effected by applying the mouth of the tube directly to the mixture, turning the tube, and depressing its posterior extremity; the rest of the mixture, which cannot be transferred into the tube in this way, is poured upon a perfectly smooth card, and finally transferred from the latter into the tube; the mortar is then rinsed with a little fresh oxide of copper, which is subsequently likewise transferred to the tube—(this will fill the latter to the point *a* or thereabout). The rest of the tube is now finally filled to within about an inch and a half of the mouth with pure oxide of copper from the crucible, and the tube is then temporarily closed with a cork. The reason why the operation of transferring the mixture to the tube is conducted over the sheet of glazed paper is that, should any of the mixture be spilled, this may be readily recovered.

c. A few gentle taps on the table suffice generally to shake together the contents of the tube, so as to free the beak perfectly from oxide of copper, and to leave a free passage above the

PLATE LIX.

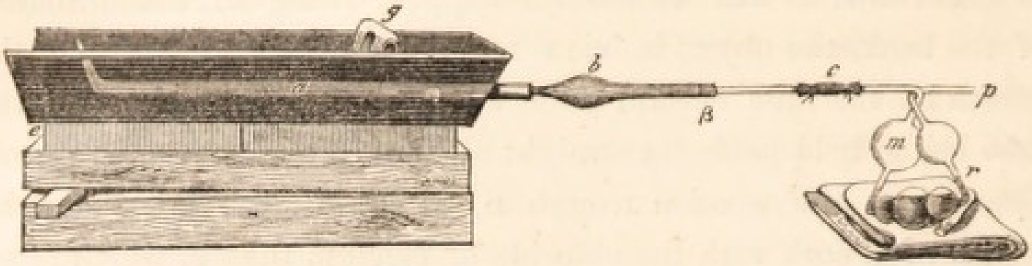


mixture, from end to end. Should a few gentle taps not suffice to effect this, as will sometimes happen, owing to malformation of the beak, the object in view may be attained by striking the mouth of the tube several times against the side of a table, the tube being held perfectly straight all the while. The tube is now placed into the wooden trough D, (Plate LIX.,) connected by means of a cork with the chloride of calcium tube B, which latter is again connected with an exhausting syringe. The combustion tube is surrounded in its whole length with the hot sand, (I., 16.) The air is now *slowly* exhausted, (quick and incautious pumping might cause a portion of the mixture to pass into the chloride of calcium tube). After a short interval, the stopcock *a* is opened, and new air is admitted, which becomes completely dried in its passage through the chloride of calcium tube; the air is then again exhausted, and fresh air admitted; this process of alternate exhaustion and readmission of air, if repeated ten or twelve times, will ensure the perfect removal of the moisture which the oxide of copper may have absorbed from the air during the operation of mixing.

d. The end *b* of the weighed chloride of calcium tube (I., 5) is now connected with the combustion tube by means of the perforated and dried cork (I., 8); the combustion tube is placed upon the supports in the furnace, (which latter rests likewise upon its supports, and is slightly inclined forward, Plate LX.,) and the end *β*. of the chloride of calcium tube, connected by means of the little caoutchouc tube with the end *m* of the potass apparatus, the caoutchouc tube is secured on both sides with silk cord, (I., 7.), taking care to press the balls of the two thumbs close together whilst tightening the cords, since otherwise, should one of the cords happen to give way, the whole apparatus might be broken. The potass apparatus is made to rest upon a folded piece of cloth. Plate LX. illustrates the whole arrangement.

e. The tightness of the junctions is examined in the following manner. A piece of wood of the size of a finger (*s*) (or a cork or other body of the kind) is placed under the bulb *r* of

PLATE LX.

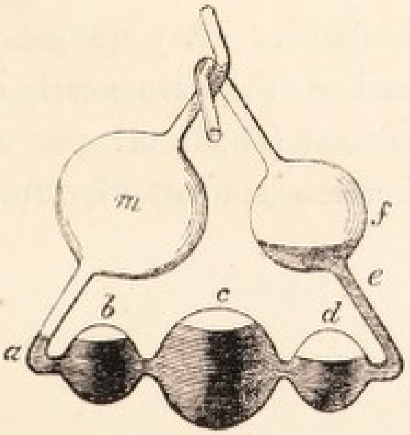


the potass apparatus, so as to raise this bulb slightly, (vide Plate LX). A live coal is then held near to the bulb *m*, until a certain portion of air is expelled through the apparatus; the piece of wood (*s*) is now removed, and the bulb *m* allowed to cool. The potass solution will now rise into the bulb *m* and fill it more or less; if the liquid in *m* preserves, for the space of a few minutes, the same level which it has found to have acquired after the perfect cooling of the bulb, the junctions may be considered perfect; should the fluid, on the other hand, gradually regain its original level in both limbs of the apparatus, this is a positive proof that the junctions are not air-tight. (The few minutes which elapse between the two observations may be advantageously employed in re-weighing the little tube in which the substance intended for analysis was originally weighed.)

f. The combustion tube is made to protrude to the extent of a full inch beyond the furnace, and the simple screen is suspended over the anterior border of the furnace so as to shield the cork. The double screen is placed over the combustion tube at a distance of about two inches, (Plate LX.), the little piece of wood (*s*) is replaced under *r*, and small live coals are placed first under that portion of the tube which is separated by the screen; this portion is now gradually altogether surrounded with live coals, and thus heated to ignition. The screen is then shifted backwards to the extent of about one inch, and fresh coals are placed upon the newly-exposed portion of the tube, which is thus likewise heated to redness; the fire is in this manner slowly and gradually extended towards the further extremity of the tube, taking care to wait always until the last exposed portion of the tube is red-hot, before shifting the screen further backwards, and taking care likewise to maintain the whole of the exposed portion of the tube before the screen in a state of ignition. The portion of the tube which protrudes beyond the furnace must be kept so hot that the fingers can hardly bear the shortest contact with it. The whole process requires generally from three-quarters to one hour. It is quite superfluous, and even injudicious, to keep on fanning the coals during the operation;—this should be done only when the process is drawing to the end, as we shall immediately have occasion to see.

The liquid in the potass apparatus is gradually displaced from the bulb *m* upon the application of heat to the anterior portions of the combustion tube; this is simply owing to the expansion of the heated air. When the heat reaches that portion of oxide of copper which has been used to rinse the mortar, a little carbonic acid and aqueous vapor begin to be evolved, which drive the whole of the air present in the apparatus before them, and force it in large bubbles through the potass apparatus. The evolution of carbonic acid and aqueous vapor acquires a greater degree of briskness when the heat begins to reach the mixture of the oxide of copper with the substance under examination; the first bubbles are only partly absorbed in the potass apparatus, since they contain still an admixture of air; but the bubbles, which are subsequently evolved, are so completely absorbed by the potass, that a solitary air-bubble only escapes from time to time through the liquid. The process should be conducted in such a manner that the gas-bubbles follow each other at intervals of from one half to one second. Plate LXI. shows the normal level of the potass ley, during the operation.

PLATE LXI.



This illustration shows how an air-bubble entering at *a* passes first into the bulb *b*, then from *b* to *c*, from *c* to *d*, and escapes finally through the tube *e* into the bulb *f*.

g. When the tube is in its whole length surrounded with red-hot charcoal, and the evolution of gas has relaxed, the burning embers should be gently fanned with a square piece of pasteboard. When the evolution of gas has entirely ceased, the operator has to adjust the position of the potass apparatus, to remove the charcoal from the posterior end of the furnace, and to place the screen before the bent and pointed extremity or beak of the combustion tube. The ensuing refrigeration of the tube, and absorption of the carbonic acid in the potass apparatus, cause the potass ley in the latter to recede, slowly at first, but with increased rapidity the moment it reaches the bulb *m*. (If the operator has taken care to adjust the position of the potass apparatus correctly, he need not fear that the contents of the latter will recede to the chloride of calcium tube.) When the bulb *m* is about half filled with potass ley, the point of the bent extremity or beak of the combustion tube is to be broken off with a pair of pliers or scissors, whereupon the fluid in the potass apparatus will immediately resume its equilibrium. The potass apparatus is now again placed into the original oblique position, and the glass tube described at § 141, I., 11, is placed over the opened end (beak) of the combustion tube, and supported by the arm of a filtering stand; the suction pipe (Plate LIV., § 141, I., 10) is then joined to the potass apparatus, and suction applied until the bubbles passing through the latter cease to diminish in size.

The analysis is now concluded. The potass apparatus is untied, and the chloride of calcium tube, together with the cork, removed from the combustion tube; the cork is now likewise removed from the chloride of calcium tube, and the latter is placed upright, with the bulb upwards. After the lapse of half an hour, the potass apparatus and chloride of calcium tube are weighed, and the results are then finally calculated. They are generally very satisfactory;—as regards the carbon, they are nearly *absolutely* accurate, rather somewhat deficient (about 0.1 per cent.) than too high. There exist indeed a few sources of error, but none of them interfere materially with the accuracy of the results; they rather compensate partially for one another. In the first place, the air which passes through the potass ley during the combustion, and finally during the process of suction, carries with it a minute amount of moisture. This source of error is increased, if the evolution of gas proceeds very rapidly, (in which case the potass ley becomes heated), and likewise if nitrogen gas or oxygen gas pass through the potass apparatus; compare § 142, *bb.*, and § 146, *a.*; this may be remedied, however, by fixing a weighed tube with solid hydrated potass to the potass apparatus. In the second place, traces of carbonic acid from the atmosphere are carried into the potass apparatus during the final process of suction; this may be likewise remedied by connecting the beak of the combustion tube with a potass tube by means of a perforated cork. In the third place, it happens frequently, in the analysis of substances containing a considerable proportion of water or of hydrogen, that the carbonic acid is not absolutely dried in passing through the chloride of calcium tube; this may also be remedied by fixing behind the chloride of calcium tube a tube filled with asbestos, moistened with hydrated sulphuric acid. Finally, I may remark that the adoption of the old equivalent for carbon=76.437 gives rise to greater differences between the results theoretically calculated and actually obtained, than the adoption of the new equivalent of carbon =75.00.

As regards the hydrogen, the results are somewhat too high, 0.1 to 0.15 per cent.; this arises principally from the circumstance that the air passing through the apparatus during the final process of suction, conveys a little moisture into the chloride of calcium tube, but it may be readily remedied by connecting the beak of the combustion tube with a potass tube. The adoption of the old equivalent for carbon increases the difference between the results calculated and obtained, so that the process was formerly assumed to yield about 0.2 per cent of hydrogen more than theoretically calculated upon. I have to remark, however, that in the far greater majority of cases, it will be quite superfluous to render the operation more complicated for the purpose simply of remedying these sources of error, the more so as we know, by innumerable experiments, the exact limits of the influence which they may exercise upon the accuracy of the results.

β. Difficultly combustible, non-volatile substances such, for instance, as many resinous and extractive matters, anthracite, &c. &c.

§ 142.

If substances of this kind are analysed after the method given above for those at *a.*, minute particles of carbon are liable to escape oxidation. To avoid this, either the one or the other of the following methods may be had recourse to, but more particularly the first.

aa. COMBUSTION WITH CHROMATE OF LEAD.

Of the apparatus and preparations enumerated at § 141, only those marked from 1 to 13 are required, and in addition to them some chromate of lead (40.2). A narrow combustion tube may be selected. A quantity of chromate of lead, more than sufficient to fill the combustion tube, is heated in a platinum or porcelain basin over a BERZELIUS' spirit lamp, until it begins to turn brown, and is then, previously to its use, allowed to cool down to 212° and even lower. The operation is conducted exactly as directed at § 141., with this difference, that the application of the exhausting syringe is omitted, since chromate of lead is not, in the slightest degree, hygroscopic like oxide of copper.

bb. COMBUSTION WITH OXIDE OF COPPER AND CHLORATE OF POTASS.

This method requires the whole of the objects enumerated at § 141., and in addition to them a small portion of dry chlorate of potass. To obtain the latter substance perfectly free from water, it is to be heated to the fusing point, and, after cooling, reduced to coarse powder, and it may then be kept in a warm place until required for use.

The operation is conducted as directed at § 141, with this difference, that the layer of oxide of copper in the hindmost part of the combustion tube is greater, and, that from 10 to 12 grains of chlorate of potass are added and intermixed with the oxide of copper by shaking the tube. When, upon the subsequent heating of the tube, the operator approaches this part, he must place the red-hot charcoal, with great care, so that the decomposition of the chlorate of potass may proceed very gradually; since, if this precaution be neglected, the impetuous rush of the gas will eject a small portion of the potass ley, and thus the analysis will be altogether vitiated.

The application of the method described sub. *bb.* is attended with an additional source of error, besides those enumerated at § 141. Part of the oxygen passing through the potass apparatus, saturates the ley in the latter and thus increases its weight. On the other hand, the excess of the oxygen carries away with it some water from the potass ley. These defects, although in some measure compensating each other, must not be neglected in very accurate analyses. **Mulder**, who was the first to point them out, has proposed to saturate the ley in the potass apparatus with oxygen previously to weighing, and to connect the exit-end of the apparatus, with a small weighed hydrate of potass tube. Compare experiment No. 68.

δ. *Volatile substances, and such bodies as undergo some alteration at* 212°, *(lose water, for instance).*

§ 143.

Were substances of this kind treated according to the directions of § 141, a portion of the substance, or of water would escape upon mixing with warm oxide of copper, and upon the application of the exhausting syringe: the results, therefore, could not possibly be accurate. On the other hand, were the substance mixed with cold oxide of copper, the mixture would absorb a considerable amount of moisture.

The process is therefore conducted according to one or other of the two following methods.

aa. COMBUSTION WITH CHROMATE OF LEAD.

The method described at § 142, *aa.* is pursued. The heated chromate of lead is introduced, while yet warm, into a wide and perfectly dry glass tube, which is then closed, and the chromate of lead allowed to cool; the further operation being subsequently conducted as directed at § 141, with this difference that the mortar is allowed to cool previously to mixing the substance under examination with the chromate of lead. There is no fear now that the mixture will absorb water, unless the substance intended for analysis be highly hygroscopic.

bb. COMBUSTION WITH OXIDE OF COPPER.

The general process is conducted as described at § 141. The only difference consists in the manner in which the operation of mixing is performed. This operation requires a copper wire, bent and twisted at one extremity into the shape of the point of a cork-screw, as illustrated by Plate LXII. And a glass tube, about two feet long closed at one end; this tube must be of sufficient width just to permit the introduction of the combustion tube into it. The ignited and still hot oxide of copper is introduced into the wide tube, when it is allowed to cool, the open end of the tube being closed air-tight with a cork-stopper, (to ensure air-tightness it will not be amiss to roll some tin-foil round the cork). The perfectly dry and just refrigerated combustion tube is mixed with a little oxide of copper, and after removing the cork from the open end of the wide tube, gradually turned into the latter, by which means, aided by some slight taps, it is filled with oxide of copper to the extent of from six to eight inches. The combustion tube is then withdrawn, and the cork is replaced into the open end of the wide tube; the substance to be analysed is now introduced into the combustion tube, and the copper wire (Plate LXII.) is turned into the contents up to about

PLATE LXII.

two inches from the bent and pointed extremity of the tube. By moving the wire repeatedly to and fro, the oxide of copper (with the exception of that portion occupying the combustion tube) is rapidly and intimately mixed with the substance to be analysed. The cork is now again removed from the open end of the wide tube, and the combustion tube is filled in the same manner as before, to two thirds of its length, with oxide of copper, which is then intermixed with the former mixture, by the aid of the copper wire. The last third of the combustion tube is now finally filled with oxide of copper, in the usual way, and the combustion is then at once commenced, without previous application of the exhausting syringe. The object of this method of mixing is to bring the oxide of copper as little as possible into contact with the air, thus preventing the absorption of moisture; it is quite evident, therefore, that this operation must be rapidly and skilfully performed to attain the intended end. (Many chemists, e. g. MITSCHERLICH, BUNSEN, &c., always proceed in this manner when analysing solid organic compounds.) Substances which volatilize without suffering decomposition, such as camphor, for instance, may be thrown in small fragments between the oxide of copper.

b. FLUID SUBSTANCES.

α. *Volatile fluids*, (e. g. ethereal oils, alchol, &c.

§ 144.

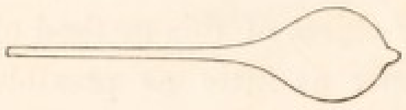
The analysis of organic volatile fluids requires all the objects enumerated at § 141, with the exception of the exhausting syringe and the apparatus serving for weighing and for mixing; it requires besides these a glass tube, such as that described at § 143 *bb.*, for the temporary reception of the oxide of copper, and finally several small glass bulbs for the reception of the fluid to be analysed. These bulbs are prepared in the following manner:

A quill tube, made of moderately thick readily fusible glass is drawn out in the manner illustrated by

PLATE LXIII.

(Let the reader imagine that the two extremities of the tube are a foot longer each than represented in the engraving.) The bulb *a* is severed by fusion at *b*, and, should it be required, the thickened part slightly expanded; the tube is then again cut at *c*. In this manner 2—3 bulbs are made of the shape illustrated by Plate LXIV.

PLATE LXIV.



The length of the ends of the tube is intended to prevent the bulbs getting moist whilst being expanded. Two of these bulbs are accurately weighed, subsequently filled with the fluid to be analysed, closed by fusion, and afterwards re-weighed. The filling of these bulbs is effected by heating them slightly over a spirit lamp and immersing their pointed extremities into the fluid to be analysed, part of which will now, upon cooling, enter the bulb. If the fluid is highly volatile, the portion entering the still warm bulb is converted into vapor, which expels the fluid again from the bulb; but the moment that the vapor is recondensed, the bulb fills the more completely. If the fluid is of a less volatile nature, a small portion only of it will enter into the bulb, at first; in such cases, the latter is to be heated again to convert the drop which has ascended into the bulb into vapor, and the point is then again immersed into the fluid to be analysed, when the bulb will subsequently, upon cooling, fill completely. The excess of the fluid is ejected from the neck of the little bulbous tube by giving the latter a sudden jerk—the point of the tube is then closed by fusion. The combustion tube is now prepared for the process by introducing into it from the wide tube, (§ 143 *bb.*,) a layer of oxide of copper occupying about two inches in length. The centre of the neck of one bulb is then slightly scratched with a file, the point is quickly broken off, and the bulb and point are dropt into the combustion tube and covered with a layer of oxide of copper of two to three inches in length;—the second bulb is then likewise, and in the same manner, dropt into the combustion tube, which is now finally nearly filled up with oxide of copper. A few gentle taps upon the table suffice to create a free passage for the evolved gases. (It is advisable to introduce into the anterior part of the combustion tube small fragments of oxide of copper, (§ 40, 1,) which will permit the free passage of the gases, even though the channel be but very narrow; since a narrow channel is in this operation preferable to a wide one, because the latter is liable to permit unconsumed vapor to escape from the combustion tube.)

The combustion of highly volatile substances demands strict attention, and requires certain modifications of the usual method. The operation commences by heating to redness the smaller anterior half of the tube, which is separated from the rest by a screen, (in the case of highly volatile substances two screens are used instead of one;) a red-hot charcoal is then placed behind the tube, so as to heat the bent and pointed extremity, and thus to prevent the condensation of vapor in this part. A red-hot charcoal is now placed at that part of the tube where the first bulb lies; this causes the efflux and evaporation of the contents of the latter; the vapor passes along over the surface of the oxide of copper, suffers combustion, and thus the evolution of gas commences, which is then maintained by heating very gradually the first and subsequently the second bulb; the operation should proceed rather too slowly than too rapidily. Sudden heating of the bulbs would at once cause such an impetuous rush of gas as to eject the ley from the potass apparatus. The whole tube is finally surrounded with red-hot charcoal, and the rest of the operation conducted in the usual manner. Should the air, which is drawn through the apparatus by the mouth, taste of the analysed substance, this is a sure sign that the combustion was not complete.

β. *Fluid, non-volatile substances,* (fatty or fixed oils.)

§ 145.

The combustion of substances of this kind is invariably effected with chromate of lead, or oxide of copper and chlorate of potass, the general operation being conducted as directed at § 142.

The substance to be examined is weighed in a small tube, and the process of mixing is then accomplished in the following manner:

In the first place, a layer, two inches in length, of chromate of lead; or of oxide of copper and chlorate of potass, is introduced into the combustion tube; the small cylinder with the substance is then dropt into the latter and the whole of the oil is allowed to flow out into the combustion tube; by turning and inclining the latter, the oil is made to flow about in it, but, in such a manner as to leave the upper side of the tube (intended for the channel) and about one-third to one-fourth of its anterior part entirely clean. The rest of the tube is now nearly filled up with chromate of lead, or oxide of copper—which has been cooled in a tube—taking care to fill the little cylinder which contained the oil intended for analysis, completely with the combustion agent. The combustion tube is then placed in hot sand, which will cause the oil to acquire a high degree of fluidity and thus effect its perfect absorption by the combustion agent; the exhausting syringe is then applied, should this be necessary, and the combustion is then proceeded with in the usual manner. It is advisable to select a tolerably long tube. Chromate of lead is usually preferable to oxide of copper with chlorate of potass. When chromate of lead is used, a very intense heat, sufficiently strong to fuse the contents of the tube, is to be applied cautiously towards the end of the operation.

Solid fats, or waxy substances which do not admit of pulverization, and consequently of mixing in the usual way, are treated in a similar manner to fixed oils. They are introduced into a small, weighed, canoe-shaped glass gutter—(which may be prepared by cutting a tube asunder in its whole length)—and melted; when cool, the little canoe, with its contents, is weighed and dropt into the combustion tube which has previously been filled to the extent of two inches with chromate of lead, or with a mixture of oxide of copper and chlorate of potass. Heat is then applied to the combustion tube to melt the substance, and thus to permit its spreading about in the tube in the same manner as described with fixed oils, the rest of the operation being conducted exactly as in the latter case.

B. ANALYSIS OF COMPOUNDS, CONSISTING OF CARBON, HYDROGEN, OXYGEN, AND NITROGEN.

§ 146.

The principle of the method applicable to compounds of this description, is in general this: the substance to be analysed is divided into two portions—and the carbon is determined as carbonic acid, the hydrogen as water, in the *one* portion; the nitrogen is determined in the *other* portion, either in the gaseous form or as double chloride of platinum and ammonium—the oxygen being finally calculated from the difference between the united weight of the carbon, hydrogen, and nitrogen, and the original weight of the analysed substance.

Since the presence of the nitrogen exercises a certain influence upon the determination of the carbon and hydrogen, we shall have to consider here not simply the method of determining the nitrogen, but likewise the modification which the presence of the nitrogen renders necessary in the usual method of determining the carbon and hydrogen.

a. DETERMINATION OF THE CARBON AND HYDROGEN IN NITROGENOUS SUBSTANCES.

Upon igniting nitrogenous substances with oxide of copper or with chromate of lead, a portion of the nitrogen present escapes in the gaseous form, together with the carbonic acid and aqueous vapor, whilst another portion is converted into nitric oxide gas, which is subsequently transformed wholly or partially into nitrous acid by the air present in the apparatus. The unmodified application of the methods described at § 141, &c., to the analysis of nitrogenous substances would accordingly produce a higher figure for the carbon ; since, besides the carbonic acid, the nitrous acid formed and a portion of the nitric oxide—(which in the presence of potass transposes very slowly to nitrous acid and nitrous oxide)—would be retained in the potass apparatus. This defect may be remedied by selecting a combustion tube about five or six inches longer than those used for the combustion of non-nitrogenous substances, filling this in the usual manner to within about four or five inches from the opening, and filling this space finally up with a loose layer of fine and clean copper turnings, (§ 40. 6.) The process is then commenced by heating these copper turnings to redness, in which state they must be maintained during the whole course of the operation. This is the only modification required to adapt the above described methods to the analysis of nitrogenous substances. The action of the copper turnings consists in this, that copper when in a state of ignition decomposes the whole of the oxygen compounds of nitrogen into oxygen, with which it combines, forming an oxide, and into pure nitrogen gas ;—since copper exercises the action only when in a state of intense ignition, the operator has to take care to maintain the anterior part of the tube in this state through the whole course of the process.

b. DETERMINATION OF THE NITROGEN IN ORGANIC COMPOUNDS.

I have already stated above, that two essentially different methods are pursued to effect the determination of nitrogen, viz. the nitrogen is either separated in the gaseous form and determined by measuring the volume of the isolated gas, or it is converted into ammonia, which is then determined as double chloride of platinum and ammonium.

a. Determination of the nitrogen by separating it in the gaseous state and measuring the volume of the separated gas.

The many methods which have been recommended to effect this purpose, may be brought under two general heads ; 1st, those having for their principle the separation and collection of the whole of the nitrogen contained in a weighed portion of the substance to be analysed ; and 2nd, those methods having for their principle the simple determination of the relative proportion between the evolved carbonic acid and nitrogen gas, from which proportion the amount of nitrogen is subsequently calculated. The latter methods require, that the amount of carbon contained in the substance intended for analysis should be previously known. The methods based upon the former principle are denominated *quantitative,* whilst those based upon the latter are called *qualitative.* I will describe here one of each, selecting those which are readiest of execution and yield the most accurate results.

aa. QUALITATIVE METHOD, (LIEBIG'S.)

§ 147.

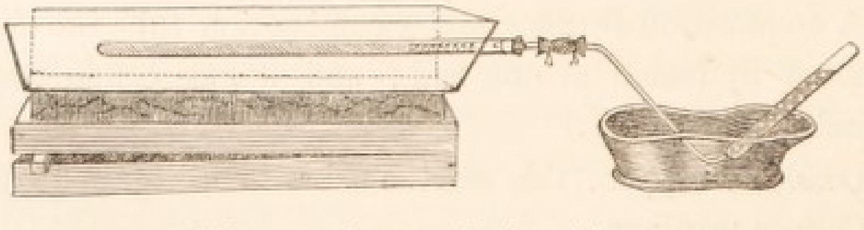
This method is applicable only when the amount of nitrogen contained in the substance to be analysed is considerable in proportion to that of the carbon.

The performance of this method requires the following apparatus and substances :

1. From six to eight accurately graduated tubes of strong glass, each about one foot long and half an inch in diameter.
2. A high cylinder of strong glass widened at the top, (vide infrà, Plate LXVI.)
3. A pipette of which the lower mouth is turned upwards, (vide infrà, Plate LXVI.)
4. A quantity of mercury more than sufficient to fill the glass cylinder.
5. A mercurial trough.
6. Potass ley.
7. A combustion furnace and a combustion tube two feet long and closed by fusion at one end ; and a gas conducting tube, (vide infrá, Plate LXV.)
8. Oxide of copper ; this need not have been ignited recently.
9. Copper turnings.

The process is conducted in the following manner : A quantity of oxide of copper, sufficient to form a layer of two inches in length, is introduced into the posterior part of the combustion tube; a quantity of about 0.5 gramme of the very finely levigated substance intended for analysis is then most intimately mixed with a portion of oxide of copper, sufficient to fill the combustion tube to the extent of about one half. This mixture is introduced into the tube and covered with a layer of oxide of copper; the rest of the tube is then filled up with copper turnings, (these latter should occupy at the least five inches of the tube). The combustion tube thus prepared is then connected with the gas conducting tube, and placed in the furnace; the anterior part of the tube is now surrounded with red-hot charcoal, and the heating is gradually proceeded with in the usual manner to that part of the tube which contains the mixture of the oxide of copper with the substance intended to be analysed. When about one-fourth part of this is decomposed, and the atmospheric air is thus nearly completely expelled from the tube by the products of the combustion, one of the graduated tubes, filled to the brim with mercury,* is placed over the mouth of the gas conducting tube which opens under mercury, and allowed to fill with gas to about three-fourths; it is then lifted out of the mercurial trough, so that the rest of the mercury flows out; if, upon looking through the tube in its whole length, the operator perceives not the slightest red coloration of the contents, he may feel convinced that the gases contain no admixture of nitric oxide. In this manner, the graduated tubes are filled one after another, (Plate LXV.), the heating being continued slowly and uniformly. This

PLATE LXV.



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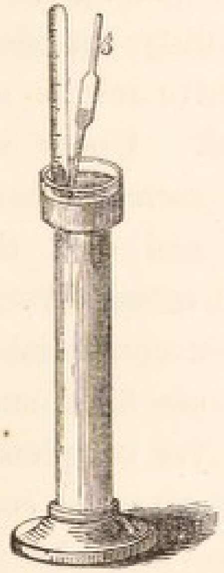
* The best way of filling a tube completely with mercury, so as to prevent any air-bubbles remaining in it, is to fill the tube nearly to the brim with mercury, to close the aperture with the finger, to invert the tube, and

operation requires an apparatus permitting the placing of six or eight tubes.* In default of an apparatus of this kind, the operator must have an assistant at hand to hold the filled tubes until they are required for measurement; care should be taken to mark the order in which the tubes are respectively filled.

When all the tubes are filled, the gas is measured successively in the following manner. The tube is, in the first place, thoroughly immersed in the mercury with which the cylinder illustrated by PLATE LXVI. is filled; this complete immersion establishes at once a perfect uniformity of temperature between the gas and the mercury. The tube is then raised until the mercury in it is on an exact level with that in the cylinder, when the volume is read off and noted, (vide § 12). A small quantity of potass ley is then made to pass from the syphon β, which is nearly filled with this liquid, into the tube; (this is effected by blowing cautiously into the syphon). The syphon is then withdrawn, and the absorption of the carbonic acid by the potass ley is promoted by moving the firmly held tube up and down in the mercury, keeping the opening firmly fixed against the wall of the cylinder; the tube is now finally again thoroughly immersed in the mercury, raised again until the mercury in it is on an exact level with that in the cylinder, and the volume is then accurately read off. (The pressure which the small column of potass ley exercises, may be altogether disregarded.) The volume of the carbonic acid is now found by subtracting the figure found in the second measurement (the nitrogen



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to compel the small bubbles of air which may adhere to the walls to unite gradually with the large bubble at the top. The tube is then again turned upwards, and slowly filled with mercury.

* Compare "Das chemische Laboratorium zu Giessen," by J. P. HOFMANN, Heidelberg, 1842.

gas) from that noted in the first, (nitrogen gas + carbonic acid gas).

When the contents of the one tube have thus been determined, the mercury is cleaned by washing with water slightly acidulated with hydrochloric acid, and subsequently with pure water, and drying between blotting paper; the contents of the second tube are then determined in the same manner.

The results which the respective measurement of the contents of the various tubes yields are usually found tolerably corresponding; in many instances, however, where the nitrogenous substance, previously to complete combustion, is resolved into products of decomposition of different degrees of volatility, considerable differences are observed between the respective results afforded by the measurement of the several tubes. Under all circumstances, the average is taken as the correct result, and this may be considered the more accurate and safe, the less the respective results of the individual tubes diverge from it. Should the first tubes, however, show a considerably larger proportion of nitrogen than those which are filled subsequently, this is a sign that the air was not yet completely expelled when the first tubes were filled; in this case the contents of the first tubes are not taken into account.

The relative proportion of the carbonic acid to the nitrogen gas expresses immediately, and 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 altering the volume of the latter element, and yields, therefore, two volumes of carbonic acid;—and one equivalent of nitrogen yields equally two volumes of nitrogen gas. Suppose we find the proportion of the carbonic acid to the nitrogen, like 4 : 1, the analysed compound contains to four equivalents of carbon$=4 \times 75=300$, one equivalent of nitrogen $=175$. If we had found, therefore, twenty-six parts of carbon in one hundred parts of the analysed substance, the latter would contain 15.17 of nitrogen, since $300 : 175 :: 26 : x$; $x=15.17$.

There is one irremediable source of error inherent in this method, viz., it is impossible to remove the air completely from the tube, and thus the resulting figure for the nitrogen is somewhat too high. This defect, however, does not materially interfere with the determination of the correct proportion, if the relative amount of nitrogen is considerable; thus, for instance, were the proportion found like 1 : 4.1, it would be evident at once that the correct proportion should be taken as 1 : 4. But if the relative proportion of the nitrogen is inconsiderable, this defect vitiates the results, and experience has proved that this method is no longer applicable to substances which contain less than one equivalent of nitrogen to eight equivalents of carbon.

bb. Quantitative method. (Dumas.)

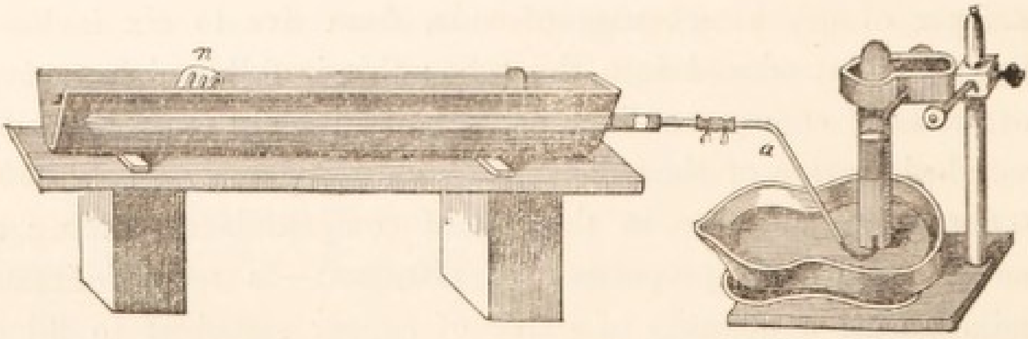
§ 148.

This method is applicable for the analysis of all nitrogenous organic compounds, and likewise for that of nitrates. The performance of the mercury processes requires, besides the objects enumerated at § 147, sub. 4 to 9, and those named at § 141, sub. 2, 9, and 12, a barometer and thermometer, and a graduated glass cylinder of a capacity of about 200 cubic centimetres; and finally a glass plate with a ground surface, to cover the latter.

The combustion tube should be about twenty-eight inches long, and closed at one end by fusion in the manner of a test cylinder; a layer of dry bicarbonate of soda, from five to six inches in length, is introduced into the tube; this is followed by a layer of oxide of copper, one inch and a half in length; an accurately weighed portion of the substance intended for analysis—(0.300—0.600 gram., or more, in the case of compounds containing but an inconsiderable proportion of nitrogen)—is most intimately mixed with a quantity of oxide of copper sufficient to fill the tube to about one half; and this mixture is then likewise introduced into the tube and covered with the oxide which has served to rinse the mortar, and also with a layer of pure oxide;

the tube is then finally filled up with a layer of copper turnings, about five inches in length. The tube thus prepared is connected with the gas conducting tube *a*, (vide infrà, Plate LXVII.), and placed in the furnace. The hindmost end of the tube (to the extent of about two inches) is then gradually heated to redness, the heat being prevented by a screen from reaching any other part of the tube. The bicarbonate of soda is decomposed by the intense heat applied to this part of the tube, and the carbonic acid thus evolved effects in its passage the expulsion of the air from the tube. When the evolution of gas has proceeded for some time, the extremity of the gas conducting tube is immersed under mercury, and a test cylinder, filled with potass ley, placed over it; the red-hot charcoals are then slightly advanced from the posterior part of the tube. If the gas bubbles entering the cylinder are completely absorbed by the potass ley, this is a sign that the air is thoroughly expelled from the tube, and the actual combustion may now be at once commenced; but should this not be the case, the evolution of carbonic acid is to be continued until the desired point is attained. The gas evolved is made to enter the graduated cylinder, which is filled to two-thirds with mercury, and one-third with strong potass ley, and placed in the mercurial trough, over the aperture of the gas conducting tube,* as the annexed illustration shows.

PLATE LXVII.



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* The following is the best way of filling the cylinder and placing it over the opening of the gas conducting tube. The mercury is introduced first, and the air-bubbles which adhere to the walls of the vessel are removed

The actual combustion is then proceeded with in the usual manner, by heating first the anterior part of the tube to redness, and advancing gradually towards the posterior part. At the conclusion of the process, the other half of the bicarbonate of soda is decomposed, and thus the whole of the nitrogen gas which still remains in the tube is forced into the cylinder. The operator must now wait until the volume of the gas in the cylinder decreases no longer, even upon slightly agitating the latter, (that is, until the whole of the carbonic acid in the cylinder has been absorbed.) The cylinder is then placed in a large and deep glass vessel, filled with water, the safe transport from the mercurial trough to this vessel being effected by keeping the aperture closed with mercury contained in a small basin. The mercury and potass ley sink to the bottom, and are replaced by water. The cylinder is totally immersed in the water, and subsequently raised again until the water in the cylinder is on an exact level with that in the vessel; the volume of the gas is then accurately read off, and the temperature of the water, and the point at which the barometer stands, are carefully marked; the weight of the nitrogen gas is finally calculated from its volume, after previous reduction to 32° of the thermometer, and 29.8 of the barometer, and with due regard to the tension of the aqueous vapor,—(compare infrà, "Calculation of analyses.") The results are generally somewhat too high, viz., by about 0.2 to 0.5 per cent.; this is owing to the circumstance, that even a protracted transmission of carbonic acid through the tube fails to expel every trace of the air adhering to the oxide of copper.

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in the usual manner. The potass ley is then poured into the cylinder, leaving the top free, to the extent of about two lines; this is then cautiously filled up to the brim with pure water, and the ground glass plate placed over it. The cylinder is now inverted, and the opening placed under the mercury in the trough; the glass plate is then finally withdrawn. In this manner the operation may be performed easily and without soiling the hands with the ley.

β. *Determination of nitrogen by weight.* (VARRENTRAPP and WILL.)

§ 149.

This method is applicable for the analysis of all nitrogenous compounds, with the exception of those which contain the nitrogen in the form of nitric acid. It is based upon the same principle as the method of examining organic compounds for nitrogen, described at § 139, 1, *a.*, viz., upon the circumstance that, when nitrogenous bodies are ignited in conjunction with the hydrate of an alkali metal, the hydration water of the latter is decomposed in such a manner, that the oxygen forms with the carbon of the organic body carbonic acid, which then combines with the alkali, whilst the hydrogen at the moment of its liberation combines with the whole of the nitrogen present, forming ammonia.

In the case of substances containing abundance of nitrogen, such as uric acid, mellon, &c., the whole of the nitrogen is not at once converted into ammonia at the commencement of the decomposition; but a portion of it enters into combination with a part of the carbon, forming cyanogen, which then combines, either as such, with the alkali metal, or in form of cyanic acid, with the alkali. Direct experiments have proved, however, that even in such cases the whole of the nitrogen is finally obtained as ammonia, provided the hydrated alkali be present in excess, and the heat applied be sufficiently intense.

Since in all organic nitrogenous compounds the carbon predominates in proportion to the nitrogen, the oxidation of the former, at the expense of the water, will invariably liberate a quantity of hydrogen more than sufficient to convert the whole of the nitrogen present into ammonia; thus, for instance,

$$C_2\,N + 4\,H\,O = 2\,C\,O_2 + N\,H_3 + H.$$

The excess of the liberated hydrogen escapes either in the free state, or in combination with the not yet oxidized carbon, as marsh gas, or olefiant gas, or vapor of readily condensable carburets of hydrogen, according to the respective proportions and the temperature; these gases serve in a certain measure to dilute the ammonia. Since this state of dilution of the ammonia is necessary for the success of the operation, I will remark at once in this place, that it may be produced at pleasure by admixing non-nitrogenous substances—sugar, for instance—in greater or less proportion, to substances containing a copious amount of nitrogen. The other parts of the practical process, (such as the collection and determination of the ammonia) require no theoretical explanation.

aa. Apparatus and other objects required for the process.

1. The objects enumerated at § 141, sub. 2, 9, and 12.

2. A COMBUSTION TUBE, from sixteen to eighteen inches in length, and about three lines in diameter, bent obliquely upwards, and drawn out in a point at its posterior end, and with rounded and smoothed edges, at its anterior end, (vide § 141, 3). The combustion is conducted in a common combustion furnace, (§ 141, 13.)

3. SODA-LIME. Mixture of caustic lime with hydrate of soda, § 40, 4. It is advisable to heat a sufficient portion of the soda-lime gently in a platinum—or porcelain—basin, in order to procure a perfectly dry mixture for combustion. In the analysis of non-volatile substances, the best way is to use the soda-lime while yet warm.

4. ASBESTOS.—A small portion of this substance is to be thoroughly ignited in a platinum crucible previously to use.

5. A VARRENTRAPP AND WILL'S BULB APPARATUS, as illustrated in Plate LXVIII., (vide infrà).

This apparatus may be procured at any chemical apparatus and instrument warehouse. It is filled with hydrochloric acid of 1.13 specific weight to the point indicated in the engraving; the filling is effected by dipping the point into the acid, and applying suction to the end *d*.

6. A soft, well-perforated CORK, which closes the combustion

tube air-tight, and into the perforated hole of which the tube *d* of the bulb apparatus fits closely.

7. A SUCTION TUBE filled with hydrate of potass, and closed at its anterior end with a perforated cork, of which the hole is adapted to admit the point of the bulb apparatus.

For the reagents, &c., requisite for the subsequent treatment of the fluid obtained in the process of combustion, I refer to the end of this paragraph.

bb. THE PROCESS.

The combustion tube is filled to one half with soda-lime, which is then gradually transferred to the perfectly dry, and, if practicable, still warm mortar, where it is most intimately mixed with the weighed substance, (compare § 141,) forcible pressure being carefully avoided; a layer of soda-lime, of about one inch in length, is now introduced into the combustion tube, and placed at the remotest end; this is followed by the mixture, which will occupy about nine inches of the tube; the mixture is covered with a layer of about two inches of soda-lime, which has been used to rinse the mortar, and this is again covered finally with a layer of about five inches of pure soda-lime, so that about one inch of the tube remains clear. The tube is then closed with a loose asbestos stopper, and a canal for the free passage of the evolved gases formed by a few gentle taps; the tube is now connected with the bulb apparatus by means of the perforated cork, and is then finally placed in the combustion furnace.

Plate LXVIII shows the arrangement of the whole apparatus.

PLATE LXVIII.

The apparatus being thus prepared, the operator has now to ascertain in the first place whether it is air-tight; this is done by holding a red-hot charcoal to the bulb *a*, to expel some air from the apparatus; and watching whether the fluid will, upon subsequent refrigeration, assume a higher position in *a* than in the other limb, and whether this position will remain constant. The tube is then gradually surrounded with red-hot charcoal, commencing at the anterior part, and progressing slowly to the posterior end, the rest of the process being conducted as in common combustion, (vide § 141). The operator should take care to keep the anterior part of the tube tolerably hot throughout the process, since this will almost entirely preclude the passage of fluid carburets of hydrogen, the presence of which in the hydrochloric acid would prove injurious. The asbestos stopper should be kept sufficiently hot to guard against its retaining water, since, were this point neglected, some ammonia might be retained in conjunction with the aqueous vapor. The combustion should be conducted in such a manner as to maintain a constant and uninterrupted evolution of gas; the operator need not fear that any of the ammonia will escape unabsorbed, even though the evolution be rather brisk; there is far more danger of the hydrochloric acid receding the very moment the gas evolution stops, and this will indeed take place in some instances with such impetuosity as to force the acid into the combustion tube, which of course would spoil the whole analysis. When operating upon compounds containing a very large proportional amount of nitrogen, even the greatest care and caution in conducting the combustion process will prove unavailing against the powerful tendency of the hydrochloric acid to force its way into the tube, which is nearly filled exclusively with ammoniacal gas. This may, however, be readily remediedby mixing with the substance analysed an equal amount of sugar,since this will give rise to the evolution of other and more permanent gases which will serve to dilute the ammonia.

When the tube is ignited in its whole length, and the gas evolution has *totally* ceased, (this is indicated by the mixture re-assuming its white appearance, which shows that the whole of the carbon which had separated upon the surface of the mixture is oxidized,) the point of the combustion tube is broken off, and a certain volume of air (three or four times the volume of the tube) is drawn through the bulb apparatus, in order to force the whole of the ammonia, which may still linger in the tube, into the apparatus; the suction tube filled with hydrate of potass is used for this purpose, in order to avoid inhaling any acid fumes.

Fluid nitrogenous compounds are weighed in small sealed glass bulbs, and the process in general is conducted as directed at § 144, (determination of carbon,) with this difference, that soda-lime is substituted for oxide of copper. It is advisable to employ tubes of greater length for the combustion of fluids than are required for that of solid nitrogenous bodies. The best way of conducting the operation is to ignite, in the first place, about one-third of the tube at the anterior end, and to heat subsequently the posterior end so, as to force the substance to be analysed out of the bulbs, when it will become diffused in the central part of the tube without suffering decomposition in that part. If the application of an ignition heat be now gradually proceeded with, progressing slowly from the anterior to the posterior end, it will be very easy to maintain a steady and uniform evolution of gas.

When the combustion is accomplished, the bulb apparatus is emptied (through the aperture at the point) into a small porcelain dish, and subsequently rinsed, first with a mixture of alcohol and ether, and finally with water until the rinsings cease to manifest acid reaction. (The rinsing with a mixture of alcohol and ether is intended to effect the solution and removal of certain fluid carburets of hydrogen which are present in some instances, and shielding the internal surface of the bulb apparatus from the contact of water, render all attempts at thorough rinsing with the latter fluid ineffectual.) Solution of pure bichloride of platinum is added in excess to the fluid, and the mixture is subsequently evaporated to dryness in a water-bath, heated by a spirit-lamp; (§ 22, Plate XIV.); a mixture of two volumes of strong alcohol and one volume of ether is then poured over the residue. If the fluid acquires a bright yellow color, this is a sure sign that the quantity of bichloride of platinum added was sufficient for the intended purpose; if not, a fresh portion of this substance must be added. The undissolved double chloride of platinum and ammonia is finally collected upon a tared filter, dried at 212°, washed with the above-mentioned mixture of alcohol and ether, dried, and finally weighed, (compare § 73). This double chloride of platinum and ammonium is not invariably of a pure bright yellow color, but sometimes of a darker or brownish yellow. This is the case, especially with difficultly combustible substances containing abundance of carbon, since it is less easy in such instances to avoid the formation of fluid carburets of hydrogen, which impart a black tint to the hydrochloric acid upon the subsequent evaporation. Direct experiments have proved, however, that this darker coloration of the precipitate does not perceptibly impair the accuracy of the results. The purity of the double chloride of platinum and ammonium produced may be tested by reducing this substance to the state of metallic platinum, according to the directions given at § 94; the application of this test, however, will be necessary only in very rare instances.

The results are very accurate; usually somewhat too low, (about from 0.1 to 0.2 per cent.) which is owing to a circumstance common to all analyses, viz., that traces of salammoniac fumes escape condensation in the absorption apparatus, and are carried off with the permanent gases. The results happen sometimes also to be too high; this is mostly owing to the impurity of the bichloride of platinum used.

C. Analysis of sulphuretted organic compounds.

§ 150.

Were it attempted to determine the amount of carbon contained in sulphuretted organic compounds, in the usual manner by combustion with oxide of copper or chromate of lead, the results obtained would be too high, since part of the sulphur would form sulphurous acid, which would subsequently be absorbed in the potass apparatus, with the carbonic acid. To remedy this, it is necessary to place between the chloride of calcium tube and the potass apparatus a tube from four to five inches long filled with perfectly dry peroxide of lead. The latter substance absorbs the sulphurous acid and completely transposing with it to sulphate of lead, ($Pb\ O_2 + S\ O_2 = Pb\ O,\ S\ O_3$,) and thus the carbonic acid alone finds its way to the potass apparatus. The presence of sulphur exercises no modifying influence upon the methods described at §§ 148 and 149 for the quantitative determination of nitrogen. With regard to the determination of the amount of sulphur present in sulphuretted organic compounds, I have to state that the sulphur is invariably weighed in the form of sulphate of barytes, into which it may be converted either in the dry or in the humid way; the former, however, is preferable to the latter.

1. The weighed substance under examination is mixed with carbonate of barytes and nitrate of potass in the proportion of two parts of the former salt to one part of the latter; the mixture is introduced into a short and narrow combustion tube and covered with a layer of carbonate of barytes and nitrate of potass. The combustion tube is then heated to redness, progressing from the anterior to the posterior part, and subsequently removed from the furnace, cleaned of the ashes which adhere to the surface of the glass, and placed upright into a tall cylinder, which is then filled up with very dilute hydrochloric acid, covered with a watch-glass, and allowed to stand at rest for some time, when the nitrate of potass, together with the undecomposed portion of the carbonate of barytes, will dissolve, while the new-formed sulphate of barytes remains un-

dissolved. The latter, after previous filtration, is determined according to the directions of § 100. Volatile sulphuretted organic compounds are weighed in one or two small glass bulbs, and the fumes subsequently transmitted over the ignited mixture of carbonate of barytes and nitrate of potass. Compare § 144.

2. The substance under examination is acted upon with red fuming nitric acid, or with a mixture of nitric acid and chlorate of potass, until the whole of the substance is oxidized; towards the end of the process, the action of the oxidizing agents may be aided by the application of heat should this be necessary. Volatile sulphuretted organic compounds are weighed in a small glass bulb, (§ 144,) the point of the latter is subsequently broken off and, together with the bulb, dropped into a tall flask with a narrow neck, containing the very strongest red fuming nitric acid. The action of the acid proceeds slowly in this case, since the acid is compelled to force its way through the narrow aperture at the point of the bulb; by placing the flask in an oblique position, and taking care to keep the neck cool, the operation may be performed without suffering the slightest loss of substance. The nitric acid which contains now the new-formed sulphuric acid, is finally treated according to the directions given at § 100. If the sulphuretted compound contains oxygen, the amount of the latter is indicated by the difference between the united estimated weight of the sulphur, carbon, &c., and the original weight of the analysed compound.

D. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING CHLORINE.

§ 151.

The combustion of chlorinated organic compounds with oxide of copper gives rise to the formation of subchloride of copper, which, were the process conducted in the usual manner, would condense in the chloride of calcium tube, and would thus vitiate the determination of the hydrogen. This, and every other source of error, may be readily remedied, however, by simply substituting chromate of lead for oxide of copper, and conducting the process strictly according to the directions given at § 142. The chlorine is, in that case, converted into chloride of lead, and remains as such in the combustion tube.

With regard to the determination of the amount of chlorine present in chlorinated organic compounds, this is invariably effected by converting the chlorine into chloride of silver, in the following manner:

The substance under examination is ignited in a combustion tube, with a mixture of three parts of hydrated lime and one part of hydrated soda, (§ 40, 4). (If the substance to be analysed be volatile, the vapors are to be transmitted over the ignited mixture of hydrate of lime and hydrate of soda, compare § 149.) The ignited mass is subsequently dissolved in highly dilute nitric acid, and the solution is finally precipitated with nitrate of silver, (compare § 107.) In the analysis of chlorinated organic compounds of an acid nature, (e. g. chlorosalicylic acid,) the chlorine may frequently be determined in a more simple manner, viz., by dissolving the substance under examination in an excess of dilute potass ley, evaporating the solution to dryness and igniting the residue; this process will, in such cases, convert the whole of the chlorine present into a soluble metallic chloride.—(Löwig.)

Organic compounds containing bromine are analyzed in the same manner.

E. Analysis of organic compounds containing inorganic bodies in admixture.

§ 152.

In the analysis of organic compounds containing inorganic bodies in admixture, it is, of course, necessary to ascertain first the amount of the latter before proceeding to the determination of the carbon, since otherwise, the amount of the organic substance. the constituents of which have furnished the carbonic acid, water, &c., not being known, it would be impossible to estimate the amount of oxygen present in the organic compound, from the difference between the united estimated weight of the carbon, hydrogen, &c., and the original weight of the analysed compound.

If the bodies in question are salts or similar compounds, their bases are to be determined respectively by the methods described in the fourth section; but in cases where the inorganic admixtures are to be looked upon more or less as contaminations of the organic substance to be analysed,—(e. g. lime in gum arabic)—their quantity may usually be determined with sufficient accuracy by the combustion of a weighed portion of the substance in an obliquely placed platinum crucible. Substances which contain fusible salts frequently resist total combustion even upon long-continued ignition, the charcoal of the fused salt being protected against the action of the oxygen The best way of attaining the end in view in such cases, is to carbonize the substance under examination, to extract the carbonized mass subsequently with water, and to incinerate the residue; the aqueous solution is, of course, likewise evaporated to dryness, and the weight of the residue added to that of the ashes.

If the compound, the ashes of which contain potass, soda, barytes, lime, or strontia, is burnt with oxide of copper, part of the carbonic acid evolved remains behind in combination with these alkalies or earths. Since the amount of carbonic acid thus retained is not constant, and since the results are, at all events, more accurate, if the whole amount of the carbon is expelled as carbonic acid, and weighed as such; the oxide of copper is to be mixed with substances which will effect the decomposition of the carbonates at a high temperature, e. g., with oxide of antimony, phosphate of copper, &c.; or the combustion is to be effected with chromate of lead according to the directions given at § 142, recommend the latter method. Precise experiments have shown that not a trace of carbonic acid remains behind in combination with the above enumerated bases, if the combustion is effected with chromate of lead: the fusion of an alkaline carbonate, in conjunction with neutral chromate of lead, giving rise to the formation of basic chromate of lead and neutral alkaline chromate, whilst the whole of the carbonic acid escapes, [$2\ (Pb\ O, Cr\ O_3) + Ba\ O,\ C\ O_2 = 2\ Pb\ O, Cr\ O_3 + Ba\ O, Cr\ O_3 + C\ O_2$.]

III. DETERMINATION OF THE ATOMIC WEIGHT OF ORGANIC COMPOUNDS.

The methods of determining the atomic weight of organic compounds differ essentially from one another, according to the nature and properties of the various compounds. There are three general methods to attain the end in view, viz.,

§ 153.

1. WE TAKE A SUBSTANCE OF KNOWN ATOMIC WEIGHT AND DETERMINE THE EXACT PROPORTIONAL AMOUNT OF THIS SUBSTANCE, WHICH FORMS A CHARACTERIZED AND DEFINITE COMPOUND WITH THE BODY OF WHICH WE WANT TO DETERMINE THE ATOMIC WEIGHT.

This method is pursued in determining the atomic weight of the organic acids and organic bases, and of many indifferent bodies possessing the property of entering into combination with bases. I shall, in this place, simply describe the performance of the analytical process; for the manner in which the atomic weight is calculated from the results obtained, I refer to the chapter on calculation of the analyses.

a. The atomic weight of *organic acids* is in most cases determined from their respective silver salts, because the analysis of these salts is very simple, and there is commonly the positive certainty that the analysed salt is not a basic or hydrated compound. Other salts are, however, frequently used for the same purpose, particularly the lead, barytes, and lime salts of organic acids. (In the analysis of the lead salts of organic acids, especial care should be taken not to mistake basic for neutral salts, whilst in the analysis of the barytes and lime salts the mistaking hydrated for anhydrous salts is to be more particularly guarded against.) For the manner in which the quantitative determination of the bases in question is effected, I refer to section IV. I.

b. The atomic weight of *alkaloids* forming crystallizable salts with sulphuric acid, hydrochloric acid, or any other readily determinable acid, is best ascertained by estimating the proportion of the acid contained in a weighed portion of the salts. For the manner in which the quantitative estimation of the respective acids is effected, I refer to section IV, II.

If the salts do not crystallize, a weighed amount of the dried alkaloid under examination, is introduced into a bulbous tube, which is then accurately weighed with its contents; a slow stream of dry hydrochloric acid gas is now transmitted through the tube; the transmission of the hydrochloric gas is continued for some time, and finally succeeded by that of atmospheric air; the amount of hydrochloric acid absorbed is found from the increase in weight which the tube gains in the process. The accuracy of the results may be controlled by dissolving the new-formed hydrochlorate in water and precipitating the chlorine from this solution, by means of nitrate of silver. (LIEBIG). The atomic weight of the alkaloids may be determined also from the insoluble double salts produced by precipitating the solutions of their hydrochlorates with bichloride of platinum; the double chlorides thus produced are cautiously ignited (§ 94. *a.*) and the residuary platinum is accurately weighed.

c. In the case of *indifferent bodies,* such as gum, sugar, starch, extractive matter, &c., we have usually no other choice than to determine their atomic weight from the analysis of their lead compounds, since these substances either refuse altogether to enter into combination with other bases besides lead, or form with them compounds only which it is impossible to obtain in a state of perfect purity.

§ 154.

2. WE ASCERTAIN THE SPECIFIC WEIGHT OF THE VAPOR OF THE COMPOUND UNDER EXAMINATION.

The following are the outlines of DUMAS' method, which I shall immediately after proceed to describe more in detail: a glass vessel filled with dry air, and the exact capacity of which is subsequently ascertained, is accurately weighed; the weight of the air which the vessel contains at the temperature, and atmospheric pressure, noticed during the process of weighing, is calculated and subtracted from the first weight: the difference expresses the weight of the exhausted vessel. A more than sufficient portion of the substance, the density of the vapor of which it is intended to determine, is then introduced into the balloon, and the latter is exposed to a uniform temperature exceeding the boiling point of the substance, until this is completely converted into vapor, and the excess is expelled together with the atmospheric air originally contained in the balloon; the balloon is then closed air-tight, and accurately weighed. By subtracting from the resulting weight, that of the perfectly exhausted balloon, as previously ascertained, we find the exact weight of a given volume of the vapor, (viz. the volume corresponding to the capacity of the balloon,) and we have consequently now the necessary data for calculating the specific weight of the vapor.

I think I need hardly mention that the volume of the vapor requires to be reduced first upon the normal state of the barometer, and 32° (0° C) of the thermometer, and consequently that the state of the barometer and of the thermometer must be correctly noted both during the process of the first weighing, and at the time of sealing the balloon.

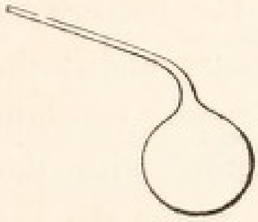
This method is of course applicable only to such substances as volatilize without suffering decomposition; to obtain accurate results, it is indispensable that the examined substance be perfectly pure. I will now proceed to enumerate the apparatus, &c., and to describe the practical process. For the manner of correcting and calculating the results, I refer to the chapter on "Calculation of Analyses."

a. Apparatus and other requisites.

1. THE SUBSTANCE.—From six to eight grammes are required. The boiling point of the substance must be pretty accurately known.

2. A GLASS BALLOON WITH DRAWN-OUT NECK.—A common balloon of pure glass, free from flaws, holding from 250 to 500 cubic centimeters is carefully mixed with water, and afterwards thoroughly dried; it is then completely exhausted, and dry air subsequently re-admitted; these alternate exhaustions and re-admissions of dry air are repeated several times (the apparatus illustrated by Plate LIX., § 141, is used for this purpose). The neck of the balloon is then softened near the bulb, and drawn out in the manner indicated by

PLATE LXIX.



The extreme point is cut off and the borders are slightly rounded over the spirit lamp; (since, it is necessary, at a subsequent stage of the process, to close this point air-tight, with great rapidity, it is advisable to ascertain, in the first place, whether the glass of the balloon is readily fusible or not; this may be done by trying to seal the point of the original neck of the balloon, previously to drawing it out; should this present any difficulty, the balloon is totally unfit for the purpose in view).

3. A SMALL IRON OR COPPER BOILER for the reception of the fluid in which the balloon is to be heated (vide infra, Plate LXX.) The fluid which is to serve as *bath*, must admit of being heated to 36 degrees at the least beyond the boiling point of the substance under examination. It is preferable that the bath should admit

being heated to from 54 to 72 degrees beyond the boiling point of the substance; water or oil will answer the purpose in all cases; a chloride of calcium bath, however, is more convenient than an oil bath, because the balloon may be more readily cleaned; the temperature of a perfectly saturated chloride of calcium bath may be raised to 356°.

4. AN APPARATUS TO FIX THE BALLOON.—This may be readily made of a stick or rod and some iron wire. During the operation, this is supported by the arm of a retort stand (vide infra, Plate LXX.

5. A quantity of MERCURY more than sufficient to fill the balloon.

6. An accurately GRADUATED MEASURING TUBE of about 100 cubic centrimeters capacity.

7. SPIRIT-LAMP and BLOW-PIPE.

8. A correct BAROMETER.

9. A correct THERMOMETER able to rise as high as the respective case under examination may require.

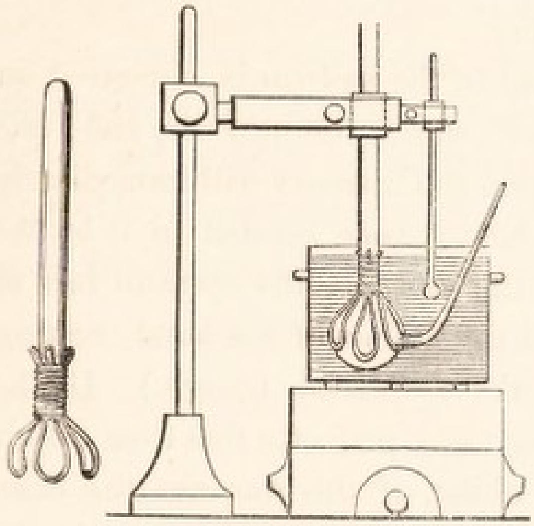
b. Practical process.

α. The balloon is equipoised in the balance; a thermometer being placed at the same time within the balance case. The balloon is allowed to remain for ten minutes undisturbed in the scale, to ascertain whether its weight remains constant. If so, the weight of the balloon is noted, together with the state of the barometer and thermometer, placed within the case of the balance.

β. About eight grammes of the substance which it is intended to examine, are introduced into a glass; should the substance be solid, it is necessary to liquify it by the application of a gentle heat. The balloon is gently heated, and its point is dipped deep into the fluid in the glass; (should the substance under examination have a very high fusing point, the neck and point of the balloon will likewise require heating, to guard against the entering fluid solidifying in the neck). As soon as the balloon cools, (which in the case of very volatile substances, may be accelerated by dropping ether upon it,) the fluid enters and spreads in the balloon; the operator should not allow more than from five to seven grammes to enter.

γ. The contents of the little boiler (3) are heated to from 104° to 122°, and the balloon, together with a thermometer, are immersed in the bath as illustrated in Plate LXX.

PLATE LXX.



The temperature of the bath is then increased to the desired point.* As soon as the temperature in the balloon has risen somewhat beyond the boiling point of the substance, the vapor of the latter rushes out at the point; the force of the stream increases at first with the temperature of the bath, but diminishes subsequently by degrees, and ceases finally altogether (after the lapse of about fifteen minutes.) Should any of the vapor have condensed into drops in the point of the balloon which protrudes beyond the surface of the bath, this may be at once reconverted into vapor by moving a red-hot charcoal to and fro along the protuding part. The moment that a perfect equilibrium is fully established at the desired temperature, the point of the balloon is rapidly sealed air-tight, by means of a spirit-lamp and blow-pipe, and the state of the thermometer is noted immediately after. A very simple test will show whether the point is sealed really air-tight or not; the operator need, for this purpose, simply direct a stream of air through the blow-pipe upon the protruding point of the balloon: if the tube is closed hermetically, a small

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* If the balloon is immersed in a chloride of calcium or oil bath, the operator must endeavour to maintain the temperature constant towards the end of the process, which may be readily effected by regulating the fire.

portion of the vapor will condense and form a small column of fluid, which will be retained in the end of the tube, by the capillary attraction of the latter; this will not take place, if the tube is not sealed hermetically. The state of the barometer is likewise noted, should it have altered since the first observation.

δ. The sealed balloon is now removed from the bath, allowed to cool, washed most carefully, wiped perfectly dry, and weighed again in the same manner as before.

ε. The whole of the pointed end of the balloon is immersed in mercury, and a mark is scratched with a file near the end; the point is then broken off, whereupon the mercury will immediately rush into the balloon, a vacuum having been created in it by the condensation of the vapor. (In this process, the operator has to place the bulb of the balloon in the hollow of his hand, resting the latter upon the border of the mercurial trough.) If the balloon, at the moment of sealing, was perfectly free from air, it will fill completely with mercury whilst, if this was not the case, an air bubble will remain in it. In either case the mercury in the balloon is accurately measured in the graduated tube (6), but in the latter case it is necessary, besides, to fill the balloon with water, and to measure also the volume of the latter liquid: the difference between the volume of the mercury and that of the water shows the volume of the air which had remained in the balloon.

This method, if properly executed, yields pretty accurate results; for the manner of calculating the latter, I refer to the chapter on "Calculation of Analyses."

§ 155.

3. A great number of the indifferent organic bodies refuse absolutely to combine with bases or acids, such as, for instance, the various fats, salicine, the ethyle and methyle compounds, &c. The atomic weight of such substances is determined either according to the directions of the preceding paragraph, or, should this be impracticable from the decomposition products

obtained by the action of acids, bases, &c., upon the substance, and which admit always of the determination of their atomic weight, according either to § 153, and to § 154, or finally the atomic weight is inferred from the mode of formation of the compound in question. In cases of this description, that atomic weight is taken as the correct one which permits the most simple explanation of the respective processes of the formation and decomposition of the compound in question.

This mode of determining the atomic weight of substances is intimately connected with the higher branches of organic chemistry, and cannot be considered here more in detail, as it is impossible to give universally applicable methods for determining the atomic weight of substances in this manner.

CHAPTER II.

CALCULATION OF ANALYSES.

§ 156.

THE calculation of the results obtained by the analysis of substances presupposes as an indispensable preliminary, a knowledge of the general stöchiometrical laws (laws of the combining proportions of substances), on the one, and of the more simple rules of arithmetic on the other hand. The working of chemical calculations does not necessarily require a thorough knowledge of mathematics, as is often very erroneously supposed: a clear head and a knowledge of decimal fractions, and of simple equations, will sufficiently enable the student to work all the more common calculations. These remarks are not by any means intended to dissuade the students of chemistry and pharmacy from pursuing the highly important study of mathematics; I intend to give confidence to those who have not had opportunity to acquire a more profound knowledge of this science, and who, as I have experienced often, are afraid to venture upon chemical calculations. For this reason I have worked the whole of the calculations given in the succeeding paragraphs, in the most intelligible manner possible, and without logarithms.

I. CALCULATION OF THE PROPORTIONAL AMOUNT OF THE CONSTITUENT SOUGHT FOR, FROM THE COMPOUND PRODUCED BY THE ANALYTICAL PROCESS, AND EXHIBITION OF THE RESULTS IN PER CENTS.

§ 157.

The substances, the weight of which it is intended to determine are separated, as we have seen in the chapter on the "practical performance of the analytical process," either in an isolated state, or, and this most frequently, in forms and combinations of known composition. The results are, under all circumstances, calculated upon 100 parts of the examined substance, since this places them in a clearer and more intelligible point of view. In cases where the several constituents have been ascertained separately, the percentage calculation may proceed directly, but if the constituents, the weight of which it is intended to determine, have been separated in combination with some other substance, the proportional amount of the constituent in question is to be calculated first from the compound produced

1. CALCULATION OF THE RESULTS OBTAINED UPON 100 PARTS OF THE ANALYSED SUBSTANCE IN CASES WHERE THE LATTER HAS BEEN OBTAINED IN AN ISOLATED STATE.

a. Solid substances, fluids, or gases, which have been determined by weight.

§ 158.

The calculation here is so exceedingly simple that I will adduce but one illustration for the sake of completeness.

Suppose protochloride of mercury has been analysed, and the mercury separated in the metallic state (§ 89. 1.) 2.945 grammes of protochloride of mercury yielded 2.499 grammes of metallic mercury.

$$2.945 : 2.499 :: 100 : x$$

$$x = 84.85,$$

which means that our analysis shows 100 parts of protochloride of mercury to contain 84.85 of mercury, and consequently is 15.15 of chlorine.

Now the protochloride of mercury is known to consist of 2 equivalents of mercury and 1 equivalent of chlorine, and the equivalent numbers of both these elements are likewise known, the real percentage composition of this compound may be readily calculated. When analyzing substances of known composition, for practice, the results theoretically calculated and those obtained by the analysis are usually placed in juxtaposition, as this enables the student at once to mark the degree of correctness and accuracy with which the analysis has been performed.

Thus for instance—

	found	calculated (compared § 58. *b.*)
Mercury . .	84.85 . . .	84.95
Chlorine . .	15.15 . . .	15.05
	100.00	100.00

b. Gases which have been determined by measure.

§ 159.

When a gas has been determined by measure it is necessary to know the exact weight to which the volume found corresponds, before we can proceed to calculate the weight of the gas in per cents.

Now as the exact weight of a certain definite volume of the various gases has been severally determined by minute and accurate experiments, this calculation is also a simple rule of three question, provided of course the gas be measured under the same circumstances to which the proportion of the volume to the weight ascertained by former experiments relates. The circumstances which we have to take into consideration here, are:

Temperature and atmospheric pressure,

Besides these, the

Tension of the aqueous vapor

may likewise claim consideration in cases where water is used as the confining fluid.

The respective weights assigned in Table V. to one litre of the gases enumerated, refer to a temperature of 0° C. (= to 32° Fahrenheit) and an atmospheric pressure of 0.76 (760 millimeters) of mercury (=29.8 of the English scale). We have, therefore, in the first place, to consider the manner in which volumes of gases measured at a different temperature and different state of the barometer, are to be reduced upon 0° of the C. (Celsius') thermometer, and 0.76 of the barometer.

a. REDUCTION OF A VOLUME OF GAS OF ANY GIVEN TEMPERATURE TO 0°C. OR UPON ANY OTHER TEMPERATURE BETWEEN 0° AND 100° C.

The following propositions of the expansion of gases were formerly universally adopted.

1. All gases expand equally between the same extremes of temperature.
2. The expansion of one and the same gas between the same extremes of temperature is independent of its original density.

Although the correctness of these propositions has not been fully confirmed by the minute investigation of MAGNUS and REGNAULT, yet they may be safely followed in temperature reductions of those gases which are most frequently measured in the course of analytical processes, since the expansion coefficients of these gases scarcely differ from one another, and since there is never any very considerable difference in the respective atmospheric pressure under which the gases are measured.

According to the investigations alluded to, we have to assume

0.3665

as that expansion coefficient of the gases which nearest approaches truth, that is, in other words, as the extent to which gases expand when heated from the freezing to the boiling point of water. Gases expand accordingly for every degree of Celsius' thermometer $\frac{0.3665}{100} = 0.003665$.

If we ask, therefore, how much space a cubic centimeter of gas of 0° C will occupy at 10° C, we find

$$1 \times (1 + 10 \times 0.003665) \text{ i. e.} = 1.03665.$$

If we ask how much space 100 cubic centimeters of 0° C will occupy at 10° C, we find

$$100 \times (1 + 10 \times 0.003665) \text{ i. e.}$$
$$100 \times 1.03665 = 103.665.$$

If we ask how much space 1 cubic centimeter of 10° C will occupy at 0° C, we find

$$\frac{1}{(1 + 10 \times 0.003665} = 0.965.$$

How much is 103.665 cubic centimeters of 10° C at 0° C?

$$\frac{103.665}{1 + (10 \times 0.003665} = 100.$$

The general rule of these calculations may be briefly expressed as follows:

If we wish to calculate a volume of gas of a lower upon a higher temperature, we have in the first place to find in the expansion for the volume unit, by adding to 1, the product obtained by multiplying with 0.003665 the number of degrees of heat above 0° C, and subsequently to multiply the product of this calculation with the given number of volume units found in the analytical process. If, on the other hand, we wish to reduce a volume of gas of a higher upon a lower temperature, we have to divide the number of volume units found in the analytical process, by the product of the multiplication of the thermometrical difference with 0.003665.

β. REDUCTION OF A VOLUME OF GAS OF A CERTAIN GIVEN

DENSITY UPON 0.76 METER BAR. OR ANY OTHER GIVEN PRESSURE.

According to the law of MARIOTTE, the volume of gases is inversely proportioned to the pressure that weighs upon them; which means, in other words, that a gas occupies the greater space, the less considerable the pressure that weighs upon it, and the less space, the greater the pressure upon its surface.

Supposing a gas to occupy a space of 10 cubic centimeters, at a pressure of one atmospheric, it will occupy 1 cubic centimeter at a pressure of 10 atmospheres and 100 cubic centimeters at a pressure of $\frac{1}{10}$ atmosphere.

Nothing, therefore, is more easy than the reduction of a gas of a certain given tension upon 760 millimeters bar. or any other given pressure.

Supposing a gas to occupy 100 cubic centimeters, at 780 millemeters bar., how much space will it occupy at 760 millimeters?

$$760 : 780 :: 100 : x$$
$$x = 102.63$$

How much space do 100 cubic centimeters at 750 millimeters bar. occupy at 760 millimeters?

$$760 : 750 :: 100 : x$$
$$x = 98.68$$

γ. REDUCTION OF A VOLUME OF GAS MIXED WITH AQUEOUS VAPOR TO ITS ACTUAL VOLUME IN A DRY STATE.

It is a well-known fact that water has a tendency at all temperatures, to assume the gaseous state. The degree of force of this tendency (the tension of the aqueous vapor) which is dependent solely and exclusively upon the temperature, and not upon the circumstance of the water being *in vacuo*, or in the air, or any other gaseous atmosphere,—is usually expressed by the height of the volume of mercury which counterbalances this tension. The following table indicates the respective degrees of tension for the various temperatures at which analyses are likely to be made. (Compare Magnus, Poggand. Ann. 61, p. 247.)

TABLE.

Temperature in degrees (Celsius.)	Force of the aqueous vapor expressed in millimeters.	Temperature in degrees (Celsius.)	Force of the aqueous vapor expressed in millimeters.
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		

If, consequently, we have a gas confined over water, its volume is, *cæteris paribus*, always greater than if it were confined over mercury, since a quantity of aqueous vapor proportional to the temperature of the water, mixes with the gas, and since the tension of this vapor counterbalances part of the column of air that presses upon the gas, and thus neutralizes the action of this part. If we wish, therefore, now to ascertain the actual pressure which weighs upon the gas, we must subtract from the apparent pressure that portion of which the action is neutralized by the tension of the aqueous vapor. Suppose we had found a gas to measure 100 cubic centimeters at 770 millimeters bar., the temperature of the confining water being 10° C: how much space would this volume of gas occupy in the dry state and at 760 millimeters bar.?

According to the above given table, the tension of aqueous vapor at 10° C is$=$9.126, and the gas is consequently not under the apparent pressure of 770, but under the actual pressure of $770-9.126=760.874$.

The calculation is now very simple; it proceeds upon the formula given sub. β., viz.,

$$760 : 760.874 :: 100 : x$$
$$x=100.115$$

When the volume of the gas, the percentage weight of which we wish to ascertain, has thus been calculated, according to α. and β., and γ., respectively upon the thermometrical and barometrical conditions to which the data of Table V. relate, the purpose which we have in view is readily attained by substituting the weight for the volume, and proceeding to calculate by simple rule of three.

How many percentage parts of nitrogen are contained in an analysed substance, of which 5 grammes have yielded 300 cubic centimeters of dry nitrogen gas at 0° C, and 760 millimeters bar.?

In Table V. we find that one litre (1000 cubic centimeters) of nitrogen gas of 0° C, and 760 millimeters bar., weighs 1.2609 grammes.

The formula is accordingly:

$$1000 : 1.2609 :: 300 : x$$
$$x=0.378 \text{ grammes.}$$

And further:

$$5 : 0.378 :: 100 : x$$
$$x=7.56.$$

The analysed substance contains consequently 7.56 per cent. by weight of nitrogen.

2. CALCULATION OF THE RESULTS OF ANALYSES UPON THE PERCENTAGE WEIGHT, IN CASES WHERE THE SUBSTANCE, THE PERCENTAGE WEIGHT OF WHICH WE WISH TO ASCERTAIN, HAS BEEN SEPARATED IN COMBINATION WITH ANOTHER, OR WHERE WE HAVE TO ESTIMATE THE WEIGHT OF A COMPOUND FROM THAT OF ONE OF ITS CONSTITUENTS.

§ 160.

In cases where a substance has not been weighed or measured by itself, but in some other form or combination, e. g. carbonic acid as carbonate of lime,—sulphur as sulphate of barytes,—ammonia as nitrogen, &c., we have to calculate the quantity of the substances sought from that of the compound or element found, in order to reduce the calculation to that considered sub. 1.

This may be accomplished either by rule of three or by some abridged method.

Suppose we have weighed hydrogen in the form of water, and have found 1 gram. of water, how much hydrogen does this contain?

One equivalent of water consists of:

$$\begin{array}{rl} 12.5 & \text{of hydrogen} \\ \underline{100.0} & \text{of oxygen} \\ 112.5 & \text{water.} \end{array}$$

The formula is accordingly:

$$112.5 : 12.5 :: 1.00 : x$$

$$x = 0.\dot{1}\dot{1}\dot{1}11$$

From this formula result the following equation:

$$\frac{12.5}{112.5} \times 1.00 = x$$

i. e.

$$0.\dot{1}\dot{1}\dot{1}11 \times 1.00 = x$$

Or, expressed in general terms:

WATER × $0.11\dot{1}\dot{1}\dot{1}$=HYDROGEN.

EXAMPLE—

517 of water; how much hydrogen?

$517 \times 0.11111 = 57.444.$

Besides this, the following equation results likewise from the above given formula:

$$\frac{112.5}{12.5} = \frac{1.00}{x}$$

$$\frac{112.5}{12.5} = 9$$

$$\text{consequently} \quad 9 = \frac{1.00}{x}$$

$$\text{consequently} \quad x = \frac{100}{9}$$

Or, expressed in general terms,

WATER DIVIDED BY 9=HYDROGEN

EXAMPLE.—

517 of water, how much hydrogen?

$$\frac{517}{9} = 57.444$$

In this manner we may find for every compound constant numbers with which to multiply or divide them, in order to find the percentage weight of the constituent sought, (compare Table III.)

Thus, for instance, the nitrogen may be estimated from the double chloride of platinum and ammonium by dividing the weight of the latter with 15.915, or by multiplying it with 0.06283; thus the carbon may be estimated from the carbonic acid by multiplying the weight of the latter with 0.2727, or by dividing it with 3.666.

These numbers are by no means so simple, convenient, and easy of retention as that which we found for hydrogen. It is therefore advisable, in the case of carbonic acid, for instance, to fix upon another general term, viz.,

$$\frac{\text{Carbonic acid} \times 3}{11} = \text{Carbon};$$

which is derived from the formula

$$275 : 75 :: \text{carbonic acid found} : x$$

For $275 : 75 :: 55 : 15 = 11 : 3$

The object in view may be likewise attained in a very simple manner, by reference to Table IV. In this table will be found the amount of the constituent sought for every number of the compound found, from 1—9, and the operator need, therefore, simply add these values.

Thus we find, for instance,

TABLE.

Found	sought	1	2	3	4	5	6	7	8	
water	hydrogen	0.11111	0.22222	0.33333	0.44444	0.55555	0.66667	0.77778	0.88889	1.00000

From this table we see that one part of water contains 0.11111 parts of hydrogen, that five parts of water contain 0.55555 parts of hydrogen, nine parts 1.00000, &c.

Now if we wish to know, for instance, how much hydrogen is contained in 5.17 parts of water, we find this by adding the values for five parts, for $\frac{1}{10}$ part, and for $\frac{7}{100}$ parts, viz.,

$$\begin{array}{l} 0.55555 \\ 0.011111 \\ 0.0077777 \\ \hline 0.5744387 \end{array}$$

Why the numbers are to be placed in this manner, and not as follows,

$$\begin{array}{l} 0.55555 \\ 0.11111 \\ 0.77777 \\ \hline 1.44443 \end{array}$$

is self-evident, since, were we to arrange them in the latter way, we would add the values for 5, for 1, and for 7 $(5+1+7=13)$

and not for 5.17. This reflection shows likewise that, to find the amount of hydrogen contained in 517 of water, we have to transpose the point as follows:

$$\begin{array}{r} 55.555 \\ 1.1111 \\ 0.77777 \\ \hline 57.44387 \end{array}$$

3. Calculation of the results of indirect analyses upon percentage weights.

§ 161.

The import of the term "*indirect analysis,*" as defined at page 286, shows sufficiently that no universally applicable rules can be laid down for the calculations occurring in indirect analyses. The selection of the right way must be left in every individual case to the intelligence of the operator. I will give in this place the mode of calculating the results in two of the indirect analyses described in section V. They may serve as examples for other similar calculations.

a. Indirect separation of soda from potass, (compare § 115, 1. *b.*)

Suppose we had found 1979.85 grammes of sulphate of soda + sulphate of potass, and in these 1000 grammes of sulphuric acid: how much potass is present, and how much soda?

Expressing sulphate of potass by K, and sulphate of soda by N, we get at the following equation;

$$K + N = 1979.85.$$
$$\text{or } K \quad = 1979.85 - N$$

One part of sulphate of soda contains 0.56123 parts, one part of sulphate of potass, 0.45916 parts of sulphuric acid.

The amount of sulphuric acid present in the mixture of sulphate of soda and sulphate of potass, viz., 1000 grammes must consequently be = 0.56123 × the quantity of the units present of sulphate of soda, (i. e. × the quantity of the sulphate of soda present) + 0.45916 × the quantity of the units present of sulphate of potass (i. e. × the quantity of the sulphate of potass present.)

This gives us the second equation :

$$(K \times 0.45916) + (N \times 0.56123) = 1000$$

$$\text{or } K = \frac{1000 - (N \times 0.56123)}{0.45916}$$

Substituting for K its value according to the first equation, we obtain

$$1979.85 - N = \frac{1000 - (N \times 0.56123)}{0.45916}$$

and, taking off the nominators of the fraction

$$(1979.85 \times 0.45916) - (N \times 0.45916) = 1000 - (N \times 0.56123)$$

that is,

$$909.068 - (N \times 0.45916) = 1000 - (N \times 0.56123).$$

Placing now the two N on one side, we obtain

$$(N \times 0.56123) - (N \times 0.45916) = 1000 - 909.068,$$

or

$$N = \frac{1000 - 909.068}{0.56123 - 0.45916} = \frac{90.932}{0.10207} = 890.90$$

The analysed mixture contains accordingly 890.90 of sulphate of soda, and consequently

$$1979.85 - 890.90 = 1088.95$$

of sulphate of potass. From these figures the operator has to deduce, according to 2, the quantities of potass and soda present, and, according to 1, the respective percentage weight of these substances.

The following general formula may be deduced from the above calculation :—Assuming A to stand for the mixture, N for the NaO, SO_3, K for the KO, SO_3, and S for the SO_3, contained in the mixture :

$$N = \frac{S - (A \times 0.45916}{0.10207}$$

$$\text{and } K = A - N.$$

Suppose we had found 20 grammes of sulphate of potass + sulphate of soda, and in these, 10.5 grammes of sulphuric acid, how much sulphate of potass is present, and how much sulphate of soda ?

$$N = \frac{10.5-(20\times 0.45916)}{0.10207}$$

$$= \frac{10.5-9.1832}{0.10207} = \frac{1.3168}{0.10207} = 12.9$$

$$K = 20-12.9 = 7.1$$

The 20 grammes of the mixture consist accordingly of 12.9 NaO, SO_3, and 7.1 KO, SO_3.

b. Indirect separation of chlorine from bromine, (§ 133, 1, *β*.)

Let us suppose the mixture of bromide of silver and chloride of silver to have weighed 20 grammes, and the decrease of weight consequent upon the transmission of the chlorine to have amounted to 1 gramme. How much chlorine does the mixture contain, and how much bromine ?

Here it need simply be borne in mind that the decrease of weight is the difference between the weight of the bromide of silver originally present and that of the chloride of silver which has replaced it, to understand the following formula without difficulty. The difference between the respective equivalents of bromide of silver and chloride of silver is to the equivalent of bromide of silver as the ascertained decrease of weight is to x, i. e. to the bromide of silver originally present in the mixture; or, expressed in numbers:

$$556.43 : 2348.64 :: 1 : x$$

$$x = 4.221$$

The twenty grammes of the analysed mixture contained accordingly 4.221 grammes of bromide of silver, and consequently 20—4.221=15.779 grammes of chloride of silver.

It results from this calculation, that we need simply multiply the ascertained decrease of weight with

$$\frac{2348.64}{556.43} \text{ i. e. with } 4.221,$$

in order to find the amount of bromide of silver originally present in the analysed mixture. And if we once know this, we know of course likewise the amount of the chloride of silver, and from these data we deduce subsequently, according to 2. the respective amount of bromine and chlorine present in the analysed mixture, and, according to 1. the respective percentage weight of these elements.

APPENDIX TO I.

AVERAGE VALUES, DFFICIENCY, AND SURPLUS IN ANALYSES.

§ 162.

If, in the analysis of a substance, we estimate one constituent from the deficiency, or, in other words, if we estimate the amount of one constituent by subtracting from the original weight of the analysed substance the omitted weight of the remaining constituents, it is quite evident that in our subsequent calculation upon percentage weights, we must of necessity invariably obtain 100 as sum total. Every deficiency or surplus occurring in the determination of the respective individual constituents will fall exclusively upon the one constituent which is estimated from the difference between the original weight of the analysed compound and the united weight of the constituents which have been *directly* determined; it is evident, accordingly, that quantitative estimations of this kind afford a sufficient degree of accuracy only in cases where the other constituents have been determined with great precision. The accuracy of the results will be greater, of course, the less the number of the constituents that have been determined in the direct way.

If, on the other hand, every constituent of the analysed compound has been determined individually, it is obvious that, were the results absolutely accurate, the united weight of the several constituents must be exactly equal to the original weight of the analysed substance. Since, however, as we have seen at § 70, certain inaccuracies attach to every analysis, without exception, the sum total of the results in the calculation upon percentage weights will sometimes exceed, and at others fall short of one hundred.

In all cases of this description, the operator should express the results actually found.

Thus, for instance, Pelouze found, in his analysis of chromated chloride of potassium,

Potassium	21.88
Chlorine	19.41
Chromic acid	58.21
	99.50

Thus Berzelius found in his analysis of potasso-peroxide of uranium :

Potass	12.8
Peroxide of uranium	86.8
	99.6

Thus Plattner found in his analysis of magnetic iron pyrites,

	OF FAHLUN.	OF BRASIL.
Iron	59.72	59.64
Sulphur	40.22	40.43
	99.94	100.07

It is altogether inadmissible to distribute any chance deficiency or surplus, proportionally upon the whole of the constituents, since such deficiency or surplus is not equally attributable to the several estimations of the individual constituents, and, moreover, because this way of arranging the calculation of the results deprives other chemists of all power of judging of the accuracy of the analysis. No one need be ashamed to confess having obtained somewhat too little or somewhat too much in his analysis, provided, of course, the deficiency or surplus be confined within certain limits, which are different in different analyses, and which the experienced chemist knows invariably how to fix properly.

In cases where an analysis has been made twice or several times, it is usual to take the average value as the most correct result. It is obvious that this average result deserves the greatest confidence the less it differs from the results of the individual analysis, (which should always be given either fully, or at least, as regards the maximum and minimum.)

Since the accuracy of an analysis is not dependent upon the quantity of substance subjected to the analytical process, (provided always this quantity be not altogether too small,) the average of the results of several analyses is to be taken quite independently of the quantities respectively used in the several analyses, which means, in other words, that the operator must not add together the quantities respectively used, on the one, and the respective weights of the determined constituent on the other hand, and deduce from these data the percentage amount; but the latter is to be calculated for every individual analysis and the average is to be subsequently deduced from the results.

Suppose a substance AB. to contain fifty per cent. of A.; and suppose two analyses of this substance to have yielded the following results:

1) 2 grammes of AB. yielded 0.99 grammes of A.
2) 50 ,, ,, ,, 24.00 ,, ,,

From analysis

No. 1, it results that AB. contains 49.50 per cent. of A.
,, 2, ,, ,, ,, 48.00 ,, ,,

Sum total . . 97.50
Mean . . 48.75

It would be quite erroneous to say

$$2+50=52 \text{ of AB yielded } 0.99+24.00=24.99 \text{ of A.}$$

which would give for 100 of AB. . . . 48.06 of A;
for it will be readily perceived that this way of calculating destroys nearly altogether the influence of the better analysis of the two, (1) upon the average, on account of the proportionally small amount of substance subjected to the analytical process.

II. Deduction of empirical formulæ.

§ 163.

If the percentage composition of a substance is known, a so styled *empirical* formula may be deduced from this under any circumstances, which means, in other words, the relative proportion of the several constituents may be expressed in equivalents—in a formula which, upon re-calculation upon percentage weights, gives figures corresponding perfectly or nearly with those deduced from the analysis of the substance in question. For all those substances of which we cannot determine the atomic weights, such, for instance, as mannite, wood fibre, mixed substances, &c., we are compelled to confine ourselves to the expression of empirical formulæ.

The method of deducing empirical formulæ is very simple and will be readily understood from the following reflections:

How would we proceed to find the relative number of equivalents in carbonic acid?

We would say:

The equivalent of the oxygen is to the proportional amount of oxygen in the atomic weight of carbonic acid, as 1 is to x, i. e. to the number of atoms of oxygen contained in carbonic acid; accordingly

$$100 : 200 :: 1 : x$$
$$x = 2$$

In the same manner we would find the number of atoms of carbon present in carbonic acid, by the following proportion:

$$\underset{\text{(equivalent of carbon)}}{75} \quad : \quad \underset{\substack{\text{(carbon in one equivalent}\\ \text{of carbonic acid.)}}}{75} \quad :: \quad 1 : x$$
$$x = 1$$

Now let us suppose, we did not know the atomic weight of carbonic acid, but simply the percentage composition of this acid, viz.,

$$\begin{array}{l} 27.27 \text{ of carbon} \\ \underline{72.73} \text{ of oxygen} \\ 100.00 \text{ of carbonic acid;} \end{array}$$

yet the relative proportion of the equivalents must appear, even though we select any other given number, e. g. 100, as the atomic weight of carbonic acid. Let us suppose we adopt 100 as the atomic weight of carbonic acid; thus,

$$100 : 72.73 :: 1 : x$$

(Equ. of O) (Amount of oxygen in the assumed atomic weight of 100)

$$x = 0.7273;$$

and further,

$$75 : 27.27 :: 1 : x$$

(Equ. of C) (Amount of carbon in the assumed atomic weight of 100)

$$x = 0.3636$$

We see here that although the *numbers* which express the relative proportion of the atoms of oxygen and carbon, have changed, yet their *relative proportion* remains the same, for

$$0.3636 : 0.7272 :: 1 : 2$$

The method is accordingly in general this:

Assume any number, say 100, (because this is the most convenient,) as the atomic weight of the compound for which you wish to establish an empirical formula, and ascertain how often the equivalent number of every individual constituent is contained in the amount of the same constituent resulting for the assumed atomic weight of the compound. When you have thus formed the number expressing the relative proportion which the several constituents bear to one another, you have attained your purpose, viz., the deduction of an empirical formula. It is, however, usual to reduce these numbers to the most simple expression possible.

Now let us take a somewhat more complicated example, e. g. the deduction of the empirical formula for mannite.

The percentage composition of mannite, is

39.56	of carbon
7.69	of hydrogen
52.75	of oxygen
100.00	

Thence,

1. $100 : 52.75 :: 1 : x$

$x = 0.5275$

2. $12.5 : 7.69 :: 1 : x$

$x = 0.6152$

3. $75 : 39.56 :: 1 : x$

$x = 0.5275$

Here we have now already the empirical formula for mannite, viz.,

$$C_{5275} \quad H_{6152} \quad O_{5275}$$

A glance shows us that the number of the atoms of carbon is equal to that of those of oxygen; and the question is now whether the relative proportion found may not be expressed by smaller numbers.

A simple calculation suffices to answer this question, viz.,

$$5275 : 6152 :: 60 : x$$

(Any other number might be substituted for 60, as the third value of the proportion, but 60 is the most convenient, since it is divisible without remainder by most of the numbers.)

$$x = 70$$

We have now accordingly the more simple formula.

$$C_{60} \quad H_{70} \quad O_{60} = C_6 \quad H_7 \quad O_6$$

The percentage composition of mannite upon which this calculation is based, is that theoretically calculated, and consequently there can be no doubt regarding the correctness of the formula. Now let us take the results of a direct analysis of mannite.

OPPERMAN obtained, upon the combustion of 1.593 grm. of mannite, with oxide of copper, 2.296 grammes of carbonic acid and 1.106 grm. of water. This gives by calculation upon percentage weights

39.31	of carbon
7.71	of hydrogen
52.98	of oxygen
100.00	

which, calculated as above, furnish us with

$$C_{5241} \quad H_{6168} \quad O_{5298}$$

as the first expression of the empirical formula; and thence:

$$5298 : 6168 :: 60 : x$$

$$x = 69.8$$

Upon looking at these numbers we see at once that 69.8 may be properly exchanged for 70, and likewise that the difference between 5241 and 5298 is so trifling, that both may be expressed by the same number. These considerations lead likewise to the formula

$$C_6 \quad H_7 \quad O_6$$

The proof whether this formula is correct or not, is obtained by the re-calculation of the formula upon the percentage weight. The less the percents calculated differ from those found, the more reason there is to consider the empirical formula correct. If both differ more considerably than can be accounted for by the defects inherent in the methods, there is every reason to consider the formula fallacious, and it becomes necessary to establish a more correct one; for it will be readily perceived that from one and the same, or several very nearly corresponding analyses, different formula may be deduced for substances of which the atomic weight is not known; since the numbers found are never absolutely correct, but only approximate.

Thus, for instance, in the case of mannite, calculated

for		for		found
C_6	39.56	C_8	39.67	39.31
H_7	7.69	H_9	7.44	7.71
O_6	52.75	O_8	52.89	52.98
	100.00		100.00	100.00

III. DEDUCTION OF RATIONAL FORMULA.

§ 164.

If, besides the percentage composition, we know also the atomic weight of a substance, we are enabled to deduce for it under all circumstances a *rational* formula, which means a formula expressing not merely the relative proportion of the atoms, but also their absolute number.

The following example may serve for illustration:

1. DEDUCTION OF THE RATIONAL FORMULA FOR HYPOSULPHURIC ACID.

The analysis has shown, in the first place, the percentage composition of hyposulphuric acid, and, in the second place, the percentage composition of hyposulphate of potass, viz.,

Sulphur	44.44	Potass	39.554
Oxygen	55.56	Hyposulphuric acid	60.446
Hyposulphuric acid	100.00	Hyposulphate of potass	100.000

(Equivalent of potass = 588.94.)

From the proportion:

$$39.554 : 60.446 :: 588.94 : x$$
$$x = 900$$

results as x, the sum of the equivalent numbers of the constituents contained in hyposulphurous acid, which means, in other terms, the atomic weight of hyposulphuric acid.

Having thus found the correct atomic weight of hyposulphuric acid, we need not trouble ourselves to assume a hypothetical, atomic weight, as we were obliged to do in the case of mannite.

Thus we write at once:

$$100 : 44.44 :: 900 : x$$
$$x = 400$$

i. e. like the sum of the equivalent number of the sulphur, and further:

$$100 : 55.56 :: 900 : x$$
$$x = 500$$

i. e. like the sum of the equivalent numbers of the oxygen.

Now the equivalent number of sulphur, i. e. 200, is contained twice in 400; and the equivalent number of oxygen, i. e. 100, is contained five times in 500; the rational formula for hyposulphuric acid is accordingly,

$$S_2 \quad O_5$$

2. Deduction of the rational formula of benzoic acid.

Stenhouse obtained from 0.3807 grm. of hydrated benzoic acid dried at 212° F., 0.9575 of carbonic acid and 0.1698 of water; 0.4287 grm. of benzoate of silver, dried at 212° F. yielded 0.202 of silver. From these figures results the following composition:

Carbon	68.67	Oxide of silver	50.67
Hydrogen	4.95	Benzoic acid	49.33
Oxygen	26.38	Benzoate of silver	100.00
Hydrated benzoic acid	100.00		

(Atomic weight of the oxide of silver = 1449.)

$$50.67 : 49.33 :: 1449 : x$$
$$x = 1410.6$$

i. e. the atomic weight of anhydrous benzoic acid; the atomic weight of the hydrated acid is accordingly = 1410.6 + 112.5 = 1523.1; and thus

$$100 : 68.67 :: 1523 : x$$
$$x = 1045.84$$
$$100 : 4.95 :: 1523 : x$$
$$x = 75.39$$
$$100 : 26.38 :: 1523 : x$$
$$x = 401.77$$

75	is contained in	1045.84	13.94 times
12.5	,,	75.39	6.03 ,,
100	,,	401.77	4.02 ,,

A glance at the figures resulting from these divisions suffices to show that 13.94 may be exchanged for 14, and that 6 may be substituted for 6.03, and 4 for 4.02 The rational formula for the hydrate of benzoic acid is accordingly

$$C_{14} \quad H_6 \quad O_4$$

This acid yields by theoretical calculation:	The numbers found by Stenhouse, were
C 68.85	C 68.67
H 4.92	H 4.95
O 26.23	O 26.38
100.00	100.00

3. Deduction of the rational formula of theine.

Stenhouse's analysis of theine gave the following results:

1. 0.285 grm. of theine yielded 0.5125 of carbonic acid and 0.132 of water.

2. The combustion of theine in conjunction with oxide of copper yielded a gaseous mixture of $CO_2 : N = 4 : 1$.

3. 0.5828 grm. of the double salt of hydrochlorate of theine and bicloride of platinum, yielded 0.143 platinum.

From these numbers results the following percentage composition:

Carbon . .	49.05
Hydrogen	5.14
Nitrogen .	28.61
Oxygen . .	17.20
	100.00

and 2451.4 as the atomic weight of theine; for we have every reason to suppose that the composition of the double salt of hydrochlorate of theine and bicloride of platinum is

$$\text{Theine} + \text{Cl H} + \text{Pt Cl}_2.$$

The proportion

$$0.143 : 0.5828 : : 1233.5 \text{ (atomic weight of platinum)} : x$$

$$x = 5027$$

gives consequently the atomic weight of this double salt=5027;—the atomic weight of theine is now found by subtracting from 5027 the sum of the atomic weight of one equivalent of bichloride of platinum (2119.9) and one equivalent of hydrochloric acid (455.7)

$$5027-(2119.9+455.7)=2451.4.$$

From the percentage composition of theine we may now deduce the empirical formula for this substance as follows:

$$75 : 49.05 : : 1 : x$$
$$x=0.654$$
$$12.5 : 5.14 : : 1 : x$$
$$x=0.411$$
$$175.2 : 28.61 : : 1 : x$$
$$x=0.163$$
$$100 : 17.20 : : 1 : x$$
$$x=0.172$$

$$C_{654}\ H_{411}\ N_{163}\ O_{172}$$

By reducing these numbers in the manner stated at page 452 (i. e. substituting 60 for the smallest of them and reducing the others in the same ratio), we get at the formula

$$C_{241}\ H_{151}\ N_{60}\ O_{63}$$

and dividing these figures by 30, we find

$$C_{8\cdot 03}\ H_{5\cdot 03}\ N_{2}\ O_{2\cdot 1}$$

for which we may at once substitute

$$C_{8}\ H_{5}\ N_{2}\ O_{2}$$

as the following percentage arrangement will clearly prove:

	calculated.	found.
8 C=600.0	49.47	49.05
5 H= 62.5	5.15	5.14
2 N=350.4	28.89	28.61
2 O=200.0	16.49	17.20
1212.9	100.00	100.00

Now, looking at the atomic weight corresponding to the formula $C_8\ H_5\ N_2\ O_2$ viz. 1212.9, we find that this is contained twice in the atomic weight, deduced from the analysis of the double salt of hydrochlorate of theine and bichloride of platinum, viz. 2451.4; we find accordingly the rational formula for theine

$$2+C_8\ H_5\ N_2\ O_2{=}C_{16}\ H_{10}\ N_4\ O_4$$

The correctness of our assumption that the formula for the above mentioned double salt is:

$$\text{Theine}+\ Cl\ H+Pt\ Cl_2$$

may now be readily tested and confirmed by comparing whether the amount of platinum expressed in this formula agrees with the quantity found.

		in 100 parts.	
		calculated.	found.
$C_{16}\ H_{10}\ N_4\ O_4$	=2425.8		
Cl H	= 455.7		
Platinum	=1233.5 .	24.66 . .	24.53
Cl_2	= 886.0		
	5001.0		

4. DEDUCTION OF THE RATIONAL FORMULÆ FOR OXYGEN SALTS IN GENERAL.

a. In the case of compounds containing no isomorphous constituents.

The rational formulæ for oxygen salts may be deduced also by a different method from the foregoing, viz. by ascertaining the ratio in which the respective quantities of oxygen stand to one another. This method is exceedingly simple.

In an analysis of crystallized sulphate of soda and ammonia, I found

Soda	17.93
Oxide of ammonium	15.23
Sulphuric acid	46.00
Water	20.84
	100.00

391 of $Na\,O$ contain 100 of O consequently 17.93 of $Na\,O$ contain 4.58 of O
325 ·· NH_4O ·· 100 ·· O ·· 15.23 ·· NH_4O ·· 4.68 ·· O
500 ·· SO_3 300 ·· O ·· 46.00 ·· SO_3 ·· 27.60 ·· O
112.5 ·· HO ·· 100 ·· O ·· 20.84 ·· HO ·· 18.52 ·· O

The respective quantities of oxygen

4.58 : 4.68 : 27.60 : 18.52

stand to one another in the same ratio

as 1 : 1.02 : 6.02 : 4.04

for which we may at once substitute, without any material inaccuracy, the following numbers:

1 : 1 : 6 : 4

which lead to the formula

$$Na\,O, NH_4\,O, 2\,SO_3 + 4\,HO$$
$$\text{or } Na\,O, SO + hH_4\,O, SO_3 + 4\text{ aq.}$$

b. In the case of compounds containing isomorphous constituents.

It is a well known fact that isormorphous constituents may replace one another in every proportion. In adducing a formula for compounds containing isomorphous constituents, the latter are therefore to be taken *collectively;* which means that they are to be expressed in the formula, as if they consisted of but *one and the same* substance. This occurs very frequently in the deduction of formulæ for minerals.

A. Erdmann found in monradite

			Proportion of oxygen.
Silicic acid	56.17		29.179
Magnesia	31.63	12.204	14.153
Protoxide of iron	8.56	1.949	
Water	4.04		3.590
	100.40		

Now the ratio between

$$3.59 : 14.153 : 29.179$$

is like $1 : 3.94 : 8.1$

for which we may substitute without any material inaccuracy

$$1 : 4 : 8$$

Designating one equivalent of metal by R, we find from those numbers the formula:

$$4\,(\mathrm{R\,O,\ Si\,O_2})+\mathrm{HO}\ \text{or}\ 4\left\{\begin{matrix}\mathrm{Mg}\\ \mathrm{Fe}\end{matrix}\right\}\mathrm{O,\ Si\,O_2})+\mathrm{aq}.$$

Besides isomorphous substances, all bodies of analogous composition possess the faculty of replacing one another in compounds; thus we find that $\mathrm{K\,O}$, $\mathrm{Na\,O}$, $\mathrm{Ca\,O}$, $\mathrm{Mg\,O}$, &c. replace one another. These substances likewise must be expressed collectively in the formula.

Abich found in andesine

			Proportion of oxygen.
Silicic acid	59.60		30.90
Alumina	24.28	11.22	11.70
Peroxide of iron	1.58	0.48	
Lime	5.77	1.61	3.79
Magnesia	1.08	0.37	
Soda	6.53	1.65	
Potass	1.08	0.16	
	99.92		

The ratio between 3.79 : 11.70 : 30.90

is as : 1 : 3.08 : 8.1

for which we may substitute, without any material inaccuracy,

1 : 3 : 8.

Designating one equivalent of metal by R, we find from these numbers the formula:

$$\begin{aligned} & \mathrm{R\,O + R_2\,O_3 + 4\,Si\,O_2} \\ = & \mathrm{R\,O,\ Si\,O_2 + R_2\,O_3,\ 3\,Si\,O_2} \end{aligned}$$

which may likewise be written:

$$\left.\begin{matrix}\mathrm{Ca} \\ \mathrm{Mg} \\ \mathrm{Na} \\ \mathrm{K}\end{matrix}\right\} \mathrm{O,\ Si\,O_2} + \left.\begin{matrix}\mathrm{Al_2} \\ \mathrm{Fe_2}\end{matrix}\right\} \mathrm{O_3,\ 3\,Si\,O_2}$$

Which formula shows that this mineral is Leucite ($\mathrm{K\,O,\ Si\,O_2 + Al_2\,O_3,\ 3\,Si\,O_2}$), in which the greater part of the potass is replaced by lime, soda, and magnesia, and a portion of the alumina by peroxide of iron.

These remarks, upon the deduction of formulæ for oxygen salts, apply of course equally to metallic sulphurets.

IV. CALCULATION OF THE DENSITY OF THE VAPOR OF VOLATILE BODIES AND APPLICATION OF THE RESULTS, FOR CONTROLLING THE ANALYSES AND DETERMINING THE ATOMIC WEIGHT OF THE ANALYZED SUBSTANCE.

§ 165.

The specific weight of a compound gas is equal to the sum of the specific weights of its respective constituents in one volume, e. g. Two volumes of hydrogen gas, and one volume of oxygen gas yield two volumes of aqueous vapor. If they yielded simply one volume of aqueous vapor, the specific weight of the latter would be equal to the sum total of the specific weight of the oxygen and double the specific weight of the hydrogen, viz.:

$$\begin{array}{r} 2 \times 0.0693 = 0.1386 \\ +1.1093 \\ \hline =1.2479 \end{array}$$

But as they yield two volumes, these 1.2479 are to be distributed upon these two volumes; accordingly

$$\frac{1.2479}{2}=0.6239$$

It will be readily seen that the knowledge of the density which the vapor of a compound substance exhibits, furnishes us with a most excellent means of controlling the correctness of a formula with regard to the relative proportions of the equivalents.

For instance: from the results of the elementary analysis of camphor, we have deduced the empirical formula:

$$C_{10}\ H_8\ O$$

Dumas found the specific weight of the vapor of camphor= 5.298.* Now, by what means do we find whether the deduced formula is correct with respect to the relative proportions of the equivalents?

Specific weight of the vapor of carbon	0.8320
,, ,, ,, hydrogen gas	0.3693
,, ,, ,, oxygen gas	1.1093

$$\begin{aligned}
10 \text{ equ. C} &= 10 \text{ volumes} = 10 \times 0.8320 = 8.3200 \\
8 \text{ equ. H} &= 16 \text{ volumes} = 16 \times 0.0693 = 1.1088 \\
1 \text{ equ. O} &= 1 \text{ volume} = 1 \times 1.1093 = \underline{1.1093} \\
& \qquad\qquad\qquad\qquad\qquad\quad 10.5381
\end{aligned}$$

This sum is almost exactly twice as large as the specific weight found by direct experiment ($\frac{10.5381}{2}=5.269$) which proves at once that the above given formula for camphor is correct with respect to the relative proportions of the equivalents. But whether the formula is correct, also, with regard to the number of equivalents, cannot be determined from the density of the vapor, because we do not know to how many volumes of camphor vapor an atom of camphor corresponds. Liebig assumes the atom

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* This is the number resulting from Dumas' experiment if we adopt the corrected expansion coefficient of the air, viz., 0.00366; but if the old coefficient, viz., 0.0037 be adopted, the resulting number will be 5.337.

of camphor to correspond to two volumes, and gives accordingly the formula $C_{10} H_8 O$, whilst DUMAS assumes it to correspond to four volumes, and gives the formula accordingly $C_{20} H_{16} 0_2$.

The knowledge of the density of the vapor affords, therefore, simply a means of controlling the correctness of the analysis, but not of establishing a rational formula, and, although it is made, nevertheless, to serve sometimes for the latter purpose, yet this can be done only in the case of substances for which we are able to infer from analogy, a certain ratio of condensation; thus, for instance, experience proves that one equivalent of most of the hydrates of the volatile organic acids corresponds to 4 volumes.

Thus we found, (vide § 164,) $C_{14} H_6 O_4$ as the rational formula for hydrated benzoic acid. DUMAS and MITSCHERLICH found the density of the vapor of this acid=4.260.

Now nearly the same number is found by dividing by 4 the sum total of the specific weights of the several constituents contained in one atom of hydrated benzoic acid.

$$\begin{array}{rr} \text{14 volumes C} = & 11.6480 \\ \text{12 volumes H} = & 0.8316 \\ \text{4 volumes O} = & 4.4372 \\ \hline & \frac{16.9168}{4} = 4.2292 \end{array}$$

Having thus endeavoured to estimate the degree of assistance which the knowledge of the density of the vapor of substances affords us in controlling the results of elementary analysis, I will now proceed to show how the results obtained according to § 154 are to be calculated.

I will select as an illustration DUMAS' estimation of the specific weight of camphor.

The immediate results of the analysis were as follows:

Temperature of the air . . .	13.5° C.
State of the barometer . . .	742 millimeters.
Temperature of the bath the moment of sealing the balloon	244° C.

Increase of weight of the balloon	0.708 grm.
Volume of the mercury which penetrates into the balloon . . .	295 cubic centimeters
Air remaining in the balloon . .	0

Now to find the specific weight of the vapor, we have to answer three questions, viz.,

1. What is the weight of the amount of air which the balloon holds? (This we must necessarily know for the solution of the second question.)

2. What is the weight of the camphor vapor which the balloon holds?

3. What is the volume to which the camphor vapor corresponds at 0° C, and 0.760 millimeters bar.?

The solution of these questions is evidently quite simple; and if the calculation appears in reality somewhat circuitous and complicated, this is merely owing to the several reduction and correction calculations which are required.

1. The balloon holds 295 cubic centimeters as we see from the volume of mercury that penetrated into it.

Now, how much are 295 cubic centimeters of air of 13.5° C and 0.742 millimeters bar. at 0° C and 760 millimeters bar.?

This question is solved according to the direction of § 159, as follows:

$$760 : 742 :: 295 : x$$

$$x = 288 \text{ cubic centimeters.} \quad \text{(Of } 13.5^\circ \text{ C and } 760 \text{ millimeters bar.)}$$

and further,

$$\frac{288}{1+(13.5 \times 0.00366)} = \frac{288}{1.04941} = 274 \text{ cubic centimeters (of } 0^\circ \text{ C and } 760 \text{ millimeters bar.)}$$

Now one cubic centimeter of air of 0° C and 760 millimeters bar. weighs 0.0012991 grm.; 274 cubic centimeters weigh accordingly

$$0.0012991 \times 274 = 0.35595 \text{ grm.}$$

2. What is the weight of the vapor?

At the outset of the experiment, we tared the balloon + the air within it; we weighed subsequently the balloon + the vapor, (but without the air);—to find, therefore, the actual weight of the vapor, it is not sufficient to subtract the tare from the weight of the vapor filled-balloon, since (*glass* + *vapor*)—(*glass* + *air*) is not equal to *vapor;* but we have either to subtract, in the first place, the weight of the air from the tare, or to add the weight of the air to the increment of weight of the balloon. Let us do the latter:

Weight of the air in the balloon = 0.35595 gramme
Increment of weight of the balloon = 0.70800 gramme

The weight of the vapor is accordingly = 1.06395 gramme

3. *What is the volume at* 0° C *and* 760 *millimeters bar. to which this* 1.06395 *gramme of vapor corresponds?*

We know from the above data that this weight corresponds to 295 cubic centimeters at 244° C, and 742 millimeters bar. Before we can proceed to reduce this volume according to the directions of § 159, the following corrections are necessary:

a. 244° C of the mercurial thermometer correspond, according to Magnus' experiments, to 239° C of the air thermometer—(vide Table VI.)

b. According to Dulong and Petit, glass expands, proceeding from 0° C. $\frac{1}{35000}$ of its volume for every one degree, C. The volume of the balloon, at the moment of sealing, was accordingly:

$$295 + \frac{295 \times 239}{35000} = 297 \text{ cubic centimeters.}$$

If we now proceed to reduce this volume upon 0° C and 760 millimeters bar. we find by the position

$$760 : 742 :: 297 : x$$

x (i. e. cubic centimeters of vapor at 760 millimeters bar. and 239° C) =290, and by the equation,

$$\frac{290}{1 + (239 \times 0.00366} = x$$

x (i. e. cubic centimeters of vapor at 760 millimeters bar. and 0° C) =154.6

154.6 cubic centimeters of camphor vapor of 0° C, and 760 millimeters bar.

weigh accordingly 1.0639 grammes. One litre (1000 cubic centimeters weighs consequently 6.882 grm., for

154.6 : 1.0639 : : 1000 : 6.882

Now, one litre of air of 0° C, and 760 millimeters bar. weighs 1.2991 grammes.

The specific weight of the camphor vapor consequently is= 5.298 ; for

1.2991 : 6.882 : : 1 : 5.5298

PART II.

SPECIAL PART.

I. ANALYSIS OF MINERAL WATERS.

§ 166.

THE principles upon which the analysis of mineral waters is based, have been sufficiently discussed already in the first part of this work, and I may, therefore, at once proceed to describe the most advantageous systematic process for performing these analyses. This I am enabled to do with tolerable minuteness and accuracy, because mineral waters contain usually but a limited number of substances.

The substances which occur most frequently are,

a. BASES: Potass, soda, lithia, ammonia.
Strontia, lime, magnesia.
Alumina.
Protoxide of manganese, protoxide of iron.

b. ACIDS: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid.
Nitric acid.
Chlorine, iodine, bromine, fluorine, sulphuretted hydrogen.
Crenic acid, apocrenic acid.

c. NON-COMBINED ELEMENTS: Oxygen, nitrogen.

d. INDIFFERENT ORGANIC SUBSTANCES.

Many of these substances occur in most springs, in predominant proportions; of the bases, particularly soda, lime, magnesia, and sometimes also iron; and of the acids, — sulphuric acid, carbonic acid, chlorine, and sometimes likewise sulphuretted hydrogen. The rest are almost invariably found in exceedingly minute proportions only.

I shall consider the subject of the analysis of mineral waters under two heads, viz., 1. *The performance of the analytical process;* and, 2. *The calculation and arrangement of the results.*

1. PERFORMANCE OF THE ANALYTICAL PROCESS.

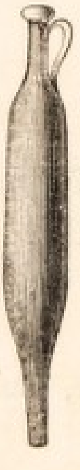
The performance of the analytical process is divided into two parts, viz., 1. operations and experiments at the spring; and, 2, operations and experiments in the laboratory.

A. OPERATIONS AND EXPERIMENTS AT THE SPRING.

§ 167.

1. APPARARUS AND OTHER NECESSARIES.

1. A COMMON SYPHON, of from three hundred to four hundred cubic centimeters capacity, (vide Plate LXXI.) The exact capacity of the syphon is to be correctly ascertained by filling it with water, and measuring the contents subsequently in a graduated jar.



2. FIVE BOTTLES, provided with good cork stoppers; each of these bottles should be able to hold about one and a half times the contents of the syphon. (In cases where the mineral water to be analysed contains sulphuretted hydrogen, about nine flasks of this description are required.)

3. A GOOD THERMOMETER. One with cut or etched divisional lines answers best.

4. From eight to ten ounces of CAUSTIC AMMONIA, which must be entirely free from admixture of carbonate of ammonia.

5. From six to eight ounces of SOLUTION OF CHLORIDE OF CALCIUM.

6. From two to three ounces of SOLUTION OF ARSENIOUS ACID IN HYDROCHLORIC ACID.

7. ALL SORTS OF TEST PAPERS.

8. ABOUT EIGHT WHITE GLASS BOTTLES, of three pounds capacity, and provided with close-fitting cork stoppers.

9. An oil of vitriol carboy of about one hundred pounds capacity. (This is required only under certain circumstances: compare II. *h.*)

If it is intended to determine the free gases, (nitrogen and oxygen,) the operator requires, besides the above,

10. A GLASS BALLOON of about twenty-four ounces capacity; (the exact capacity of this balloon must be correctly known).

11. A GAS CONDUCTING TUBE. This is fitted air-tight into the balloon (10) by means of a perforated cork.

12. A STRONG BOTTLE of about six ounces' capacity; this must be provided with a case, in which it may be packed up securely.

13. A SMALL PNEUMATIC TROUGH.

14. POTASS LEY.

15. A TRIPOD adapted to support the balloon (10).

16. A SMALL SPIRIT-LAMP.

17. Some BEES-WAX.

II. OPERATIONS AT THE WELL.

a. The *taste* and *smell* of the water are examined to detect the presence of very minute quantities of odoriferous matter, a tumbler is half filled with the water, covered with the hand, and vigorously shaken; the hand is then removed and the water smelt.

b. The water is tested with the various *reagent papers;* the operator has to observe whether the color which the papers acquire change upon drying in the air.

c. The *temperature* of the water is examined. The statement of the temperature must be accompanied by the notes, of *a*. The date. *β*. The temperature of the air. *γ*. The constancy or variability of the temperature at different seasons of the year, which may generally be ascertained on the spot.

d. About 1 ounce of solution of chloride of calcium, and about 1½ ounce of ammonia, are introduced into each of the five bottles (I. 2.)

e. The syphon is dipt slowly into the spring below the surface of the water; the upper aperture is closed tight with the thumb, the crane is lifted out of the spring and the contents are transferred to one of the five bottles, which is then immediately corked tight. The remaining four bottles are then filled in the same manner. For greater safety, the cork-stoppers are to be carefully tied over with a bit of string.

f. (This operation is necessary only in cases when the water smells of sulphuretted hydrogen.) A small portion of the solution of arsenious acid in hydrochloric acid (I. 6.) is poured into each of the remaining four bottles (I. 2.); the neck of the bottles is carefully rinsed with pure water, to remove every trace of the arsenical solution, since were this precaution neglected, the syphon would get soiled on the outside upon its subsequent introduction into the neck of the bottles. The bottles are then filled with the water and carefully corked, and the corks tied over, in the same manner as at *e*.

g. (This operation is necessary only if the operator wishes to determine the gases which the water may contain besides carbonic acid and sulphuretted hydrogen.) The glass balloon (I. 10.) is filled entirely with the water, and the gas-conducting tube (I. 11.) which is likewise filled entirely with the water, is fixed in it; the anterior aperture of this tube is then to be closed with a little wax stopper. The bottom is now placed upon the tripod (I. 15.) and the gas-conducting tube is made to dip into the phneumatic-trough, (I. 13.) which is filled with a weak solution of potass, and in which the little bottle, (I. 12.) likewise filled with the same solution of potass, stands inverted. The wax stopper is then removed, and the aperture of the tube is introduced into the mouth of the bottle.

The spirit-lamp is now placed under the balloon, and the water is then heated to ebullition, in which state it is to be maintained for about ten minutes; the gas-conducting tube is then removed from the trough. The bottle which now contains the expelled gases, is allowed to remain for some time longer in the trough, to ensure the complete absorption of the carbonic acid; it is then carefully corked, and the cork tied over with string: this operation is to be performed without changing the inverted position of the bottle in the trough. The bottle is now finally removed from the trough, placed into its case, and carried home to the laboratory, taking care to keep its aperture constantly turned downwards.

h. The bottles (I. 8.) and the carboy (I. 9.) are filled with the water. The filling of the carboy may be dispensed with if the operator can manage to evaporate on the spot, in porcelain basins, about 100 pounds of the water to three pounds. In this case the evaporated water, together with the sediment, are introduced into one of the bottles.

i. The operator should pay attention to every particular connected with the spring, and to every circumstance that may be interesting for the investigation: thus he should mark, for instance, the quantity of water which the spring yields; whether its level remains constant or not; whether a deposit is formed in the outlet tubes; whether the water is clear or not; the formation of the mountain from which it springs; the depth at which it originates; the nature of the basin; the medicinal action of the water, &c.

B. OPERATIONS AND EXPERIMENTS IN THE LABORATORY.

I. QUALITATIVE ANALYSIS.

§ 168.

In the qualitative analysis of mineral waters, the principal constituents only are usually attended to, the detection of those substances which are present in very minute proportions, being more appropriately effected in the course of the quantitative investigation.

a. The detection of free carbonic acid and sulphuretted hydrogen* seldom require any special experiment, since the taste and smell of the water are sufficient in most cases to indicate their presence or absence. Should the application of more positive tests be required, however, the following is the best way of attaining the desired object:—

α. A little lime-water is added to a portion of the water.

The formation of a precipitate which re-dissolves subsequently upon addition of a further measure of mineral water, indicates the presence of FREE CARBONIC ACID.

β. A little test-tube is filled with the water nearly to the brim, and a small quantity of solution of acetate of lead added; the tube is then vigorously shaken, and afterwards placed upon a sheet of white paper. If the operator, looking in at the top of the tube, perceives a black precipitate, or even simply a brownish coloration of the fluid, this indicates the presence of SULPHURETTED HYDROGEN.

b. About 24 ounces of the water are introduced into a glass flask, (or better still, into a porcelain basin,) and boiled down to about 12 ounces. The water generally becomes turbid in this process, owing to the precipitation of those constituents which are kept in solution solely by the agency of the carbonic acid, and which consequently fall down the moment this acid is removed. The water is, therefore, filtered, and the precipitate thoroughly washed with distilled water.

In testing the precipitate and filtrate, we have to look more particularly for the following substances:

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* Mineral waters which have been long kept in stone jars, frequently smell of sulphuretted hydrogen, even though they were entirely free from this odor when fresh. This is owing to the circumstance that the contact with the moist cork reduces a portion of the sulphates to sulphurets, from which the free carbonic acid present, subsequently evolves sulphuretted hydrogen.

IN THE PRECIPITATE.	IN THE FILTRATE.
Carbonate of lime.	Soda, potass, lime, magnesia.
Carbonate of magnesia.	Sulphuric acid, chlorine, iodine.
Peroxide of iron.	Bromine.

c. Examination of the precipitate of b.

The precipitate is dissolved in hydrochloric acid—(effervescence indicates the presence of CARBONIC ACID.) The solution is divided into two portions, and ferrocyanide of potassium is added to the one, ammonia to the other; the formation of a blue precipitate in the first portion, and that of a brownish red precipitate in the second portion, indicate the presence of IRON. (Should the precipitate produced by ammonia be of a pale yellow instead of a brownish red tint, there is reason to suspect the presence of alumina, or of phosphoric acid, which is to be borne in mind in the subsequent processes of quantitative analysis.) That portion of the fluid to which the ammonia has been added is, after previous filtration, (should this be necessary) tested for LIME by means of oxalate of ammonia, and the fluid filtered off from the precipitated oxalate of lime, is finally tested for MAGNESIA, with phosphate of soda.

d. Examination of the filtrate of b.

α. The reaction of the filtrate is tested; a strong alkaline reaction indicates the presence of an alkaline carbonate, possibly also of an alkaline sulphuret, in the latter case the water will acquire a black color upon addition of solution of acetate of lead. The filtrate may manifest a feebly alkaline reaction, although neither alkaline carbonates nor alkaline sulphurets be present; this reaction may be owing to the presence of chloride of magnesium in the water, since this compound upon ebullition transposes partly with water, in such a manner that hydrochloric acid escapes and basic chloride of magnesium remains in solution. To obtain positive information of the presence or absence of an alkaline carbonate, a portion of the filtrate is evaporated nearly to dryness, and a strong acid subsequently added, when ensuing effervescence will decide this point.

β. Another portion of the filtrate is acidified with hydrochloric acid, and subsequently tested for SULPHURIC ACID, by means of chloride of barium.

γ. Another portion of the filtrate is acidified with nitric acid, and subsequently tested for CHLORINE, by means of nitrate of silver.

δ. Another portion of the filtrate is mixed with sal ammoniac, and oxalate of ammonia is subsequently added. The formation of a precipitate indicates LIME. The precipitate is filtered off.

ε. A portion of the filtrate (obtained in δ.) is tested for MAGNESIA, by means of phosphate of soda and ammonia.

ζ. The rest of the filtrate obtained in δ, is evaporated to dryness, and the residue ignited until the whole of the ammoniacal salts have been expelled; the ignited residue is subsequently dissolved in water, and the magnesia and sulphuric acid are precipitated from the solution, with water of barytes; the fluid is filtered off from the precipitate, and the excess of barytes is then thrown down from the filtrate by means of carbonate of ammonia; the fluid is again filtered, and the filtrate evaporated to dryness; the residue is ignited and subsequently tested for SODA by the alcohol flame, and for POTASS by means of bichloride of platinum.

η. To test satisfactorily for iodine and bromine, it is indispensable, at least in most cases, to evaporate larger quantities of water. The residual fluid is tested for IODINE by means of starch in conjunction with chlorine water, which latter is to be added with the greatest caution. For BROMINE, by mixing a portion of the fluid with chlorine water and ether, shaking the mixture, decanting, and evaporating the ethereal solution, (which will appear yellow if bromine is present); with potass ley, igniting the residue, heating it subsequently in conjunction with some peroxide of manganese and sulphuric acid, in a small retort provided with condensing tube, and collecting the distillate which passes over first, in small test-tubes, containing some moistened starch; these test-tubes are then finally sealed and placed in an inverted position. Compare my volume in "QUALITATIVE ANALYSIS."

II. QUANTITATIVE ANALYSIS.

§ 169.

The systematic course to be pursued in the quantitative analysis of mineral waters, varies according to the presence or absence of alkaline carbonates. Since this course is more simple in the case of alkaline than in the case of non-alkaline water, we will here principally consider the course adapted for the quantitative analysis of the latter, because this includes every thing necessary for the quantitative analysis of alkaline water.

In the course which I am now going to describe, I proceed upon the assumption that all those substances are present which usually occur, associated, in saline waters. The modifications which the presence of alkaline carbonates requires, and likewise those demanded by the presence of sulphuretted hydrogen or sulphurets will be found appended to the general course (§ 170 and 171).

The actual analysis is usually preceded by the

DETERMINATION OF THE SPECIFIC WEIGHT.

The respective temperatures of a bottle of the mineral water and a bottle of distilled water are equalized, and the temperature within accurately marked. A small bottle of about 100 grammes capacity, and provided with a close-fitting glass stopper is then accurately tared, and subsequently filled, first with the distilled water and weighed, afterwards with the mineral water and weighed again. The quotient produced by dividing the weight of the mineral water by that of the distilled water, is the specific weight of the former.

The respective quantities required for the estimation of the several constituents, may be determined either directly by weight, or by measure, in the latter case the little flask is to be employed, which has served for the determination of the specific weight. I prefer weighing to measuring. To estimate the whole of the ingredients the operator requires, besides the water, the mother liquor obtained by evaporating 100 pounds down to 3, together with the precipitate, or sediment, which has subsided in the process of evaporation. Should the operator not have been able to evaporate the water on the spot, he has to commence his operation in the laboratory by evaporating the water contained in the large carboy. The evaporation is conducted best in porcelain basins, over spirit-lamps.

1. ESTIMATION OF THE TOTAL AMOUNT OF THE FIXED INGREDIENTS.

From 200 to 300 grammes of the mineral water are introduced into a tall beaker glass, which is then covered with a glass plate, and gently heated in the sand-bath until the whole of the free carbonic acid present is expelled. The water together with the precipitate which may have formed, is to be carefully transferred to an accurately tared small platinum basin, and evaporated to dryness, in the water-bath; the residue is subsequently dried in the air or oil-bath, at about 318 F., until *repeated weighings* continue to furnish the same constant result; the weight is then accurately marked.*

2. JOINT ESTIMATION OF THE CHLORINE, IODINE AND BROMINE.

About 100 grammes of the water are acidified with nitric acid precipitated subsequently with nitrate of silver, and the precipitate is finally determined according to the instruction given at § 107, I. *a.*

3. ESTIMATION OF THE TOTAL AMOUNT OF LIME, MAGNESIA, IRON, SILICIC ACID.

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* The quantity of the chloride of magnesium suffers some slight diminution in this process, a small portion of it transforming with water, into hydrochloric acid which escapes, and magnesia which remains. The diminution in the quantity of chloride of magnesium is, however, so trifling that it may be safely disregarded. Should the operator, nevertheless, feel disposed to prevent it, he need simply evaporate the water with a weighed amount of ignited carbonate of soda.

About 800 grammes of the water are introduced into a capacious glass flask, and mixed with some nitric acid; heat is then applied until the whole of the carbonic acid is expelled, when the water is transferred to a porcelain basin, and evaporated to dryness in the water bath. The residue is heated in the sand-bath until every trace of moisture is completely expelled; the dry residue is now digested with hydrochloric acid, some water added and the silicic acid determined according to the instructions given at § 106, II. *a*. From the filtrate, the iron is precipitated with ammonia (§ 122, *b*, 4), the lime subsequently with oxalate of ammonia, and the magnesia finally with phosphate of soda (§ 117, 6, *a*.) Should the iron precipitate not exhibit a fine brownish red colour, and should the operator accordingly have reason to suspect the presence of alumina or of phosphoric acid, he must pursue the following process. The precipitate is thoroughly washed, and subsequently dissolved in hydrochloric acid; the solution is precipitated with caustic potass, which should be added slightly in excess, and the fluid filtered off from the precipitate formed, which latter is then to be washed, redissolved in hydrochloric acid, ammonia added in excess, and subsequently sulphuret of ammonium, the iron in the sulphuret of iron produced, being finally determined according to § 85, *b*; should it be found now that the alkaline filtrate contains alumina, this is to be estimated according to § 123, A. *a*.

4. ESTIMATION OF THE LIME, MAGNESIA, AND IRON IN THE PRECIPITATE WHICH FORMS UPON EBULLITION OF THE WATER, AND ALSO OF THE LIME AND MAGNESIA IN THE FLUID FILTERED OFF FROM THE PRECIPITATE.

From 600 to 800 grammes of the water are introduced into a glass flask, and boiled for about one hour, the evaporating water being replaced from time to time by distilled water. (If this precaution is neglected, gypsum may precipitate in conjunction with the carbonates of the earths.) The fluid is then filtered off from the precipitate formed, and the latter is carefully washed.

The lime and magnesia in the filtrate are determined according to the instructions given at §117. 6. *a.* The precipitate is dissolved in diluted hydrochloric acid, and the solution heated with some nitric acid; the iron, lime, and magnesia are then finally determined as at 3.

5. ESTIMATION OF THE ALKALIES.

About 600 grammes of the water are introduced into a glass flask, cautiously evaporated to 400 grammes, and subsequently mixed with water of barytes in excess; the mixture is then filtered, and the lime and the excess of barytes are removed by means of carbonate of ammonia (§ 74. 2. *a.*); the fluid is again filtered off, and the filtrate subsequently evaporated to dryness; the residue is ignited, (§71. 3.) weighed, and the soda finally separated from the potass, (should the latter substance be present) as directed at § 115. 1. *a.*

6. ESTIMATION OF THE SULPHURIC ACID.

About 600 grammes of the water are acidified with hydrochloric acid, and chloride of barium is subsequently added; the sulphate of barytes which forms upon the addition of this reagent, is allowed 24 hours to subside, and is then finally determined according to the directions of § 74. 1. *a.*

7. ESTIMATION OF THE TOTAL AMOUNT OF CARBONIC ACID PRESENT.

The precipitates which have formed in the bottles containing chloride of calcium and ammonia (and which were filled on the spot by means of the syphon) are collected severally upon tared filters,* dried at 212° F., and subsequently weighed. If the operations have been properly conducted, the respective weights of the several precipitates will differ but little; the arithmetical mean is in that case taken as the most accurate. The precipitates are now triturated together, and the carbonic acid is then estimated in 2 or 3 portions of the mixture, according to the directions of § 105. *b.*, *β.* *bb.*; the mean of the results obtained are taken, and the amount of carbonic acid then found is calcu-

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[*] Should the precipate be copious, those of three bottles will be sufficient for the further operation.

lated upon the total amount of the precipitate, or, what comes to the same point, upon the total amount of the water from which the precipitate had separated. This quantity being known only by volume, and the specific weight of mineral water exceeding that of pure water, it is necessary to multiply the number of cubic-centimeters found with the specific weight of the analyzed mineral water, in order to find the number of grammes corresponding to the cubic-centimeter.

8. Estimation of the iodine and bromine.

Both of these constituents are determined in the mother liquor, the iodine by means of protochloride of palladium, the bromine in the indirect way. Since protochloride of palladium fails to precipitate the whole of the iodine present as protiodide, whenever metallic chloride, and particularly the chloride of calcium and magnesium, are present to a considerable amount, the following process is to be resorted to :

The mother liquor, obtained by evaporating 100 pounds of the mineral water to three, is filtered off from the sediment ; the latter is washed and the rinsings are added to the filtrate and mixed with it; the fluid is then accurately weighed, and so is the sediment. The quantity of the water from which the mother liquor has been prepared, being known, it is easy to calculate the amount of the mineral water corresponding to a definite portion of the filtered fluid.

About 1000 grammes of the concentrated fluid are evaporated to dryness, in conjunction with carbonate of soda to remove the dissolved lime and magnesia, and the residue is repeatedly extracted with alcohol of 85 per cent., until the last produced extracts cease to manifest the faintest indication of the presence of iodine ; the alcoholic extract is then evaporated to dryness, the residue again completely extracted with alcohol, the alcoholic solution once more evaporated to dryness, the residue treated with water and the iodine finally precipitated from the solution, with protochloride of palladium, according to § 109. I. The fluid filtered off from the precipitated protiodide of palladium is acidified with nitric acid, and subsequently precipitated with nitrate of silver; the precipitate which contains the whole of the bromine present as bromide of silver together with a considerable portion of chloride of silver, is determined according to § 107. I. *a.*, and the amount of the bromine present is then finally calculated according to the instructions given at § 133. 1. *β.*

9. DETECTION AND ESTIMATION OF THE LITHIA.

About 400 grammes of the filtered mother-liquor (vide 8.) are boiled with an excess of carbonate of soda, until evaporated to dryness; the residue is treated with boiling water, the aqueous solution is filtered, mixed with phosphate of soda, and subsequently again evaporated to dryness; the residue is treated with cold water, and the fluid is subsequently filtered off from the undissolved phosphate of soda and lithia, which is then washed with cold water, dried, ignited, and weighed; the washing with cold water should not be continued too long. The purity of the residual phosphate of soda and lithia is to be tested before the blow-pipe.*

10. DETECTION AND ESTIMATION OF PROTOXIDE OF MANGANESE, ALUMINA, AND STRONTIA.

The precipitate remaining upon the filtration of the mother-liquor (vide 8.) is dried in the water-bath and weighed. The quantity of the water from which the precipitate has been obtained, being known, it is easy to calculate the amount of mineral water corresponding to any given definite portion of this precipitate.

About one fourth part of the precipitate is dissolved in hydro-

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* *Phosphate of soda and Lithia* is a white light powder, very sparingly soluble in cold but somewhat more readily in hot water, and nearly altogether insoluble in water containing phosphate of soda in solution. (According to Brandes its solution requires 1400 parts of water of 59° F., 1233 parts of 140° F., and 951 parts of 212° F.) Exposed on platinum wire to the flame of the blow-pipe, it fuses pretty readily to a transparent button, which, upon solidifying, turns white, opaque, and crystalline; fused upon charcoal it is imbibed by the latter. Exposed to the flame of the blow-pipe upon a platinum wire, with carbonate of soda, it fuses to a transparent mass,

chloric acid, and the solution subsequently supersaturated with ammonia. Sulphuret of ammonium is then added, and the fluid is afterwards filtered off from the precipitate, which contains, besides sulphuret of iron, sulphuret of manganese, and alumina. The precipitate is thoroughly washed and subsequently dissolved in hydrochloric acid; the solution is heated with nitric acid and the alumina separated from the iron and manganese, by means of potass (§ 123. A. *a.*); the iron is finally separated from the manganese by means of succinate of ammonia (§ 124. 1. α.). The filtrate is mixed with solution of gypsum to precipitate the strontia, should any of this substance be present.

11. DETECTION AND ESTIMATION OF THE PHOSPHORIC ACID.

Another fourth of the precipitate (vide 10) is dissolved in hydrochloric acid, and the phosphoric acid determined in the solution according to § 101. II. *d.* α.

12. DETECTION OF THE FLUORINE.

The third fourth of the precipitate (vide 10) is dissolved in hydrochloric acid, and the solution is subsequently precipitated with ammonia; the fluid is filtered off from the precipitate, and

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which loses its transparency upon cooling. In this it differs more particularly from the phosphate of the alkaline earths. It is anhydrous and its composition remains consequently unaltered upon ignition. According to RAMMELSBERG (Poggend. Annal., XLVI. 79—91,) the formula of the ignited phosphate of soda and lithia is not, as was formerly supposed, PO^5, Na O, Li O,—but PO_5, 3 RO, i. e., it contains three equivalents of base to one equivalent of phosphoric acid, and since soda and lithia, as isomorphous substances, may replace one another, the relative proportions in which these two bases are present in the salt are variable. To determine the actual amount of lithia present, it is indispensable, therefore, to analyse the salt. This is effected by separating the phosphoric acid from the two alkalies according to § 101, II. *a.* γ., and the lithia subsequently from the soda by converting the mixed alkalies into chlorides, and separating the latter by means of absolute alcohol, which dissolves the chloride of lithium, leaving the chloride of sodium undissolved.

the latter is washed, and tested for fluorine by heating with sulphuric acid in a platinum crucible covered with a glass plate.

13. DETECTION AND ESTIMATION OF THE AMMONIA.

From 3000 to 4000 grammes of the water are evaporated at from 176 to 194° F., with some hydrochloric acid, the residue is introduced into a capacious flask and soda ley added in excess; the contents of the flask are then heated to boiling, and kept for some time in a state of ebullition, the evolved vapour being transmitted through diluted hydrochloric acid in a flask surrounded with cold water. The ammonia in the sal ammoniac formed, is finally determined according to § 73. 2. *a.*

14. DETECTION AND ESTIMATION OF THE CRENIC ACID AND APOCRENIC ACID.

The last fourth of the precipitate (vide 10) is boiled for about one hour, with potass ley; the fluid is then passed through the filter, the filtrate is acidified with acetic acid, and neutral acetate of copper subsequently added. If a brownish precipitate forms upon the addition of this reagent, this consists of apocrenate of copper (which, according to MULDER, contains variable quantities of ammonia in admixture, and dried at 284° F., 42.8 per cent. of oxide of copper.) The fluid filtered off from this precipitate, is mixed with carbonate of ammonia until the green colour has changed to blue; heat is then applied. If a bluish green precipitate forms, this is crenate of copper, which dried at 284° F., contains 74.12 per cent. of oxide of copper (MULDER.*)

15. DETECTION AND ESTIMATION OF THE SO CALLED ORGANIC EXTRACTIVE MATTER.

Nearly all mineral waters, when boiled in large quantities, and, subsequently filtered and evaporated, leave a residue which, when heated, turns brown and black; this is owing to the presence of

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* For further information regarding crenic acid and apocrenic acid, I refer to MULDER's paper on these acids.—Journal für prakt. Chemie. XXXII. pag. 321—344.

organic extractive matter. To determine the amount of the latter, a weighed portion of the filtered mother-liquor is evaporated to dryness, with carbonate of soda; the residue is boiled with water and the solution subsequently filtered; the filtrate is evaporated to dryness, and the residue dried at 284° F. until the weight ceases to vary. The dry residue is then gently ignited until the black color which it acquires at first has disappeared. The difference between the weight of the dry and that of the ignited residue shows the amount of the extractive matter. The residue contains sometimes an admixture of resinous matter, in which case it is to be treated with alcohol, water being subsequently added to the alcoholic solution; upon evaporating the alcohol the resinous matters will separate, being insoluble in water.

16. Estimation of the free gases present in mineral waters.

The gaseous mixture collected according to § 167. II. *g.*, and which usually contains only oxygen gas and nitrogen gas, and perhaps some marsh gas, is introduced (under water) into a measuring tube, and the volume accurately noted. The amount of the oxygen is then determined by removing this gas, according to § 187, by means of copper, moistened with hydrochloric acid. The gas residue is again measured, and some chlorine gas conducted into it; the gaseous mixture is allowed to stand for some time freely exposed to the day light, when the marsh gas, ($C\,H_2$) which may be present, will transpose with four equivalents of chlorine and two equivalents of the confining water to $4\,Cl\,H$ and $C\,O_2$. The tube is now placed in fresh and pure water, and a fragment of caustic potass attached to a bent wire quickly introduced into it, beyond the surface of the confining water. When the volume of the gas ceases to decrease, the potass is withdrawn, and the remaining nitrogen gas is then finally measured. The volume of marsh gas (should this have been present) is found by subtracting the joint volume of the oxygen and nitrogen gas from the total volume of the original gaseous mixture.

MODIFICATIONS REQUIRED BY THE PRESENCE OF A FIXED ALKALINE CARBONATE.

§ 170.

A mineral water, which contains an alkaline carbonate, cannot contain soluble lime and magnesia salts; all the lime and magnesia which are found are to be considered as carbonates kept in solution by the agency of carbonic acid, although the whole of the magnesia present does not precipitate upon ebullition, since a small portion of the double carbonate of soda and magnesia is invariably formed under these circumstances. The best way, therefore, is to determine the lime and magnesia, together with iron and silicic acid, according to the instructions given at § 169. 3.

The estimation of the carbonated alkali, or speaking more correctly, of the carbonic acid combined with alkalies to simple carbonates, is effected best in the following manner.

From three hundred to four hundred grammes of the water are boiled for a considerable time, and the fluid is subsequently filtered off from the precipitate formed, which latter is thoroughly washed with hot water, the rinsings being added to and intimately mixed with the filtrate. The fluid is then divided into two equal portions; nitric acid is added to the one portion, and the chlorine subsequently determined in the usual manner. Pure hydrochloric acid is added to the other portion until the fluid acquires a decidedly acid reaction; it is then evaporated to dryness, and the residue dried, gently ignited, and subsequently dissolved in water; the amount of chlorine present in this solution is determined likewise. It is evident that this second estimation must of necessity yield more chlorine than the first; now every one equivalent of chlorine obtained in the second estimation, beyond the amount obtained in the first, corresponds to one equivalent of carbonic acid originally combined with an alkali.

With regard to the estimation of the total amount of the alkalies present, this is effected best in the following manner. The water is boiled for some time, with chloride of barium, and some water of barytes subsequently added, the boiled mixture being then finally filtered after the lapse of some time. The filtrate is precipitated with carbonate of ammonia, and the fluid filtered off from the precipitated carbonate of barytes. The filtrate is evaporated to dryness when the whole of the alkalies originally present in the water will be left behind as chlorides.

MODIFICATIONS REQUIRED BY THE PRESENCE OF SULPHURETTED HYDROGEN OR OF ANOTHER SULPHUR COMPOUND.

§ 171.

Mineral waters smelling of sulphuretted hydrogen, and manifesting a non-alkaline reaction, contain sulphuretted hydrogen alone; but if the water manifests alkaline reaction, it may, besides sulphuretted hydrogen, contain likewise an alkaline sulphuret. The estimation of the total amount of sulphur present is by no means difficult. The sulpharsenious acid produced, according to § 167. II. *f.*, is carefully collected upon the filter, washed, dried, and weighed. (Compare § 111. I. *a.*)

The methods which have hitherto been recommended to effect the estimation of the amount of sulphur present in the form of sulphurets, besides the free sulphuretted hydrogen, are so very imperfect, that I venture here to propose a new method, although I have not yet had any opportunity of testing its practical merits.

Having determined the total amount of sulphur present in the analysed water, the free sulphuretted hydrogen is to be estimated in a fresh portion of the water; this is effected in the following manner:

The water is introduced into a glass balloon, and digested for some considerable time, with an excess of pure magnesia. This process serves to bind the free sulphuretted hydrogen, and likewise the free carbonic acid. The contents of the balloon are now heated to boiling, and maintained in ebullition for some considerable time, the escaping aqueous vapor which is accompanied by the free sulphuretted hydrogen evolved, being conducted into a solution of arsenious acid in hydrochloric acid, supersaturated with potass, and which is kept surrounded with cold water. The sulphuret of arsenic formed is then determined according to § 111. II. *b. a. bb.* The difference between the amount of sulphur calculated from this, and the total weight of the sulphur present, as ascertained in the first process, shows the proportion of sulphur originally present in the form of sulphuret. This method is based upon the circumstance that the sulphuret of sodium and hydrogen is resolved, upon boiling, into sulphuretted hydrogen and sulphuret of sodium, (GUERANGER), and also that an aqueous solution of sulphuret of magnesium is, upon boiling, resolved into magnesia and sulphuretted hydrogen (BERZELIUS).

2. METHOD OF CALCULATING, CONTROLLING, AND ARRANGING THE RESULTS OF THE ANALYSIS OF MINERAL WATERS.

§ 172.

The results found at 1. are the immediate products of direct experiments; they are altogether independent of any theoretical views which may be entertained of the manner in which the various constituents are combined or associated with one another. Since all theoretical views on this subject may change as chemistry advances, it is absolutely indispensable that reports of analyses of mineral waters should above all give the direct results together with the methods pursued; for analyses thus reported are of service for all times.

With respect to the principles which guide chemists in inferring what manner the acids and bases are combined, as salts in the water, it is assumed that the bases and acids are combined according to their relative degrees of affinity, i. e. the strongest acid is assumed to be combined with the strongest base, &c. ; due attention being paid, however, to the greater or less degree of solubility of the salts, since it is well known that this exercises a considerable influence upon the manifestations of the force of affinity. Thus, for instance, when lime, potass, and sulphuric acid are found in the boiled water, the sulphuric acid is assumed in the first place to exist in combination with the lime. It cannot be denied, however, that this way of proceeding leaves much to the individual views and discretion of the analyst, and consequently that different modes of associating the several ingredients found may lead to different results for one and the same analysis.

A general understanding upon this point would be very desirable, because without it the comparison of two mineral waters is beset with difficulties. As long as a general understanding of this kind is wanting, a comparison between mineral waters can only be made with the direct and immediate results of the respective analyses.

One point, I think, should be at once agreed upon, viz., to assume the whole of the salts to be present in the anhydrous state ; and, moreover, the carbonates as neutral salts, and the surplus carbonic acid as free acid.

To illustrate the principles which I conceive ought to guide chemists in this matter, and the way of controlling the results obtained, I select the following example.

ANALYSIS OF THE BONIFACE WELL AT SALZSCHLIRF.*

a. Direct results of the analysis in per cents.

SPECIFIC WEIGHT = 1.011164.

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* Compare "Chemical Investigations of the mineral spring at Salzschlirf in the bishopric of Fulda, (Electorate of Hesse,) by FRESENIUS and WILL :

1. TOTAL AMOUNT OF THE FIXED CONSTITUENTS: 1.3778 per cent.

2. JOINT AMOUNT OF CHLORINE, IODINE, AND BROMINE: 2.8071 per cent. silver precipitate.

3. TOTAL AMOUNT OF LIME, MAGNESIA, IRON, AND SILICIC ACID:

   a. Lime 0.10442 per cent.

   b. Silica 0.00114 per cent.

(The gross amount of magnesia and iron was not determined.)

4. LIME, MAGNESIA, AND IRON IN THE PRECIPITATE WHICH SEPARATES UPON EBULLITION:

   a. Lime 0.03642 per cent.

   b. Magnesia 0.00041 per cent.

   c. Peroxide of iron 0.00066 per cent.

5. LIME AND MAGNESIUM IN THE BOILED AND FILTERED WATER:

   a. Lime 0.064724 per cent.

   b. Magnesium 0.028855 per cent.

6. ALKALIES:

   a. Potass 0.00865 per cent.

   b. Soda 0.54783 per cent.

7. SULPHURIC ACID: 0.10853 per cent

8. TOTAL AMOUNT OF CARBONIC ACID: 0.194301 per cent.

9. BROMINE AND IODINE:

   a. Bromine: 0.000402 per cent.

   b. Iodine: 0.000447 per cent.

The respective weights of the remaining ingredients, such as lithium, phosphoric acid, protoxide of manganese, crenic acid, apocrenic acid, and extractive matter, were not determined.

b. Calculation of the results.

α. Of the salts which precipitate upon boiling, we have to

Annalen der Chemie und Pharmacie, LII., page 66. I have copied the results from the papers, and have refrained from altering them according to the corrected atomic weights.

assume that they are present as carbonates which are maintained in solution by the agency of free carbonic acid.

1. 0.00066 peroxide of iron correspond to 0.00096 of PROTOCARBONATE OF IRON which contain 0.00038 of carbonic acid.

2. 0.03642 of lime correspond to 0.06533 of CARBONATE OF LIME, which contain 0.02891 of carbonic acid.

3. 0.00041 of magnesia correspond to 0.00085 of CARBONATE OF MAGNESIA, ($Mg\,O, C\,O_2$), which contain 0.00044 of carbonic acid.

β. The amount of free carbonic acid present is now readily found by subtracting the amount of the acid which exists in combination, from the total weight of the acid present in the analysed water, viz.,

Total amount of the carbonic acid . . .		0.194301
Carbonic acid existing in combination		
With lime . . .	0.02891	
With magnesia . . .	0.00044	
With protoxide of iron . .	0.00038	
Sum total		0.029730
Remains FREE CARBONIC ACID		0.164571

γ. The sulphuric acid is assumed to exist in combination with lime, in the first place; should a surplus remain, this is assumed to exist in combination with potass, and, should there still remain a surplus, this is supposed to exist as sulphate of soda.

1. The boiled water contains 0.064724 of lime, which combines with 0.09261 of sulphuric acid to 0.15733 of SULPHATE OF LIME.

2. 0.00865 of potass combine with 0.00737 of sulphuric acid to 0.01602 of SULPHATE OF POTASS.

3. Total amount of sulphuric acid present . .		0.10853
Of which there are combined		
With lime	0.09261	
With potass	0.00737	
Sum total . . .		0.09998
There remains . .		0.00855

of sulphuric acid, which combine with 0.00666 of soda to 0.01521 of SULPHATE OF SODA.

δ. The rest of the soda present exists evidently as chloride of sodium.

Total amount of the soda present . . .	0.54583
Of which	0.00666 are
combined with sulphuric acid; there remain accordingly . . .	0.53917

which correspond to 0.40123 of sodium, which latter combine with 0.61040 of chlorine to 1.01163 of CHLORIDE OF SODIUM.

ε. The whole of the iodine and bromine must evidently be assumed as existing in combination with magnesium, and the rest of the magnesium must be considered to exist as chloride of magnesium.

1. 0.000447 of iodine combine with 0.000044 of magnesium to 0.000491 of IODIDE OF MAGNESIUM.

2. 0.000402 of bromine combine with 0.000065 of magnesium to 0.000467 of BROMIDE OF MAGNESIUM.

Total amount of the magnesium contained in the boiled water		0.028855
Of which there are combined		
With iodine	0.000044	
With bromine . . .	0.000065	
Sum total . . .		0.000109
There remain accordingly . .		0.028746

which are combined with 0.080220 of chlorine to 0.108966 of CHLORIDE OF MAGNESIUM.

c. Control.

I. The joint amount of the lime in the boiled water and in the precipitate which forms upon ebullition must be equal, or, at least, nearly equal, to the total amount of the lime.

Total amount of the lime . . .		0.10442
Combined with carbonic acid .	0.03642	
Combined with sulphuric acid .	0.06472	
Sum total. . . .		0.10114

II. The amount of chlorine directly determined must correspond with the joint amount of the chlorine contained in the chlorides of sodium and magnesium.

The joint amount of the chloride, bromide, and iodide of silver is		2.807100
Subtract from this the amount of iodide of silver corresponding to 0.000491 of iodide of magnesium, viz.	0.000828	
Together with the amount of bromide of silver corresponding to 0.000467 of bromide of magnesium, viz. . . .	0.000958	
Sum total		0.001786
There remains		2.805314
which corresponds to Chlorine		0.69202
According to δ. . . . 0.61040 of chlorine is combined with sodium.		
And according to ε. . . 0.08022 of chlorine is combined with magnesium.		
Sum total 0.69062		0.69062

III. The total amount of the fixed constituents must correspond to the joint amount of the several ingredients, (the iron is to be counted as peroxide, since it is contained as such in the residue.)

Total amount of the fixed constituents = 1.37780

The estimation of the several constituents yielded respectively:

Carbonate of lime . . .	0.06533
,, magnesia .	0.00085
Sulphate of lime . . .	0.15733

Sulphate of potass	0.01602
,, soda	0.01521
Chloride of sodium	1.01163
,, magnesium .	0.10896
Iodide of magnesium . .	0.00049
Bromide of magnesium .	0.00047
Peroxide of iron	0.00066
Silica	0.00114
Sum total	1.37809

d. Arrangement and classification of the results.

The analyst should state, in the first place, how many parts of the several constituents are contained in 100 (or 1000 or 10000) parts of the water; and, in the second place, how many grains (1 lb. = 7680 grs.) of the several constituents are contained in one pound of the water.

The most appropriate way of classifying the results, is to enumerate them under the following heads :

A. Fixed Constituents.

a. Present in appreciable quantity.

b. Present in inappreciable quantity.

B. Volatile Constituents.

Besides stating the weight of the carbonic acid and the gases in general, it is customary to give the volumes likewise, calculated upon the temperature of the spring ; (the volumes should be given, in the first place, in cubic centimeters, and, in the second place, in cubic inches, [1 lb. of water = 32 cubic inches]).

As similar examples to guide the young chemist in calculating and controlling the results of analyses of alkaline waters, I adduce :

Analysis of the spring at Geilnau, by Liebig.—Annalen der Chemie und Pharmacie XLII. 88., and

Analysis of the hot spring at Asmannshausen.

By Fresenius and Will.—Annalen der Chemie und Pharmacie, XLVII. 198.

ANALYSIS OF THE ASHES OF PLANTS.

§ 173.

The recent researches and discoveries of agricultural chemistry have fully established the fact, that plants require for their growth and development certain inorganic constituents, which are different for the divers classes of plants; the discovery of this fact has created a very natural desire to ascertain *which* inorganic constituents are respectively indispensable for the growth of the various species of plants, and more particularly for that of the cultivated plants, and also the various weeds, since the knowledge of the constituents of these latter enables us to infer the nature of the soil from which they spring.—This knowledge may be attained, to a degree of preciseness sufficient at least for the purposes of agriculture, by the analysis of the ashes remaining upon the combustion of either the whole plants or particular parts of them, (the fruits, for instance).

The experiments which have been made hitherto show that the ashes of plants contain only a limited number of bases and acids; viz.

BASES.	ACIDS, OR SALT RADICALS.
Potass	Silicic acid
Soda	Phosphoric acid
Lime	Sulphuric acid
Magnesia	Carbonic acid
Peroxide of iron	Chlorine
Peroxide of manganese.	

And, besides these, we find sometimes fluorine, iodine, and bromine; and, in some cases, also oxide of copper.

The diversity of these ingredients, and the circumstance that some of them are usually present only in very minute proportions, render the devising of universally applicable methods a task of no inconsiderable difficulty, especially as such methods ought to combine the necessary degree of preciseness with a certain degree of rapidity of execution.

The general process of analysing the ashes of plants, is properly divided into four parts; viz.

1. *The incineration of the plant.*

2. *The estimation of the total amount of ashes yielded by a vegetable substance.*

3. *The actual analysis of the ashes.*

4. *The statement and arrangement of the results.*

1. Incineration.

§ 174.

The first condition requisite for the proper incineration of plants is, that the plant, or the part of it which it is intended to reduce to ashes, be perfectly free from extraneous impurities; the second condition is, that the ashes contain as little as possible of unconsumed organic ingredients.

To satisfy the first condition, it is necessary to select and clean with great care, the plant, or part of the plant, intended for incineration, without, however, having recourse to washing, since this would cause a loss of part of the soluble salts. To satisfy the second condition, the kind and nature of the plant, or part of the plant intended for incineration, must be had regard to.

Woods, stalks, and matter of similar descriptions are incinerated best after having previously been most thoroughly dried at a brisk fire, either upon a clean iron plate, or in a perfectly clean small iron stove. Dry seeds are incinerated in hessian crucibles, which latter, are to be placed obliquely amidst red-hot charcoal. In some cases, perfect incineration is readily accomplished, when the ashes will speedily acquire a white appearance. On the other hand, there are many seeds that require long-protracted ignition, even to the extent of several days, to effect the consumption of the whole, or at least of the greatest part of the carbon which they contain. The temperature ought to be kept within certain limits, to prevent the fusion, or agglutination of the ashes, since this would protect the still admixed carbon from the access of air, and would consequently prevent its combustion. The whitest and purest ashes are obtained, if the operator refrains altogether from stirring, or shaking the carbonized matter in the crucible, since this will leave the whole mass bulky and porous, and thus facilitate the free access of air to all parts. Succulent roots and fruits are to be cut in slices, which latter are thoroughly dried on glass plates, and subsequently incinerated in hessian crucibles in the same manner as seeds.

The ashes thus prepared, in either manner, are, if necessary, kept for some time longer, in a state of feeble ignition, for which purpose they are to be transferred to a flat platinum dish, which is then to be exposed to the heat of a spirit- lamp, the ashes being stirred all the time. The ashes are then, while still warm, reduced to a very fine powder, which is uniformly intermixed and kept in well-stoppered bottles.

2. ESTIMATION OF THE TOTAL AMOUNT OF ASHES YIELDED BY A VEGETABLE SUBSTANCE.

§ 175.

To determine the total amount of ashes which a given vegetable substance yields upon incineration; it is necessary, in the first place, to dry the substance in question, in the water-bath, or should it contain volatile ingredients under a bell-glass over sulphuric acid, (§ 14.) without applying heat; the process of exsiccation is in either case continued until the weight of the substance ceases to vary. The quantity to be used for incineration depends upon the proportion of fixed constituents present; in the case of herbs or seeds containing abundance of fixed constituents, from 2 to 3 grammes will yield sufficiently accurate results, whilst in the case of woods, which yield sometimes as little as 0.2 per cent. of ashes, 10 times the amount and more will be required. The process of incineration is conducted best in a covered platinum crucible with thin sides. At the commencement of the process, a gentle heat only should be applied, which is to be increased afterwards, the crucible being opened and placed in an oblique position, with the removed lid leaning against it. (Compare § 32. Plate XXIX.)

This method of estimating the quantity of the ashes which a plant yields, is not free from defects, whence it happens that the results of repeated incinerations of one and the same substance do not perfectly correspond. Thus the amount of carbonate of lime undergoing calcination, and also that of the sulphates passing to the state of sulphurets, depend upon the degree of heat applied, and upon the application of an intense heat whilst a considerable portion of charcoal remains; carbonate of soda and chloride of sodium undergo decomposition when intensely ignited with silicic acid, and even simply with charcoal. Upon the degree of heat applied, the duration of the process of ignition, the presence of alkaline carbonates, &c., depends the form in which the phosphoric acid is obtained, and likewise the more or less complete combustion of the charcoal, &c. As the quantity of ashes, however, which a plant yields is not constant, since two specimens of the same plant never produce exactly the same amount of ashes, we rest usually satisfied with the results obtained in the manner described, although some of the indicated defects admit of a remedy. Thus, ashes which do not effervesce with acids may be readily freed from charcoal by moistening them with nitric acid, and igniting them again; the same end may be attained in the case of ashes containing carbonates and sulphurets, by mixing them with peroxide of mercury, and exposing the mixture subsequently to an intense and protracted ignition, which will moreover serve to effect the reconversion into sulphuric acid of the whole of the sulphur present; thus, carbonic acid which has escaped may be replaced by moistening the ashes with solution of carbonate of ammonia, drying, and subsequent gentle ignition, &c.

3. Actual analysis of the ashes.

§ 176.

The ashes of plants may be classed under the following heads, according to their respective principal constituents.

a. Ashes in which *carbonates of the alkalies and alkaline earths* predominate; e. g. the ashes of woods, of herbaceous plants, &c.

b. Ashes in which *phosphates of the alkalies and alkaline earths* predominate; to this class belong the ashes of nearly all kinds of seeds.

c. Ashes in which silicic acid predominates; e. g. those of the stalks of the graminaceæ, of the equisetaceæ, &c.

This classification, although it is quite obvious that the limits between the different classes cannot be drawn very strictly, must be maintained, in order to impart a certain degree of clearness and simplicity to the analytical methods which I am now going to describe; for the general process requires of course certain modifications according to the respective class to which the ashes under examination belong.

a. QUALITATIVE ANALYSIS.

The general constituents of the ashes of plants being already known, a perfect qualitative analysis of every kind of ashes which may happen to come under our notice would be superfluous. A few preliminary experiments suffice to ascertain the presence or absence of the more rarely occurring constituents, and more particularly the class to which the ashes under examination belong. This preliminary investigation proceeds as follows:

1. *The operator has to ascertain whether the ashes under examination decompose completely when heated with concentrated hydrochloric acid.* Ashes which effervesce strongly when concentrated hydrochloric acid is poured over them, may be at once considered decomposed by this menstruum. The ashes of the stalks of the graminaceæ, &c., which contain a large proportion of

silicic acid, are usually the only kind of ashes that resist complete decomposition.

2. Upon mixing the hydrochloric solution of any kind of ashes whatsoever, (after separation of the silicic acid,) with an alkaline acetate, or neutralizing it with ammonia, and adding subsequently free acetic acid, a gelatinous yellowish white precipitate of perphosphate of iron will almost invariably separate. Now it becomes necessary to ascertain *whether, besides the phosphoric acid in this precipitate, the ashes contain still a further portion of this acid or not.* For this purpose, the fluid is filtered off from the precipitated perphosphate of iron, and ammonia in excess is added to the filtrate; should this fail to produce a precipitate, or should the precipitate produced be red, and consequently consist of hydrated peroxide of iron, this is a proof that the ashes contain no more phosphoric acid; but if, on the contrary, a white precipitate is formed, (phosphate of lime, and phosphate of magnesia and ammonia), this is a positive proof that the ashes contain more phosphoric acid than the peroxide of iron present is able to combine with, and the ashes are consequently to be classed under the second head.

3. *The ashes are tested for manganese*, by mixing a small portion of them with carbonate of soda, and (exposing the mixture on a platinum plate, to the external flame of the blow-pipe. (Compare "Elementary instruction in Qualitative Analysis.")

4. *The ashes are tested for iodine, bromine, and fluorine*, (compare "Elementary instruction in Qualitative Analysis,") for the two former elements if the analyst has reason to suspect their presence, and for fluorine in cases when it is intended to ascertain whether traces of this element are present or not.

b. QUANTITATIVE ANALYSIS.

I. *Ashes in which the carbonate of the alkalies or alkaline earths predominate, and in which the whole of the phosphoric acid present is combined with peroxide of iron.*

§ 177.

The ashes are divided into three portions, which we will call respectively A, B, and C.

In C we determine the carbonic acid.

In B the chlorine.

In A the whole of the remaining constituents.

A.

1. ESTIMATION OF THE SILICIC ACID, CHARCOAL, AND SAND.

From four to five grammes of the ashes are introduced into a flask, and concentrated hydrochloric acid is poured over them, the flask being held in an oblique position, to preclude the carrying off of small drops of the fluid by the evolved carbonic acid; a gentle heat is then applied until you perceive no more undecomposed ashes, (with the exception of the carbonaceous and sandy particles which are almost invariably present, and may be readily distinguished). The solution is now carefully transferred to a porcelain basin, and evaporated to dryness in the water-bath; the residue is then heated somewhat more intensely, as is invariably required to effect the separation of silicic acid; compare § 106. II. *a.* (If the ashes effervesce only feebly when treated with hydrochloric acid, the operator need not use the flask at the commencement of the process, but may conduct the operation at once in the porcelain basin, taking care simply to cover the latter with a glass plate.)

The dry residue is, after cooling, moistened with concentrated hydrochloric acid, which is allowed to act upon it for the space of about thirty minutes; the mass is then heated with the necessary amount of water, to incipient ebullition, and the acid fluid is subsequently passed through a tared filter, made of strong paper and dried at 212° F.

The silicic acid remains upon the filter, together with the charcoal and sand, should these latter substances be present. The mass upon the filter is thoroughly washed, carefully dried, and subsequently transferred from the filter to a platinum basin, without injuring the filter. (If the powder be perfectly dry, this may be readily accomplished, a few particles of charcoal alone adhering to the paper.) The powder is now heated to boiling with pure dilute potass ley, and kept in ebullition for half an hour, whereupon the whole of the silicic acid present will gradually dissolve, without the sand or charcoal being affected. The fluid is passed through the same filter as before, and the undissolved residue is thoroughly washed and subsequently dried upon the filter at 212° F. until the weight ceases to diminish. The weight is then accurately determined, and, after subtracting the tare of the filter, taken into account as CHARCOAL and SAND.

The filtrate is supersaturated with hydrochloric acid, and the amount of the SILICIC ACID contained in it, is then finally determined according to § 106. II. *a*.

2. ESTIMATION OF THE WHOLE OF THE REMAINING CONSTITUENTS, WITH THE EXCEPTION OF CHLORINE AND CARBONIC ACID.

The hydrochloric solution filtered from the silicic acid, charcoal, and sand, is most intimately mixed with the rinsing water, and the whole fluid subsequently divided, by weight or measure, into three or, better still, four parts, since this will leave one part for unforeseen accidents. The best way of proceeding is to measure the whole of the fluid in an accurately graduated tube, and to divide it subsequently into three or four perfectly, or nearly equal portions, which we call *a*, *b*, and *c*, (the fourth portion being kept for unforeseen accidents, as just now stated).

In *a*, we determine the perphosphate of iron, and the alkaline earths, and also the free peroxide of iron and the manganese which may happen to be present.

In *b* we determine the alkalies, and

In *c* the sulphuric acid.

a. Estimation of the perphosphate of iron, &c., and of the alkaline earths.

Ammonia is added to the fluid until the precipitate produced is not entirely redissolved upon agitation; acetate of soda is then added, and sufficient free acetic acid, to impart a strongly acid reaction to the fluid; the character of the precipitate formed will readily show whether it still contains phosphate of lime, in which case a further addition of acetic acid is required. The permanent, yellowish white precipitate, which separates best upon the application of a gentle heat, is PERPHOSPHATE OF IRON, ($3\ PO_5,\ 2\ Fe_2\ O_3,\ 3\ HO + 10$ aq.). The fluid is now filtered off from the precipitate, which is then washed with hot water and subsequently dried, ignited and weighed, the weight being stated in the account as that of perphosphate of iron. The formula of this salt, after ignition, is $3\ P\ O_5,\ 2\ Fe_2, O_3$, (compare § 67. 4 *c.*)

The filtrate is supersaturated with ammonia and the LIME and MAGNESIA are subsequently determined according to § 117. 6. *a.*

Should, however, a precipitate of hydrated peroxide of iron form upon the addition of the ammonia, this precipitate must first be filtered off and determined; and should an appreciable amount of MANGANESE be present either alone or with iron, the filtrate is, after the supersaturation with ammonia, first to be precipitated with sulphuret of ammonium, before proceeding to the estimation of the alkaline earths. The precipitated sulphuret of manganese, if pure, is to be treated according to § 81. 1. *c.*; if containing an admixture of iron, according to § 124. 1.

b. Estimation of the alkalies.

The fluid *b* is mixed with water of barytes to alkaline reaction, heated and subsequently filtered. This process serves to remove the whole of the sulphuric acid, phosphoric acid, peroxide of iron, and magnesia present. The precipitate is washed until the last washings are no longer rendered turbid by solution of nitrate of silver; the excess of barytes is removed from the filtrate by means of carbonate of ammonia mixed with caustic ammonia; the barytes precipitate is allowed to subside, and the fluid is subsequently filtered off; the filtrate is evaporated to dryness in a platinum basin, and the residue subsequently ignited, and the chloride of the alkalies produced, are weighed, the SODA and POTASS being subsequently separated according to § 115. 1. *a.*

c. Estimation of the sulphuric acid.

The fluid *c* is precipitated with chloride of barium, and the precipitated sulphate of barytes determined according to the directions of § 100.

B.

ESTIMATION OF THE CHLORINE.

A second portion of the ashes (from one to two grammes) is accurately weighed off, and extracted with hot water mixed with a few drops of nitric acid; the solution is precipitated with nitrate of silver, and the precipitated chloride of silver is finally determined according to the instructions given at § 107. 1. *a.*

C.

ESTIMATION OF THE CARBONIC ACID.

The carbonic acid is determined in a third portion of the ashes, according to the directions of § 105. II. *b.* (The quantity of the ashes to be operated upon for this purpose, depends upon the greater or less proportion of carbonic acid which they may happen to contain.)

II. *Ashes which are decomposed by hydrochloric acid; and contain an additional amount of phosphoric acid, besides that which is combined with peroxide of iron.*

§ 178.

The general process is the same with that described sub. I. (§ 177); it undergoes, however, certain modifications in the following numbers.

1. In A. 2. *a.*

The fluid filtered off from the precipitated perphosphate of iron, is precipitated with neutral oxalate of ammonia, (§ 76. 2. *b.* *β.*), and the fluid is then filtered off from the precipitated oxalate of lime, the magnesia being finally precipitated from the filtrate, by means of phosphate of soda and ammonia. But should an appreciable amount of manganese be present, perchloride of iron is to be added to the fluid filtered off from the perphosphate of iron (and which contains still acetated alkali), until the mixture appears distinctly red from the peracetate of iron formed; the mixture is then boiled for a considerable time and subsequently filtered hot. This process serves to eliminate the whole of the phosphoric acid present, leaving manganese, lime, and magnesia alone in solution as chlorides. The latter three substances are then separated according to § 122. *a.* Should the precipitate of sulphuret of manganese contain an admixture of iron, (which is generally the case,) these two metals are to be separated from one another according to the directions given at § 124. 1.

2. In A. 2. *c.*

Besides the sulphuric acid, the total amount of the phosphoric acid is to be determined in the fluid *c.*

For this purpose the fluid filtered off from the precipitated sulphate of barytes is concentrated by evaporation, neutralized nearly with ammonia, acetate of soda added in excess, and subsequently perchloride of iron, and the further operation proceeded with strictly according to the directions given at § 101. II. *d.*

III. *Ashes which are not completely decomposed by hydrochloric acid.*

§ 179.

Carbonic acid is rarely found in ashes of this description; should any of this acid be present, however, this is to be determined according to the directions of I. (§ 177). The same applies to chlorine. With regard to the estimation of the other constituents, I have to observe that the ashes require to be decomposed by alkalies, first, before they are to be acted upon with hydrochloric acid in the usual manner; it is consequently necessary to determine the alkalies in a separate portion of the ashes. The operation proceeds as follows:

a. ESTIMATION OF THE SILICIC ACID, THE PERPHOSPHATE OF IRON, THE ALKALINE EARTHS, &c.

Pure potass or soda ley is poured over about four grammes of the ashes, and the mixture is then evaporated to dryness in a platinum or silver basin. This process serves to decompose the whole of the silicates contained in the ashes, without affecting the sand that may happen to be present, or, at all events, affecting the latter substance only to an exceedingly trifling extent. The heat should not be raised sufficiently high, towards the end of the process, to fuse the mass. Dilute hydrochloric acid is now poured over the residue, the mixture is evaporated, and the residue again acted upon with hydrochloric acid; the hydrochloric solution is filtered off from the insoluble residue, (silicic acid, charcoal, and sand,) and the latter subsequently treated as directed at I. A. 1. (§ 177.) The filtrate is treated as directed at I. A. 2. (with the exception, of course, of that part of the process which relates to the estimation of the alkalies, since these must of necessity be determined in a separate portion of the ashes, as already stated.)

b. ESTIMATION OF THE ALKALIES.

A second portion of the ashes (about three grammes) are decomposed with four times the amount of hydrated barytes, in a platinum—or silver—crucible, (compare § 20. *b.* *β.*) The residue is treated with hydrochloric acid, the mixture is evaporated, the residue again acted upon with hydrochloric acid, and the solution filtered off from the silica, the filtrate being finally treated, strictly according to the directions of I. A. 2. *b.* (§ 177).

4. METHOD OF STATING AND ARRANGING THE RESULTS.

§ 180.

It is only very recently that chemists have begun to turn their attention seriously to the analysis of the ashes of plants, for the benefit of vegetable physiology and agriculture. The questions which it is intended to solve by the analysis of the ashes of plants, are in the main the following:

1. Do plants absolutely require certain constituents in certain definite proportions? and if they do, *what* are those constituents?

2. May some of the inorganic constituents of plants be replaced by others?

3. Has every plant a definite saturation capacity, that is, in other terms, is the amount of oxygen contained in the bases present, invariably the same?

It is quite obvious that a proper and satisfactory solution of these questions can be expected only from the results of an exceedingly large number of analyses, and that consequently a great many chemists must contribute towards the final solution.

Under these circumstances, it is of the utmost importance that the respective results of the various analyses should be stated and arranged in a uniform and corresponding manner, so that they may readily and without previous calculation admit of mutual comparison.

Since the manner in which the bases and acids found were originally combined in the plants cannot be inferred from the ashes with any degree of positive certainty, and since, moreover, as I have already had occasion to state, the form in which the phosphoric acid is obtained, &c. differs according to the degree of heat employed, &c., it is unquestionably the most judicious way to enumerate the percentage weights of the bases and acids separately. Chlorine, however, is to be arranged as chloride of sodium; (and, should the quantity of soda present be insufficient for this purpose, chloride of potassium); the proportion of sodium contained in the chloride is to be calculated upon soda, and the calculated weight of the latter finally subtracted from the total amount of soda formed; since, otherwise, a surplus would be invariably obtained in the analysis, the chloride of sodium originally present in the ashes being reckoned as chlorine and soda, instead of chlorine and sodium, as it ought to be. Should any manganese have been found, this is to be given as manganoso-manganic oxide, since it exists as such in the ashes.

The following analysis of the ashes of beech seeds, by **Souchay** may serve as an illustration:

Potass	18.13
Soda	7.55
Lime	19.47
Magnesia	9.25
Peroxide of iron	2.12
Manganoso-manganic oxide	2.47
Phosphoric acid	16.53
Sulphuric acid	1.75
Chloride of sodium	0.69
Silica	1.49
Carbonic acid	9.11
Charcoal and sand	9.39
	97.95

It is evident, however, that this kind of statement is not sufficiently precise for an accurate comparison of the results given with those of another analysis, since we find here near twenty per cent. of substances enumerated which are altogether immaterial, viz., carbonic acid, charcoal, and sand. For the proportion in which these substances are present in the ashes of plants, nay, their very presence, depends altogether upon accidental circumstances, such as the degree of care with which the vegetable substances are cleaned previously to incineration, the degree of heat used, and the extent of time that the process of ignition lasts.

To render the mutual comparison of the results obtained in several analyses practicable, it is necessary to strike out the numbers for the inessential ingredients, viz., carbonic acid, sand, and charcoal, and to calculate the weight of the remaining essential constituents upon one hundred parts.

This calculation will give the following results for the above quoted analysis:

Potass	22.82
Soda	9.50

Lime	24.50
Magnesia	11.64
Peroxide of iron	2.67
Manganoso-manganic oxide	3.11
Phosphoric acid	20.81
Sulphuric acid	2.20
Chloride of sodium	0.87
Silica	1.88
	100.00

To satisfy all demands, it is therefore necessary to state the results of every analysis of vegetable ashes, both ways. The first statement will enable chemists to pronounce upon the accuracy of the results, whilst the second statement will render mutual comparisons between the results of several analyses practicable. Should the analyst feel desirous to render his statement still more complete, he may also calculate the proportional amount of oxygen contained in the several bases, and communicate the resulting sum total of this element.

III. ANALYSIS OF SOILS.*

§ 181.

The proposition being established that every plant requires for its growth and development certain inorganic matters which are provided by the soil in which it grows, it is self-evident that the knowledge of the composition of the soil must be a subject of paramount importance to the practical farmer, whether he wishes to know to which kind of plants a given soil will afford the re-

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* I cannot begin this chapter without expressing my warmest thanks to Professor Otto for the great benefit which I have derived from his excellent paper on the analysis of soils, (vide Sprengell's Bodenkunde.)

quisite sustenance—or whether he wishes to adapt a soil for the cultivation of a certain definite plant by a proper supply of manure.

But as plants can absorb with their roots substances in a state of solution only, it is not sufficient for their growth and proper development that the necessary ingredients should be present in the soil; but it is necessary, moreover, that these ingredients should be present in a form admitting of their absorption by the roots of the plants. If, therefore, the analysis of a soil is intended to enable the agriculturist to judge of the appropriateness of the analysed soil for the cultivation of a certain plant, it is necessary not only to know what are its constituents, but the form or state in which these constituents are present in the examined soil.

In this point of view, the inorganic constituents of the soil may be ranged under three heads:

1. Constituents which dissolve in water.

2. Constituents which, though not dissolving in water, dissolve in dilute acids.

3. Constituents which dissolve neither in water nor in dilute acids.

The ingredients belonging to the first class are supplied directly to the plants with the water which they imbibe from the soil. The absorption of the ingredients of the second class is somewhat more difficult, since these ingredients are rendered soluble only by the agency of carbonic acid, and of the acid decomposition products of decaying organic substances, (humic acid). The constituents belonging to the third class require a thorough modification, before they can exercise any influence upon the development of plants; and this modification they suffer slowly and gradually by the progressive disintegration and decomposition of their particles.

The ingredients which are soluble in water serve therefore for immediate use, whilst those soluble in acids exercise a more permanent action, and those, finally, which are altogether insoluble, afford a prospect of future nourishment for plants, although, for the time being, they possess no nutritive powers.

But besides the inorganic constituents, we find in most, in fact nearly in all soils, organic substances (vegetable and animal remains) and the products of their decomposition. That these organic substances exercise a material influence on the fertility of the soil is unquestionable; and, whatever views we may entertain as to the manner of this influence, this much is certain, that it is highly important to obtain also a knowledge of the quantity contained in the soil, and their exact nature.

Having thus briefly indicated the object which the analysis of soil is intended to attain, I will now proceed to describe a simple and accurate method of proceeding in the analysis, arranged under three heads, viz., 1, Qualitative analysis; 2, Quantitative analysis, and, 3, the way of stating and arranging the results. To enter into a minute investigation into the physical and mineralogical conditions of soils, or to draw conclusions for the practical purposes of agriculture, from the analytical results, would, of course, be altogether beside the purpose of the present work.

1. QUALITATIVE ANALYSIS.

§ 182.

A simple reflection upon the origin of arable soil suffices to show that a soil may contain all elements without exception. In most cases, however, we have to deal only with a limited number of elements and compounds, and more particularly with the following:

Inorganic constituents.

Chlorine, sulphuric acid, phosphoric acid, silicic acid, carbonic acid, and sometimes also nitric acid.

Potass, soda, ammonia, lime, magnesia, alumina, manganese and iron

Organic constituents.

Vegetable remains, humic acid, humine, waxy and resinous matters.

The object of the qualitative analysis of soils is twofold, viz., 1, to detect all the constituents present, and the form and state in which they exist; and, 2, to indicate which of these constituents are present in appreciable quantities. These objects the qualitative analysis ought to attain in the most simple and expeditious manner.

The earth intended for analysis is collected from a great number of different parts and various depths of the surface-soil; the collected mass is triturated, spread upon a sheet of paper, and allowed to dry in the air on a spot well protected against dust. The dry earth is then uniformly mixed, and kept in a well-stoppered bottle.

In the following instructions I suppose that the earth is to be subjected both to the processes of qualitative and to those of quantitative analysis, and I have therefore given the quantities which will suffice for both purposes. If the analyst purposes a qualitative investigation only, he may, of course, operate upon a smaller quantity, and omit altogether the process of weighing &c., which is only required for the purposes of the quantitative analysis.

a. DETECTION OF THOSE INGREDIENTS OF THE SOIL WHICH ARE SOLUBLE IN WATER.

1200 grammes of the uniformly mixed dry earth are introduced into a porcelain basin, a sufficient quantity of water is poured over them, and the mixture is then heated nearly to the boiling point, and kept thus for about one hour; the solvent action of the water being aided by frequent stirring. The fluid is then passed through a moistened filter,* and the residue repeat-

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* The best way is to transfer first the larger fragments of the undissolved sediment to the filter, and then to pour the fluid upon it, since otherwise

edly washed with fresh quantities of hot water, until a portion of the last rinsings, upon evaporation on a platinum plate, leaves at least only a hardly perceptible, residue. (Earths containing much gypsum require long protracted washing.) The filtrate and the rinsing water are uniformly mixed, and the whole fluid is then accurately weighed. The aqueous solution corresponds to the whole amount of earth from which it has been prepared, viz., to 1200 grammes; we may therefore take from this, at pleasure, the quantities necessary for the qualitative analysis, since it is easy to calculate afterwards every weighed portion of the remainder of the fluid, upon the original total amount.

α. A small portion of the fluid is acidified with nitric acid and divided into two portions, one of which is tested for SULPHURIC ACID, with chloride of barium, and the other for HYDROCHLORIC ACID, with nitrate of silver.

β. About one-sixth part of the total quantity of the fluid is acidified with hydrochloric acid, and subsequently concentrated by evaporation; a small portion of the concentrated fluid is then tested for AMMONIA, with hydrate of lime.

Some nitric acid is added to the rest of the concentrated fluid, and the mixture evaporated to dryness; the residue is very feebly ignited, to consume any organic substance which may happen to be present and when this has been effected, heated with hydrochloric acid; the white sediment which remains undissolved consists of SILICIC ACID. (The reaction with carbonate of soda before the blow-pipe may be resorted to as a conclusive test—compare "Elementary instructions in Qualitative Analysis.")

The solution filtered off from the silicic acid is divided into two portions, and ammonia added to the one; should a precipitate form, this may consist of a mixture of HYDRATED ALUMINA, with HYDRATED PEROXIDE OF IRON, which may subsequently be

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the minute particles which are suspended in the fluid might tend to choke up the pores of the filter.

separated from one another by means of potass, and of which the former may be more positively identified by adding sal ammoniac to the potass solution, and the latter by means of ferrocyanide of potassium. Whether the detected iron existed in the soil in the form of peroxide or of protoxide, may be decided by testing a portion of the original solution (which may be concentrated, if necessary) with ferro and ferri-cyanide of potassium.

The fluid which has been filtered off from the mixed precipitate of iron and alumina, is tested for MANGANESE, with sulphuret of ammonium.

The fluid filtered off from the sulphuret of manganese, which may precipitate upon the addition of the sulphuret of ammonium, is tested for LIME, with oxalate of ammonia; the fluid is again filtered off from the precipitated oxalate of lime, and the filtrate is subsequently tested for MAGNESIA by means of phosphate of soda.

The second portion of the fluid filtered off from the silicic acid is evaporated to dryness, and the residue subsequently gently ignited; the residue is dissolved in water, an excess of water of barytes added, and heat applied; the fluid is passed through the filter, and the excess of the barytes is subsequently removed from the filtrate by means of carbonate of ammonia, which serves also to remove the lime which may happen to be present. The fluid is filtered off from the precipitated carbonate of barytes, (and carbonate of lime,) and the filtrate is subsequently evaporated to dryness, and the residue ignited; the POTASS in the ignited residue is identified by means of tartaric acid or bichloride of platinum; and the SODA by the blow-pipe flame.

γ. Another sixth of the original solution is concentrated by evaporation, and the concentrated fluid is divided into four portions.

The *first* portion is tested with turmeric paper; if this turns brown, and if the addition of hydrochloric acid to the heated solution causes effervescence, this indicates the presence of CARBONIC ACID (in combination with an alkali.) The *second* portion is tested for NITRIC ACID, with pure concentrated sulphuric acid and solution of indigo. The *third* portion is tested for PHOSPHORIC ACID, by acidification with acetic acid, and subsequent addition of an exceedingly minute amount of perchloride of iron and of an excess of acetate of soda. The *fourth* portion is tested for ORGANIC SUBSTANCES (humic acid, &c.) by evaporation to dryness and gentle ignition of the residue. If the latter turns black without emitting the odor of singed hair, this is a sign that the organic substances present are free from nitrogen ; the emission of this odor, during the ignition of the residue, indicates the presence of nitrogenous organic substances. In the latter case, the fumes which escape upon the carbonization of the residue, impart a brown tint to turmeric paper.

The remainder of the aqueous extract is kept in a well-stoppered bottle, marked SOLUTION I., to serve subsequently for the processes of the quantitative estimation.

b. DETECTION OF THOSE CONSTITUENTS OF THE SOIL WHICH ARE INSOLUBLE IN WATER, BUT SOLUBLE IN DILUTE HYDROCHLORIC ACID.

The insoluble part of the earth which remains upon the filtration of the aqueous extract (vide *a.*) is dried on the filter, separated from it, carefully intermixed in a mortar, and the sixtieth part of the whole amount accurately weighed off, and introduced into a glass flask containing some water,* with which it is made into a uniform thin pasty mass, by gentle agitation. Heat is then applied, and a sufficient excess of hydrochloric acid gradually poured into the flask.† When the mixture is thus kept from one to two hours longer, exposed to a temperature approaching the boiling point, the action of the acid

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* Should the earth contain a somewhat considerable proportion of organic ingredients, the transfer of this portion of the earth to the flask is to be preceded by gentle ignition, which should be maintained until the organic constituents are completely consumed.

† Should this cause effervescence, the hydrochloric acid is to be added in small portions, to guard against loss by foaming.

being aided by frequent shaking of the flask. The fluid is subsequently passed through a moist filter with the same precaution as at *a*, vide page 512, foot note,) and the insoluble residue washed with water until the rinsings cease to manifest an acid reaction.

The filtrate and rinsing water are intimately mixed and the whole fluid is accurately weighed; it corresponds to twenty grammes of the earth.

This fluid is now subjected to the following tests:

α. A portion of the fluid is tested with chloride of barium, for SULPHURIC ACID.

β. Another portion is tested with ferricyanide of potassium, for PROTOXIDE OF IRON.

γ. Another portion is tested with ferrocyanide of potassium, for PEROXIDE OF IRON.

δ. Another portion (about two-fifths of the whole) is evaporated to dryness; some nitric acid being added during the process of evaporation; the residue is tested with concentrated hydrochloric acid; should an insoluble white sediment remain, this consists of SILICIC ACID.

ε. The fluid filtered off from the undissolved silicic acid (should there have been any) is divided into two parts, in the proportion of two-thirds to one-third, and of which we will call the former *aa*, the latter *bb*.

aa. is mixed with ammonia until a precipitate begins to form; some acetic acid is then added and subsequently acetate of soda in excess;* the mixture is boiled for some time and filtered hot. The precipitate (which, under all circumstances, contains the whole of the phosphoric acid present) is washed with hot water, transferred together with the filter to a porcelain dish, and dissolved in a little hydrochloric acid; the solution is then mixed with water, and ammonia added to alkaline reaction; sulphuret of ammonium is then finally added in excess. The fluid is filtered off from the precipitated sulphuret of iron,

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* Should the hydrochloric solution contain no iron, perchloride of iron is to be added until the fluid appears distinctly red.

and the latter is washed with water mixed with sulphuret of ammonium. The filtrate is concentrated by evaporation, sulphate of magnesia added, and the mixture stirred; the formation of a crystalline precipitate shows the presence of PHOSPHORIC ACID. The fluid filtered off from the precipitate produced upon boiling *aa* with acetate of soda, is tested for LIME, by means of oxalic acid, and the fluid filtered off from the precipitated oxalate of lime is subsequently tested for MAGNESIA by means of phosphate of soda.

bb. is evaporated nearly to dryness, and the residue subsequently dissolved in water, an excess of barytes is then added, and the further process of testing for SODA and POTASS conducted exactly as at *α. β.*

The precipitate produced by the water of barytes is tested for MANGANESE, with carbonate of soda before the blow-pipe, and for ALUMINA, by boiling with potass, and mixing the potass solution subsequently with sal ammoniac.

The remainder of the hydrochloric solution, which will consist of about one half of the total amount, is kept in a well-stoppered bottle, to serve for the processes of the quantitative estimation. This bottle is marked SOLUTION II.

c. DETECTION OF THOSE CONSTITUENTS OF THE SOIL WHICH ARE INSOLUBLE BOTH IN WATER AND DILUTE ACIDS.

That part of the soil which is insoluble both in water and hydrochloric acid, consists generally of a mixture of clay with the detritus of various minerals. In many cases it will be sufficient to wash off the finer from the coarser particles, and to subject the latter to a microscopic examination. But in cases when it is desirable to discover the composition of this undissolved part more accurately, it is necessary to decompose and dissolve it. This may be accomplished in many instances by treating the undissolved residue with concentrated sulphuric acid. In some cases, however, even this powerful acid leaves still an undissolved residue, which requires for its decomposition and ultimate solution to be fluxed with alkalies.

The process is conducted as follows :

The washed residue of *b* is thoroughly dried, carefully separated from the filter, and very finely levigated in an agate mortar; the powder is transferred to a platinum basin, (glass or porcelain vessels do not answer equally well,) and from 6 to 8 times its weight of pure concentrated sulphuric acid poured over it. The mixture is then heated to gentle ebullition and maintained in this state under a good drawing chimney, until nearly the whole of the sulphuric acid is expelled, and the residue appears almost dry. The residue is then treated with hydrochloric acid, water added, and the mixture heated once more: the fluid is now finally filtered off from the undissolved residue, and the latter is thoroughly washed.

The filtrate is divided into two equal portions, and one half tested for iron, manganese, alumina, lime, magnesia, potass, soda, and phosphoric acid, according to the directions given at *b*, with this difference, that the silicic acid need not be separated. The other half is kept in a well-stoppered bottle, to serve for the subsequent operations of the quantitative estimation. This bottle is marked SOLUTION III.

The residue, which consists either simply of separated silicic acid, or contains also undecomposed minerals, is dried on a filter, separated from it, and boiled with dilute potass ley, or with a solution of carbonate of soda. If the residue dissolves completely in the potass or the solution of carbonate of soda, this is a proof that it consisted of silicic acid alone; but if a residue remains, this consists of undecomposed minerals.

To discover the constituents of the latter the solution is to be filtered off from the undissolved sediment, and the latter thoroughly washed. The whole of the filtrate is kept for the quantitative estimation of the silicic acid; the bottle is marked SOLUTION IV. The residue is dried, weighed, and divided into two equal portions, which we will call respectively *aa* and *bb*;—*aa* is fluxed with carbonate of soda, *bb* with hydrate of barytes. (Compare § 20 α. and β.) The silicic acid is then separated from both portions, in the usual manner, the hydrochloric solutions obtained are weighed, and the one half of the solution of *aa* is tested for iron, manganese, alumina, lime, magnesia, and phosphoric acid, and one half of the solution of *bb* for potass and soda —compare *b*. The other halves of *aa* and *bb* are kept for the subsequent operation of the quantitative estimation, that of *aa* being marked SOLUTION V., that of *bb* SOLUTION VI.

d. DETECTION OF THE ORGANIC SUBSTANCES PRESENT IN THE SOIL.

If the analytical processes *a* and *b* indicate the presence of organic substances, and the analyst wishes to discover the kind and nature of these substances, he must take fresh portions of the soil to operate upon. The method of detecting the organic constituents serves also for their quantitative estimation, and I therefore refer the student to § 183, from *e* to *i*.

2. QUANTITATIVE ANALYSIS.

§ 183.

The method described in the last section besides effecting the detection of the constituents of the soil, serves also, as we have seen, to prepare these constituents for quantitative estimation; since we have now already the whole of the constituents in solution corresponding to a known quantity of the earth, and may thus readily calculate them upon one hundred parts.

a. ESTIMATION OF THE WATER.

Ten grammes of the earth are dried in the water-bath until the weight ceases to vary; the loss of weight is then ascertained. (The dry earth is preserved for *g*.)

b. ESTIMATION OF THE CONSTITUENTS WHICH ARE SOLUBLE IN WATER.

" SOLUTION I." (§ 182) is divided (by weighing or measuring) into four parts, which we will call respectively α, β, γ, and δ; the three former should consist each of about one-fifth part of the whole, and δ contain the two remaining fifths.

α. is evaporated in the water bath, and the residue dried at 212°, until the weight ceases to vary. The dry residue is weighed, and the weight found is noted as THE TOTAL AMOUNT OF THE CONSTITUENTS SOLUBLE IN WATER. The residue is gently ignited for some time in a small platinum basin, and afterwards re-weighed. The loss of weight which the residue has suffered in the ignition process is taken into account as ORGANIC SUBSTANCES, NITRIC ACID, and AMMONIA, should the qualitative analysis have revealed the presence of these substances.*

In β. we have to estimate the SULPHURIC ACID and the CHLORINE, according to the directions given at § 132.

In γ. we estimate the CARBONIC ACID which may happen to be present, by evaporating the fluid to a small residue, and treating this subsequently according to § 105 II., *b.*, β.

δ. is evaporated with hydrochloric acid, and the SILICIC ACID in the residue determined according to § 106. II., *a.*; the acid solution obtained in the process is divided into two equal parts, in one of which we determine the alkalies. (Compare § 177. A. 2. *b.*)

The other portion serves for the estimation either of the PHOSPHORIC ACID, (§ 101. II. *d.*), or of the IRON, ALUMINA, MANGANESE, LIME, and MAGNESIA, (compare Part I., Section V.,) since it is not very likely that these bases should occur in the aqueous extract with phosphoric acid, or *vice versâ*, the acid with these bases.

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* Should the qualitative analysis indicate the presence of a considerable proportion of ammonia, this substance may be determined in a separate portion of the solution, by boiling the latter in a flask, with caustic soda, conducting the evolved ammonia into hydrochloric acid, and estimating the sal ammoniac produced finally as double chloride of platinum and ammonium.

c. ESTIMATION OF THE CONSTITUENTS WHICH ARE SOLUBLE IN DILUTE HYDROCHLORIC ACID.

" SOLUTION II." (§ 182) is evaporated to dryness, nitric acid being added during the evaporation; the residue is treated with hydrochloric acid, and the residual SILCIC ACID afterwards determined according to the directions of § 106. II. *a*. The hydrochloric solution is divided into three parts, which we will call respectively α. β. and γ.

In α. we have to determine the SULPHURIC ACID, according to the directions given at § 100.

In β., the alkalies according to the directions given at § 177. A. 2. *b*.

γ. is treated in strict conformity with the directions of § 182. *b*. ϵ. *aa*.

The precipitate of basic phosphate of magnesia and ammonia is ignited, and the amount of the PHOSPHORIC ACID subsequently estimated from the residual pyrophosphate of magnesia. The precipitate of sulphuret of iron is dissolved in hydrochloric acid and the solution subsequently boiled with nitric acid; the fluid is then added to the first filtrate, (which contains the lime and the magnesia, together with the excess of the acetate of soda,) and the IRON, MANGANESE, ALUMINA, LIME, and MAGNESIA, contained in the mixed fluid, are finally separated from one another by the appropriate methods. (Part I., section V.)

A weighed portion of the earth remaining after the extraction of the soil with water (vide § 182. *b*.) is treated according to the directions of § 105. II. *b*. β., to determine the amount of CARBONIC ACID contained in the insoluble carbonates present in the soil.

d. ESTIMATION OF THOSE CONSTITUENTS WHICH ARE INSOLUBLE BOTH IN WATER AND DILUTE ACIDS.

α. *The part of the soil remaining after the extraction with hydrocloric acid is completely decomposed by concentrated sulphuric acid.*

"SOLUTION III." (§ 182) is divided into two portions; in the one we have to determine the ALKALIES; in the other the PHOSPHORIC ACID, on the one hand, and the IRON, MANGANESE, ALUMINA, LIME, and MAGNESIA, on the other. (Compare § 183. *c*. β. and γ.)

The solution of silicic acid, which is obtained by the action of caustic potass or of carbonate of soda, is treated according to the directions of § 106. II. *a*. to determine the amount of SILICIC ACID contained in it.

β. *The concentrated sulphuric acid fails to decompose the whole of the residual earth.*

One half of "SOLUTION III." is mixed with "SOLUTION V.," and the PHOSPHORIC ACID, IRON, MANGANESE, ALUMINA, LIME, and MAGNESIA, present in the mixed fluid, are determined as directed at § 183. *c*. γ.

"SOLUTION VI." is mixed with the other half of "SOLUTION III.,' and the POTASS and SODA present in the mixed fluid are then determined. (Compare § 177. A. 2. *b*.)

In "SOLUTION IV." we have to determine the amount of SILICIC ACID which has been separated from the earth by the action of the concentrated sulphuric acid. This amount is added to that of the silicic acid which remains after fluxing the final residue of § 182. *c*. with carbonate of soda and hydrate of barytes, and acting upon the fluxed mass with hydrochloric acid; both these amounts are, of course, calculated first upon one hundred parts of the analysed earth. By adding the resulting figures, we find the total amount of silicic acid which we have to consider in *d*.

e. ESTIMATION OF THE HUMIC ACID.

From ten to one hundred grammes of the earth (according to the greater or less proportion of humic acid, indicated by the qualitative investigation,) are digested for several hours at from 176° to 194° F. with a solution of carbonate of soda; the fluid is then filtered off from the undissolved sediment, and the filtrate subsequently mixed with hydrochloric acid to incipient acid reaction. This process effects the separation of the humic acid in the form of brown flakes, which are collected upon a tared filter, washed, dried, and weighed; the dry mass is then incinerated, and the weight of the residual ashes (after subtraction of the filter ashes) is subtracted from the weight of the dry flakes; the difference is put down in the calculation of the results as the weight of the HUMIC ACID.

f. ESTIMATION OF THE HUMINE.

A quantity of the earth, equal to that operated upon in *e.*, is introduced into a porcelain basin, potass ley is poured over it, and the mixture boiled for several hours, the evaporated water being replaced from time to time; the mixture in the basin is then diluted with water, passed through the filter, and the undissolved sediment is washed. The total amount of humic acid present in the filtrate is then determined as at *e.* The difference between the respective weights of *e.* and *f.* indicates the quantity of humic acid formed from humine upon boiling with potass. This differential weight is usually put down in the calculation as HUMINE.

g. ESTIMATION OF THE ORGANIC MATTERS WHICH HAVE NOT YET SUFFERED CONVERSION INTO HUMIC ACID, HUMINE, OR SIMILAR PRODUCTS.*

The dried (anhydrous) earth of *a.* (which corresponds to ten grammes of fresh earth as taken directly from the soil) are heated in a platinum basin, until the whole of the organic matter present is completely consumed; the residue is moistened with solution of carbonate of ammonia, and the mass subsequently again evaporated; the residue very feebly ignited, and afterwards

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* If the quantity of the humine is very considerable, the fluid alone should be transferred to the filter, and the sediment boiled once more with potass ley, the boiled mixture to be afterwards likewise transferred to the filter.

weighed. The loss of weight which the earth has suffered in the process expresses the total proportion of organic substances present in the soil. From this we subtract the united weight of the humic acid and humine, and consider the remainder as undecomposed ORGANIC MATTER.

h. ESTIMATION OF THE NITROGEN PRESENT IN THE SOIL.

This is effected in strict accordance with the directions of § 149. (Estimation of nitrogen.) The quantity of earth which is to be subjected to the analytical process, depends upon the greater or less proportion of nitrogen present. The amount of chloride of platinum and ammonium produced should be 0.1 grammes, at the least, otherwise the results deserve but little reliance. (The weight of the nitrogen present in the analysed soil being included already in the results of *g.*, the separate statement of it is to be omitted, of course, from the list of the results.)

i. ESTIMATION OF WAXY AND RESINOUS SUBSTANCES.

These substances occur in appreciable quantities, in some kinds of soil only. This estimation may be effected in the following manner: 100 grammes of the earth are dried in the water-bath, and subsequently boiled repeatedly with strong alcohol; the filtrates are transferred into a flask, and one half of the spirits of wine distilled off. The residual fluid in the flask is then allowed to cool, when the wax which may happen to be present will separate; this is collected upon a tared filter, washed with cold spirits of wine, and weighed. The filtrate is evaporated until the whole of the alcohol is expelled, water being added towards the termination of the process; the separated resin is washed, dried, and weighed. (Should the quantities of the wax and resin be rather considerable, the united weight of these substances must be subtracted from the weight of the humic acid, since this acid is obtained and weighed in conjunction with the waxy and resinous ingredients.)

3. METHOD OF STATING AND ARRANGING THE RESULTS.

§ 184.

The following three points, with respect to the plan adopted for stating the results of the analyses of soils, seem to me deserving of particular attention.

a. The respective results of different analyses must readily admit of mutual comparison.

b. They should admit, moreover, of ready comparison with the results of analyses of vegetable ashes.

c. They should give a most perfect and accurate notion of the nature of the analysed soil.

That any single method of arranging the results should satisfy these requirements cannot reasonably be expected; three differently arranged statements are required to meet the exigencies of the case. The additional labor which this may be thought to impose upon the analyst is but trifling in comparison with that bestowed upon the analysis itself, and surely ought not to be permitted to weigh against the great advantages to chemical science, which may be expected to accrue from a full and universally intelligible statement of the results of all important investigations.

I therefore propose the following three methods of arranging the results.

I. ANHYDROUS EARTH (direct results of the analysis).

A. *Inorganic constituents.*

a. Soluble in water.
    Potass.
    Soda.
    Lime.
    Sulphuric acid.
        &c.

b. Soluble in dilute hydrochloric acid :

Peroxide of iron.
Peroxide of manganese.
Alumina.
Lime.
Carbonic acid.
Phosphoric acid.
&c.

c. Insoluble in water and in dilute hydrochloric acid :

Silicic acid.
Lime.
Alumina.
&c.

B. *Organic constituents.*

Humic acid.
Humine.
Undecomposed organic matter.
&c.

II. ANHYDROUS EARTH (calculated results.)*

A. *Inorganic constituents.*

a. Soluble in water :

Sulphate of lime.
Chloride of potassium.
Chloride of sodium.
Nitrate of magnesia.
&c.

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* The acids and bases are to be associated here according to their relative forces of affinity. Phosphoric acid, silicic acid, and humic acid, however, and the bases with which they are assumed to be in combination, are to be enumerated separately, since we are without sufficiently fixed and definite data as to the combining proportions of these acids.

b. Soluble in dilute hydrochloric acid :
   Carbonate of lime.
   Lime (combined with silicic acid).
   Peroxide of iron (combined with silicic acid and phosphoric acid).
   Phosphoric acid.
   Silicic acid.
      &c.

c. Insoluble in water and dilute hydrochloric acid :
   Lime } (combined with silicic acid).
   Alumina }
   Silicic acid.
      &c.

B. *Organic constituents.*

Humic acid.
   &c

III. AIR-DRY EARTH.

Anhydrous earth (for instance) . .	90
Water	10
	100

Should the analyst wish to make the last statement more precise, he may determine, by a single experiment, the quantity of the minute insoluble particles of the soil which may be washed off, and state likewise the results of the microscopic examination of the sandy residue. The statement would now run, for instance :

Particles that may be removed by washing .	10
Quarz-sand, detritus of felspar, mica, &c. . .	80
Water	10
	100

If the analyst thinks he can dispense with the advantages resulting from a more precise knowledge of the respective forms and states in which the various constituents exist in the soil, he may save himself much time and labor, by dividing the whole of the ingredients of the soil into two classes only, viz., into, 1, constituents which are *soluble* in water or dilute acids; and 2, constituents which are *insoluble* in water and dilute acids; since if he adopts this classification he may treat the soil at once with dilute hydrochloric acid, and subsequently determine the constituents of the hydrochloric solution, by the appropriate methods.

ANALYSIS OF ATMOSPHERIC AIR.

§ 185.

I will describe here two methods of analysing atmospheric air, i. e. determining the respective proportion of nitrogen and of oxygen which it contains. The first of these methods (BRUNNER'S) yields the most accurate results; the results of the second method, although very satisfactory, are not by any means equally accurate; but, on the other hand, the second method is recommended by the very great simplicity of the process, and is, therefore, particularly adapted for practical purposes. The principle upon which it is based, was first applied by GAY LUSSAC—the practical process which I recommend here, is my own.

FIRST METHOD.

§ 186.

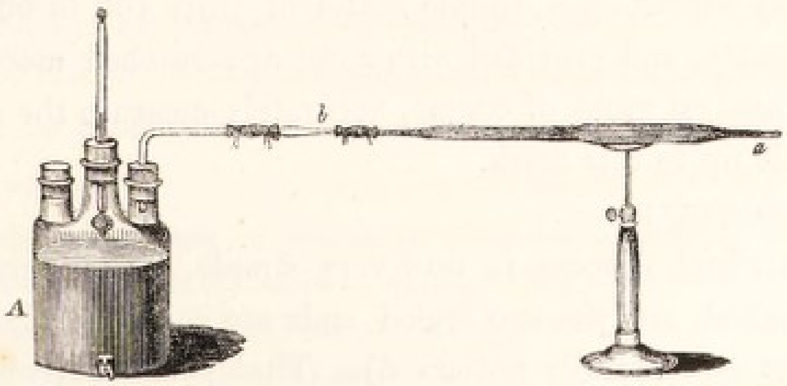
The principle upon which BRUNNER'S method is based, is this: heated phosphorus and phosphorous acid deprive the air with which they come into contact, of the whole of its oxygen. The practical process requires the following apparatus and preliminary operations:

1. A GLASS TUBE OF THE FORM ILLUSTRATED IN THE ANNEXED ENGRAVING.

PLATE LXXII.

From *c to d* should be four inches long and about three lines in diameter; the length of the narrowed part *d* to *g* should be about six inches. Before the tube is drawn out at *c* into the point *a*, the space from *f* to *g* is to be be filled with very loose cotton and any adhering moisture is withdrawn by heating the tube moderately and applying suction to the point *b*, (either by the mouth, an aspirator, or a small exhausting syringe.) One gramme of carefully dried phosphorus is now introduced into the tube and placed at *e*; the space intervening between the phosphorus and *c* is then filled up with loose asbestos (this is intended to divide and diffuse the passing air so thoroughly as to bring every particle of it into contact with the phosphorus.) The tube is now drawn out at *c* to the point *a*, the phosphorus is melted by the application of a gentle heat, and diffused as much as possible on the internal surface of the tube, by turning and inclining the latter. The end *a* is then connected with a chloride of calcium tube (vide § 141. 5.) by means of a good caoutchouc tube (§ 141. 6); the end *b* is connected, in the same manner with an aspirator, or three necked bottle filled with oil and provided with a stop-cock. The annexed sketch shows the whole arrangement of this apparatus.

PLATE LXXIII.



The heat of a spirit-lamp is then applied to the tube, to melt the phosphorus; when this is effected the spirit-lamp is withdrawn, and immediately after about four ounces of oil are made to trickle slowly from the stop-cock. The moment that the air rushes into the tube, the phosphorus begins to burn feebly, and is partly converted into phosphorous acid, which is deposited throughout the whole mass of the cotton; this phosphorous acid serves in the subsequent operation to deprive the atmospheric air passing through the tube, of the last trace of oxygen. Besides this, another object is attained by this preliminary operation, viz., the tube is filled with nitrogen gas, and thus the same state is induced in which the tube is afterwards found at the termination of the analytical process. The stop-cock of the aspirator is now closed, the chloride of calcium tube is withdrawn, the phosphorus tube disconnected from the aspirator, and the two ends of the phosphorus tube are sealed.

2. A CHLORIDE OF CALCIUM TUBE.

3. A TUBE FILLED WITH SMALL FRAGMENTS OF HYDRATE OF POTASS.

4. A THREE-NECKED BOTTLE, or similarly shaped metallic vessel, (aspirator,) filled with oil and provided with a stop-cock at the bottom, (vide Plate LXXIII. A.) The three apertures of the aspirator are closed air-tight, the one with a plain, the other two with perforated corks. A thermometer is closely fitted into the hole of the central cork.

5. A LARGE SIZED GRADUATED CYLINDER. For this the analyst may substitute a simple bottle of from 400 to 600 centimeters capacity, and provided with a cut or scratched mark in the neck; the analyst must, of course, accurately measure the capacity of the bottle up to this mark.

6. A BAROMETER.

The analytical process is now very simple. The phosphorus tube is weighed, and the two sealed ends are subsequently cut off, (these must be carefully preserved). That part from which the point *b* has been removed is then connected with the aspirator, whilst the other end is connected with the potass tube, the latter is connected with a chloride of calcium tube, caoutchouc tubes being used as the connecting medium in all three instances. The graduated cylinder or a bottle of known capacity is placed under the cock of the aspirator. The phosphorus is now gently heated, that part of the tube which is filled with cotton, is surrounded with moist blotting paper, and the oil is made to trickle slowly from the stop-cock. The phosphorus re-ignites immediately and continues to burn uniformly, if the gradual flowing off of the oil is properly managed. The first quarter of the oil should be made to drip off very slowly, to guard against the carrying off of phosphorous acid fumes by the gaseous stream. When about from 400 to 600 cubic centimeters of the oil have been thus withrawn from the aspirator, the experiment may be considered at an end. The stop-cock is closed, the state of the barometer, as well as that of the thermometer, introduced into the aspirator, are observed, the quantity of oil which has flown into the graduated cylinder is accurately measured,* and the phosphorus tube, when cold and after being most carefully wiped dry, is finally weighed. The measured volume of the oil expresses directly the volume of the nitrogen contained in the analysed bulk of air; the increment of weight which the phosphorus tube exhibits after the termination of the process, expresses the weight of the oxygen contained in the analysed air.

If the analyst wishes to express the results in percentage numbers by weight, he must calculate the weight of the volume of nitrogen gas at the temperature and atmospheric pressure indicated by the thermometer and barometer; if, on the other hand, he wishes to express the results in percentage numbers by volume, he must calculate the volume to which the weight of the

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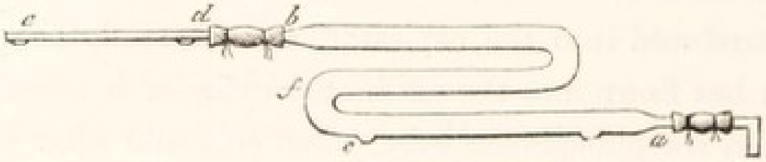
* The measuring may of course be altogether dispensed with, in cases where a marked bottle of known capacity, (vide 5.) has been used instead of a graduated cylinder, since the process is terminated, in such cases, the moment that the oil reaches the mark.

oxygen corresponds at the temperature and atmospheric pressure observed. For the manner of performing the arithmetical operations, I refer to § 159.

The amount of aqueous vapor, and carbonic acid, present in the atmosphere, may be determined in an analogous manner. A volume of air which is measured by the volume of oil or water that flows from the aspirator, is transmitted, first through a weighed tube filled with asbestos moistened with sulphuric acid, and subsequently through another weighed tube half filled with hydrated lime, and half with asbestos moistened with sulphuric acid. The most appropriate shape for the second tube is that illustrated by the annexed engraving:

PLATE LXXIV.



The part *a c*, which is turned towards the aspirator, should be one foot long; the asbestos is placed in this part; the rest of the tube (with the exception of the bend *f*) is filled with hydrated lime, prepared from recently calcined lime, and moistened with water so as to cause it to form into small lumps, which are kept separate by means of some loose cotton; the bend *f* is filled with cotton to separate the hydrated lime from the asbestos. The purpose of the latter is to retain the water which is carried off from the hydrate of lime by the current of air.

It will be readily understood that the small proportion of carbonic acid present in the air, renders it necessary to employ a large bulk of air (25000 cubic centimeters at the least) in the analytical process. Should the aspirator be too small for this purpose, this may be remedied by filling it several times. The analysis of a smaller volume of air than 25000 cubic centimeters cannot be expected to yield accurate results.

After the termination of the experiment, the analyst may either calculate the weight of the analyzed air, with due regard to the actual state of the thermometer and barometer, (the tension of the aqueous vapor may be disregarded without any material inaccuracy,) and may thus find the amount of carbonic acid and water in percents by weight; or he may calculate the weight of the carbonic acid and water upon volumes at the temperature and atmospheric pressure observed, and may thus find the result in percents by volume.

Second Method.

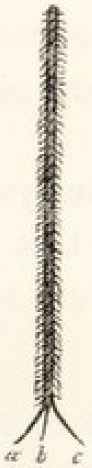
§ 187.

This method is based upon the circumstance that copper moistened with hydrochloric, or dilute sulphuric acid rapidly withdraws from atmospheric air the whole of its oxygen. The performance of the process requires the following:—

1. A GRADUATED TUBE, about one foot long, and half an inch in diameter.

2. A SMALL SLIP OF SHEET COPPER, somewhat longer than the graduated tube, and of the shape illustrated by the annexed sketch.

PLATE LXXV.



Copper turnings are tied round this slip in its whole length, by means of a piece of hempen string, in such a manner, however, as not to impede the ready introduction of the slip into the graduated tube.

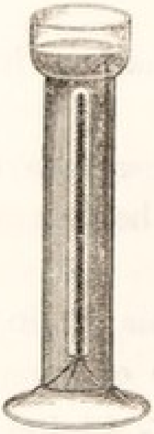
3. A common GLASS CYLINDER, a few inches taller than the graduated tube, and filled with a mixture of equal parts of hydrochloric acid and water. This cylinder should not be too narrow, and should be widened at the top.

4. A THERMOMETER.

The performance of the process is exceedingly simple.

The copper slip (2) is introduced into the cylinder, at the bottom of which it is kept fixed by means of the three divergent slips *a*, *b*, and *c*; the fluid in the cylinder should stand about one inch above the top of the slip. Some time is now allowed for the perfect escape of the air in the string, and the temperature of the fluid in the cylinder is observed. The graduated tube is then filled with water, and from two-thirds to three-fourths of this fluid are poured out again. The tube is now inverted and completely immersed in the fluid in the cylinder, (to give the confined air the temperature of the dilute hydrochloric acid). The tube is then raised again until the fluid within is on a perfect level with the surrounding fluid; the volume of the gas is then read off. The tube is now cautiously pushed over the copper-slip,* and pressed down. The annexed engraving shows the arrangement of the apparatus.

PLATE LXXVI.



The whole apparatus is now kept standing at rest for the space of one and a half to two hours, and the residue is subsequently measured; the tube is then once more pushed over the copper-slip, and, after the lapse of half an hour, the residual gas is measured again. If no further decrease has taken place in the interval, the operation may be considered at an end. The temperature is now once more observed, and if it is found to be the same as at the commencement of the process, the percentage volumes of the oxygen and nitrogen are found by the following simple calculation:

The first measurement shows the volume of the analysed air, the second that of the nitrogen, and the difference that of the oxygen. Suppose the bulk of the analysed air amounts to three

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* The analyst must take care to guard against any escape of air from the tube during the operation; it is on this account that the tube should be filled only with two-thirds or three-fourths of air, otherwise it might be impractiacble to prevent its escape.

hundred cubic centimeters, and the second shows the volume of the residual gas to be 237 cubic centimeters, the volume of the oxygen will be : 300—237=63, and accordingly 100 volumes of air consist of

79.0 of nitrogen
21.0 of oxygen.

Should the temperature of the confining water have changed during the process, this calculation is to be preceded, of course, by the correction of the volume of the nitrogen, in conformity with the original temperature.

The results are as accurate as can possibly be expected from a method requiring measurement over water. The action of a copper-slip prepared as described above is far more rapid than that of a simple slip of copper, since the surface offered to the air is greater, and besides the string keeps the copper turnings constantly moistened with hydrochloric acid.

PART III.

EXAMPLES FOR PRACTICE.

When the student has become tolerably proficient in qualitative analysis, he proceeds naturally to the study of quantitative. Now every one who has endeavoured to pursue this study in the laboratory, systematically, will have found that it is very difficult to occupy every moment of time judiciously, since he is frequently obliged to stop in his operations; thus, for instance, he has to wait some time for the subsidence of a precipitate, or a precipitate requires protracted washing or slow drying. I have, therefore, always deemed it judicious to advise my pupils to fill up their intervals with the preparation of substances which may afterwards be analyzed. This system offers the following advantages:—

1. The whole of the time of the student is fully and judiciously occupied, without confusing his ideas, as might be the case were he to undertake several analyses at the same time.

2. It ensures the purity of the substances which are to be analysed for practice.

3. The mode of combining the preparation of chemically pure substances, with their analysis, is unquestionably the best introduction to subsequent original investigations.

I have given here 50 examples for practice, of which 40 comprise inorganic, and the remaining 10, organic substances. The principal point I had in view in the selection of these substances, was this, that the analysis of most of them, and more particularly those of the inorganic class, permits the most precise control of the results. This point is of the utmost importance to the student of quantitative analysis, since a certain degree of self-reliance is amongst the most indispensable requisites for a successful pursuit of quantitative investigation; and this self-reliance the student can acquire only if he possesses the means of testing and controlling the accuracy of his results.

A perfectly strict and precise control is practicable only in cases when the analyst has to examine pure salts of known composition, or substances which he himself has previously prepared, and of which he knows the constituents, and the relative proportions in which they are combined. When the student has acquired by these means the necessary degree of confidence in his own abilities, he may gradually proceed to analyses of a somewhat more difficult and intricate nature.

The second point which I had in view in the selection of these examples for practice, was to make the latter comprise not only the whole of the more important analytical methods, but also the most important compounds, so as to afford the student sufficient opportunity to acquire a thorough knowledge of every branch of quantitative analysis. I have therefore not always indicated the most simple methods.

Organic analysis offers far less variety than the analysis of inorganic substances—the examples relating to the former branch, are therefore less numerous here than those relating to the latter. I would advise the student to analyse the same organic substance repeatedly until the results prove quite satisfactory.

In conclusion, I have to remark, that I do not mean to say that it is absolutely necessary to go through the whole of these examples; the time which a student may require to attain proficiency in analysis, depends entirely upon his own abilities. One may be a good analyst without having applied *every method* or analyzed EVERY compound. I would, however, warn students to guard against prematurely attempting new discoveries. The safest way is to wait until he has acquired a certain degree of proficiency in general chemistry, and more particularly in practical analysis.

EXAMPLES.

1. COMMON SALT.

The pure salt is gently ignited.

a. Estimation of the chlorine from 0. 5 to 1 gramme if the salt is dissolved in water, and the solution is acidified with nitric acid and precipitated with nitrate of silver. (§ 107. I. *a.*)

b. Estimation of the soda. About one gramme of the salt is dissolved in water, and subsequently converted into sulphate of soda by evaporation with sulphuric acid. (§ 72. 1.)

(For the calculated percentage composition, I refer to the " corrections" at the end of the work.)

2. CRYSTALLIZED CARBONATE OF SODA.

The pure nonefflorescced salt is finely powdered, and subsequently repeatedly pressed between sheets of blotting paper, fresh sheets being used every time, (§ 14. *a.*)

a. Estimation of the water, (1—2 grammes). The salt is cautiously ignited, (§ 17. *a.*)

b. Estimation of the carbonic acid, (residue of *a*, or 1—2 grammes).

The salt is decomposed by means of sulphuric acid, and the carbonic acid determined by the loss of weight which the decomposed salt suffers in the process, (§ 105. II. *b. β. aa.*)

(For the calculated percentage composition I refer to the " corrections" at the end of the work.

3. CARBONATE OF LIME.

The carbonate of lime is gently ignited.

a. Estimation of the lime. About 1 gramme of the carbonate is dissolved in hydrochloric acid, and the solution is supersaturated with ammonia, and subsequently precipitated with oxalate of ammonia, (§ 76. 2. *b.*)

b. Estimation of the carbonic acid. About one gramme of the carbonate is ignited with borax glass. (§ 105. II. *b. a.*)

Ca O	350.00	56.00
$C O_2$	275.00	44.00
	625.00	100.00

4. Chloride of barium.

The pure salt is gently ignited.

a. Estimation of the barytes. About one gramme of the chloride is dissolved in water, and the solution is subsequently precipitated with sulphuric acid. (§ 74. 1. *a.*)

Ba.	854.85	65.86
Cl.	443.20	34.14
	1298.05	100.00

5. Crystallized sulphate of magnesia.

The salt is levigated and dried according to the directions of § 14. *b.*

a. Estimation of the crystallization water. This is effected by drying 1.5 to 2 grammes of the salt, at from 266° to 284° F.

b. Estimation of the basic water. The residue of *a.* is gently ignited.

c. Estimation of the sulphuric acid. From one to two grammes of the salt are dissolved in water, some hydrochloric acid is added to the solution, and subsequently chloride of barium. (§ 100. I.)

d. Estimation of the magnesia. From one to two grammes of the salt are dissolved in water, sal ammoniac is added to the solution, and subsequently ammonia, and the mixture is finally precipitated with phosphate of soda. (§ 77. 2.)

Mg. O	257.75	16.68
$S O_3$	500.00	32.36
H O	112.50	7.28
6 aq.	675.00	43.68
	1545.25	100.00

6. Bitartrate of potass.

The salt is powdered and dried at 212. (§ 14. *d.*)

Estimation of the potass. From 1.5 to 2 grammes of the salt are ignited, and the residue is extracted with solution of sal ammoniac; the solution is evaporated to dryness, and the residue subsequently ignited. (§ 71.)

KO	588.94	25.05
$2\,C_4\,H_2\,O_5$	1650.00	70.17
HO	112.50	4.78
	2351.44	100 00

7. Bichromate of potass.

The levigated salt is dried in the water-bath.

Estimation of the chromic acid. From one to two grammes of the salt are dissolved in water; the chromic acid is then reduced by means of hydrochloric acid and alcohol, and the solution is finally precipitated with ammonia. (§ 99. I. *a.*)

KO	588.94	31.12
$2\,Cr.\,O_3$	1303.64	68.88
	1892.58	100.00

8. Crystallized sulphate of copper.

The finely-powdered salt is pressed repeatedly between blotting-paper. (§ 14. *a.*)

a. Estimation of the crystallization water. From 1 to 1.5 gramme of the salt is dried in the water-bath. (§ 14. *d.*)

b. Estimation of the basic water. The residue of *a* is heated in a crucible over a spirit-lamp until the whole of the water present is expelled; a very high temperature, however, is to be carefully avoided.

c. Determination of the oxide of copper. About 1.5 gramme of the salt is dissolved in water; the solution is boiled, and precipitated boiling with potass. (§ 90. 1. *a.*)

$Cu.\,O$	496.00	31.83
$S\,O_3$	500.00	32.08
HO	112.50	7.22
4 aq.	450.00	28.87
	1558.50	100 00

9. ACETATE OF LEAD.

Large nonefflorescced crystals should be used; they are to be finely powdered, and the powder subsequently repeatedly pressed between blotting-paper, fresh paper being used every time. (§ 14. *a.*)

Estimation of the lead.

a. One gramme of the salt is dissolved in water, and the solution subsequently precipitated with carbonate of ammonia. (§ 87. 1.)

b. A portion of 1 to 1.5 gramme of the salt is ignited in a porcelain dish, and the residue is subsequently treated with acetic acid, etc. (§ 87. 4.)

Pb. O	1394.50	58.85
$\bar{A}$	637.50	26.91
3 aq.	337.50	14.24
	2369.50	100.00

10. OXIDE OF ANTIMONY.

From 0.5 to 0.8 gramme of pure oxide of antimony is dissolved in hydrochloric acid, and some tartaric acid added to the solution, which is then diluted with water, and subsequently precipitated with sulphuretted hydrogen. (§ 95. 1.)

11. PERCHLORIDE OF MERCURY.

Pure perchloride of mercury, perfectly soluble in water, should be selected, and about one gramme used to separate the mercury in the dry way according to the method described at § 89. 1. *a.*

Hg.	1250.90	73.84
Cl.	443.20	26.16
	1694.10	100.00

12. ANALYSIS OF PHOSPHATE OF SODA.

Pure and recently crystallized phosphate of soda is powdered, and the powder pressed repeatedly between blotting-paper, fresh paper being used every time.

a. Estimation of the crystallization water. This is effected by drying the salt first at 212° F., and finally in the air or oil bath at about 572° F. (§ 14. *d.*)

b. Estimation of the basic water. This is effected by igniting the residue of *a.*

c. Estimation of the phosphoric acid. A portion of about 1.5 gramme of the salt is dissolved in water, and sal ammoniac added to the solution; the fluid is subsequently precipitated by sulphate of magnesia with ammonia. (§ 101. I. *b.*)

d. Estimation of the soda.

The filtrate of *c.* is treated according to the instructions given at § 101. II., *a.*, *β.*

$2\,NaO$	781.80	17.29
PO_5	891.55	19.91
HO	112.50	2.51
24 aq.	2700.00	60.29
	4485.85	100.00

13. ALKALIMETRICAL EXAMINATIONS according to GAY-LUSSAC, (§ 135.)

14. ALKALIMETRICAL EXAMINATIONS according to FRESENIUS and WILL, (§ 136.)

In both experiments (13 and 14) the student has to analyse, in the first place, recently ignited pure carbonate of soda, since this will afford him the means of controlling the results of the subsequent analysis of commercial specimens of soda.

15. ACIDIMETRICAL METHODS, (§ 112. I. *b.*)

Two experiments are to be made with unequal portions of one and the same acid, since this will enable the student to control the results.

16. EXAMINATION OF PEROXIDE OF MANGANESE, (§ 125.)

Every sort is to be analysed twice.

17. EXAMINATION OF CHLORIDE OF LIME.

One and the same sort is analysed by every one of the three methods described at § 137.

18. DETERMINATION OF THE DEGREE OF SOLUBILITY OF COMMON SALT.

a. At the boiling point (229.5° F.) Perfectly pure, powdered chloride of sodium is dissolved in distilled water, in a glass flask; the solution is heated to boiling, and kept in a state of ebullition until part of the salt has separated again. The boiling fluid is then speedily filtered into an accurately tared capacious flask, through a funnel, which is to be kept surrounded with boiling water, and covered with a glass plate. When a few ounces of fluid have been thus introduced into the flask, the latter is to be corked, allowed to cool, and accurately weighed. A definite portion of the solution is then evaporated in a platinum basin, to determine the proportional amount of common salt contained in it. Some sal ammoniac should be added in the process of evaporation, since this will, in some measure, prevent the decrepitation which attends the ignition of common salt.

b. In water of 57.2 F. The boiling saturated solution is allowed to cool down to 57.2° F., (the liquid should be frequently shaken), and the further process is conducted as directed in *a*.

100 parts of water dissolve at 229.5° F. . . 40.35 of common salt
100 ,, ,, ,, 57.2° F. . . 35.87 ,, ,,

19. DETERMINATION OF THE DEGREE OF SOLUBILITY OF GYPSUM.

a. In water of 212° F.

b. In water of 53.6° F.

Pure, levigated sulphate of lime is digested for some time with water, at last at a temperature of from 104° to 122° F. (This is the temperature at which the largest proportion of gypsum dissolves.)

The clear solution, together with the undissolved gypsum, is poured into two flasks, and the fluid in the one flask is then heated to boiling, and kept for some time in a state of ebullition; the fluid in the other flask is allowed to cool down to 53.6° F., (being frequently shaken the while,) and is then kept at rest for some time. Both solutions are now filtered, and the filtrate weighed, the amount of gypsum present in each being finally determined by evaporating the respective solutions, and igniting the residues.

100 parts of water of 212° F. dissolve . . 0.217 of anhyd. gypsum
100 ,, ,, 53.6° F. dissolve . . 0.233 ,, ,,

20. Analysis of atmospheric air.

Method 2 (§ 187).

O	20.8 vol.
N	79.2 vol.
	100.0

21. Separation of potass from soda.

Weighed quantities of pure chloride of sodium and pure chloride of potassium are mixed, and the separation of the alkalies from one another is then effected.

a. In the direct way, according to § 115. 1. *a.*

b. In the indirect way, according to § 115. 1. *b.*

22. Separation of iron from manganese.

Weighed quantities of pure peroxide of iron and pure manganoso-manganic oxide are mixed, and the metals are subsequently separated.

a. By means of carbonate of barytes (§ 124. 1. *β.*)

b. By means of succinate of ammonia (§ 124. 1. *α.*)

23. Separation of arsenic, iron, lime, and potass from one another.

Weighed quantities of pure arsenious acid, peroxide of iron, carbonate of lime, and chloride of potassium are mixed, and the mixture is subsequently dissolved in dilute hydrochloric acid, and

a. The arsenic is precipitated from the solution by means of sulphuretted hydrogen (§ 97. 2. *a.*)

b. The iron from the filtrate of *a.* with ammonia (§ 85. *a.*)

c. The lime from the filtrate of *b.* with oxalate of ammonia (§ 76. 2. *b.*)

d. The potass is determined in the filtrate of *c.*, for which purpose the filtrate is to be evaporated to dryness, the residue ignited, subsequently redissolved in water, some hydrochloric acid added to the solution, the fluid once more evaporated to dryness, and the residue finally again ignited (§ ~~72~~ 71. 3.)

24. SEPARATION OF SILVER FROM MERCURY.

Weighed quantities of pure peroxide of mercury and pure nitrate of silver are mixed, and the mixture is subsequently dissolved in dilute nitric acid; the solution is precipitated with sulphuretted hydrogen, and the precipitates are finally exposed to a current of chlorine gas (§ 127. I. γ.)

25. ANALYSIS OF WATER.

Pure oxide of copper is introduced into a bulbous tube and ignited; the tube (with its contents) is then accurately weighed. A slow stream of hydrogen gas—(which has been perfectly purified, and dried by transmission through potass ley, and subsequently through sulphuric acid)—is then transmitted through the tube; a weighed chloride of calcium tube being previously affixed to the other end, by means of a perforated cork. When every trace of air is expelled from the apparatus, the oxide of copper is to be heated to intense redness, and jointly with this, the posterior part of the bulbous tube, together with the cork, are to be heated with a little spirit-lamp, beyond 212° F. When the whole of the oxide of copper is reduced, the lamp is withdrawn from the bulb, the other lamp being subsequently also removed. The transmission of the hydrogen gas is continued until the tube has cooled; the bulbous tube is then weighed, and so is the chloride of calcium tube. The increase in the weight of the latter expresses the quantity of water that has been formed in the process, whilst the decrease of weight, which the bulbous tube exhibits, indicates the amount of oxygen contained in the water.

26. ANALYSIS OF BRASS.

The essential constituents of brass are from twenty-five to thirty-five per cent. of zinc, and from sixty-five to seventy-five per cent. of copper. Besides these, it contains usually small quantities of tin and lead. About four grammes of the brass which it is intended to analyse are dissolved in nitric acid, and the solution is separated from the undissolved peroxide of tin, according to the instructions given at § 129. 6. *a.* The solution is considerably concentrated by evaporation, pure sulphuric acid being added during the process; the concentrated solution is then again diluted with water, and the sulphate of lead which will separate after some time, is determined according to the directions of § 87. 2. *a.* The filtrate is weighed, and a weighed portion of it (about one half) treated with sulphuretted hydrogen to precipitate the copper (§ 90. 1. *c.*) The zinc is finally determined in the fluid filtered off from the precipitated sulphuret of copper, according to the directions of § 80. *a.*

Pinchbeck, prince's metal, gold of Mannheim, and other alloys analogous to brass, are analysed in exactly the same manner.

27. ANALYSIS OF ALLOYS OF COPPER AND TIN. (Bronze, Gun-metal, &c.)

These usually contain, besides copper and tin, small admixtures of lead and iron, and sometimes likewise of zinc.

Alloys containing only a comparatively small proportion of tin may be analysed as directed in 26. But alloys containing a considerable proportion of tin are to be analysed in the following manner:

About three grammes of the alloy are heated in a bulbous tube, in a stream of chlorine gas, and the volatile chlorides formed (the chlorides of tin, zinc, and iron) are received in water mixed with hydrochloric acid; the chlorides of lead and copper remain in the tube (§ 127. 1. γ.) A stream of hydrogen gas is now transmitted through the tube, heat being at the same time applied to the chlorides. This effects the reduction of the latter to the metallic state. The reduced metals are then weighed in the tube, subsequently dissolved in nitric acid, and the empty tube weighed again; the difference between the former and the latter weight expresses the joint weight of the copper and lead. The lead is now estimated in the solution, according to the directions of § 127. 14. and the weight found subtracted from the joint weight of the copper and lead; the difference shows the amount of copper contained in the analysed alloy. The tin is precipitated from the hydrochloric solution by means of sulphuretted hydrogen, (§ 96. *c.*), and the iron and zinc in the filtrate are then finally separated by means of succinate of ammonia (§ 124. 4.)

28. ANALYSIS OF GERMAN SILVER.

German silver consists of zinc, nickel, and copper. Besides these, it contains mostly some iron, sometimes tin and cobalt, and rarely appreciable traces of arsenic.

The following process relates to the estimation of the principal constituents alone.

About three grammes of the German silver which it is intended to analyse are dissolved in nitric acid, and the copper is subsequently precipitated from the solution by means of sulphuretted hydrogen (§ 90. 1. *c.*)

The excess of sulphuretted hydrogen is removed from the filtrate, and the zinc and nickel are then precipitated with carbonate of soda, and finally separated from one another, by one of the methods described at § 124. 10.

29. ANALYSIS OF GUNPOWDER. (GAY-LUSSAC.)

a. Estimation of the moisture.

From two to three grammes of the finely-levigated powder are weighed off, and subsequently dried at 212° F. (The result will be found more accurate still if the powder be dried *in vacuo* over sulphuric acid).

b. Estimation of the nitrate of potass.

About three grammes of the finely-levigated powder are weighed off, drenched with hot water, digested for some time, and the insoluble residue subsequently collected upon a tared filter, thoroughly washed, dried at 212° F., and weighed. The difference between the former and the latter weight expresses the amount of nitrate of potass contained in the analysed powder. Should the analyst desire to weigh the nitrate of potass directly, he need simply evaporate the filtrate to dryness (§ 71. 2.)

c. Estimation of the sulphur.

One part (about 1 to 1.5 gramme) of the finely-levigated powder is mixed with an equal amount of pure, anhydrous carbonate of soda; the mass is then mixed with one part of pure nitrate of potass and four parts of pure and dry chloride of sodium. The whole mixture is introduced into a platinum crucible, and heated until combustion ensues and the mass appears white. The fused saline mass is then dissolved in water, the solution is acidified with hydrochloric acid, and the sulphuric acid which has been formed in the process by the oxidation of the sulphur is then finally precipitated with chloride of barium (§ 100. I.)

Estimation of the charcoal.

The difference between the joint weight of the moisture, nitre, and sulphur, and the original weight of the analysed powder, indicates the amount of the charcoal.

30. ANALYSIS OF NATROLITE.

The essential constituents of natrolite are: soda, alumina, silicic acid, and water. Besides these, this mineral sometimes contains lime, and peroxide of iron.

From four to five grammes of the mineral are finely levigated, the powder is dried at 212° F., and divided into two portions of about two grammes each.

a. The water is determined in the one portion (§ 14. *e.*)

b. The other portion is digested at a gentle heat with concentrated hydrochloric acid until completely decomposed. The silicic acid is then removed in the manner directed at § 106. II. *b.*; the alumina is subsequently precipitated from the filtrate, as directed at § 78. *a.*, and the soda is then finally determined, according to § 72. 3.

31. ANALYSIS OF STEATITE.

The essential constituents of steatite are magnesia and silicic acid; besides these substances, this mineral contains water and usually also iron and alumina.

The mineral is finely levigated, and the powder dried in the water-bath.

a. About four grammes are treated according to § 14. *e.*, to determine the amount of water present.

b. The residue of *a.* is accurately weighed, fluxed with carbonate of soda, (§ 20. *a.*), and the silicic acid separated in the usual manner; the peroxide of iron and the alumina are then precipitated with ammonia—(and subsequently separated from one another according to the directions of § 123. A. *a.*)—and the magnesia is finally precipitated with phosphate of soda (§ 77. 2.)

32. ANALYSIS OF KAOLIN.

The principal constituents of kaolin are alumina, silica, and water; besides these, it contains frequently small quantities of alkalies, carbonate of lime, magnesia, peroxide of manganese, and peroxide of iron, and usually a larger or smaller admixture of quartz-sand.

The finely-levigated clay is dried in the water-bath, and

a. About two grammes are treated as directed at § 14. *e.*, to determine the amount of the water.

b. About five grammes are digested and boiled with pure concentrated sulphuric acid until completely decomposed (this operation is conducted best in a platinum crucible). The solution is then evaporated nearly to dryness, and the residue subsequently digested, and heated with concentrated hydrochloric acid; the solution is diluted with water, filtered, and the residue thoroughly washed. The alumina is determined in the filtrate, and so are the lime, magnesia, iron, and manganese, should these substances be present; the residue consists of separated silicic acid mixed with quartz-sand; the separation of the former from the latter is effected by boiling with a solution of carbonate of soda.

c. Should carbonic acid be present, this is to be determined in a third portion of the levigated clay, according to the directions of § 105. II. *b.* *β.* *aa.*

33. Analysis of glass.

a. About three grammes of finely-levigated glass are fluxed with carbonate of soda, and the silicic acid, lime, magnesia, alumina, iron, manganese, &c., are subsequently determined in the fused mass.

b. Another portion of about three grammes—(which must be most finely elutriated)—is fluxed with hydrate of barytes, (§ 20. *β.*), or with fluor-spar and sulphuric acid, (§ 106. II. *c.* *β.*), and the alkalies are subsequently determined in the fluxed mass.

34. Analysis of magnetic iron ore (ferroso-ferric oxide.)

(Compare the methods described at § 124. 5.)

$Fe\,O$	450.00	31.04
$Fe_2\,O_3$	1000 00	68.96
	1450.00	100.00

Sulphuret of Lead

35. Analysis of ~~litharge.~~ (Vide § 111. II. *c.*)

(Percentage composition, vide § 57. *f.*)

36. Analysis of dolomite.

Constituents: Lime, magnesia, carbonic acid.

The mineral is levigated and dried at 212° F.

a. About two grammes of the powder are treated according to the directions of § 105. II. *b.* *α.* or *β.*, to determine the amount of the carbonic acid.

b. Another portion of about two grammes is cautiously (in an obliquely placed flask) dissolved in hydrochloric acid, and the lime and magnesia in the solution are subsequently separated from one another, according to the directions of § 117. 6. *a.* Should the hydrochloric acid leave a residue undissolved, this consists generally of quartz-sand.

37. Analysis of grey cobalt ore.

Constituents: Sulphur, arsenic, cobalt, iron.

About three or four grammes of the finely-levigated mineral are introduced into a flask, and digested with strong nitric acid, until the action of the acid begins to relax; strong hydrochloric acid is then added, and heat applied, until the eliminated sulphur appears of a pure yellow. The solution is now diluted, and the sulphur collected upon a tared filter; the sulphuric acid which has been formed in the process is precipitated from the filtrate with chloride of barium, and the excess of barytes subsequently removed by means of dilute sulphuric acid; the arsenic acid is reduced by means of sulphurous acid, (§ 97. 2. *b.*), the reduced arsenic subsequently precipitated with sulphuretted hydrogen, and the cobalt and iron are finally separated accordingly to the directions of § 124. 2.

38. Analysis of the ashes of a plant.

(Method described in §§ 173—180.)

39. Analysis of a soil.

(Methods described in §§ 181—184)

40. Analysis of a mineral water.

Method described in §§ 166—172.)

B. Organic analysis.

41. Analysis of cane sugar.

Perfectly pure, white crystals of cane sugar are powdered, and the powder is dried at 212° F. (§ 140. *a. a.*)

12 C	900.00	42.10
11 H	137.50	6.44
11 O	1100.00	51.46
	2137.50	100.00

42. Analysis of oil of turpentine.

(Vide § 144.)

A recently rectified and perfectly anhydrous oil is selected for the analysis.

5 C	375.00	88.24
4 H	50.00	11.76
	425.00	100.00

43. ANALYSIS OF A FATTY SUBSTANCE.

(Stearine, oleic acid, wax, &c. § 145.)

44. ANALYSIS OF UREA.

a. Estimation of the carbon and hydrogen. (Vide § 146. *a.*)

b. Estimation of the nitrogen; vide § 149. Method of VARRENTRAPP and WILL.

2 C	150.00	19.99
2 N	350.50	46.70
4 H	50.00	6.66
2 O	200.00	26.65
	750.50	100.00

45. ANALYSIS OF URIC ACID.

a. Estimation of the carbon and hydrogen (§ 146. *a.*)

b. Estimation of the nitrogen (§ 148. DUMAS' method.)

5 C	375.00	35.69
2 N	350.50	33.37
2 H	25.00	2.38
3 O	300.00	28.56
	1050.50	100.00

46. ANALYSIS OF PERCYANIDE OF MERCURY.

Estimation of the nitrogen by LIEBIG's method (§ 147.)

Hg	1250.90	79.36
2 C	150.00	9.52
N	175.25	11.12
	1576.15	100.00

47. ANALYSIS OF TARTRATE OF SILVER.

a. Estimation of the silver, vide § 86. 4.

b. Estimation of the carbon and hydrogen, vide § 140. *a.* *a.*

Ag O	1449.01	63.72
$C_4 H_2 O_5$	825.00	36.28
	2274.01	100.00

48. Analysis of ferrocyanide of potassium.

a. Combustion with chromate of lead (§ 146. *a.*)

b. Estimation of the nitrogen by the method of Varrentrapp and Will (§ 149.)

c. Estimation of the potass (as chloride of potassium) vide § 71.

d. Estimation of the iron, vide § 110. III. *b.*

e. Estimation of the water (§ 14. *d.*)

2 K	977.88	37.03
6 C	450.00	17.04
3 N	525.75	19.90
1 Fe	350.00	13.25
3 Aq.	337.50	12.78
	2641.13	100.00

49. Analysis of quinine.

a. Estimation of the carbon and hydrogen, vide § 146.

b. Estimation of the nitrogen (§ 149.)

c. Determination of the atomic weight.

α. From the double platinum salt (§ 94. *a.*)

β. From the increase of weight upon the transmission of hydrochloric acid gas (§ 153. *b.*)

20 C	1500.00	74.06
12 H.	150.00	7.41
1 N	175.25	8.65
2 O	200.00	9.88
	2025.25	100.00

50. Determination of the specific weight of the camphor vapor.

Vide § 154.

(For the calculated result, vide § 165.)

APPENDIX.

I. EXPERIMENTS.

1. WATER DISTILLED FROM GLASS VESSELS. (§ 34. 1.)

42.41 grammes of water which had been distilled with extreme caution from a tall glass flask with a LIEBIG's condensing tube, left upon evaporation in a platinum basin, a residue weighing after ignition 0.0018 grm., consequently $\frac{1}{23561}$.

2. SULPHATE OF POTASS AND ALCOHOL, (§ 42. *a.*)

a. Ignited pure sulphate of potass was digested cold with absolute alcohol, for the space of several days, the solvent action of the alcohol being aided by frequent agitation of the mixture; the fluid was then filtered off, the filtrate diluted with water, and subsequently mixed with chloride of barium. It remained perfectly clear upon the addition of this reagent, but after the lapse of a considerable time it began to exhibit a slight opalescence. Upon evaporation to dryness there remained a very trifling residue, which manifested however a distinct reaction of sulphuric acid.

b. The same salt treated in the same manner, with addition of some pure concentrated sulphuric acid, yielded a filtrate, which upon evaporation in a platinum dish left a perfectly distinct fixed residue of sulphate of potass.

3. DEPORTMENT OF CHLORIDE OF POTASSIUM IN THE AIR, AND AT A HIGH TEMPERATURE. (§ 42. *c.*)

0.9727 grm. of ignited (not fused) pure chloride of potassium were heated to dull redness in an open platinum basin, and kept ten minutes at this temperature, when loss of weight of 0.0007 gramme was observed; maintained for ten minutes longer in this state, the weight remained the same. Heated to bright redness and semi-fusion, the salt suffered a further loss of weight to the extent of 0.0009 gramme. Ignited intensely and to perfect fusion, it lost 0.0034 gramme, in addition to the former 0.0007 and 0.0009 gramme.

Eighteen hours exposure to the air produced not the slightest increase of weight.

4. SOLUBILITY OF POTASSIO-CHLORIDE OF PLATINUM IN ALCOHOL. (§ 42. *d.*)

a. In absence of free hydrochloric acid.

α. An excess of perfectly pure, recently precipitated, potassio-chloride of platinum was digested for six days at from 59° to 68° F., with alcohol of 97.5 per cent., in a stoppered bottle, the solvent action of the alcohol being aided by frequent agitation of the mixture. 72 5 grammes of the perfectly colorless filtrate left upon evaporation in a platinum basin, a residue which dried at 212° weighed 0.006 grammes. The solution of one part of potassio-chloride of platinum require therefore 12083 parts of alcohol of 97.5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was nearly colorless; upon evaporation, slight nigrescence ensued, in which account the residue was determined as platinum. 75.5 grammes yielded 0.008 gramme of platinum corresponding to 0.02 gramme of the potassio-chloride. One part of this salt dissolves accordingly in 3775 parts of spirit of wine of 76 per cent.

δ. The same experiment was made with spirit of wine of 55 per cent: the filtrate was distinctly yellowish. 63.2 grammes left 0.0241 gramme of platinum corresponding to 0.06 gramme of the potassio-chloride. One part of this salt dissolves accordingly in 1053 parts of spirit of wine of 55 per cent.

b. In presence of free hydrochloric acid.

Recently precipitated potassio-chloride of platinum was digested cold with spirit of wine of 76 per cent. containing an admixture of hydrochloric acid. The solution was yellowish ; 67 grammes left, 0.0146 gramme of platinum, which corresponds to 0.0365 gramme of the potassio-chloride. One part of this salt, therefore, dissolved in 1835 parts of spirit of 76 per cent., containing an admixture of hydrochloric acid.

5. SULPHATE OF SODA AND ALCOHOL. (§ 43. *a.*)

Experiments made with pure anhydrous sulphate of soda, in the manner described at 2., showed that this salt comports itself both with pure alcohol, and alcohol containing sulphuric acid in admixture, exactly like the sulphate of potass.

6. DEPORTMENT OF THE IGNITED SULPHATE OF SODA IN THE AIR. (§ 43. *a.*)

2.5169 grammes of anhydrous sulphate of soda were exposed in a watch glass to the open air on a hot summer day. The first few minutes passed without any increase of weight, but after the lapse of five hours an increase of 0,0061 gramme was observed.

7. EXPERIMENTS WITH NITRATE OF SODA. (§ 43. *b.*)

a. 4.5479 grammes of pure nitrate of soda exposed in a state of fusion, to the air, (in April, the weather being fine,) exhibited after the lapse of twenty-four hours, an increase of weight of 0.0006 gramme.

b. 4.5479 grammes of pure nitrate of soda were dissolved in water, in a platinum basin, and pure nitric acid was added to the solution ; the mixture then evaporated to dryness in the water-bath, and the residual mass cautiously heated to incipient fusion. The contents of the basin weighed, after cooling 4.5503 grammes. The mass was now again heated to complete fusion ; after cooling it was found to weigh 4.5474 grammes.

8. DEPORTMENT OF CHLORIDE OF SODIUM IN THE AIR. (§ 43. *c.*)

4.3281 grammes of chemically pure intensely ignited (but not fused) chloride of sodium which has been cooled under a glass jar over sulphuric acid, acquired during forty-five minutes exposure to the (somewhat moist) air, an increase of weight of 0.0009 gramme.

9. DEPORTMENT OF CHLORIDE OF SODIUM UPON IGNITION WITH AND WITHOUT SAL AMMONIAC.

4.3281 grammes of chemically pure ignited chloride of sodium were dissolved in water in a moderately sized platinum basin, and pure sal ammoniac added to the solution, which was then evaporated and the residue gently heated until the evolution of sal-ammoniac fumes had apparently ceased. The weight of the residue was now 4.3334 grammes. The residue was then again very gently ignited for about two minutes, and subsequently re-weighed, when the weight was found to be 4.3314 grammes. After a few minutes strong ignition, the weight of the residue was 4.3275 grammes. After two minutes intense ignition, (upon which occasion white fumes were seen to escape,) the weight of the residue was found to be 4.3249 grammes.

10. DEPORTMENT OF SAL AMMONIAC UPON EVAPORATION AND EXSICCATION. (§ 44. *a.*)

0.5625 gramme of pure and perfectly dry sal ammoniac were dissolved in water in a platinum basin, and the solution was subsequently evaporated and dried in the water-bath; the weight was now found to be 0.5622 gramme, (ratio 100 : 99.94.) The mass was again heated for fifteen minutes in the water-bath, and afterwards re-weighed, when the weight was found to be 0.5612 grm. (ratio 100 : 99.77.) Exposed once more for fifteen minutes to the same temperature; the weight was afterwards found to be 0.5608 grammes, (ratio 100 : 99.69.)

11. SOLUBILITY OF AMMONIO-CHLORIDE OF PLATINUM IN ALCOHOL. (§ 44. *b.*)

a. In the absence of free hydrochloric acid.

α. An excess of perfectly pure recently precipitated ammonio-chloride of platinum was digested for six days, at from 59° to 68° F., with alcohol of 97.5 per cent., in a stoppered bottle, the solvent action of the alcohol being aided by frequent agitation of the mixture.

74.03 grammes of the perfectly colorless filtrate left, upon evaporation in a platinum basin, a residue of platinum which, after ignition, weighed 0.0012 grm., corresponding to 0.0028 of the ammonio-chloride. One part of this salt, therefore, dissolves in 26535 parts of the alcohol of 97.5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was distinctly yellowish.

81.75 grammes left 0.0257 grm. of platinum, which corresponds to 0.0584 grm. of the ammonio-chloride. Therefore, one part of the salt dissolves in 1406 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellow. Slight nigrescence ensued upon evaporation, and 56.5 grammes of the filtrate left 0.0364 grm. of platinum, which corresponds to 0.08272 grm. of the ammonio chloride. Consequently one part of the salt dissolves in 665 parts of spirit of wine of 55 per cent.

b. In presence of hydrochloric acid.

The experiment described in *β.* was repeated, with this modification, that some hydrochloric acid was added to the spirit of wine. 76.5 grammes left 0.0501 grm. of platinum, which correponds to 0.1139 grm. of the ammonio-chloride. 672 parts of the acidified alcohol had dissolved one part of ammonio-chloride of platinum.

12. SOLUBILITY OF CARBONATE OF BARYTES IN WATER. (§ 45. *b.*)

a. In cold water. Perfectly pure, recently precipitated carbonate of barytes (Ba O, CO_2) was digested for five days with water of from 60.8 to 68° F., the solvent action of the water being aided by frequent agitation of the mixture. The solution was then filtered, and a sample of the filtrate tested with sulphuric acid, and another sample with ammonia; the former reagent produced immediate turbidity in the fluid, the latter only after the lapse of a considerable time. 84.82 grammes of the solution left 0.006 of Ba O, CO_2. One part of this salt, consequently, dissolves in 14137 parts of cold water.

b. In hot water. The same carbonate of barytes being boiled for ten minutes with pure distilled water, yielded a filtrate manifesting the same reactions as that prepared with cold water, and remained perfectly clear upon cooling. 84.82 grammes of the hot solution left, upon evaporation, 0.0055 grm. of carbonate of barytes. One part of this salt, therefore, dissolves in 15421 parts of boiling water.

13. SOLUBILITY OF CARBONATE OF BARYTES IN WATER CONTAINING AN ADMIXTURE OF AMMONIA AND CARBONATE OF AMMONIA. (§ 45. *b.*)

A solution of chemically pure chloride of barium was mixed with ammonia, and carbonate of ammonia in excess, and the mixture gently heated and left standing at rest for twelve hours; the fluid was then filtered off and a sample of the filtrate treated with sulphuric acid; it remained perfectly clear, but after the lapse of a very considerable time a hardly perceptible precipitate separated. 84.820 grammes of the filtrate left, upon evaporation in a small platinum basin, and subsequent gentle ignition of the residue, 0.0006 grm. of carbonate of barytes. One part of this salt had dissolved in 141000 parts of the fluid.

In another experiment sal ammoniac was added to the solution of the chloride of barium, previously to precipitation; the results were the same.

14. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER. (§ 45. *c.*)

a. Recently precipitated, thoroughly washed silico-fluoride of barium was digested for four days with cold water; the fluid was then filtered off, and one sample of the filtrate tested with dilute sulphuric acid, and another sample with solution of gypsum; both reagents produced turbidity, the former immediately, the latter after one or two seconds,—precipitates separated from both samples after the lapse of some time. 84.82 grammes of the filtrate left a residue which, after being thoroughly dried, weighed 0.0223 grm. One part of the salt, therefore, required 3802 parts of cold water for solution.

b. Recently precipitated silico-fluoride of barium was heated with water to ebullition, and the solution subsequently allowed to cool (upon which a portion of the dissolved salt separated again from the solution). The cold fluid was left for a considerable time longer in contact with the undissolved salt, and was then filtered off. The filtrate showed the same deportment with solution of gypsum as that of *a.* 84.82 grammes of it left 0.025 grm. of silico-fluoride of barium. One part of this salt dissolved in 3392 parts of water.

15. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER, ACIDIFIED WITH HYDROCHLORIC ACID. (§ 45. *c.*)

a. Recently precipitated pure silico-fluoride of barium was digested for three weeks with cold water acidified with hydrochloric acid, the solvent action of the water being aided by frequent agitation of the mixture. The filtrate yielded with sulphuric acid a tolerably copious precipitate. 84.82 grammes left 0.1155 grm. of thoroughly dried residue which, calculated as silico fluoride of barium, shows that the solution of one part of this salt requires 733 parts of acidified water for solution.

b. Recently precipitated, pure silico-fluoride of barium was mixed with water very slightly acidified with hydrochloric acid, and the mixture heated to boiling, and subsequently cooled down to 53.6° F. and filtered. 84.82 grammes of the filtrate left a residue of 0.1322 grm. The proportion between the salt and the fluid which it requires for solution is as 1 : 640.

N.B. The solution of silico-fluoride of barium in hydrochloric acid is not effected without decomposition; at all events, the residue contains, even after ignition, a large proportion of chloride of barium.

16. SOLUBILITY OF SULPHATE OF STRONTIA IN WATER. (§ 46. *a.*)

a. In water of 57.2° F.

84.82 grammes of a solution prepared by four days' digestion of recently precipitated sulphate of strontia with water of the common temperature, left 0.0123 grm. of sulphate of strontia. One part of $Sr O, SO_3$, therefore, dissolves in 6895 parts of water.

b. In water of 212° F.

84.82 grammes of a solution prepared by boiling recently precipitated sulphate of strontia several hours with water, left 0.0088 grm. of sulphate of strontia. Consequently one part of this salt dissolves in 9638 parts of boiling water.

17. SOLUBILITY OF SULPHATE OF STRONTIA IN WATER CONTAINING AN ADMIXTURE OF HYDROCHLORIC ACID AND SULPHURIC ACID. (§ 46 *a.*)

a. 84.82 grammes of a solution prepared by three days' digestion, left 0.0077 grm. of $Sr O, SO_3$.

b. 42.41 grammes of a solution prepared by four days' digestion, left 0.0036 grm.

c. Pure carbonate of strontia was dissolved in an excess of hydrochloric acid, and the solution precipitated with an excess of sulphuric acid, and kept standing in the cold, for a fortnight. 84.82 grammes of the filtrate left 0.0066 grm.

In *a*.	1 part of $Sr\,O, SO_3$	required	11016	parts
,, *b*.	1 ,,	,,	11780	,,
,, *c*.	1 ,,	,,	12791	,,
		Average	11862	

18. SOLUBILITY OF CARBONATE OF STRONTIA IN COLD WATER. (§ 46. *b*.)

Recently precipitated thoroughly washed carbonate of strontia ($Sr\,O, C\,O_2$) was digested several days with distilled cold water, the solvent action of the water being aided by frequent agitation of the mixture. 84.82 grammes of the filtrate left, upon evaporation, a residue weighing, after ignition, 0.0047 grm. One part of carbonate of strontia requires accordingly 18045 parts of water.

19. SOLUBILITY OF CARBONATE OF STRONTIA IN WATER CONTAINING AN ADMIXTURE OF AMMONIA AND CARBONATE OF AMMONIA. (§ 46. *b*.)

Recently precipitated, thoroughly washed carbonate of strontia was digested for four weeks, with cold water containing an admixture of ammonia and carbonate of ammonia, the operation being aided by frequent agitation of the mixture. 84.82 grammes of the filtrate left 0.0015 grm. of $Sr\,O, CO_2$. Consequently one part of the salt requires 56545 parts of this fluid for its solution.

If solution of chloride of strontium is precipitated with carbonate of ammonia in conjunction with ammonia (§ 75. 2. *a*.), sulphuric acid produces no turbidity in the filtrate, after previous addition of alcohol.

20. SOLUBILITY OF CARBONATE OF LIME IN COLD WATER. (§ 47. *b*.)

A hot prepared solution of carbonate of lime (vide infrà 21.) was digested cold, for four weeks, with the undissolved residue; the operation being aided by frequent agitation of the mixture. 84.82 grammes of the filtrate left 0.0080 of $Ca\,O, CO_2$. One part of the carbonate required 10601 parts of cold water for solution.

21. SOLUBILITY OF CARBONATE OF LIME IN BOILING WATER. (§ 47. *b.*)

Recently precipitated Ca O, CO_2 was boiled with distilled water, and the ebullition maintained for a considerable time. 42.41 grammes of the filtrate left upon evaporation and subsequent gentle ignition of the residue 0.0048 grm. of Ca O, CO_2. The solution of one part of carbonate of lime requires accordingly 8834 parts of boiling water.

22. SOLUBILITY OF Ca O, CO_2 IN WATER CONTAINING AN ADMIXTURE OF AMMONIA AND CARBONATE OF AMMONIA. (§ 47. *b.*)

Pure solution of chloride of calcium was precipitated with carbonate of ammonia in conjunction with ammonia, and the precipitate allowed twenty-four hours to subside; the fluid was then filtered off. 84.82 grammes of the filtrate left 0.0013 grm. of Ca O, CO_2. One part of carbonate of lime requires accordingly 65246 parts of this fluid for solution.

23. DEPORTMENT OF CARBONATE OF LIME, UPON IGNITION IN A PLATINUM CRUCIBLE. (§ 47. *b.*)

0.7955 grm. of perfectly dry carbonate of lime were introduced into a small and thin platinum crucible, and exposed to the gradually increased, and finally most intense heat of a good BERZELIUS lamp. The crucible was open and placed obliquely. (Plate XXIX.) After the first fifteen minutes the mass weighed 0.6482 grm.,—after half an hour 0.6256 grm.,—after one hour 0.5927 grm., which latter weight remained unaltered after fifteen minutes' additional heating. This corresponds to 74.5 per cent., whilst the proportion of lime in the carbonate is calculated at 56 per cent. A considerable proportion of the carbonic acid evidently remained.

24. COMPOSITION OF OXALATE OF LIME, DRIED AT 212°. (§ 47. *c.*)

0.8510 grm. of pure, thoroughly dry carbonate of lime were dissolved in hydrochloric acid, and the solution was subsequently precipitated with oxalate of ammonia, in conjunction with ammonia; the precipitate was collected upon a tared filter, dried at 212° F. until the weight ceased to vary. The oxalate of lime thus produced weighed 1.2461 grm. Calculating this as $CaO, C_2O_3 + aq$, the amount found contained 0.4772 of CaO, which corresponds to 56.07 per cent in the carbonate of lime; the calculated proportion of lime in the latter is 56 per cent.

25. DEPORTMENT OF SULPHATE OF MAGNESIA IN THE AIR AND UPON IGNITION. (§ 48. *a.*)

0.8135 grm. of perfectly pure, anhydrous MgO, SO_3 in a covered platinum crucible, acquires on a fine and warm June day, in half an hour's time, an increase of weight of 0.004 grm., and in the course of twelve hours, 0.067 grm. Exposed to the air in the open crucible, the salt could not be accurately weighed, owing to the continuous increase of the weight.

0.8135 grm., exposed for some time to a very faint red heat, suffered no diminution of weight; but, after five minutes exposure to an intense red heat, they were found to have lost 0.0075 grm., and the residue, upon re-solution, in water, yields no longer a clear fluid.

26. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN PURE WATER. (§ 48.)

a. Recently precipitated basic phosphate of magnesia and ammonia was thoroughly washed with water, and subsequently digested for twenty-four hours with water of about 59° F.; the operation being aided by frequent agitation of the mixture.

84.42 grammes of the filtrate left . . 0.0047 grm. of pyrophosphate of magnesia.

b. The same precipitate was digested in the same manner for seventy-two hours.

84.42 grammes of the filtrate left . . 0.0043 grm.

Average 0.0045 grm.

which correspond to 0.00552 grm. of the anhydrous double salt. One part of this salt dissolves therefore in 15293 parts of pure water. The cold saturated solution yielded with ammonia, after the lapse of a short time, a clearly perceptible crystalline precipitate;—treated with phosphate of soda, it remained perfectly clear, and even after the lapse of two days no precipitate had formed; phosphate of soda and ammonia produced a precipitate of equal bulk to that produced by ammonia.

27. SOLUBILITY OF BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN AMMONIATED WATER. (§ 48. *b.*)

a. Pure basic phosphate of magnesia and ammonia was dissolved in the least possible amount of nitric acid, and a large quantity of water added to the solution, and subsequently ammonia in excess. The mixture was allowed to stand at rest for twenty-four hours, and was then filtered; its temperature being 57.2° F. 84.42 grammes of the filtrate left 0 0015 gramme of pyrophosphate of magnesia, which corresponds to 0.00184 grm. of the anhydrous double salt. Consequently one part of this salt requires 45880 parts of ammoniated water for solution.

b. Pure basic phosphate of magnesia and ammonia was digested for four weeks with ammoniated water, the operation being aided by frequent agitation of the mixture; the fluid (temperature 57.2° F.) was then filtered off, 126.63 grammes of the filtrate left 0.0024 gramme of the pyrophosphate of magnesia, which corresponds to 0.00296 gramme of the double salt. One part of this double salt therefore dissolves in 42780 parts of ammoniated water; taking the average of *a.* and *b.*, one part of the double salt required 44330 parts of ammoniated water for solution.

28. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING AN ADMIXTURE OF SAL AMMONIAC. (§ 48. *b.*)

Recently precipitated, thoroughly washed basic phosphate of magnesia and ammonia was digested cold with a solution of one part of sal ammoniac in five parts of water. 18.4945 grammes of the filtrate left 0.002 grm. of pyrophosphate of magnesia, which corresponds to 0.00245 grm. of the double salt. One part of the salt dissolves in 7548 parts of the fluid.

29. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING ADMIXTURES OF AMMONIA AND SAL AMMONIAC. (§ 48. *b.*)

Recently precipitated, thoroughly washed phosphate of magnesia and ammonia was digested cold with a solution of one part of sal ammoniac in seven parts of ammoniated water. 23.1283 grammes of the filtrate left 0.0012 gramme of pyrophosphate of magnesia, which corresponds to 0.00148 grm. of the double salt. One part of the salt requires accordingly 15627 parts of this fluid for solution.

30. SOLUBILITY OF PURE MAGNESIA IN WATER. (§ 48. *d.*)

a. In cold water.

Perfectly pure, well crystallized sulphate of magnesia was dissolved in water, and the solution subsequently precipitated with carbonate of ammonia in conjunction with caustic ammonia; the precipitate was most thoroughly washed—(and yet, notwithstanding, it retained still a perceptible trace of sulphuric acid)—and subsequently dissolved in pure nitric acid. The solution (which contained no free acid) was then again precipitated with carbonate of ammonia in conjunction with caustic ammonia, and the precipitate again thoroughly washed. The thus prepared perfectly pure basic carbonate of magnesia was ignited in a platinum crucible until the weight ceased to vary. The residual pure magnesia was then digested cold for twenty-four hours with distilled water, the operation being aided by frequent agitation of the mixture. (The distilled water was perfectly free from chlorine, and left no fixed residue upon evaporation.)

α. 84.82 grammes of the filtrate were cautiously evaporated in a platinum basin; a residue remained which, after ignition,

weighed 0.0015 gramme. One part of the pure magnesia requires 56546
parts of cold water for solution.

The digestion was continued for forty-eight hours longer, when

β. 84.82 grammes of the filtrate left 0.0016 gramme. One part of the magnesia required . . 53012

γ. 84.82 grammes of the filtrate left 0.0015 gramme. One part required . . . 56546

On an average 55368

The cold prepared solution of magnesia in water has a feeble yet distinctly alkaline reaction, which is most perceptible upon admixture of very faintly-reddened tincture of litmus; the alkaline reaction of the solution is perfectly manifest, with slightly-reddened litmus paper, or with turmeric or georgina paper, when these test-papers are left for some time in contact with the solution.

Alkaline carbonates fail to render the solution turbid, even upon ebullition. Phosphate of soda also fails to impair the clearness of the solution, but upon subsequent addition of ammonia and agitation of the fluid, the latter becomes turbid, and deposits after some time a distinctly perceptible precipitate of basic phosphate of magnesia and ammonia.

b. In hot water.

Upon boiling pure magnesia with water, a solution is obtained which comports itself in every respect like the cold prepared solution of magnesia. A hot prepared solution of magnesia does not become turbid upon cooling, nor does a cold prepared solution upon ebullition. 84.82 grammes of hot prepared solution of magnesia left 0.0016 gramme of $Mg\,O$.

31. Precipitation of alumina by ammonia, &c. (§ 49. *a.*)

a. Ammonia produces in neutral solutions of alumina, or of alum, gelatinous precipitates of hydrate of alumina. Upon further addition of ammonia in considerable excess, the precipitate redissolves gradually, without however disappearing altogether.

b. If a drop of a dilute solution of alum is mixed with a copious amount of ammonia, and the mixture shaken, the solution appears almost perfectly clear, but, after standing at rest for some time, slight flakes of hydrated alumina separate.

c. If a solution of alumina, mixed with a copious amount of ammonia, is filtered, and

α. The filtrate is heated to boiling, and maintained for some considerable time in a state of ebullition, flakes of hydrated alumina separate gradually as the excess of ammonia escapes.

β. The filtrate is mixed with solution of sal ammoniac, a very perceptible flocculent precipitate of hydrate of alumina separates immediately; the whole of the hydrated alumina present in the solution separates if the sal ammoniac be added in sufficient quantity.

γ. The filtrate is mixed with sesquicarbonate of ammonia, the same reaction takes place as in β.

δ. The filtrate is mixed with solution of chloride of sodium or chloride of potassium, no precipitate separates, but after several days' standing, slight flakes of hydrated alumina subside, owing to the decrease of ammonia by evaporation.

d. If a neutral solution of alumina is precipitated with carbonate of ammonia, or a strongly acidified (with hydrochloric or nitric acid) solution, with pure ammonia, or if to a neutral solution, after precipitation with ammonia, or sufficient amount of sal ammoniac is added, even a considerable excess of the precipitant will fail to redissolve the precipitated alumina, as appears from the undisturbed limpidity of the filtrate upon continued boiling and evaporation.

32. PRECIPITATION OF OXIDE OF CHROMIUM BY AMMONIA. (§ 50. *a.*)

Solutions of protochloride of chromium and of chrome alum (both concentrated and dilute, neutral and acidified with hydrochloric acid,) were mixed with ammonia in excess. The whole of the filtrates drawn off immediately after precipitation appeared red, but when filtered after previous ebullition, they all became colorless, whenever the ebullition was continued sufficiently long.

33. SOLUBILITY OF THE BASIC CARBONATE OF ZINC IN WATER (§ 51. *a.*)

Perfectly pure, recently (hot) precipitated basic carbonate of zinc was heated with distilled water, and subsequently digested cold for many weeks, the operation being aided by frequent agitation of the mixture. The clear solution yielded not the slightest precipitate with sulphuret of ammonium, not even after long standing.

84.82 grammes left 0.0014 gramme of oxide of zinc, which corresponds to 0.0019 of basic carbonate of zinc ($Zn\,O$ assumed =74 per cent. in this salt). One part of the basic carbonate requires accordingly 44642 parts of water for solution.

34. DEPORTMENT OF SULPHURET OF NICKEL WITH SULPHURET OF AMMONIUM, &c., (§ 53. *c.*)

A dilute solution of pure protosulphate of nickel and potass was mixed with a very slight excess of colorless hydrosulphuret of ammonia, perfectly saturated with sulphuretted hydrogen. The following experiments were then made with the precipitated fluid.

a. One portion was filtered off at once. The filtrate was and remained perfectly clear and colorless.

b. Another portion was digested with an excess of colorless and perfectly saturated hydrosulphuret of ammonia, and α. Filtered without previous application of heat. The filtrate presented a hardly perceptible shade of yellow; no precipitate separated, even after long standing.

β. Filtered after previous application of heat. The filtered fluid exhibited a more marked shade of yellow, and deposited some sulphuret of nickel after several days' standing.

c. Another portion was digested with an excess of yellow sulphuret of ammonium (prepared by exposing perfectly saturated hydrosulphuret of ammonia to the action of the air). The filtrate was yellow without the slightest shade of brown; after several days' standing, a slight precipitate of sulphuret of nickel had separated.

d. Another portion was digested cold with ammoniated water. The filtrate presented a faint brownish tint.

e. Another portion was digested with ammonia and colorless hydrosulphuret of ammonia. The filtrate was of a distinct light brown color. After several days' standing a light precipitate of sulphuret of nickel had separated.

f. Another portion was digested with ammonia and yellow sulphuret of ammonium. The filtrate was likewise of a brownish color, and comported itself like the filtrate of *e.*

35. SOLUBILITY OF CARBONATE OF LEAD. (§ 57. *a.*)

a. In pure water.

Recently precipitated, pure, and thoroughly-washed carbonate of lead was digested for eight days with water at the common temperature, the operation being aided by frequent agitation of the mixture. 84.42 grammes of the filtrate were evaporated, some pure sulphuric acid being added during the process; the residual sulphate of lead weighed 0.0019 gramme, which corresponds to 0.00167 gramme of carbonate of lead. One part of this salt dissolves therefore in 50551 parts of water. A sample of the solution was mixed with sulphuretted hydrogen water; it remained perfectly colorless, not the slightest coloration being detected, even upon looking through it from the top of the test-cylinder.

b. In water containing a slight admixture of acetate of ammonia, and, moreover, carbonate of ammonia and pure ammonia.

A highly dilute solution of pure acetate of lead was mixed with carbonate of ammonia and pure ammonia in excess, and the mixture gently heated and allowed to stand at rest for several days. 84.42 grammes of the filtrate left, upon evaporation with a little sulphuric acid, 0.0041 gramme of sulphate of lead, which corresponds to 0.0036 gramme of carbonate of lead. One part of this salt, therefore, requires 23450 parts of this fluid for solution. A sample of the solution was mixed with sulphuretted hydrogen water; when looking through the fluid from the top of the cylinder, a distinct coloration was visible, but when looking through the cylinder laterally, this coloration was hardly perceptible. Traces of sulphuret of lead separated after the lapse of some time.

c. In water containing a large proportion of nitrate of ammonia in admixture, together with carbonate of ammonia and caustic ammonia.

A highly dilute solution of acetate of lead was mixed with nitric acid, and subsequently with carbonate of ammonia and caustic ammonia in excess; the mixture was gently heated, and allowed to stand at rest for eight days. The filtrate, when mixed with sulphuretted hydrogen, exhibited a very distinct brownish coloration, upon looking through it from the top of the cylinder, but this coloration appeared very slight only when looking through the cylinder laterally. The amount of lead dissolved was unquestionably more considerable than the quantity dissolved in *b*.

36. SOLUBILITY OF OXALATE OF LEAD. (§ 57. *b*.)

A dilute solution of acetate of lead was precipitated with oxalate of ammonia and pure ammonia, and the mixture allowed to stand at rest for some time, and subsequently filtered. The filtrate, when mixed with sulphuretted hydrogen, comported itself exactly like the filtrate of 35. *b*. The same deportment was observed in another similar experiment, in which nitrate of ammonia had been added to the solution.

37. Solubility of sulphate of lead in pure water. (§ 57. *d.*)

Thoroughly washed and still moist sulphate of lead was digested for five days with water, at a temperature of from 50 to 59° F., the operation being aided by frequent agitation of the mixture. 84.42 grammes of the filtrate (filtered off at 51.8° F.) left 0.0037 gramme of sulphate of lead. Consequently one part of this salt requires 22816 parts of pure water of 51.8° F. for solution.

The solution, when mixed with sulphuretted hydrogen, exhibited a distinct brown color when looking through it from the top of the cylinder, but this coloration appeared very slight upon looking through the cylinder laterally.

38. Solubility of sulphate of lead in water acidified with sulphuric acid. (§ 57. *d.*)

A highly dilute solution of acetate of lead was mixed with an excess of dilute pure sulphuric acid; the mixture was very gently heated, and the precipitate allowed several days to subside. 80.31 grammes of the filtrate left 0.0022 gramme of sulphate of lead. One part of this salt requires 36504 parts of water acidified with sulphuric acid for solution. The solution, when mixed with sulphuretted hydrogen, remained colorless when looking through the cylinder laterally, and very little darker when looking through it from the top.

39. Solubility of sulphate of lead in water containing ammoniacal salts and free sulphuric acid.

A highly dilute solution of acetate of lead was mixed with a tolerably large amount of nitrate of ammonia, and sulphuric acid in excess added. After several days' standing, the mixture was filtered. The filtrate was nearly indifferent to sulphuretted hydrogen water, the mixed fluid appearing hardly perceptibly darker than pure water, when looking through it from the top of the cylinder.

40. DEPORTMENT OF SULPHATE OF LEAD UPON IGNITION. (§ 40. *d.*)

Speaking of the determination of the atomic weight of sulphur, ERDMANN and MARCHAND (Journal für Praktische Chemie, xxxi. page 385) state that sulphate of lead loses some sulphuric acid upon ignition. To test the correctness of this statement, and to ascertain in how much this loss might impair the accuracy of the method of determining lead as a sulphate, I heated 2.2151 grammes of absolutely pure $Pb\,O,\ S\,O_3$ to the most intense redness, over a spirit-lamp with double draught. I could not perceive the slightest decrease in the weight of the ignited compound; at all events, the decrease did not amount to 0.0001 gramme.

41. DEPORTMENT OF SOLUTIONS OF LEAD WITH SULPHURETTED HYDROGEN. (§ 57. *f.*)

It is a well known fact that solutions of lead which contain much free acid are not precipitated by sulphuretted hydrogen unless diluted with water. TRIBOULET (Archives de Pharmacie xxix., page 234) maintains that sulphuretted hydrogen fails to precipitate the whole of the lead from solutions of lead, mixed with solution of acetate of potass, but that the whole of the lead present precipitates subsequently upon addition of ammonia. To test the correctness of this statement, I added to a concentrated solution of acetate of potass, mixed with solution of neutral acetate of lead, and which I acidified with a drop of acetic acid, *a.* sulphuretted hydrogen water in excess; *b.* sulphuretted hydrogen gas in excess. In both cases, the precipitation was so complete that the filtrates drawn off after vigorous agitation of the mixture suffered not the slightest alteration upon addition of ammonia and sulphuret of ammonium. It is *certain*, therefore, that TRIBOULET's statement is erroneous, and *probable* that this error was caused by the presence of iron in the fluid upon which this chemist operated.

42. DEPORTMENT OF METALLIC MERCURY AT THE COMMON TEMPERATURE, AND UPON EBULLITION WITH WATER. (§ 58. *a.*)

To ascertain in what manner loss of metallic mercury occurs upon drying, and likewise upon boiling with water, and to determine which is the best method of drying, I made the following experiments:

I placed 6.4418 grammes of perfectly pure mercury upon a watch-glass, poured distilled water over the metal, removed the water again as far as practicable, (by decantation, and subsequently by means of blotting-paper,) and weighed. I found the weight to be 6.4412 grammes, which after several hours' exposure to the air were reduced to 6.4411 grammes. I placed these 6.4411 grammes under a bell jar over sulphuric acid, the temperature being about 62 or 63° F. After the lapse of twenty-four hours, the weight had not altered in the least. I introduced the 6.4411 grammes of mercury into a flask, poured a copious quantity of distilled water over it, and boiled the mixture for fifteen minutes. I now placed the mercury again upon the watch-glass, dried it most carefully with blotting-paper, and weighed. The weight was now 6.4402 grammes. Finding that a trace of mercury had adhered to the paper, I repeated the same experiment with the 6.4402 grammes. After fifteen minutes boiling with water, the mercury had again lost 0 0004 gramme. The remaining 6.4398 grammes were exposed to the air for six days, (during summer, and the heat being considerable,) after which they were found to have lost only 0.0005 gramme.

43. DEPORTMENT OF BISULPHURET OF MERCURY WITH

POTASS, SULPHURET OF AMMONIUM, &c. (§ 58. *c.* where experiment 44 is referred to, by mistake, instead of 43.)

a. Pure potass ley fails to dissolve the slightest trace of pure recently precipitated bisulphuret of mercury upon ebullition; the filtrate yields no precipitate, nor exhibits even the slightest coloration upon addition of hydrochloric acid.

b. If bisulphuret of mercury is boiled with potass ley in conjunction with some sulphuretted hydrogen water, sulphuret of ammonium, or sulphur, complete solution is effected.

c. Digestion of bisulphuret of mercury with sulphuret of ammonium (no matter whether colorless or yellow) fails to dissolve the slightest trace of the bisulphuret—cyanide of potassium equally fails to dissolve bisulphuret of mercury. Hydrochloric acid produces in the fluid filtered off from the mixture of sulphuret of ammonium with bisulphuret of mercury, a purely white turbidity or a white precipitate, and in the fluid filtered off from a mixture of bisulphuret of mercury and cyanide of potassium, this acid fails altogether to produce the slightest turbidity or precipitate.

d. Thoroughly washed bisulphuret of mercury moistened with water, suffers no alteration upon exposure to the air; at all events the fluid which I obtained by washing peroxide of mercury which had been thus exposed to the air for twenty-four hours, did not manifest acid reaction, nor did it contain mercury or sulphuric acid.

44. DEPORTMENT OF OXIDE OF COPPER UPON IGNITION. (§ 59. *a.*)

Pure oxide of copper (prepared from nitrate of copper) was ignited in a platinum crucible, subsequently cooled under a bell jar, over sulphuric acid, and finally weighed. The weight was 3.542 grammes. These 3.5420 grammes were then most intensely ignited for five minutes, over a BERZELIUS lamp, cooled and re-weighed, when the weight was found unaltered; the oxide was then once more ignited for five minutes, but with the same result.

45. DEPORTMENT OF OXIDE OF COPPER IN THE AIR. (§ 59. *a.*)

A platinum crucible containing 4.3921 grammes of feebly ignited oxide of copper (prepared from the nitrate) was placed for ten minutes (covered with the lid) in a warm room (in winter); the weight of the oxide of copper was now found to have increased to 4.3939 grammes.

The oxide of copper was then intensely ignited over a spirit-lamp; after ten minutes standing in the covered crucible, the weight had hardly perceptibly increased—after twenty-four hours it had increased by 0.0036 gramme.

46. DEPORTMENT OF SULPHURET OF CADMIUM WITH AMMONIA, &c. (§ 61. *c.*)

Pure recently precipitated sulphuret of cadmium was diffused through water, and the following experiments were made with the fluid.

a. One portion was mixed with ammonia in excess, and the mixture digested cold and subsequently filtered. The filtrate remained perfectly clear upon addition of hydrochloric acid.

b. Another portion was digested hot with excess of ammonia, and the mixture subsequently filtered. This filtrate likewise remained perfectly clear upon addition of hydrochloric acid.

c. Another portion was digested for a considerable time with solution of cyanide of potassium, and the mixture subsequently filtered. This filtrate likewise remained perfectly clear upon addition of hydrochloric acid.

d. Another portion was digested with hydrosulphuret of ammonia, and the mixture subsequently filtered. The turbidity which hydrochloric acid imparted to this filtrate was of a pure white.

(A remark made by WACKENRODER, in BUCHNER's Repertorium der Pharmacie, 46, page 226, induced me to make these experiments.)

47. ESTIMATIN OF SODA IN SALTS WITH ORGANIC ACIDS. (§ 72. 4.)

1.154 gramme of paratartrate of soda yielded, upon intense ignition, after deduction of 0.004 gramme of charcoal, 0.63 gramme of $Na\ O, C\ O_2$, which corresponds to 0.3698 of $Na\ O$= 32.05 per cent. (calculated 32.14 per cent.); this gives 99.7 instead of 100.

48. ESTIMATION OF BARYTES BY PRECIPITATION WITH CARBONATE OF AMMONIA. (§ 74. 2. *a.*)

0.7553 gramme of pure ignited chloride of barium were precipitated according to § 74. 2. *a*; the precipitate of $Ba\ O, CO_2$ weighed 0.7142 gramme, which corresponds to 0.554719 gramme of $Ba\ O$=73.44 per cent. (100 parts of $Ba\ Cl$ should have yielded 73.59 parts. The result accordingly was 99.79 instead of 100.

49. ESTIMATION OF BARYTES IN ORGANIC SALTS. (§ 74.2. *b.*)

0.686 gramme of paratartrate of barytes [2. (R, Ba + O.) + 5 aq.] treated according to § 74. 2. *b.*, yielded 0.408 gramme of carbonate of barytes. = 0.3168936 of $Ba\ O$ = 46.20 per cent. (calculated 46.38 per cent.), which gives 99.61 instead of 100.

50. ESTIMATION OF STRONTIA AS SULPHATE OF STRONTIA. (§ 75. 1.)

a. An aqueous solution of 1.2398 grm. of $Sr\ Cl$ was precipitated with $S\ O_3$ in excess, and the precipitated sulphate of strontia washed with water. It weighed 1.4113 gramme, which corresponds to 0.795408 gramme of $Sr\ O$ = 64.15 per cent. (calculated 65.38 per cent.); this gives 98.12 instead of 100.

b. A tolerably dilute solution of 1.1510 gramme of $Sr\ O, CO_2$ in an excess of hydrochloric acid was precipitated with $S\ O_3$, and the precipitated sulphate of strontia washed with water. It weighed 1.4024 gramme, which corresponds to 0.79039 of $Sr\ O$

= 68.68 per cent. (calcutated 70.07 per cent.); this gives 98.02 instead of 100.00.

51. ESTIMATION OF STRONTIA AS SULPHATE, WITH CORRECTION. (§ 75. 1.)

The fluid filtered off in the experiment described at 50. *b.*, weighed 190.84 grammes. According to experiment No. 17., 11862 parts of water acidified with sulphuric acid dissolve one part of sulphate of strontia. 190.84 grammes of the filtrate contain accordingly 0.0161 gramme of this salt in solution. The *rinsing water* weighed 63.61 grammes. According to experiment No. 15. 6895 parts of water dissolve one part of $Sr\ O.\ S\ O_3$; the 63.61 grammes of the rinsing water contain therefore 0.0092 gramme in solution.

Adding then 0.0161 and 0.0092 gramme to the 1.4024 gramme of precipitated sulphate of strontia, we find the total amount = 1.4277 gramme, which corresponds to 0.80465 of Sr. O = 69.91 per cent. in $Sr\ O,\ C\ O_2$ (calculated 70.07 per cent.); this gives 99.77 instead of 100.

52. ESTIMATION OF STRONTIA AS CARBONATE OF STRONTIA. (§ 75.2.)

1.3104 of chloride of strontium, precipitated according to § 75. 2.; yielded 1.2204 gramme of $Sr\ O,\ CO_2$. containing 0.8551831 of Sr O = 65.26 per cent. (calculated 65.38), which gives 99.82 instead of 100.

53. ESTIMATION OF LIME AS SULPHATE OF LIME, BY PRECIPITATION. (§ 76. 1. *a.*)

(In the experiments described from 53, to 57, chemically pure air-dried carbonate of lime was used, in a portion of which the amount of anhydrous carbonate had been determined by very cautious heating. 0.7647 gramme of the heated carbonate left 0.7581 gramme, which weight did not suffer any further decrease upon the carbonate being once more gently ignited. It results from these data that the air-dried carbonate of lime which was used in this and the following four experiments, contained 55.516 per cent. of lime.)

1.186 gramme of the said air-dried carbonate of lime were dissolved in hydrochloric acid, and the solution was subsequently precipitated with sulphuric acid in conjunction with alcohol. (Vide § 76. 1. *a.*) The precipitated sulphate of lime weighed 1.5949 gramme, corresponding to 0.65598 of $Ca\,O$ = 55.31 per cent. (calculated at 55.51), which gives 99.64 instead of 100.

54. Estimation of $Ca\,O$ as $Ca\,O, CO_2$, by precipitation with carbonate of ammonia and subsequent washing of the precipitate with pure water. (§ 76. 2. *a.*)

A solution of 1.1437 gramme of the air-dried carbonate of lime of 53 in hydrochloric acid, yielded upon precipitation with carbonate of ammonia (vide § 76. 1. *a.*) 1.1243 gramme of anhydrous carbonate of lime, corresponding to 0.629608 of $Ca\,O$ = 55.05 per cent. (calculated 55.51 per cent., which gives 99.17 instead of 100.

55. Estimation of $Ca\,O$ as $Ca\,O, CO_2$, by precipitation with oxalate of ammonia from alkaline solutions. (§ 76. 2. *b. a.*)

1.1734 gramme of the air-dried carbonate of lime of 53, dissolved in hydrochloric acid, and treated as stated at § 76. 2. *b. a.*, yielded 1.1632 gramme of $Ca\,O, CO_2$ (reaction non-alkaline), containing 0.651392 of $Ca\,O$ = 55.513 per cent. (calculated 55.516 per cent.), which gives 99.99 instead of 100.

56. Estimation of lime as oxalate. (§ 76. 2. *b. a.*)

0.857 gramme of the air-dried carbonate of lime of 53, were dissolved in hydrochloric acid, the solution was precipitated with oxalate of ammonia in conjunction with ammonia, the precipitate washed, and subsequently dried at 212° until the weight ceased to vary. The precipitate ($Ca\,O, \bar{O}$ + aq. weighed 1.2461 gramme, corresponding to 0.477879 of $Ca\,O$ = 55.76 per cent. (calculated 55.516 per cent.), which gives 100.45 instead of 100.

57. ESTIMATION OF $Ca\,O$, AS $Ca\,O, CO_2$ BY PRECIPITATION AS $Ca\,O, \bar{O}$, FROM ACID SOLUTION. (§ 76. 2. *b.* *β.*)

0.857 gramme of the dry carbonate of lime of 53., dissolved in hydrochloric acid and precipitated from this solution according to § 76. 2. *b.* *β.*, yielded 0.8476 gramme of carbonate of lime, (which did not manifest alkaline reaction, and the weight of which did not vary in the least upon evaporation with carbonate of ammonia,) corresponding to 0.474656 of $Ca\,O$ = 55.39 per cent. (calculated 55.51) which gives 99.78 instead of 100.

58. ESTIMATION OF MAGNESIA AS $2\,Mg\,O, PO_5$. (§ 77. 2.)

a. A solution of 1.0587 gramme of pure anhydrous sulphate of magnesia in water, yielded upon precipitation, according to § 77. 2. 0.9834 of pyrophosphate of magnesia, containing 0.3606128 of magnesia = 34.06 per cent. (calculated 34.01 per cent.), which gives 100.14 instead of 100.00.

b. 0.9672 gramme of sulphate of magnesia yielded 0.8974 pyrophosphate of magnesia = 34.02 per cent. of magnesia (calculated 34.01 per cent.) which gives 100.03 instead of 100.

59. ESTIMATION OF MAGNESIA IN SALTS WITH ORGANIC ACIDS BY IGNITION. (§ 77. 3. *a.*)

1.0965 of paratartrate of magnesia ($Mg\,O, \bar{R} + 5$ aq.), treated according to § 77. 3. *a.*, yielded 0.171 of $Mg\,O$ = 15.59 per cent. (calculated 15.69 per cent.), which gives 99.36 instead of 100.00.

60. PRECIPITATION OF ACETATE OF ZINC WITH SULPHURETTED HYDROGEN. (§ 80. *b.*)

a. A solution of pure acetate of zinc was treated with sulphuretted hydrogen in excess, and the mixture allowed to stand at rest for some time, and subsequently filtered. The filtrate was mixed with ammonia; it remained perfectly clear at first, and even after long standing, a few, hardly visible flakes only had separated.

b. A solution of acetate of zinc to which a tolerably large amount of acetic acid had been added previously to the precipitation with sulphuretted hydrogen, presented exactly the same deportment.

61. ESTIMATION OF MERCURY AS METAL IN THE HUMID WAY BY MEANS OF PROTOCHLORIDE OF TIN. (§ 89. 1. *b.*)

2.01 grammes of perchloride of mercury yielded 1.465 gramme of metallic mercury = 72.88 per cent. (calculated 73.83 per cent.), which gives 98.71 instead of 100. (SCHAFFNER.)

62. PRECIPITATION OF NITRATE OF BISMUTH BY MEANS OF CARBONATE OF AMMONIA. (§ 91. 1. *a.*)

If a solution of nitrate of bismuth, no matter whether containing much or little free nitric acid, is mixed with water, subsequently precipitated with carbonate of ammonia and caustic ammonia, and filtered without applying heat, the filtrate turns blackish brown, upon addition of sulphuretted hydrogen water. But if the mixture before filtering is heated, for a short time, nearly to boiling, sulphuretted hydrogen fails to impart this coloration to the filtrate, or, at all events, the brownish tint is so little apparent, that it can hardly be perceived when looking through the fluid, from the top of the test-tube, although the latter be filled to the brim.

63. ESTIMATION OF PHOSPHORIC ACID AS PYROPHOSPHATE OF MAGNESIA. (§ 101. I. *b.*)

In the following experiments I used perfectly pure air-dried crystallized phosphate of soda, of which I had most carefully determined the amount of water by heating and ignition.

1.3123 gramme of the substance left 0.4899 gramme of pyrophosphate of soda. This shows a percentage amount of water = 62.67. The formula $2\ NaO, HO, PO_5 + 24\ aq.$ requires 62.71 per cent.

a. 1.9847 gramme of the air-dried crystallized phosphate of soda was dissolved in water, and the solution subsequently precipitated, (according to § 101. I. *b.*) with sulphate of magnesia, sal ammoniac, and ammonia. The precipitate was thoroughly washed with ammoniated water. It yielded, after ignition and after deducting for the filter ashes, 0.6336 gramme of pyrophosphate of magnesia, which corresponds to 0.3945328 of phosphoric acid. This shows the amount of phosphoric acid in the crystallized phosphate of soda = 19.87 per cent. ;—the above-given formula demands 19.9—and, corrected upon the amount of water found, 19.91 per cent.

b. 3.0676 grammes of the same crystallized phosphate of soda were dissolved in water ; the solution was mixed with hydrochloric acid and subsequently with perchloride of iron and solution of alum, tartaric acid was then added, and finally ammonia until the precipitate which had formed at first, was completely re-dissolved. The mixture was then precipitated with sulphate of magnesia, and allowed to stand at rest for twelve hours, when it was filtered and the precipitate washed with ammoniated water, so thoroughly that a drop of the last rinsings left not the slightest residue upon evaporation on a platinum plate; and yet nevertheless I did not succeed to get the precipitate so white as it ought to have been; but it retained to the end a faint shade of yellow, and turned upon ignition slightly blackish throughout the whole mass. It weighed, after deduction of 0.0026 gramme filter ashes, 0.9786 gramme, which corresponds to 0.6181 of phosphoric acid = 20.14 per cent., (calculated 19.91 per cent.) The 0.23 per cent. surplus, was owing to the presence of a trace of charcoal and a minute amount of peroxide of iron; the charcoal separated subsequently upon the solution of the residue in hydrochloric acid; the peroxide of iron was detected distinctly in the solution upon testing with sulphocyanide of potassium.

64. SEPARATION OF MAGNESIA FROM SODA. (§ 116. *a.*)

1.1864 gramme of pure ignited chloride of sodium, and 1.4252 gramme of pure, anhydrous sulphate of magnesia were dissolved in water, the solution was heated to 212° F., and mixed with water of barytes in excess. The fluid was filtered off from the precipitate formed, and the excess of barytes removed from the filtrate by means of carbonate of ammonia. The filtrate was then evaporated with sulphuric acid: it yielded 1.4371 gramme of neutral sulphate of soda, which corresponds to 0.4694 of sodium. The precipitate produced by the water of barytes, was washed, and subsequently heated with dilute hydrochloric acid; the solution was filtered off from the undissolved sulphate of barytes and the filtrate subsequently evaporated in conjunction with sulphuric acid (upon the addition of which a small precipitate of sulphate of barytes separated). The gently ignited residue weighed 1.4308 gramme. This was treated with water, and the undissolved sulphate of barytes filtered off and weighed; its weight was 0.0889 gramme. Thus there remained for sulphate of magnesia 1.4308 gramme which corresponds to 0.48668 of $Mg\,O$.

This gives in 100 parts of the mixture,

	found	calculated
Na	17.84	17.86
$Mg\,O$	18.63	18.56

Now, although these numbers correspond, yet the result of the analysis would have been more satisfactory still, had the amount of magnesia found been somewhat deficient, and that of sodium somewhat too high. From the results which I obtained, I was led to conclude that the precipitate by the water of barytes had not been thoroughly washed, and I was indeed able to detect the presence of a trace of soda in the separated sulphate of magnesia.

65. SEPARATION OF BARYTES FROM STRONTIA, BY MEANS OF HYDROFLUOSILICIC ACID. (§ 117. 1.)

1.9676 gramme of carbonate of strontia, and 1.5202 gramme of chloride of barium were dissolved in hydrochloric acid and water, and the two bases were subsequently separated from one another, according to § 117. 1.

The results obtained were; 2.403 grammes of $Sr\ O, SO_3$, and 2.141 grammes of $Ba\ Fl, Si\ Fl_2$.

From these data results as the percentage amount of barytes and strontia contained in the above mixture:

	Synthesis.	*Analysis.*
Sr O	39.56	38.81
Ba O	32.35	33.55

It will be seen at one glance that the result would have been more accurate had the rinsings of the silicofluoride of barium been longer continued. But we possess no means of hitting the right point in this respect. In the present instance the fluid filtered off from the silicofluoride of barium weighed 177 grammes, and the total amount of the rinsing water, 54 grammes. These 54 grammes were accordingly not sufficient for the thorough rinsing of a precipitate of 2 grammes weight.

66. SEPARATION OF BARYTES FROM STRONTIA BY ALCOHOL. (§ 117. 1.)

0.6853 gramme of pure chloride of barium and 0.697 gramme of pure chloride of strontium were mixed and the finely levigated mixture was introduced into a bottle provided with a glass stopper, and digested for twenty-four hours, at the common temperature, with 100 grammes of alcohol of 97 per cent., the operation being aided by frequent agitation of the mixture. The mixture was then filtered, and the undissolved residue gradually washed with 70 grammes of alcohol of the same strength. Both bases were now converted into sulphates and weighed as such. The weight of the sulphate of strontia was 0.728 gramme, that of sulphate of barytes, 0.833 gramme.

From these data results as the percentage amount of barytes and strontia contained in the above mixture:

	Synthesis.	*Analysis.*
Ba O	36.49	39.61
Sr O	32.94	29.70

67. Experiments in alkalimetry (to page 359.)

Although the little work on alkalimetry, chlorimetry, and acidimetry, published by Professor Will and myself, contains comparative experiments upon the respective efficiency and preciseness of the two alkalimetrical methods, yet I will communicate here the results of several experiments made by my pupils during a practical course of analytico-technical investigations, since these results will tend to show the extent of the deviations likely to occur in alkalimetrical experiments.

a. Potash made from husks of grapes was examined by Gay-Lussac's method; the results of eight experiments were respectively:

81 — 81 — 80.5 — 81. — 81 — 80.4 — 83 — 81.

b. Pure carbonate of soda was examined by Fresenius and Will's method; the results of five experiments were respectively:

100.5 — 100.0 — 100.2 — 100.5 — 99.5.

c. A soda of commerce was examined by the same method; the results of four experiments were respectively:

Hygroscopic water.	*After ignition.*		
Water	$\mathrm{Na\,O, C\,O_2}$	$\mathrm{Na\,O}$	$\mathrm{Na\,O, C\,O_2 + Na\,O}$ assumed as $\mathrm{Na\,O, C\,O_2}$
19.9	78.7	6.8	90.2
19.8	81.5	5.0	90.2
20.3	79.5	6.2	90.3
19.6	80.0	5.9	90.0

The percentage amount of $\mathrm{Na\,O, C\,O_2}$ ($\mathrm{Na\,O}$ being likewise calculated as $\mathrm{Na\,O, C\,O_2}$) contained in the examined commercial soda was accordingly:

72.25 — 72.34 — 71.96 — 72.36.

d. The same sort of soda was examined by Gay-Lussac's method; the results of five experiments were respectively:

73.0 — 72.7 — 73.0 — 73.0 — 73.0.

68. Note to "COMBUSTION OF ORGANIC SUBSTANCES WITH OXIDE OF COPPER AND CHLORATE OF POTASS." (§ 142. *bb.*)

Absolutely dry oxygen gas was transmitted, for a short time, through a potass apparatus filled with potass ley of 1.27 specific gravity, and at the anterior end a small tube containing hydrated potass was attached; the excess of oxygen was subsequently withdrawn from the apparatus by suction. The bulb apparatus and potass tube had been weighed separately before the operation. After the termination of the experiment, the weight of the potass apparatus had increased by 0.0048 grm., that of the potass tube by 0.0029 grm. The potass ley had accordingly absorbed 0.0077 grm. of oxygen, and yielded 0.0029 grm. of water.

II. TABLES FOR THE CALCULATION OF ANALYSES.

TABLE I.

EQUIVALENTS OF THE ELEMENTS WHICH OCCUR IN THE PRESENT WORK. (O=100.)*

Aluminium, *a*	Al	170.42	(Berzelius)
Antimony	Sb	1612.90	,,
Arsenic, *b*	As	936.48	,,
Barium, *c*	Ba	854.85	,,

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* The equivalent numbers given in this table have been calculated from the best and most precise investigations made both at former periods and recently. The equivalents of many substances, differ from those which were formerly adopted, although no investigations have been recently made upon them. These equivalents are derived from others which have been experi-

Bismuth, *d*	Bi	2660.75	(Lagerhjelm)
Boron, *e*	B	136.31	(Berzelius)
Bromine	Br	999.63	(Marignac)
Cadmium	Cd	696.77	(Stromeyer)
Calcium	Ca	250.00	(Dumas. Erdmann and Marchand)
Carbon	C	75.00	,,
Chlorine	Cl	443.20	(Marignac)
Chromium, *f*	Cr	349.83	(Berzelius)
Cobalt, *g*	Co	368.44	(Rothoff)
Copper,	Cu	396.00	(Erdmann and Marchand)
Fluorine, *h*	Fl	235.71	(Berzelius)
Gold, *i*	Au	2456.72	,,
Hydrogen	H	12.50	(Dumas)
Iodine	I	1585.57	(Marignac)
Iron	Fe	350.00	(Erdmann and Marchand)
Lead	Pb	1294.50	(Berzelius)
Lithium, *k*	L	81.85	,,
Magnesium, *l*	Mg	157.75	,,
Manganese, *m*	Mn	344.44	,,
Mercury	Hg	1250.90	(Erdmann and Marchand)
Nickel, *n*	Ni	369.14	(Rothoff)
Nitrogen	N	175.25	(Marignac)
Oxygen	O	100.00	
Palladium, *o*	Pd	662.54	(Berzelius)
Phosphorus, *p*	P	391.55	,,
Platinum, *q*	Pt	1233.50	,,
Potassium	K	488.94	(Marignac)

mentally corrected. It became necessary, therefore, to re-calculate the results of the original experiments upon the corrected equivalent numbers. I have done this, and I add the necessary explanations subsequently by way of appendix; the small letters by the side of the elements in question refer to these explanations. The names of the chemists who have furnished the analytical results are likewise stated.

Silicon, *r*	Si	184.88	(Berzelius)
Silver	Ag	1349.01	(Marignac)
Sodium	Na	287.17	(Pelouze)
Strontium, *s*	Sr	545.60	(Stromeyer)
Sulphur	S	200.00	(Erdmann and Marchand)
Tin	Sn	735.30	(Berzelius)
Zinc	Zn	406.59	(Axel Erdmann)

Explanations of the foregoing table.

a. Equivalent of aluminium.

100 parts of anhydrous sulphate of alumina left, after expulsion of the acid by intense ignition, 29.934 parts of alumina. Consequently, 100 parts of sulphuric acid are saturated by 42.7227 parts of alumina (Berzelius).

$$100 : 42.7227 :: 1500\ (3\text{ equ. of } S\,O_3) : x$$

$$x\ (\text{equivalent of } Al_2\,O_3) = 640.8405$$

$$640.8405 - 300 = 340.8405\ (2\,Al)$$

$$\frac{340.8405}{2} = 170.42$$

b. Equivalent of arsenic.

2.203 grammes of arsenious acid yielded, upon being heated with sulphur, 1.069 grm. of $S\,O_2$, which corresponds to 0.5345 O (Berzelius). 2.203 grammes of $As\,O_3$ consist accordingly of 0.5345 O and 1.6685 As.

$$5345 : 16685 :: 300 : x$$

$$x = 936.48$$

(Pelouze (Comptes Rendus xx., page 1047) found, by precipitation of protochloride of arsenic with solution of nitrate of silver, 937.5.)

c. Equivalent of barium.

100 of Ba Cl yielded in two experiments respectively 138.06 and 138.08 of Ag Cl. Mean 138.07 (Berzelius).

$$138.07 : 100 :: 1792.21 \text{ (equ. of Ag Cl)} : x$$
$$x = 1298.05$$
$$1298.05 - 443.20 \text{ (equivalent of chlorine)} = 854.85$$

(PELOUZE (Comptes Rendus xx., page 1047) found 858.01. The results obtained by Berzelius correspond so perfectly in the two experiments quoted, and correspond, moreover, so accurately with two other experiments in which the Ba Cl was converted into Ba O, S O_3 (and which gave as equivalent 856.08) that their accuracy cannot be questioned.

d. EQUIVALENT OF BISMUTH.

The equivalent number 2660.75 is based upon the assumption that the composition of oxide of bismuth is Bi O_3.

e. EQUIVALENT OF BORON.

100 of borax (Na O, 2 B O_3 + 10 aq.) yielded in three experiments, without deviation, 47.1 per cent. of water (BERZELIUS).

$$47.1 : 100 :: 1125.0 \text{ (10 equ. of H O)} : x$$
$$x = 2388.53$$

2388.53 — 2115.90 (viz. the sum of one equivalent of Na O = 390.9, 10 equivalents of H O = 1125.0, and six equivalents of O=600)=272.63.

$$\frac{272.63}{2} = 136.31$$

f. EQUIVALENT OF CHROMIUM.

100 of Pb O, N O_5 yielded 98.772 Pb O, Cr O_3 (BERZELIUS).

$$100 : 98.772 :: 2069.75 \text{ (equ. of Pb O, N } O_5) : x$$
$$x = 2044.333 \text{ (equ. of Pb O, Cr } O_3).$$

2044.333 — 1694.5 (viz. the sum of one equivalent of Pb O = 1394.5 and three equivalents of O=300)=349.833.

g. EQUIVALENT OF COBALT.

269.2 parts of Co O, converted into neutral protochloride and precipitated subsequently with nitrate of silver, yielded 1029.9 parts of Ag Cl (Rothoff).

1029.9 : 269.2 : : 1792.21 (equivalent of Ag Cl) : x

x = 468.44 (equivalent of Co O).

468.44 — 100.00 = 368.44.

h. EQUIVALENT OF FLUORINE.

100 parts of Ca Fl yielded in three experiments respectively 174.9 — 175.0 — and 175.1 of Ca O, S O_3. Mean 175 (BERZELIUS).

175 : 100 : : 850 (equivalent of Ca O, S O_3) : x

x = 485.71 (equivalent of Ca Fl).

485.71 — 250.00 = 235.71

i. EQUIVALENT OF GOLD.

142.9 parts of mercury precipitate from perchloride of gold, (Au Cl_3,) 93.55 of gold (BERZELIUS).

142.9 : 93.55 : : 3752.7 (3 equivalents of Hg) : x

x = 2456.72

k. EQUIVALENT OF LITHIUM.

1.874 grm. of Li O, S O_3 yielded 3.9985 grm. of Ba O, S O_3 (BERZELIUS).

3.9985 : 1.874 : : 1454.85 (equivalent of Ba O, S O_3) : x

x = 681.85

681.85 — 600 (viz. the sum of one equivalent of S O_3=500, and 1 equivalent of O =100) = 81.85.

BERZELIUS' other experiment, in which 4.4545 grammes of fused Li O, C O_2 yielded 6.653 grammes of Li O, S O_3, tallies tolerably well with the preceding experiment (basing the calculation upon the above deduced equivalent = 81.85, the result ought to have been 6.648 grammes of Li O, S O_3). Since the method pursued in the first experiment admits of greater preciseness than that pursued in the other experiment, I deemed it preferable to calculate the equivalent from the results of the first experiment alone.

l. Equivalent of magnesium.

100 of Mg O yielded 293.985 of $Mg O, S O_3$ (Berzelius).

193.985 : 293.985 : : 500 (equivalent of $S O_3$) : x

x = 757.74 (equivalent of $Mg O, S O_3$)

757.75 — 600 (viz. the sum of one equivalent of $S O_3$ = 500, and one equivalent of O = 100) = 157.75.

m. Equivalent of manganese.

a. 4.20775 of Mn Cl yielded 9.575 of Ag Cl } Berzelius.
b. 3.063 of Mn Cl ,, 6.96912 of Ag Cl

ad. *a.*) 9.575 : 4.20775 : : 1792.21 (equ. of Ag Cl) : x

x = 787.59 (equ. of Mn Cl)

787.59 — 443.20 (equ. of Cl) = 344.39

ad. *b.*) 6.96912 : 3.063 : : 1792.21 : x

x = 787.69

787.69 — 443.20 = 344.49

Mean of 344.39 and 344.49 = 344.44.

n. Equivalent of nickel.

188 of Ni O, converted into neutral protochloride, yielded 718.2 of Ag Cl (Rothoff).

718.2 : 188 : : 1792.21 (equ of Ag Cl) : x

x = 469.14 (equ. of Ni O)

469.14—100 = 369.14

o. Equivalent of palladium.

2.606 grammes of (K Cl+Pd Cl) yielded 0.563 gramme of chlorine,—0.851 grm. of palladium,—and 1.192 grm. of chloride of potassium (Berzelius).

1.192 : 2.606 : : 932.14 (equ. of K Cl) : x

x = 2037.88 (equ. of [K Cl+Pd Cl]).

2037.88 — 1375.34 (viz. the sum of one equ. of K Cl=932.14, and one equ. of chlorine = 443.20) = 662.54.

p. Equivalent of phosphorus.

100 parts of phosphorus absorbed 127.45 parts of oxygen (calculated from the reduced silver) Berzelius.

100 (equ. of O) : 1351.61 (equ. of Ag which Berzelius assumed)
: : 127.65 O : x
$x = 1722.627$ Ag

1722.627 of silver must accordingly have been precipitated in Berzelius' experiment, and these correspond (calculated upon 1349.01 as equivalent of Ag) to 127.695 O; for

1349.01 : 100 : : 1722.627 : 127.695

127.695 : 100 : : 500 (5 equ. of O) : x
$x = 391.55$

Pelouze (Comptes Rendus xx., page 1047) found, by precipitation of protochloride of phosphorus with solution of nitrate of silver, 400.3 as the equivalent of phosphorus.

I have, however, based my calculation upon the results of Berzelius' experiment, since the method pursued by Pelouze might be less accurate than that adopted by Berzelius, considering the nature of the analysed phosphorus compound.

q. Equivalent of platinum.

6.981 grammes of $K\,Cl + Pt\,Cl_2$ yielded 2.024 grammes of chlorine, (which were originally combined with the platinum,) 2.822 grammes of Pt, and 2.135 grammes of K Cl (Berzelius).

α. Calculated from the chlorine.

2.024 : 6.981 : : 886.4 (2 equ. of chlorine) : x
$x = 3057.28$

3057.28—1818.54 (viz the sum of 2 equ. of chlorine=886.40, —one equivalent of chlorine = 443.20; and one equivalent of potassium = 488.94) = 1238.74.

β. Calculated from the chloride of potassium.

2.135 : 6.981 : : 932.14 (equ. of K Cl) : x
$x = 3047.90$
3047.90 — 1818.54 = 1229.36

The mean of 1238.74 and 1229.36 = 1234.5.

r. Equivalent of silicon.

This was found by Pelouze (Comptes Rendus xx., page 1047) as 88.94 × 2=177.88. I consider the method pursued by Pelouze less accurate than that pursued by Berzelius, and I have therefore retained the number of Berzelius, viz. in the ratio of 3 : 2, since silicic acid is $Si\,O_2$.

s. Equivalent of strontium.

100 Sr Cl yielded 181.25 of Ag Cl (Stromeyer).

$$181.25 : 100 : : 1792.21 : x$$
$$x = 988.80$$
$$988.80 - 443.20 = 545.60$$

Pelouze found 548.02 (Comptes Rendus xx., page 1047). His statements, however, leave some doubt regarding the purity of the salt used.

TABLE II.

COMPOSITION OF THE BASES AND OXYGENATED ACIDS.

a. BASES.

Group:				
I.	Potass	K	488.94	83.02
		O	100.00	16.98
		K O	588.94	100.00
	Soda	Na	287.17	74.17
		O	100.00	25.83
		Na O	387.17	100.00
	Lithia	Li	81.85	45.01
		O	100.00	54.99
		Li O	181.85	100.00
	Ammonia	NH_4	225.25	69.25
		O	100.00	30.75
		NH_4O	325.25	100.00
II.	Barytes	Ba	854.85	89.53
		O	100.00	10.47
		Ba O	954.85	100.00
	Strontia	Sr	545.60	84.51
		O	100.00	15.49
		Sr O	645.60	100.00
	Lime	Ca	250.00	71.43
		O	100.00	28.57
		Ca O	350.00	100.00
	Magnesia	Mg	157.75	61.20
		O	100.00	38.80
		Mg O	257.75	100.00

Group :				
III.	Alumina	Al_2	340.84	53.19
		O_3	300.00	46.81
		Al_2O_3	640.84	100.00
	Chromium, oxide	Cr_2	699.66	70.11
		O_3	300.00	29.89
		Cr_2O_3	999.66	100.00
IV.	Zinc, oxide	Zn	406.59	80.26
		O	100.00	19.74
		ZnO	506.59	100.00
	Manganese, protoxide	Mn	344.44	77.50
		O	100.00	22.50
		MnO	444.44	100.00
	Manganoso-manganic oxide	Mn_2	688.88	69.67
		O_3	300.00	30.33
		Mn_2O_3	988.88	100.00
	Nickel, protoxide	Ni	369.14	78.68
		O	100.00	21.32
		NiO	469.14	100.00
	Cobalt, protoxide	Co	368.44	78.65
		O	100.00	21.35
		CoO	468.44	100.00
	Cobaltoso-cobaltic oxide	Co_2	736.88	71.07
		O_3	300.00	28.93
		Co_2O_3	1036.88	100.00
	Iron, protoxide	Fe	350.00	77.78
		O	100.00	22.22
		FeO	450.00	100.00
	Iron, peroxide	Fe_2	700.00	70.00
		O_3	300.00	30.00
		Fe_2O_3	100.000	100.00

Group :				
V.	Silver, oxide	Ag	1349.01	93.10
		O	100.00	6.90
		Ag O	1449.01	100.00
	Lead, oxide	Pb	1294.50	92.83
		O	100.00	7.17
		Pb O	1394.50	100.00
	Mercury, protoxide	Hg_2	2501.80	96.16
		O	100.00	3.84
		Hg_2O	2601.80	100.00
	Mercury, binoxide	Hg	1250.90	92.60
		O	100.00	7.40
		Hg O	1350.90	100.00
	Copper, protoxide	Cu_2	792.00	88.79
		O	100.00	11.21
		Cu_2O	892.00	100.00
	Copper, oxide	Cu	396.00	79.84
		O	100.00	20.16
		Cu O	496.00	100.00
	Bismuth, oxide	Bi	2660.75	89.87
		O_3	300.00	10.13
		BiO_3	2960.75	100.00
	Cadmium, oxide	Cd	696.77	87.45
		O	100.00	12.55
		Cd O	796.77	100.00
VI.	Gold, peroxide	Au	2456.72	89.12
		O_3	300.00	10.88
		AuO_3	2756.72	100.00
	Platinum, peroxide	Pt	1233.50	86.05
		O_2	200.00	13.95
		PtO_2	1433.50	100.00

Group:				
VI.	Antimony, oxide	Sb	1612.90	84.32
		O_3	300.00	15.68
		SbO_3	1912.90	100.00
	Tin, protoxide	Sn	735.30	88.02
		O	100.00	11.98
		SnO	835.30	100.00
	Tin, peroxide	Sn	735.30	78.62
		O_2	200.00	21.38
		SnO_2	935.30	100.00
	Arsenious acid	As	936.48	75.74
		O_3	300.00	24.26
		AsO_3	1236.48	100.00
	Arsenic acid	As	936.48	65.19
		O_5	500.00	34.81
		AsO_5	1436.48	100 00

b. ACIDS.

Chromic acid	Cr	349.83	53.83
	O_3	300.00	46.17
	CrO_3	649.83	100.00
Sulphuric acid	S	200.00	40.00
	O_3	300.00	60.00
	SO_3	500.00	100.00
Phosphoric acid	P	391.55	43.92
	O_5	500.00	56.08
	PO_5	891.55	100.00
Boracic acid	B	136.31	31.24
	O_3	300.00	68.76
	BO_3	436.31	100.00

Oxalic acid	C_2	150.00	33.33
	O	300.00	66.67
	C_2O_3	450.00	100.00
Carbonic acid	C	75.00	27.27
	O_2	200.00	72.73
	CO_2	275.00	100.00
Silicic acid	Si	184.88	48.03
	O_2	200.00	51 97
	SiO_2	284.88	100.00
Nitric acid	N	175.25	25.95
	O_5	500.00	74.05
	NO_5	675.25	100.00
Chloric acid	Cl	443.20	46.99
	O_5	500.00	53.01
	ClO_5	943.20	100.00

TABLE III.

Reduction to constituent parts by simple multiplication or division of the compounds obtained.

(This table contains some of the most frequently occurring compounds.)

INORGANIC ANALYSIS.

Potash.

$$\left.\begin{array}{l} \text{Chloride of platinum and potassium} \times 0{,}3054 \\ \text{or} \\ \dfrac{\text{Chloride of platinum and potassium}}{3{,}274} \end{array}\right\} = \text{Chloride of potassium.}$$

$$\left.\begin{array}{c}\text{Chloride of platinum} \\ \text{and potassium} \quad \times 0{,}193 \\ \text{or} \\ \dfrac{\text{Chloride of platinum and potassium}}{5{,}182} \quad . \; . \; . \; .\end{array}\right\} = \text{Potash.}$$

Sodium.

Chloride of sodium × 0,5301 = Soda.

Lime.

! * Carbonate of lime × 0,56 = Lime.

Magnesia.

Pyrophosphate of magnesia × 0,3664 = 2 Magnesia.

Iron.

! Oxide of iron × 0,7 = 2 Iron.

! Oxide of iron × 0,9 = 2 Protoxide of iron.

Sulphuric acid.

$$\left.\begin{array}{c}\text{Sulphate of barytes} \times 0{,}3436 \\ \text{or} \\ \dfrac{\text{Sulphate of barytes}}{2{,}91} \quad . \; . \; . \; .\end{array}\right\} = \text{Sulphuric acid.}$$

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* Those marked with ! yield very accurate results.

Carbonic acid.

! Carbonate of lime × 0,44 = Carbonic acid.

Chlorine.

Chloride of silver × 0,2473 = Chlorine.

ORGANIC ANALYSIS.

Carbon.

$$\left.\begin{array}{l} \text{Carbonic acid} \times 0{,}2727 \\ \qquad \text{or} \\ \dfrac{\text{Carbonic acid}}{3{,}666} \quad . \quad . \\ \qquad \text{or} \\ ! \ \dfrac{\text{Carbonic acid}}{11} \times 3 \end{array}\right\} = \text{Carbon.}$$

Hydrogen.

$$\left.\begin{array}{l} \text{Water} \times 0{,}11111 \\ ! \ \dfrac{\text{Water}}{9} \quad . \quad . \quad . \end{array}\right\} = \text{Hydrogen.}$$

Nitrogen.

$$\left.\begin{array}{l} \text{Chloride of platinum} \\ \quad \text{and ammonium} \times 0{,}06284 \\ \qquad \text{or} \\ \text{Chloride of platinum} \\ \quad \dfrac{\text{and ammonium}}{15{,}9} \quad . \quad . \quad . \quad . \end{array}\right\} = \text{Nitrogen.}$$

TABLE IV.

Elements.	Found.	Sought.	1.
Barium	Silico-fluoride of barium $BaFl, SiFl_2$	Barytes BaO	0.54661
Bismuth	Oxide of bismuth BiO_3	Bismuth Bi	0.89867
Boron	Boracic acid BO_3	Boron B	0.31241
Bromine	Bromide of silver $AgBr$	Bromine Br	0.42562
Cadmium	Oxide of cadmium CdO	Cadmium Cd	0.87449
Calcium	Lime CaO	Calcium Ca	0.71429
	Sulphate of lime CaO, SO_3	Lime CaO	0.41176
	Carbonate of lime CaO, CO_2	Lime CaO	0.56000
Carbon	Carbonic acid CO_2	Carbon C	0.27273
	Carbonate of lime CaO, CO_2	Carbonic acid CO_2	0.44000
Chlorine	Chloride of silver $AgCl$	Chlorine Cl	0.24729
	Chloride of silver $AgCl$	Hydrochloric acid ClH	0.25427
Chromium	Oxide of chromium Cr_2O_3	Chromium Cr	0.70108
	Oxide of chromium Cr_2O_3	Chromic acid $2CrO_3$	1.29891
	Chromate of lead PbO, CrO_3	Chromic acid CrO_3	0.31853
Cobalt	Cobalt Co	Protoxide of cobalt CoO	1.27141
Copper	Oxide of copper CuO	Copper Cu	0.79839

continued.

2.	3.	4.	5.	6.	7.	8.	9.
1.09322	1.63983	2.18644	2.73304	3.27965	3.82626	4.37287	4.91948
1.79735	2.69602	3.59470	4.49337	5.39204	6.29072	7.18939	8.08807
0.62483	0,93724	1.24966	1.56207	1.87449	2.18690	2.49932	2.81173
0.85124	1.27686	1.70248	2.12810	2.55373	2.97935	3.40497	3.83059
1.74899	2.62348	3.49797	4.37246	5.24696	6.12145	6.99594	7.87044
1.42857	2.14286	2.85714	3.57143	4.28571	5.00000	5.71429	6.42857
0.82353	1.23529	1.64706	2.05882	2.47059	2.88235	3.29412	3.70588
1.12000	1,68000	2.24000	2.80000	3.36000	3.92000	4.48000	5.04000
0.54545	0.81818	1.09091	1.36364	1.63636	1.90909	2.18181	2.45455
0.88000	1.32000	1.76000	2.20000	2.64000	3.08000	3.52000	3.96000
0.49458	0.74188	.098917	1.23646	1.48375	1.73104	1.97834	2.22563
0.50853	0.76280	1.01707	1.27133	1.52560	1.77987	2.03414	2.28840
1.40217	2.80325	2.80434	3.50542	4.20651	4.90759	5.60868	6.30976
2.59783	3.89674	5.19566	6.49457	7.79349	9.09240	10.39132	11.69023
0.63707	0.95560	1.27413	1.59266	1.91120	2.22973	2.54826	2.86680
2.54283	3.81424	5,08566	6.35707	7.62849	8.89990	10.17132	11.44273
1.59677	2.39516	3.19355	3-99193	4.79032	5.58871	6.38710	7.18548

TABLE IV.

Elements.	Found.	Sought.	1.
Fluorine	Fluoride of calcium	Fluorine	0.48528
	$Ca\,Fl$	Fl	
	Fluoride of silicon	Fluorine	0.71829
	$Si\,Fl_3$	$2\,Fl$	
Hydrogen	Water	Hydrogen	0.11111
	$H\,O$	H	
Iodine	Iodide of silver	Iodine	0.54031
	$Ag\,J$	J	
Iron	Oxide of iron	Iron	0.70000
	$Fe_2\,O_3$	Fe_2	
	Oxide of iron	Protoxide of iron	0.90000
	$Fe_2\,O_3$	$2\,Fe\,O$	
Lead	Oxide of lead	Lead	0.92829
	$Pb\,O$	Pb	
	Sulphate of lead	Oxide of lead	0.73608
	$Pb\,O,\,S\,O_3$	$Pb\,O$	
	Chloride of lead	Oxide of lead	0.80250
	$Pb\,Cl$	$Pb\,O$	
	Chloride of lead	Lead	0.74495
	$Pb\,Cl$	Pb	
	Sulphuret of lead	Oxide of lead	0.93309
	$Pb\,S$	$Pb\,O$	
Magnesium	Magnesia	Magnesium	0.61203
	$Mg\,O$	Mg	
	Sulphate of magnesia	Magnesia	0.34015
	$Mg\,O,\,S\,O_3$	$Mg\,O$	
	Pyrophosphate of magnesia	Magnesia	0.36637
	$P\,O_5\;2\,Mg\,O$	$2\,Mg\,O$	
Manganese	Protoxide of manganese	Manganese	0.77500
	$Mn\,O$	Mn	
	Manganoso-manganic oxide	Manganese	0.72093
	$Mn\,O+Mn_2\,O_3$	Mn_3	
	Protosulphate of manganese	Protoxide of manganese	0.47059
	$Mn\,O,\,S\,O_3$	$Mn\,O$	

continued.

2.	3.	4.	5.	6.	7.	8.	9.
0.97056	1.45584	1.94112	2.42640	2.91168	3.39695	3.88223	4.36751
1.43658	2.15487	2.87316	3-59145	4.30975	5.02804	5.74633	6.46462
0.22222	0.33333	0.44444	0.55555	0.66667	0.77778	0.88889	1.00000
1.08061	1.62092	2.16122	2.70153	3.24184	3.78214	4.43245	4.86275
1.40000	2.10000	2.80000	3.50000	4.20000	4.90000	5.60000	6.30000
1.80000	2.70000	3.60000	4,50000	5.40000	6.30000	7.20000	8.10000
1.85658	2.78487	3.71316	4.64145	5.56974	6.49803	7.42632	8.35461
1.47216	2.20823	2.94431	3.68039	4.41647	5.15255	5.88862	6.62470
1.60500	2.40749	3.20999	4.01249	4.81499	5.61749	6.41998	7.22248
1.48990	2,23485	2.97980	3.72475	4.46970	5.21465	5.95960	6.70455
1,86618	2.79926	3.73235	4.66544	5.59853	6.53162	7.46470	8.39779
1.22405	1.83608	2.44811	3.06013	3.67216	4.28419	4.89622	5.50824
0.68030	1.02046	1.36061	1.70076	2.04091	2.38106	2.72122	3.06137
0.73274	1.09911	1.46548	1.83184	2.19821	2.56458	2,93095	3.29732
1.55000	2.32499	3.09999	3.87499	4.64999	5.42499	6.19998	6.97498
1.44186	2.16278	2.88371	3.60464	4.32557	5.04650	5.76742	6.48835
0.94117	1.41176	1.88234	2.35293	2.82352	3.29410	3.76469	4.23527

TABLE IV.

Elements.	Found.	Sought.	1.
Mercury	Mercury Hg_2	Protoxide of mercury $Hg_2 O$	1.03997
	Mercury Hg	Binoxide of mercury $Hg O$	1.07994
	Protochloride of mercury $Hg_2 Cl$	Mercury Hg_2	0.84951
	Sulphide of mercury $Hg S$	Mercury Hg	0.86215
Nickel	Protoxide of nickel $Ni O$	Nickel Ni	0.78684
Nitrogen	Ammonio-chloride of platinum $N H_4 Cl, Pt Cl_2$	Nitrogen N	0.06285
	Platinum Pt	Nitrogen N	0.14207
	Sulphate of barytes $Ba O, S O_3$	Nitric acid $N O_5$	0.46414
	Carbonic acid $2 C O_2$	Nitric acid $N O_5$	1.22773
	Cyanide of silver $Ag, C_2 N$	Cyanogen $C_2 N$	0.19426
	Cyanide of silver $Ag, C_2 N$	Hydrocyanic acid $C_2 N, H$	0.20173
Phosphorus	Phosphoric acid $P O_5$	Phosphorus P	0.43918
	Pyrophosphate of magnesia $2 Mg O, P O_5,$	Phosphoric acid $P O_5$	0.63363
	Phosphate of iron $2 Fe_2 O_3, 3 P O_5,$	Phosphoric acid $3 P O_5$	0.57216
	Phosphate of silver $3 Ag O, P O_5,$	Phosphoric acid $P O_5$	0.17019
	Pyrophosphate of silver $2 Ag O P O_5,$	Phosphoric acid $P O_5$	0.23526
Potassium	Potash $K O$	Potassium K	0.83020

continued.

2.	3.	4.	5.	6.	7.	8.	9.
2.07994	3.11991	4.15988	5.19985	6.23983	7.27980	8.31977	9.35974
2.15988	3.23983	4.31977	5.39971	6.47965	7.55959	8.63954	9.71948
1.69902	2.54852	3.39803	4.24754	5.09705	5.94656	6.79606	7.64557
1.72431	2.58646	3.44862	4·31077	5.17293	6.03508	6.89724	7.75939
1.57369	2.36053	3.14738	3.93422	4.72106	5.50791	6.29475	7.08160
0.12570	0.18855	0.25140	0.31425	0.37711	0.43996	0.50281	0.56566
0.28415	0.42622	0.56830	0.71037	0.85245	0.99452	1.13660	1.27867
0.92827	1.39241	1.85655	2.32068	2.78482	3.24896	3.71310	4.17723
2.45545	3.68318	4.91091	6.13863	7.36636	8.59409	9.82182	1.104954
0.38853	0.58279	0.77706	0.97132	1.16559	1.35985	1.55412	1.74838
0.40346	0.60519	0.80692	1.00865	1.21039	1.41212	1.61385	1.81558
0.87836	1.31754	1.75672	2.19589	2.63507	3.07425	3.51343	3.95261
1.26726	1.90089	2.53452	3.16815	3.80179	4.43542	5.06905	5.70268
1.14431	1.71647	2.28862	2.86078	3.43294	4.00509	4.57725	5.14940
0.34038	0.51057	0.68076	0.85094	1.02113	1.19132	1,36151	1.53170
0.47053	0.70579	0.94106	1.17632	1.41158	1.64685	1.88211	1.11738
1.66041	2.49061	3.32081	4.15101	4.98122	5.81142	6.64162	7.47183

TABLE IV.

Elements.	Found.	Sought.	1.
Potassium	Sulphate of potash	Potash	0.54084
	KO, SO_3	KO	
	Nitrate of potash	Potash	0.46586
	KO, NO_5	KO	
	Chloride of potassium	Potassium	0.52454
	KCl	K	
	Chloride of potassium	Potash	0.63182
	KCl	KO	
	Potassio-chloride of platinum	Potash	0.19297
	$KCl, PtCl_2$	KO	
	Potassio-chloride of platinum	Chloride of potassium	0.30541
	$KCl, PtCl_2$	KCl	
Silicon	Silicic acid	Silicon	0.48036
	SiO_2	Si	
Silver	Chloride of silver	Silver	0.75271
	$AgCl$	Ag	
	Chloride of silver	Oxide of silver	0.80850
	$AgCl$	AgO	
Sodium	Soda	Sodium	0.74172
	NaO	Na	
	Sulphate of soda	Soda	0.43641
	NaO, SO_3	NaO	
	Nitrate of soda	Soda	0.36442
	NaO, NO_5	NaO	
	Chloride of sodium	Soda	0.53010
	$NaCl$	NaO	
	Chloride of sodium	Sodium	0.39318
	$NaCl$	Na	
	Carbonate of soda	Soda	0.58470
	NaO, CO_2	NaO	
Strontium	Strontia	Strontium	0.84510
	SrO	Sr	
	Sulphate of strontia	Strontia	0.56355
	SrO, SO_3	SrO	

continued.

2.	3.	4.	5.	6.	7.	8.	9.
1.08168	1.62251	2.16335	2.70419	3.24503	3.78587	4.32670	4.86754
9.93173	I.39759	1.86346	2.32232	2.79518	3.26105	3.72691	4.19278
1.04908	1.57362	2.09816	2.62270	3.14724	3.67178	4.19632	4.72086
1.26364	1.89546	2.52728	3.15909	3.79091	4.42273	5.05455	5.68637
0.38593	0 57890	0.77186	0.96483	1.15780	1.35076	1.54373	1.73669
0.61083	0.91624	1.22166	1.52707	1.83429	2.13790	2.44332	2.74873
0,96072	1.44107	1.92143	2.40179	2.88215	3.36251	3.84286	4.32322
1.50542	2,25812	3.01083	3.76354	4.51625	5.26896	6.02166	6.77437
1.61701	2.42551	3.23402	4.04252	4.85103	5.65953	6.46804	7.27654
1.48343	2,22515	2.96686	3.70858	4.45030	5.19201	5.93373	6.67544
0.87282	1.30923	1.74564	2.18205	2.61846	3.05487	3.49128	3.92769
0.72885	1.09327	1,45769	1.82211	2.18654	2.55096	2.91538	3.27981
1.06020	1.59030	2.12040	2.65050	3.18061	3.71071	4.24081	4.77091
0.78637	1.17955	1.57274	1.96592	2.35910	2.75229	3.14547	3.53866
1.16940	1,75410	2,33880	2.92349	3.50819	4.09289	4,67759	5 .26229
1.69021	2.53531	3.38042	4.22552	5.07063	5·91573	6.76084	7.60594
1.12709	1.69064	2.25419	2.81773	3.38128	3.94483	4.50838	5,07192

TABLE IV.

Elements.	Found.	Sought.	1.
Strontium	Carbonate of strontia $Sr O, S O_2$	Strontia $Sr O$	0.70128
Sulphur	Sulphate of barytes $Ba O, S O_3$	Sulphur S	0.13747
	Sulphuret of arsenic $As S_3$	Sulphur S_3	0.39050
	Sulphate of barytes $Ba O, S O_3$	Sulphuric acid $S O_3$	0.34368
Tin	Oxide of tin $Sn O_2$	Tin Sn	0.78616
	Oxide of tin $Sn O_2$	Protoxide of tin $Sn O$	0.89308
Zinc	Oxide of zinc $Zn O$	Zinc Zn	0.80260

continued.

2.	3.	4.	5.	6.	7.	8.	9.
1.40256	2.10385	2.80513	3.50641	4.20769	4.90897	5.61026	6.31154
0.27494	0.41241	0.54988	0.68735	0.82483	0.96230	1.09977	1.23724
0.78101	1.17151	1.56201	1.95251	2.34302	2.73352	3.12402	3.51453
0.68736	1.03103	1.37471	1.71839	2.06207	2.40575	2.74942	3.09310
1.57233	2.35849	3.14466	3.93082	4.71698	5.50315	6.28931	7.07547
178616	2.67924	3.57232	4.46540	5.35848	6.25156	7.14464	8.03772
1.60520	2.40781	3.21041	4.01301	4.81561	5.61821	6.42082	7.22342

TABLE V.

Specific gravity and absolute weight of several gases.

	Specific gravity, atmospheric air = 1.0000	1 litre (1000 centimetres cubes) of gas at 0° C. and 0.76 metre pressure weighs Grammes.
Atmospheric air	1.0000	1.2991
Oxygen	1.1093	1.4410
Hydrogen	0.0693	0.0901
Water, vapor of	0.6239	0.8105
Carbon, vapor of	0.8320	1.0808
Carbonic acid	1.5252	1.9814
Carbonic oxide	0.9709	1.2609
Phosphorus, vapor of . . .	4.3435	5.6422
Sulphur, vapor of	6.6556	8.6463
Hydrosulphuric acid . . .	1.1786	1.5311
Iodine	8.7944	11.4240
Bromine	5.5444	7.2023
Chlorine	2.4582	3.1932
Nitrogen	0.9706	1.2609
Ammonia	0.5893	0.7655

TABLE VI.

COMPARISON OF THE DEGREES OF THE MERCURIAL THERMOMETER WITH THOSE OF THE AIR THERMOMETER.

According to Dulong and Petit.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.	Degrees of the mercurial thermometer.	Degrees of the air thermometer.
105	104.8	220	216.2
110	109.6	230	225.9
120	119.5	240	235.4
130	129.2	250	245.0
140	139.0	260	254.6
150	148.7	270	264.0
160	158.4	280	273.5
170	168.0	290	283.2
180	177.7	300	292.7
190	187.4	320	311.6
200	197.0	340	330.5
210	206.7	350	340.0

According to Magnus.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.
100	100.00
150	148.74
200	197.49
250	245.39
300	294.51
350	320.92

According to Regnault.

Air thermometer.	Mercurial thermometer.
0	0
50	50 2
100	100.0
150	150.0
200	200.0
250	250.3
300	301.2
325	326.9
350	353.3

TABLE FOR THE CONVERSION OF DEGREES ON THE CENTIGRADE

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58°.0	—3°	26°.6	44°	111°.2	91°	195°.8
—49	—56.2	—2	28.4	45	113.0	92	197.6
—48	—54.4	—1	30.2	46	114.8	93	199.4
—47	—52.6	0	32.0	47	116.6	94	201.2
—46	—50.8	+1	33.8	48	118·4	95	203.0
—45	—49.0	2	35.6	49	120.2	96	204.8
—44	—47.2	3	37.4	50	122.0	97	206.6
—43	—45.4	4	39.2	51	123.8	98	208.4
—42	—43.6	5	41.0	52	125.6	99	210·2
—41	—41.8	6	42.8	53	127.4	100	212.0
—40	—40.0	7	44.6	54	129.2	101	213.8
—39	—38.2	8	46.4	55	131.0	102	215.6
—38	—36.4	9	48.2	56	132.8	103	217.4
—37	—34.6	10	50.0	57	134.6	104	219.2
—36	—32.8	11	51.8	58	136·4	105	221.0
—35	—30.0	12	53.6	59	138.2	106	222.8
—34	—29.2	13	55.4	60	140.0	107	224.6
—33	—27.4	14	57.2	61	141.8	108	226.4
—32	—25.6	15	59.0	62	143.6	109	228.2
—31	—23.8	16	60.8	63	145.4	110	230.0
—30	—22.0	17	62.6	64	147.2	111	231.8
—29	—20.2	18	64.4	65	149.0	112	233.6
—28	—18.4	19	66.2	66	150.8	113	235.4
—27	—16.6	20	68.0	67	152.6	114	237.2
—26	—14.8	21	69.8	68	154.4	115	239.0
—25	—13.0	22	71.6	69	156.2	116	240.8
—24	—11.2	23	73.4	70	158.0	117	242.6
—23	—9.4	24	75.2	71	159.8	118	244.4
—22	—7.6	25	77.0	72	161.6	119	246.2
—21	—5.8	26	78.8	73	163.4	120	248.0
—20	—4.0	27	80.6	74	165.2	121	249.8
—19	—2.2	28	82.4	75	167.0	122	251.6
—18	—0.4	29	84.2	76	168.8	123	253.4
—17	+1.4	30	86.0	77	170.6	124	255.2
—16	3.2	31	87.8	78	172.4	125	257.0
—15	5.0	32	89.6	79	174.2	126	258.8
—14	6.8	33	91.4	80	176.0	127	260.6
—13	8.6	34	93.2	81	177.8	128	262.4
—12	10.4	35	95.0	82	179.6	129	264.2
—11	12.2	36	96.8	83	181.4	130	266.0
—10	14.0	37	98.6	84	183.2	131	267.8
—9	15.8	38	100.4	85	185.0	132	269.6
—8	17.6	39	102.2	86	186.8	133	271.4
—7	19.4	40	104.0	87	188.6	134	273.2
—6	21.2	41	105.8	88	190.4	135	275.0
—5	23.0	42	107.6	89	192.2	136	276.8
—4	24.8	43	109.4	90	194.0		

THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
137°	278°.6	183°	361°.4	229°	444°.2	275°	527°.0
138	280.4	184	363.2	230	446.0	276	528.8
139	282.2	185	365.0	231	447.8	277	530.6
140	284.0	186	366.8	232	449.6	278	532.4
141	285.8	187	368.6	233	451.4	279	534.2
142	287.6	188	370.4	234	453.2	280	536.0
143	289.4	189	372.2	235	455.0	281	537.8
144	291.2	190	374.0	236	456.8	282	539.6
145	293.0	191	375.8	237	458.6	283	541.4
146	294.8	192	377.6	238	460.4	284	543.2
147	296.6	193	379.4	239	462.2	285	545.0
148	298.4	194	381.2	240	464.0	286	546.8
149	300.2	195	383.0	241	465.8	287	548.6
150	302.0	196	384.8	242	467.6	288	550.4
151	303.8	197	386.6	243	469.4	289	552.2
152	305.6	198	388.4	244	471.2	290	554.0
153	307.4	199	390.2	245	473.0	291	555.8
154	309.2	200	392.0	246	474.8	292	557.6
155	311.0	201	393.8	247	476.6	293	559.4
156	312.8	202	395.6	248	478.4	294	561.2
157	314.6	203	397.4	249	480.2	295	563.0
158	316.4	204	399.2	250	482.0	296	564.8
159	318.2	205	401.0	251	483.8	297	566.6
160	320.0	206	402.8	252	485.6	298	568.4
161	321.8	207	404.6	253	487.4	299	570.2
162	323.6	208	406.4	254	489.2	300	572.0
163	325.4	209	408.2	255	491.0	301	573.8
164	327.2	210	410.0	256	492.8	302	575.6
165	329.0	211	411.8	257	494.6	303	577.4
166	330.8	212	413.6	258	496.4	304	579.2
167	332.6	213	415.4	259	498.2	305	581.0
168	334.4	214	417.2	260	500.0	306	582.8
169	336.2	215	419.0	261	501.8	307	584.6
170	338.0	216	420.8	262	503.6	308	586.4
171	339.8	217	422.6	263	505.4	309	588.2
172	341.6	218	424.4	264	507.2	310	590.0
173	343.4	219	426.2	265	509.0	311	591.8
174	345.2	220	428.0	266	510.8	312	593.6
175	347.0	221	429.8	267	512.6	313	595.4
176	348.8	222	431.6	268	514.4	314	597.2
177	350.6	223	433.4	269	516.2	315	599.0
178	252.4	224	435.2	270	518.0	316	600.8
179	354.2	225	437.0	271	519.8	317	602.6
180	356.0	226	438.8	272	521.6	318	604.4
181	357.8	227	440.6	273	523.4	319	606.2
182	359.6	228	442.4	274	525.2	320	608.0

TABLE VIII.

French weights and measures.

French.	English.
Milligramme	.0154 grains.
Centigramme	.1543 ,,
Decigramme	1.5434 ,,
Gramme	15.4336 ,,

Kilogramme . . . . 15433.6 grains.
= 2.679 lbs. Troy.
= 2.205 lbs. Avoirdupoids.

	English inches.
Millimètre	.03937
Centimètre	.39371
Decimètre	3.93710
Mètre	39.37100
Decamètre	393.71000
Hectomètre	3937.10000
Kilomètre	39371.
Myriamètre	393710.

ALPHABETICAL INDEX.

ERRATA.

Page 54, line 18, *for* re-solution *read* decomposition.
91, — 2 from bottom, *for* carbonate *read* chromate.
95, — 16, *for* aq. *read* 2 aq.
117, line 24, *for* 2 aq. *read* aq.
126, — 8, *for* 55450 *read* 50550.
138, — 18, *for* paratartaric *read* tartaric.
149, — 3, *for* 505 *read* 5.05.
161, — 12, *for* zinc *read* lime.
168, — 2, *for* b. *read* a.
168, — 11, *for* c. *read* *a*.
206, — 3 from bottom, *put* *a*. at the beginning of line.
212, — 17 from bottom, *for* 1784 *read* 1844.
221, — 7 from bottom, *for* e. read c.
251, — 4 from bottom, *for* magnesia *read* manganese.
264, — 7 from bottom, *for* silica *read* silicon; and *for* hydrochloric *read* hydrofluoric.
283, — 16 from the bottom, *for* which must not lose the slight, *read* must not acquire the slightest.
296, — 6, *for* strontia *read* alumina.
312, — 4 and 5, *add* ($Co_2\ Cy_6$, 3 K.)
313, — 9, *for* 3 KO *read* 3 K.
321, — 8 from bottom, *for* 297 *read* 2.97.
548, — 7, *for* 72 *read* 71.
553, — 16, *for* litharge *read* sulphuret of lead.
601, — 8, *for* 200.90 *read* 200.00.
9, *for* 284.38 *read* 284.88.
605, — 4, *for* 9.34994 *read* 0.34994.
8, *for* 6.65102 *read* 6.05102.
607, — 12, *for* .098917 *read* 0.98917.
14, *for* 2.80325 *read* 2.10325.

When no name is attached to the degree of the thermometer, it refers invariably to the Fahrenheit scale.

Page 101. The formulæ of the salts of soda, calculated from the atomic weight of sodium = 390.90 are to be corrected as follows, according to the recent determination, by Pelouze, of the atomic weight of this element = 387, 17.

$Na\,O$ = 387.17 . . . . 43.64
$S\,O^3$ = 500.00 . . . . 56.36
887.17 100.00

Page 102.
$Na\,O$ = 387.17 . . . . 36.44
$N\,O_5$ = 675.25 . . . . 63.56
1062.42 100.00

Page 103.
Na = 287.17 . . . . 39.32
Cl = 443.20 60,68
730.37 100.00

$Na\,O$ = 387.17 . . . . 58.47
$C\,O_2$ = 275.00 . . . . 41.53
662.17 100.00

London, Princes Street, Soho,
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