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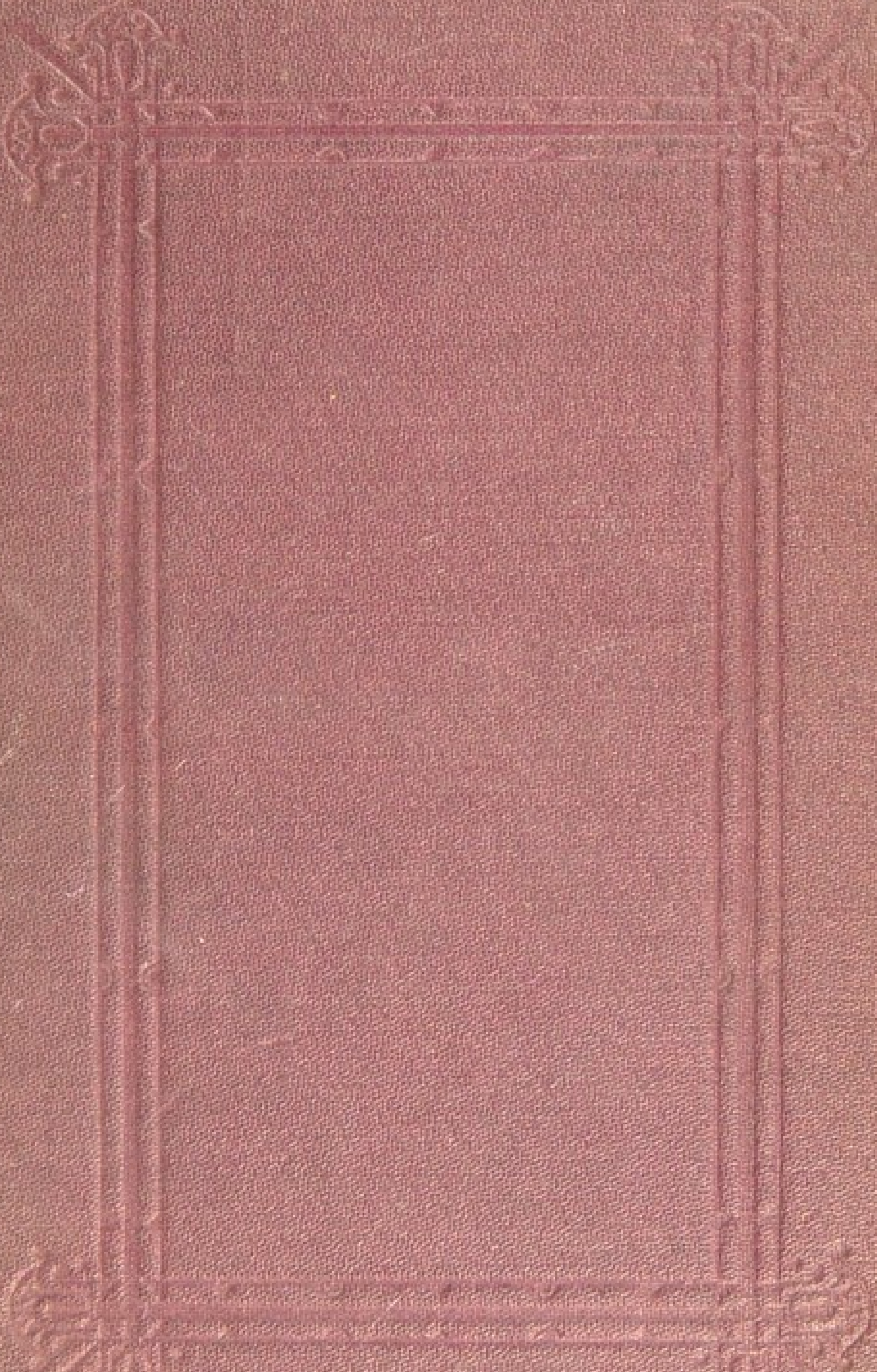

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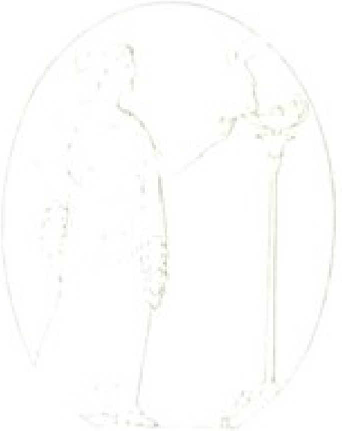

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BY

WM. GEO. VALENTIN, F.C.S.,

PRINCIPAL DEMONSTRATOR OF PRACTICAL CHEMISTRY IN THE ROYAL SCHOOL
OF MINES AND SCIENCE SCHOOLS, SOUTH KENSINGTON.

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PREFACE

TO THE FOURTH EDITION.

A NEW Edition of my Course of Qualitative Chemical Analysis having become necessary, within two years from the appearance of the last Edition, I have again been guided in the changes which I have made by the experience gained, during the last six years, of its working with large Laboratory Classes. The Plan of the Book has been left undisturbed. The few alterations and additions which the more recent progress in Chemical Analysis rendered necessary, have been carefully executed; and the original purpose strictly kept in view, for which the Book was written, viz., to serve as an Elementary Text-book for large Laboratory Classes.

The notation employed throughout is that of Dr. Frankland. An experience extending now over a number of years, and gained with students of very varying abilities, has shown me that this notation greatly facilitates the teaching. It complies with the doctrine of Atomicity, which may now be said to have struck firm root in Chemical Literature, and the Chemical Formulæ of Inorganic as well as Organic Bodies, will be found expressed in accordance with this comprehensive and elegant Law.

The study of Chemical Analysis, when properly conducted, introduces the student to a vast number of changes, the verification of which requires, in no mean degree, the cultivation of habits of close observation and exact reasoning; and as a means of mental training, Chemical Analysis cannot fail to acquire a foremost place in the Curriculum of a Liberal Education.

The methods which I selected in this work have stood the test of many years' practice under my own eyes. They are, I believe, well adapted for promoting accurate and expeditious work. Students who apply themselves steadfastly to the study of analysis, usually get through the course in about six months, and have time left to gain some practice also in Quantitative Analysis, during their first year's study. The foundation for this latter branch of Chemistry having been laid by the Qualitative Course, they have, in most cases, only to acquire the necessary manipulatory skill to conduct quantitative operations successfully.

The reactions of the Rare Metals have been treated somewhat more fully than usual, in an Appendix. The individuality of the metals as well as the classification which nature itself has traced out for them, have been retained as much as possible. I trust that the additions made in this New Edition will increase the usefulness of the Book and will gain for it many new friends.

The Analytical Tables are published also in a separate and all but indestructible form, printed on Messrs. De la Rue's parchment paper.

SCIENCE SCHOOLS,
SOUTH KENSINGTON,
September 30th, 1876.

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A COURSE
OF
QUALITATIVE CHEMICAL ANALYSIS.

Chapter I.

DEFINITION OF QUALITATIVE ANALYSIS. — REAGENTS. — CHEMICAL OPERATIONS. — GROUP-REAGENTS AND SPECIAL REAGENTS.

Chemical analysis consists in the performance of certain experiments:—with the object of putting, so to speak, certain questions to a substance, in order to ascertain the presence or absence of certain bodies. It is termed *qualitative* analysis, if the answer which is received reveals merely *what kind* of matter is present (from *qualis*), without regard to quantity. It is essential that these questions should not be put at random, but according to a well-considered systematic order; and that the answers should be interpreted correctly.

There exists a resemblance between certain elementary as well as certain compound bodies; at the same time the metallic, like the non-metallic elements, bear the stamp of a marked individuality which renders every classification, from whatever point of view we attempt it, more or less difficult—a difficulty which extends likewise to the various compounds which the elements form. Thus silver, which is classified with the monad metals potassium and sodium, differs in a marked manner from the alkali metals. Iron, which exists in the dyad form in $\mathbf{Fe}Cl_2$ (ferrous chloride), and in the tetrad condition in $\left\{\begin{array}{l}\mathbf{Fe}Cl_3\\ \mathbf{Fe}Cl_3\end{array}\right.$ (ferric chloride), partakes in the dyad form of the character of the isomorphous diatomic metals of the magnesium group, *e.g.*, manganese and zinc, and resembles in the tetrad form aluminium and chromium. Copper, which in its cupric compounds offers certain points of resemblance to the magnesium group, resembles also in many respects the metals of the mercury group;* the general composition of the cuprous and mercurous and the cupric and mercuric oxides and chlorides being the same. Inorganic (as well as organic) compound bodies bear, for the most part, the impress of the elementary bodies which enter into their composition; and compounds built up of elements which have equal numbers of bonds, frequently show a certain analogy in their structure as well as a considerable similarity in their reactions. In studying the chemical changes to which the various bodies—elementary or compound—can be submitted, our attention must be mainly directed towards discovering and defining this similarity and dissimilarity.

---

* H. Wurtz, Leçons de Philosophie chimique, p. 170.

We employ *reagents* as the means of producing chemical changes. By reagents are meant bodies—either elementary or compound—which are capable of *reacting* upon and revealing to us the nature of the substances under examination. They are usually divided, without any strict line of demarcation, into two classes, viz., *general* and *special reagents*. General reagents are those which separate a number of substances—groups in fact—at one operation; and special reagents those which are used to a limited extent only, and for the detection of *individual* substances.

In a laboratory the general reagents are most conveniently arranged over the working table within reach of each operator; whilst the special reagents intended for the use of a number of chemical students, are usually placed in a freely accessible part of the laboratory.

A list of reagents, as well as directions for their preparation, will be found in an Appendix. Chemical students who have not the advantage of working in a well-appointed laboratory, should devote much attention and care to the preparation of the reagents.

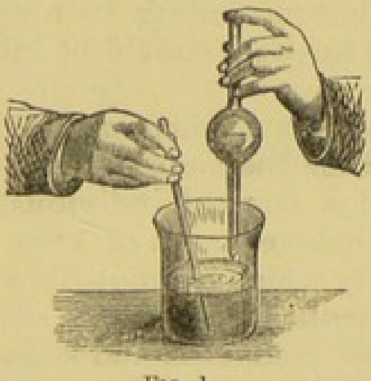

FIG. 1.

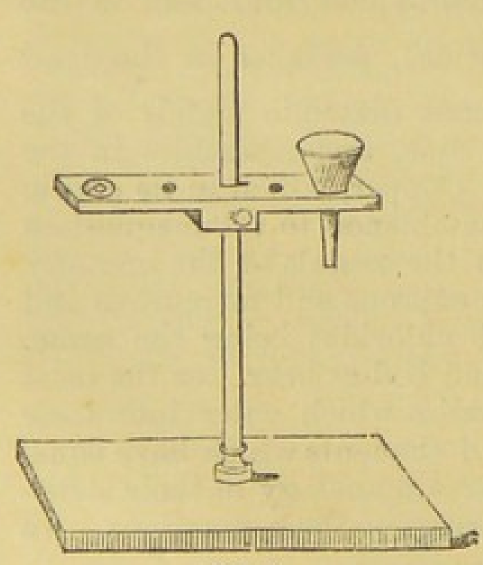

FIG. 2.

Chemical Operations.—We add a **reagent** to a solution of an unknown body either by pouring it directly from the bottle or by running it from a pipette, as shown in Fig. 1, with the view of producing a **precipitate,** *i.e.*, of converting the body from the soluble to the insoluble state. The reaction which takes place is mostly *a change by double decomposition*. Sometimes a precipitation is produced by voltaic action, sometimes merely by the substitution of one solvent for another. One or more bodies may be precipitated by one and the same reagent. As most precipitates are heavier than the liquid in which they are suspended, they fall to the bottom with more or less rapidity; and the supernatant liquid may often be poured off or **decanted,** without much disturbing the precipitate. This mode of separating fluids from precipitates is by far the most expeditious, and should be resorted to whenever it is applicable. The precipitate may be washed in the vessel itself by treatment with hot water and repeated decantation.

When a large quantity of a fluid has to be removed from a precipitate, it is best to **siphon** off the supernatant fluid. The precipitate may be washed with water, and the wash-water siphoned off repeatedly.

Small quantities of a precipitate which do not subside readily are more quickly separated by **filtration.** For this purpose

funnels are used, mostly of glass, conical in shape, and inclined at an angle of 60°. They may be conveniently supported on a wooden stand, Fig. 2, or an iron or brass **filtering stand** as seen in Fig. 3. The **filtering paper** should be porous and unsized, and cut in the form of a round sheet, which by being folded twice in the shape of a quadrant, forms, on opening up, a paper cone, at an angle of 60°. The **filter** should exactly fit the funnel, without reaching quite to the rim, and should be moistened in the funnel with distilled water before any liquid is poured through it. As most kinds of filtering paper contain traces of iron, lime, silica, etc.,—with the exception of the so-called Swedish filtering paper, which contains scarcely perceptible traces of mineral substances,—acid liquids frequently dissolve out traces of these bodies. In all accurate analyses the filtering paper should, on this account, be washed first with dilute hydrochloric or nitric acid, and then with hot water, before being used; or else Swedish filter paper only should be employed.

Most precipitates retain with great pertinacity traces of the fluid in which they were suspended, and it is therefore of the utmost importance to thoroughly wash them in order to obtain accurate results. For this purpose a **wash-bottle** (Fig. 3) is employed, whereby a fine jet of hot or cold distilled water can be directed on to the filter in such a manner as to loosen and detach the precipitate from the paper. The liquid should at no time quite fill the filter, as some precipitates have a tendency to creep up and to get between the paper and the glass, and are carried into the **filtrate.** This would entail repeated filtration. The washing of a precipitate on the filter is effected most rapidly by allowing the wash-water to run off entirely each time before adding fresh quantities of distilled water. By repeating this four or five times, most precipitates will be found sufficiently washed for qualitative purposes.

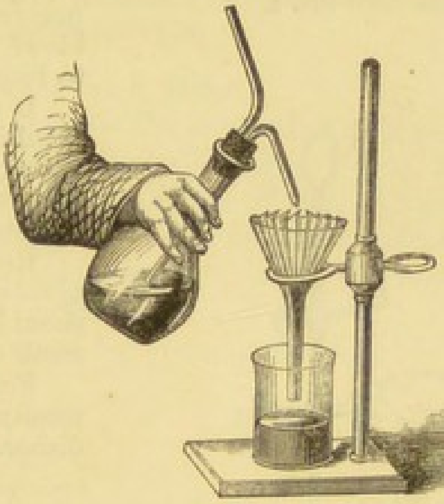
FIG. 3.

The student should guard himself against using too large a quantity of the substance which he wishes to examine. Heavy precipitates entail much washing, an operation which is most tedious and yet indispensable.

Test-tubes answer the purpose of precipitation and separation in qualitative analysis, especially as there is generally no need for collecting the wash-water

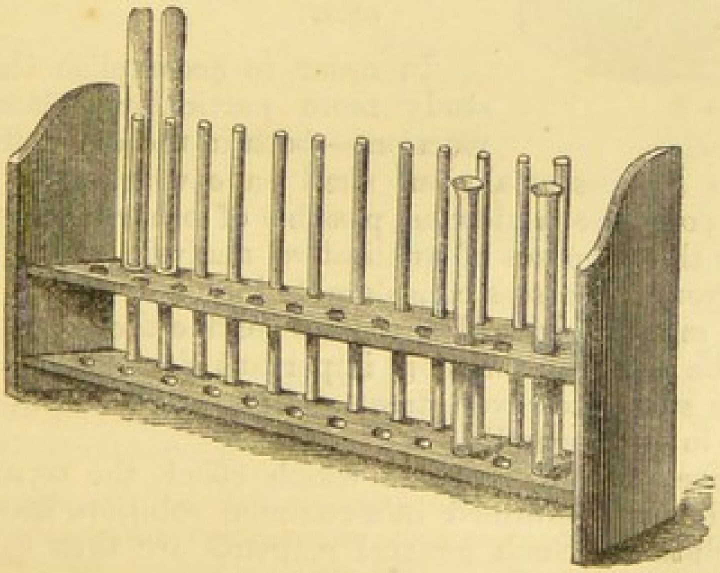
FIG. 4.

or adding it to the main filtrate. These tubes are conveniently placed in a **test-tube stand** (Fig. 4). After being well cleansed by the aid of a test-tube brush, and rinsed out with distilled water, they should be set aside to drain in a basket.

Beakers are sometimes employed if an analysis involves the separation of a small quantity of one substance from a large amount of another, and when, of necessity, large quantities of the substance must be operated upon.

Porcelain dishes are employed for the purpose of concentration, or evaporation and ignition. They can be heated either by means of a **spirit lamp** (Fig. 5), or a so-called **Berzelius lamp** (Fig. 6), or, where coal-gas can be procured, by means of a **Bunsen gas lamp,** provided with a rose top. Sometimes a sheet of iron wire gauze or a sand-bath is interposed between the porcelain vessel and the gas flame, and is supported on a retort ring, or tripod stand. Illustrations of convenient tripod supports for porcelain and glass vessels, which prevent at the same time the flame from being blown about, have been given in my Introduction to Inorganic Chemistry.

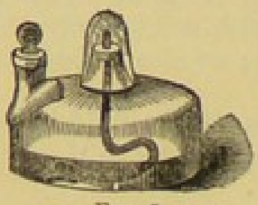

FIG. 5.

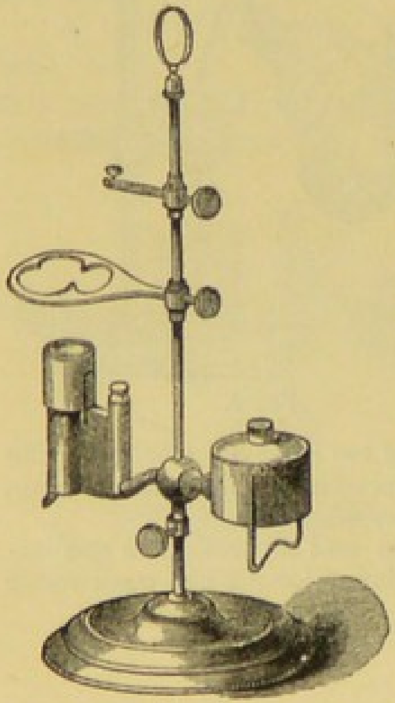

FIG. 6.

If solid substances have to be examined, they should always be **powdered** in a **mortar**—an agate mortar should be employed for hard substances, such as minerals—before being dissolved in water, acids, &c.

Reactions involving the use of valuable reagents—such as salts of gold, platinum, silver—should be performed on **watch-glasses,** with small quantities of the substance only.

For the **ignition** of precipitates we employ mostly porcelain crucibles, or small porcelain dishes.

A knowledge of qualitative analysis enables us—

1. *To recognise with speed and certainty the presence of various elementary and compound bodies.*
2. *To effect their separation from each other.*

In order to accomplish this we shall study more particularly those chemical reactions—both in the dry and in the wet way—which are essential; but shall endeavour, at the same time, to give as complete a view as possible of other chemical changes which serve the purposes of qualitative analysis, and which on this and other grounds possess considerable interest.

It is for many reasons desirable to confine the laboratory course at first to the study of the more important elements and their compounds; we shall, however, treat of the rarer elements and their compounds in an Appendix.

There are certain reagents which effect the separation of a number of bodies contained in a common solution, leaving all the others in solution. Such general reagents are then called *group-reagents.*

Dissolve in water small quantities of
Argentic nitrate*
Cupric nitrate.
Cobaltic „
Baric „
Potassic „

To the solution add—

HCl, a *white curdy* precipitate is obtained, which consists of **argentic chloride**, AgCl; filter. To the filtrate add—

SH_2, a *black* precipitate is obtained consisting of **cupric sulphide**, CuS; filter again, and to the filtrate add—

AmCl, AmHo, and SAm_2 } A *black* precipitate comes down consisting of **cobaltous sulphide**, CoS; filter, and to the filtrate add—

$COAmo_2$, a white precipitate is obtained, consisting of **baric carbonate**, COBao″; filter, evaporate the filtrate and ignite to drive off the ammonic salts. A white saline residue is left, containing the **potassic salt**.

What were the chemical changes that took place?

The changes were evidently produced *by the mutual exchange of elements in two bodies* (changes by *double decomposition*): *i.e.*, the hydrochloric acid added in Group I to the solution of the metallic nitrates, exchanged its hydrogen for the silver of the argentic nitrate; and the sulphuretted hydrogen exchanged its hydrogen for the metal copper, leaving nitric acid and cupric sulphide, etc.

The reactions will be readily expressed by equations, thus :—

NO_2Ago	+	HCl	=	AgCl	+	NO_2Ho.
Argentic nitrate.				Argentic chloride.		
$\begin{matrix}NO_2\\NO_2\end{matrix}Cuo''$	+	SH_2	=	CuS†	+	$2NO_2Ho$.
Cupric nitrate.				Cupric sulphide.		
$\begin{matrix}NO_2\\NO_2\end{matrix}Coo''$	+	SAm_2	=	CoS	+	$2NO_2Amo$.
Cobaltous nitrate.				Cobaltous sulphide.		
$\begin{matrix}NO_2\\NO_2\end{matrix}Bao''$	+	$COAmo_2$	=	COBao″	+	$2NO_2AmO$.
Baric nitrate.				Baric carbonate.		

Silver, copper, cobalt, and potassium are, however, not the only metals which might have been separated by these same reagents.

The table on the next following page exhibits the five groups into which all metallic bodies classify themselves on the addition of the several group-reagents.

---

* Solutions of salts of the different metals containing five milligrammes of the metal in a cubic centimetre are conveniently prepared and kept for use.

† It is immaterial whether we write SCu or CuS, since both sulphur and copper are dyad elements.

ANALYTICAL CLASSIFICATION OF THE METALS,

WITH THEIR RESPECTIVE GROUP-REAGENTS.

GROUP I. Hydrochloric Acid.	GROUP II. Sulphuretted Hydrogen, in acid solutions.	GROUP III. Ammonic Chloride, Ammonia, and Ammonic Sulphide.	GROUP IV. Ammonic Chloride, Ammonia, and Ammonic Carbonate.	GROUP V. (No group-reagent.)
Lead.... as $\mathbf{PbCl_2}$.*	Mercury...... as $\mathbf{HgS}$, *black.*	(1.) **Hydrates.**	Barium as $\mathbf{COBao''}$.	**In solution:**
Silver .. ,, $AgCl$.	Lead .... ,, $\mathbf{PbS}$,‡ ,,	Aluminium.. as $\mathbf{Al_2Ho_6}$.	Strontium ,, $\mathbf{COSro''}$.	Magnesium.
Mercury ,, $\mathbf{Hg_2Cl_2}$.†	Bismuth...... ,, $\mathbf{Bi_2S_3}$,,	Chromium .. ,, $\mathbf{Cr_2Ho_6}$, *green.*	Calcium ,, $\mathbf{COCao''}$.	Potassium.
	Copper ...... ,, $\mathbf{CuS}$, ,,			Sodium.
	Cadmium .... ,, $\mathbf{CdS}$, *yellow.*	(2.) **Sulphides.**		Ammonium.
	Tin (Stannosum) ,, $\mathbf{SnS}$, *black.*	Iron........ as $\mathbf{FeS}$, *black.*		
	,, (Stannicum) ,, $\mathbf{SnS_2}$, *yellow.*	Zinc........ ,, $\mathbf{ZnS}$, *white.*		
	Antimony .... ,, $\mathbf{Sb_2S_3}$, *orange.*	Manganese .. ,, $\mathbf{MnS}$, *buff.*		
	Arsenic........ ,, $\mathbf{As_2S_3}$, *yellow.*	Nickel...... ,, $\mathbf{NiS}$, *black.*		
	Gold.......... ,, $\mathbf{Au_2S_3}$, *black.*	Cobalt...... ,, $\mathbf{CoS}$, ,,		
	Platinum...... ,, $\mathbf{PtS_2}$, ,,	(3.) **Certain Salts,**		
		such as alkaline earthy phosphates, &c., &c.		

---

* When no colour is stated, the precipitate is *white.*

† Precipitated as mercurous chloride from mercurous salts.

‡ Lead being somewhat soluble in cold water in the form of plumbic chloride, $\mathbf{PbCl_2}$, occurs both in the first and second group.

Thus far *group*-reagents assist us in separating bodies, but when, as in Group IV, the white precipitate produced by the group-reagent, $\mathbf{C}OAmo_2$, leaves us still in doubt whether a barium, strontium, or calcium compound was present in the solution, further experiments must evidently be made with a view of completely identifying the substance under examination. This the student will only be able to do by making himself first practically familiar with the different changes or reactions which the members of the various groups of metals can be made to undergo: and after understanding the use of the group-reagents, he should direct his attention to the special reactions *which distinguish and separate one metal from another, or from several others.* This may frequently be done in more than one way; one reaction, however, as a rule, deserves the preference over others, on account of the greater exactness which distinguishes it, or on account of increased facility of execution, or of both.

Certain reactions, lastly, will have to be studied, which are not directly available for the separation of the members of a group from each other, but to which considerable interest is attached as being illustrative of some valuable property or other of the metals.

The tabular form, which is, no doubt, the most compact and summary mode of arranging chemical reactions, will often be adopted for embodying such reliable and expeditious methods of separation as have stood the test of experience in the laboratory. The directions given will be concise and divested of all explanatory matter. On no account should a student use any tabular directions, however, without first having made himself practically acquainted with the details of the reactions; and to counteract any pernicious influence which the use of tables might have, the student should learn to draw up tables for the several other processes of separation which are frequently possible.

A deviation from the natural course of studying the reactions of the metals by beginning with Group I, and so on, will be justified on the ground of greater simplicity, and on account of the far greater importance which is attached to the metals of Group V, especially the alkali metals. Experience has shown that students have less difficulty in mastering the reactions by reversing the order of the groups, beginning with the study of the alkali and alkaline-earthy metals; and that a thorough knowledge of the metals of these groups is of material assistance in understanding the qualitative changes to which the metals proper are subjected.

The chemical nomenclature employed in this work is that of Dr. Frankland. It will be found fully explained in my Introduction to Inorganic Chemistry. An experience extending now over several years has shown that it is readily mastered and greatly appreciated by students. It is both comprehensive and logical, for it does not require one kind of formulæ for inorganic and another for organic bodies, and it complies with the law of atomicity, observed for the different elementary bodies. The little o employed by Dr. Frankland in writing the different compound basilous radicals, such as Ho, Ko, Bao'', Bio''', Al_2o^{vi}, etc., has tended occasionally to mislead beginners. It will be found useful in all such cases to practise writing these same radicals with a big O, and using the bracket, with the atomicity indication placed outside the bracket, thus:—(OH), (OK), $(O_2Ba)''$, $(O_3Bi)'''$, $(O_6Al_2)^{vi}$. We shall employ these formulæ occasionally. Students have as a rule no difficulty in transcribing constitutional into empirical formulæ, a practice which may precede with advantage percentage calculations.

CHAPTER II.

REACTIONS OF THE METALS OF GROUP V.

THIS group comprises the metals POTASSIUM, SODIUM, AMMONIUM, and MAGNESIUM, which are not precipitated by any group-reagent.

1. POTASSIUM, K.

Atomic weight 39·1.—Occurs in nature only in a few minerals, of which *nitre* or *saltpetre* is the most important. Potassium is present in larger or smaller quantities in a few silicates and sulphates, such as *felspar*, *alumstone*. It is also found in the ashes of plants (*crude potashes*), and in the form of chloride in saline deposits (at Stassfurth, in Prussia, and elsewhere).

REACTIONS IN THE DRY WAY.

Most potassium compounds, when heated in small quantities on a thin platinum wire in the inner flame of the blowpipe, undergo dissociation, the vapour of the metal imparting a **violet colour** to the outer flame. When examined with the aid of a spectroscope,*

* When elements in the gaseous condition, or vaporised by strong ignition, are analysed by means of the spectroscope (for a description of which we refer the student to *Roscoe* or *Schellen* on the Spectroscope), they may be distinguished from each other by the respective spectra which they give. The intensity of the spectra of metallic elements is so much greater than that of the non-metals, that the latter are only rarely seen. The heat which can be produced by a good Bunsen gas burner is not strong enough to volatilize all elements, or to heat their vapour highly enough. Most heavy metals can only be volatilized by means of an electric spark, making use of an induction coil, by placing the galvanically precipitated metals between the electrodes. In order to analyse the ordinary gases spectroscopically, the spark is passed through the gases confined in Geissler tubes.

It is usual to employ the spectroscope only for the examination of those metals, or metallic compounds, which can be volatilized by means of the gas flame from a good Bunsen burner, such as the alkali metals, sodium, potassium, rubidium, caesium, lithium; the alkaline earthy metals, barium, strontium, calcium; and the heavy metals, thallium and indium. The compounds most suitable are the chlorides, nitrates, chlorates, perchlorates, and carbonates of these metals. A small portion is placed on the loop of a thin platinum wire, introduced into the non-luminous portion of the flame, and the spectrum the potassium spectrum is found to consist mainly of two lines, a comparatively strong line, Kα, in the RED, and a faint line, Kβ, in the BLUE.

This applies more particularly to potassic salts which are volatile without decomposition at a very strong heat (such as potassic chloride, bromide, iodide, and cyanide) or which are decomposed by heat; but not to non-volatile potassic salts, such as phosphates, silicates, or borates, which give scarcely any flame reaction till they are moistened with HCl, or, if HCl be without action, heated together with pure calcic sulphate. The presence of sodium compounds gives rise to an intense *golden-yellow* flame, and conceals the potassium reaction; but when seen through a blue glass, or indigo-prism, the yellow or sodium flame is entirely cut off, and the potassium flame becomes distinctly visible, and is then of a *rich reddish-violet* colour.

REACTIONS IN THE WET WAY.

WE EMPLOY A SOLUTION OF POTASSIC CHLORIDE, KCl.

$PtCl_4$ (**platinic chloride**) precipitates from potassic solutions which are not too dilute, a *yellow crystalline* precipitate of **potassic platinic chloride**, $2KCl,PtCl_4$, insoluble† in strong alcohol, or better still in alcohol and ether, as well as in acids.

$\left\{\begin{array}{l}COHo\\CHHo\\CHHo\\COHo\end{array}\right.$ (**tartaric acid**) precipitates *white crystalline* **hydric potassic tartrate,** $\left\{\begin{array}{l}COKo\\CHHo\\CHHo\\COHo\end{array}\right.$, from neutral and sufficiently concentrated solutions. The precipitate settles rapidly, especially on shaking or stirring.

$2HF, SiF_4$ (**hydrofluosilicic acid**) gives a *white gelatinous* precipitate of **potassic silicofluoride,** $2KF,SiF_4$; difficultly soluble in water (833 parts at 17·5° C.); insoluble in alcohol.

Potassic salts are for the most part soluble in water, hence so few reactions; the hydrate and carbonate constitute two important reagents, on account of the great affinity which the powerful base potassa possesses for the acids with which the metals of other groups may be combined.

2. **SODIUM,** Na. Atomic weight 23.—Occurs in nature in vast masses, as *rock salt*, NaCl; as CARBONATE, in *native soda*, $CONao_2, 10OH_2$, and in *trona*, $CONao_2,2COHoNao,3OH_2$; as NITRATE, in *cubic*

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examined. The different elements are distinguishable by their respective colours, as well as by the position which their lines occupy in the continuous solar spectrum. The lines are not at all of the same intensity, and therefore not equally available.

It is only by employing larger quantities of pure substances, and heating them very intensely, that many of the less prominent lines can be observed. The accuracy of the reactions is, however, so great that we can discover in this manner the merest traces of these elements, and are enabled to disentangle mixtures thereof, without actual separation. Spectroscopic analysis constitutes in fact, a most valuable auxiliary to chemical analysis.

† The degree of solubility of a precipitate in different media can only be ascertained by laborious *quantitative* experiments. The student will therefore be expected to verify only those statements respecting the solubility of the precipitates which require no quantitative knowledge.

nitre, or *Chili saltpetre*, $\mathbf{N}O_2Nao$; as SULPHATE or *glauber salt*, $\mathbf{S}O_2Nao_2, 10\mathbf{O}H_2$; as *biborate*, $\mathbf{B}_4O_5Nao_2,10\mathbf{O}H_2$; as *glauberite*, $\mathbf{S}_2O_4Nao_2Cao''$, and as *cryolite*, $6NaF,\mathbf{Al}_2F_6$, and in many SILICATES, of which *albite* may be taken as the representative. All natural sodium compounds, with the exception of the last two minerals, are soluble in water.

REACTIONS IN THE DRY WAY.

We almost exclusively rely for the detection of sodium upon the characteristic colour—an intense **golden-yellow**—which its compounds impart to the outer flame of the blowpipe. Its spectrum consists of one bright double line, coinciding with the D line of the solar spectrum. Some sodic salts are readily recognised by their characteristic taste, especially rock salt and cubic nitre.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF SODIC CHLORIDE, NaCl.

Sodic salts are even more freely soluble than potassic salts, and platinic chloride or tartaric acid give no precipitates. Hydrofluosilicic acid gives a gelatinous precipitate from concentrated (aqueous) solutions only; the precipitate is, however, insoluble in alcohol.

$\mathbf{Sb}O_2Ko$ (**potassic metantimonate**) produces a *white crystalline* precipitate of **sodic metantimonate** from neutral or slightly alkaline solutions, if they are not too dilute. The precipitate is insoluble in alcohol. (The solution to be tested should only contain alkali metals.)

Sodic hydrate and sodic carbonate act in every respect like potassic hydrate and carbonate. Pure sodic hydrate is now prepared from the metal sodium, and deserves the preference over potassic hydrate.*

3. AMMONIUM.—Am = NH_4. Atomic weight, 18.—

REACTIONS IN THE DRY WAY.

Ammonic salts, when heated in a test-tube, **volatilize**, either entirely or partially. Salts with fixed acids, such as phosphoric acid, lose ammonia, $\mathbf{N}H_3$. Salts of ammonium with volatile acids can be volatilised, either with decomposition, such as the nitrate, nitrite, sulphate, the latter with formation of mixed vapour of nitrogen, water, ammonia, and sulphurous anhydride; or without decomposition, such as the cyanide; or partial dissociation only, such as the chloride, bromide, iodide: the latter salts condense again, for the most part unchanged; they *sublime*, and are found in the upper part of the test-tube.

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* The student who has not the advantage of attending a course of lectures on chemistry should make himself familiar, by reading a good Manual of Chemistry, with the properties of the various salts of potassium and sodium, also with the interesting processes of manufacturing sodic carbonate from the chloride; sodic silicate (*water-glass*); potassic chlorate, &c., &c.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF AMMONIC CHLORIDE, AmCl.

$\mathbf{Pt}Cl_4$ produces a *heavy yellow* precipitate of **ammonic platinic chloride**, $2AmCl,\mathbf{Pt}Cl_4$. The precipitate is soluble in much water (hence there appears no precipitate from dilute ammonic solutions), but insoluble in alcohol and ether. Ammonic platinic chloride leaves on ignition only spongy platinum. (DISTINCTION FROM POTASSIC PLATINIC CHLORIDE, which leaves spongy platinum and potassic chloride, $Pt + 2KCl$.)

Tartaric acid produces from a concentrated solution of ammonic chloride a *white crystalline* precipitate of **hydric ammonic tartrate**, resembling the potassium precipitate in its properties. The two precipitates are readily distinguished on ignition. Hydric potassic tartrate leaves a carbonaceous residue, which is strongly alkaline, and the potassic carbonate which it contains dissolves in water. The other leaves merely a residue of carbon, devoid of any alkaline reaction.

Ammonic salts are decomposed, with evolution of ammonia gas, when heated with a hydrate of an alkali (KHo, NaHo), or alkaline earthy metal ($\mathbf{Ba}Ho_2$, $\mathbf{Ca}Ho_2$), thus:—

$$2AmCl + \mathbf{Ca}Ho_2 = 2\mathbf{N}H_3 + \mathbf{Ca}Cl_2 + 2\mathbf{O}H_2.$$

Neutral or normal salts of certain polybasic acids, *e.g.*, well dried alkaline chromates, borates, phosphates, etc., readily decompose ammonic salts, especially when heated, with evolution of ammonia gas, and formation of acid salts, thus:—

$$2\mathbf{Cr}O_2Ko_2 + 2AmCl = \left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right. + 2\mathbf{N}H_3 + 2KCl + \mathbf{O}H_2.$$

This reaction enables us, therefore, to distinguish between *normal* and *acid* salts of polybasic acids, by heating them with ammonic chloride.

Ammonia gas is readily recognised, 1st, by *its pungent odour;* 2nd, by *its turning red litmus paper*, moistened with a drop of distilled water, *blue;* 3rd, by *its combining with the vapour of volatile acids* (such as *dilute* hydrochloric acid) to form white fumes (AmCl).

Nessler's test* for *traces* of ammonia.—If a potassic solution of potassic mercuric iodide, $2KI,\mathbf{Hg}I_2$, be added to a fluid containing mere traces of ammonia or of an ammonic salt, a *brown* precipitate of dimercurammonic iodide, or a *yellow to brown coloration* is produced, according to the quantity of the ammonium compound present—

$$2(2KI,\mathbf{Hg}I_2) + 3KHo + \mathbf{N}H_4Ho = \underset{\text{Brown pp.}}{\mathbf{N}Hg''_2I,\mathbf{O}H_2} + 7KI + 3\mathbf{O}H_2.$$

Ammonic hydrate and carbonate, as well as various other ammonium compounds, *e.g.*, ammonic chloride, ammonic sulphide, are among the most useful reagents which we possess.

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* For the preparation of Nessler's solution, see Appendix.

QUESTIONS AND EXERCISES.

1. Mention some natural compounds in which potassium occurs.
2. How are potassium compounds recognised in the wet way?
3. How can potassium and sodium compounds be distinguished before the blowpipe flame?
4. State how you would ascertain whether the yellow precipitate produced by platinic chloride indicates the presence of a salt of ammonium or potassium, or of both.
5. How can hydric potassic tartrate be distinguished from hydric ammonic tartrate?
6. How can sodium compounds be recognised in the wet way?
7. Which sodic salts are found native?
8. What changes do the following ammonic salts undergo upon ignition:—ammonic chloride, ammonic nitrate, ammonic nitrite, ammonic phosphate, $\mathbf{P}\mathrm{OAmo}_3$, ammonic carbonate, $\mathbf{C}\mathrm{OAmo}_2$, ammonic iodide, and ammonic sulphate?
9. How is spongy platinum prepared?
10. How would you test for mere traces of ammonia?
11. How much spongy platinum is obtained from 2·345 grms. of ammonic platinic chloride?
12. How much dry ammonia gas by volume (litres) and weight can be obtained by distillation with calcic hydrate from 5 grms. of ammonic chloride?
13. How would you examine a mixture containing ammonic chloride and potassic chloride?
14. 2 grms. of the mixed chlorides of potassium and sodium gave by precipitation with platinic chloride 3·671 grms. of potassic platinic chloride, $2\mathrm{KCl},\mathbf{Pt}\mathrm{Cl}_4$; what is the percentage of potassium and sodium in the mixed chlorides?
15. A mixture of 1·5 grm. of sodic and ammonic chloride lost on ignition ·234 grm.; what is the percentage of ammonic and sodic chloride present in the mixture?
16. Calculate the percentage composition of borax.

4. **MAGNESIUM**, Mg''. Atomic weight, 24.—Occurs in nature as OXIDE, in the mineral *periclase*, $\mathbf{Mg}\mathrm{O}$; as HYDRATE in *brucite*, $\mathbf{Mg}\mathrm{Ho}_2$; as CARBONATE, in *magnesite*, $\mathbf{C}\mathrm{OMgo''}$, and in *hydromagnesite*, $\mathbf{C}_3\mathrm{OHo_2Mgo''_4},3\mathbf{O}\mathrm{H}_2$; as DOUBLE CARBONATE, in *dolomite*, $\begin{matrix}\mathbf{C}\mathrm{O}\\ \mathbf{C}\mathrm{O}\end{matrix}\mathrm{Cao''Mgo''}$, and *mesitine spar*, $\begin{matrix}\mathbf{C}\mathrm{O}\\ \mathbf{C}\mathrm{O}\end{matrix}\mathrm{Mgo''Feo''}$; as SULPHATE, in *kieserite*, $\mathbf{S}\mathrm{OHo_2Mgo''}$ (from Stassfurth salt), and in *epsomite*, $\mathbf{S}\mathrm{OHo_2Mgo''},6\mathbf{O}\mathrm{H}_2$; as PHOSPHATE, in *wagnerite*, $\mathbf{P}\mathrm{OMgo''}\left(\begin{matrix}\mathrm{O}\\ \mathrm{F}\end{matrix}\mathrm{Mg''}\right)$; as SILICATE, in *peridote*, $\mathbf{Si}\mathrm{Mgo''_2}$, *enstatite*, $\mathbf{Si}\mathrm{OMgo''}$, *steatite*, $\mathbf{Si}_4\mathrm{O_5Mgo''_3}$, *talc*, $\mathbf{Si}_5\mathrm{O_6Mgo''_4}$, *serpentine*, $\begin{matrix}\mathbf{Si}\mathrm{HoMgo''}\\ \mathbf{Si}\mathrm{HoMgo''}\end{matrix}\mathrm{Mgo''}$, *meerschaum*, $\mathbf{Si}_3\mathrm{O_2Ho_4Mgo''_2}$, and in *diopside*, $\begin{matrix}\mathbf{Si}\mathrm{O}\\ \mathbf{Si}\mathrm{O}\end{matrix}\mathrm{Cao''Mgo''}$; and lastly, as BORATE in *boracite*, $\mathbf{B}_8\mathrm{O_9Mgo''_3}$.

REACTIONS IN THE DRY WAY.

Magnesic salts, as such, impart *no* colour to a non-luminous gas-flame. The most characteristic reaction for magnesia, in the dry way, is the *pale rose* colour which this alkaline earth acquires on moistening with cobaltous nitrate, and then igniting it once more strongly on charcoal.

This colour can, however, only be relied on when no other metallic oxides are present; and as magnesium salts do not colour the outer blowpipe flame, recourse must almost invariably be had to the reactions in the wet way. Ignition of the sulphate on charcoal in the reducing flame yields the sulphide, $\mathbf{Mg}S$. Prolonged ignition of the carbonate yields caustic magnesia, which is almost insoluble in water.

REACTIONS IN THE WET WAY.

For this purpose a SOLUTION OF MAGNESIC CHLORIDE, $\mathbf{Mg}Cl_2$, or MAGNESIC SULPHATE, SO_2Mgo'', $(SO_2(O_2Mg)'')$, is employed.

Magnesia is not precipitated by ammonia in the presence of ammonic chloride, because it forms a *soluble double chloride*, $2AmCl,\mathbf{Mg}Cl_2$. In the absence of ammonic chloride, part of the magnesia is precipitated as hydrate, $\mathbf{Mg}Ho_2$, thus—

$$2\mathbf{Mg}Cl_2 + 2AmHo = \mathbf{Mg}Ho_2 + \underbrace{2AmCl,\mathbf{Mg}Cl_2}_{\text{Soluble double chloride.}}$$

In the presence of a sufficient amount of ammonic chloride, the magnesic hydrate is at once decomposed into magnesic chloride ($\mathbf{Mg}Ho_2 + 2AmCl = \mathbf{Mg}Cl_2 + 2AmHo$), and no precipitation takes place, nor is the double chloride precipitated by ammonic, sodic, or potassic carbonate. Hence magnesium cannot be precipitated in Groups III and IV, *provided a sufficient amount of ammonic chloride be present, and the solution be kept sufficiently dilute.*

Potassic, sodic, calcic, and baric hydrate precipitate magnesia almost completely as *white* **magnesic hydrate**, nearly insoluble in cold and hot water. Ammonic chloride, as well as other ammonic salts, dissolve it readily, or, if originally present in sufficient quantities, prevent its formation.

Sulphuric and hydrofluosilicic acid form soluble magnesic salts, even in the presence of moderate quantities of alcohol.

Ammonic oxalate gives, after some time, from moderately dilute solutions of magnesic salts, a *white crystalline* precipitate of a double oxalate of magnesia and ammonia; not so, however, in the presence of excess of ammonic chloride.

$POHoNao_2$ (**hydric disodic phosphate**), or better still, a solution of microcosmic salt, precipitates **hydric magnesic phosphate**, $POHoMgo''$.

The precipitation is complete in the presence of ammonic chloride and ammonia. $POAmoMgo''$, $6Aq$, **ammonic magnesic phosphate**, falls as *a white crystalline* precipitate. The separation from a dilute solution of a magnesic salt is promoted by gentle heat, and by stirring with a glass rod. The precipitate is but slightly soluble in water and ammonic salts. In water containing ammonia it is practically insoluble. Dilute mineral acids dissolve it, as well as acetic acid. From very dilute solutions the precipitate separates only on standing for about 24 hours in a warm place.

On heating magnesic chloride with precipitated mercuric oxide, **the chloride is converted into oxide,** mercuric chloride being volatilized. This experiment must be conducted in a closet which is provided with a good indraught of air, and is in connection with a chimney flue.

Methods for the recognition of Mg, K, Na, and Am will readily suggest themselves, if we bear in mind—

1st. *The volatility of ammonic salts* (phosphates and borates excepted).

2nd *The insolubility of* $MgHo_2$ *in water.*

3rd. *The insolubility of* $2KCl,PtCl_4$ *in alcohol.*

4th The *intense yellow coloration* which sodium imparts to the blowpipe flame.

A solution containing salts of Mg, K, Na, and Am, may be examined as follows:—

1st. Heat a portion with NaHo; ammonia gas is given off, which is recognised by its pungent odour, etc.—**presence of Am.**

2nd. To a second portion add AmCl, AmHo, and $POHoNao_2$, a *white crystalline* precipitate indicates the **presence of Mg.**

3rd. Evaporate a third portion to dryness and ignite strongly. Extract with hot water (without filtering off any magnesic oxy-chloride (Mg_2OCl_2), which may have been formed), and add sufficient $BaHo_2$ till the whole of the magnesia is precipitated as $MgHo_2$; filter. To the filtrate add $COAmo_2$, as long as a precipitate is produced, and filter again. Evaporate the filtrate to dryness, and ignite strongly to expel ammonic salts. Dissolve the residue in a little water, filter off a trace of MgO (if any), and test filtrate for potassium by means of $PtCl_4$; a *yellow crystalline* precipitate—**presence of K**; and for sodium, by heating on a platinum wire before the blowpipe flame; a *golden-yellow flame* indicates the **presence of Na.**

QUESTIONS AND EXERCISES.

1. How is magnesic sulphate prepared—1st from *magnesite*; 2nd, from *dolomite*?
2. Which are the most important magnesium minerals? Give constitutional and graphic formulæ.
3. How is magnesium detected in the dry way?
4. Explain the action which ammonia, potassic hydrate, and sodic carbonate have upon solutions of magnesic salts in the presence of ammonic salts, and also without them.
5. Describe fully the most characteristic reaction for magnesic salts in the wet way.
6. How is magnesic chloride converted into oxide in the dry way?
7. How is magnesium separated from potassium and sodium?
8. Calculate the percentage composition of *magnesite* and *epsomite*.
9. How much crystallized magnesic sulphate, $SOHo_2Mgo'',6OH_2$, can be prepared from one ton of pure *magnesite*?

CHAPTER III.

REACTIONS OF THE METALS OF GROUP IV.

THIS group comprises the metals BARIUM, STRONTIUM, CALCIUM, which are precipitated by ammonic carbonate from an ammoniacal solution in the presence of ammonic chloride. The latter (if present in sufficient quantities) prevents the precipitation of magnesium.

1. **BARIUM**, Ba''. Atomic weight, 137.—Occurs in nature chiefly in the form of *heavy spar*, SO_2Bao'', and as *witherite*, $COBao''$.

REACTIONS IN THE DRY WAY.

Barium compounds, when held in the fusing zone of a Bunsen gas burner, or when heated on thin platinum wire in the inner blowpipe flame, impart a **yellowish-green** colour to the outer flame, especially when treated with strong hydrochloric acid. When viewed through the spectroscope (the chloride* is best employed), two GREEN lines, $Ba\alpha$ and $Ba\beta$, come out most intensely; $Ba\gamma$ is less marked. Besides these, there are numerous lines in the RED and YELLOW, and one broad indistinct line in the BLUE, close to F of the solar spectrum.

Heavy spar heated on charcoal in the reducing flame is reduced to baric sulphide, BaS, which fuses readily. This reaction is made use of to prepare, on a manufacturing scale, soluble baric salts from the sulphate. Baric carbonate is decomposed only triflingly by ignition to a strong white heat.

REACTIONS IN THE WET WAY.

Baric salts are obtained by dissolving the native carbonate or *witherite* in acids.† *Heavy spar* is attacked by alkaline carbonates at a high temperature. By mixing, on a small scale, finely powdered baric sulphate with three to four times its weight of fusion mixture, and heating in a platinum crucible over a gas flame, it is converted into baric carbonate, thus:—

$$SO_2Bao'' + CONaoKo = COBao'' + SO_2NaoKo.$$

Insol. in water. Soluble in water.

On extracting the fused mass with hot water and filtering, $COBao''$ is left, from which, by the addition of the respective acids, small quantities of the different baric salts can be prepared.

The same applies to *celestine*, SO_2Sro'', and to *anhydrite*, SO_2Cao''.

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* The spectra of Ba and of the two following metals are probably those of the *oxides*, and not of the metals themselves.

† Dilute acids (HCl or NO_2Ho) should be employed, as the baric chloride and baric nitrate, which result from the action of these acids upon witherite, are insoluble in the concentrated acids.

A SOLUTION OF BARIC CHLORIDE, $BaCl_2$, is employed.

$COAmo_2$ (**group-reagent**) precipitates *white* **baric carbonate,** $COBao''$, soluble with decomposition in acids; somewhat soluble in ammonic chloride. With carbonic acid it forms a soluble acid carbonate or dihydric dicarbonate, $C_2O_2Ho_2Bao''$, but it is reprecipitated, on boiling, with evolution of carbonic anhydride. Baric carbonate is partially decomposed by alkaline sulphates, *e.g.*, potassic sulphate, into baric sulphate and alkaline carbonate. The decomposition is complete in the presence of free carbonic anhydride. $COSro''$ and $COCao''$ are not changed, not even on boiling with SO_2Ko_2.

$CONao_2$ and $COKo_2$, same precipitate.

KHo and NaHo, free from carbonates and sulphates, which they rarely are, give from highly concentrated solutions a *voluminous* precipitate of **baric hydrate,** $BaHo_2$, soluble in water. A solution of the hydrate in water is known as *baryta-water.* It possesses a strong alkaline reaction, and great affinity for carbonic anhydride.

AmHo gives no precipitate.

SO_2Ho_2, as well as all **soluble sulphates**, precipitate on boiling, especially in the presence of free acid (dilute HCl), *heavy white granular* **baric sulphate,** SO_2Bao'', even from very dilute solutions of baric salts. The precipitate is insoluble in water, dilute acids and alkalies; soluble to a perceptible extent in boiling concentrated hydrochloric and nitric acids and also in concentrated solutions of ammonic salts, but not if the precipitants are in excess; soluble also in concentrated boiling sulphuric acid, with formation of dihydric baric disulphate, $S_2O_4Ho_2Bao''$. The presence of an alkaline citrate greatly interferes with its precipitation. Solutions of strontic or calcic sulphate (two sulphates which are but slightly soluble in water, especially the former) constitute the most delicate test for barium.

SO_2Bao'' is soluble only in about 400,000 parts of pure water; SO_2Sro'' in 7,000 parts of cold water; whilst SO_2Cao'' dissolves in 390 parts of water at 35° C, and in 460 parts at 100° C, being in fact less soluble in hot than in cold water.

$POHoNao_2$ (**hydric disodic phosphate**) gives from neutral or alkaline solutions a *white* precipitate of **hydric baric phosphate,** $POHoBao''$, readily soluble in dilute nitric, hydrochloric or *acetic* acid. Perceptibly soluble in ammonic chloride.

$\left\{\begin{matrix}COAmo\\COAmo\end{matrix}\right.$ (**ammonic oxalate**) gives from a moderately dilute solution of a baric salt, a *white pulverulent* precipitate of **baric oxalate,** $\left\{\begin{matrix}CO\\CO\end{matrix}\right.Bao''$, soluble in dilute nitric or hydrochloric acid. Soluble also in oxalic and acetic acids when freshly precipitated.

CrO_2Ko_2 (**potassic chromate**) gives a bright *lemon-yellow* precipitate of **baric chromate,** CrO_2Bao'', even from very dilute *neutral* or *moderately acid* (acetic acid) solutions, readily soluble in nitric, hydrochloric or chromic acid (CrO_2Ho_2)—reprecipitated by ammonia.—(DISTINCTION FROM STRONTIC AND CALCIC SALTS, WHICH ARE NOT PRECIPITATED FROM DILUTE SOLUTIONS.)

$2HF,SiF_4$ (**hydrofluosilicic acid**) gives a colourless *crystalline* precipitate of **baric silicofluoride,** BaF_2,SiF_4, which subsides quickly, especially upon the addition of an equal bulk of alcohol. It is somewhat soluble in water and in dilute acids, insoluble in alcohol. (DISTINCTION OF BARIC FROM STRONTIC AND CALCIC SALTS, WHICH GIVE NO PRECIPITATE EVEN ON THE ADDITION OF ALCOHOL.)

Soluble baric salts, such as baric chloride, nitrate or acetate, constitute exceedingly useful reagents for the detection of acids, on account of the metal barium forming insoluble salts with most acids.

QUESTIONS AND EXERCISES.

1. How can baric sulphate be converted into baric nitrate or chloride?
2. Which are the natural compounds of barium?
3. Express in symbolic equations the different reactions for barium.
4. Which are the most delicate reactions for barium?
5. How can barium be separated from strontium and calcium?
6. 1·235 grm. of *witherite* give ·965 grm. of baric sulphate; what is the percentage of barium and of baric carbonate in the mineral?
7. A sample of *heavy spar* contains 96·5 per cent. of pure sulphate; how much baric sulphide, and how much baric nitrate can be obtained from 1 cwt. of the mineral?

2. STRONTIUM, Sr''.

Atomic weight, 87·5.—Occurs in nature as SULPHATE, in the mineral *celestine*, SO_2Sro''; and as CARBONATE or *strontianite*, $COSro''$.

EXAMINATION IN THE DRY WAY.

Strontium compounds, when heated on platinum wire in the inner flame, colour the outer flame intensely **crimson.** When the flame is viewed through the spectroscope, it shows a number of characteristic lines, more especially the $Sr\beta$ and γ lines in the RED and the line $Sr\delta$ in the BLUE, which latter is particularly suited for the detection of strontium in presence of Ba and Ca.

Celestine heated on charcoal in the reducing flame, is converted into strontic sulphide, SrS, from which the chloride may be prepared for blowpipe and other reactions, by treating the residue with hydrochloric acid. *Strontic carbonate,* heated in a platinum crucible, over a gas-blowpipe, is all but entirely converted into *oxide*, after about 20 minutes' heating.

REACTIONS IN THE WET WAY.

We use A SOLUTION OF STRONTIC CHLORIDE, $SrCl_2$.

$COAmo_2$ (**group-reagent**) gives a *white* precipitate of **strontic carbonate**, $COSro''$, less soluble in ammonic chloride than the corresponding baric carbonate; soluble in dilute acids. Carbonic acid produces the soluble dihydric strontic dicarbonate, $C_2O_2Ho_2Sro''$, which is decomposed on boiling into normal carbonate, carbonic anhydride and water.

$CONao_2$ and $COKo_2$, same precipitate.

SO_2Ho_2, or a **soluble sulphate**, produces a *white* precipitate of **strontic sulphate**, SO_2Sro''. From *dilute* solutions a precipitate appears *only after some time*, especially if calcic sulphate be used as the precipitant. Heat assists the precipitation. The precipitate dissolves perceptibly in hydrochloric or nitric acid, but is *insoluble* *in alcohol.* It is insoluble also on boiling in a concentrated solution of ammonic sulphate, SO_2Amo_2, and a little ammonia. (DISTINCTION BETWEEN STRONTIUM AND CALCIUM.)

A solution of strontic sulphate in water is not precipitated by ammonic oxalate, but readily precipitates baric salts.

$POHoNao_2$ (**hydric disodic phosphate**) gives a *white* precipitate of **hydric strontic phosphate,** soluble in acids, including acetic acid.

$\left\{\begin{array}{l}COAmo\\COAmo\end{array}\right.$ (**ammonic oxalate**) precipitates strontic salts more readily than baric salts. The *white* precipitate of **strontic oxalate,** $\left\{\begin{array}{l}CO\\CO\end{array}\right.Sro''$, is readily soluble in dilute nitric or hydrochloric acid; somewhat soluble in ammonic salts; but sparingly soluble in oxalic or acetic acid.

QUESTIONS AND EXERCISES.

1. Which are the principal strontium minerals?
2. How are strontic chloride and nitrate prepared—1st from *strontianite;* 2nd, from *celestine?*
3. Which are the most characteristic reactions for strontium?
4. How can strontium be distinguished from barium?
5. What is the percentage of strontium in *strontianite* and in *celestine?*
6. How can strontium be separated from calcium?

3. CALCIUM, Ca''. Atomic weight, 40.—Occurs in nature in the mineral, vegetable and animal kingdom, in vast masses, in combination with carbonic, sulphuric, silicic and phosphoric acids. In plants it occurs combined with carbonic, sulphuric, and phosphoric acids; in animals combined with phosphoric and carbonic acids. It is occasionally also found in minerals which result from the action of acids (such as nitric or arsenic acid) upon *calc spar.*

The principal calcium minerals are the various CALCIC CARBONATES, differing in physical properties or in crystalline structure, such as *calc spar*, $COCao''$ (containing occasionally barium, magnesium, iron, manganese, lead, in variable proportions, and passing gradually into *baryto-calcite* and *dolomite, siderite, diallogite* and *plumbo-calcite*), *arragonite, marble, limestone, chalk;* the SULPHATES, such as *gypsum*, SHo_4Cao'', *anhydrite*, SO_2Cao'', *alabaster, selenite;* the PHOSPHATES, such as *apatite*, $P_3O_3Cao''_4\left(\begin{matrix}O\\F\end{matrix}Ca''\right)'$, *bone-earth*, $P_2O_2Cao''_3$; and *fluor spar*, CaF_2.

REACTIONS IN THE DRY WAY.

Most calcium compounds, when heated in the inner flame of the blowpipe, colour the outer flame **yellowish-red**; calcic phosphate and borate excepted. The presence of barium or strontium entirely obscures the calcium reaction. The lime *spectrum* shows, among other lines in the RED and YELLOW, an intensely **green** line, $Ca\beta$, also an intensely **orange** line, $Ca\alpha$. It requires a very good spectroscope to see the faint **indigo-blue** line to the right of G in the solar spectrum.

Calcic carbonate when strongly ignited becomes converted into caustic or quicklime, **CaO**, which reacts alkaline. It combines with water very eagerly, evolving much heat, and is converted into calcic hydrate, $\mathbf{CaHo_2}$ (slaked lime), which is less soluble in water than either baric or strontic hydrate. It is also more soluble in cold than in hot water. Calcic sulphate is converted into calcic sulphide, **CaS**, when ignited on charcoal in the reducing flame. The mass reacts likewise alkaline.

REACTIONS IN THE WET WAY.

Calcic salts are readily prepared from pure *calc spar* or *marble*, by means of dilute acids.

We employ A SOLUTION OF CALCIC CHLORIDE, $CaCl_2$.

$COAmo_2$ (**group-reagent**) precipitates *white* **calcic carbonate**, $COCao''$, which is bulky and amorphous at first, but on warming gently becomes rapidly crystalline. Calcic carbonate is somewhat soluble in ammonic chloride, especially when freshly precipitated. It is in fact partially reconverted on boiling into calcic chloride.

$CONao_2$ and $COKo_2$, same reaction.

SO_2Ho_2, or **a soluble sulphate**, precipitates from concentrated solutions of a calcic salt *white* **calcic sulphate**, $SOHo_2Cao'' + Aq.$, soluble in much water, and still more soluble in acids. A precipitate is obtained on the addition of twice the volume of alcohol from solutions which are too dilute to be precipitated by sulphuric acid or a soluble sulphate. Calcic sulphate dissolves readily on boiling in a concentrated solution of ammonic sulphate.

$SOHo_2Cao'' = SO_2Cao'', OH_2$

$SO_2Cao'', 2OH_2 = SHo_4Cao''$

A solution of calcic sulphate precipitates both baric and strontic salts.

$POHoNao_2$ (**hydric disodic phosphate**) gives a *bulky white* precipitate of **tricalcic phosphate**, $P_2O_2Cao''_3$, soluble in dilute hydrochloric or nitric acid, and soluble in acetic acid; reprecipitated by ammonia.

$\left\{\begin{matrix}COAmo\\COAmo\end{matrix}\right.$ (**ammonic oxalate**) produces even from very dilute solutions of calcic salts a *white pulverulent* precipitate of **calcic oxalate**, $\left\{\begin{matrix}CO\\CO\end{matrix}\right.Cao'' + Aq.$, readily soluble in hydrochloric or nitric acid; not perceptibly soluble in oxalic or acetic acid. On gentle ignition calcic oxalate breaks up into calcic carbonate, and carbonic oxide gas, and on igniting very strongly, caustic lime is left.

Soluble calcic salts, such as the chloride or nitrate, constitute very important reagents for the detection of acids, on account of the metal calcium forming insoluble salts with most acids.

QUESTIONS AND EXERCISES.

1. Which are the most important natural lime compounds?
2. Give graphic formulæ for *gypsum, anhydrite, calc spar, fluor spar, apatite.*
3. Which are the most delicate reactions for calcium in the wet way?
4. How is *arragonite* converted into calcic oxalate?
5. Calculate the percentage composition of *bone-ash.*
6. Why can a solution of calcic sulphate be employed for the detection of barium and strontium even in the presence of calcic salts?

Separation of Barium, Strontium, and Calcium.—Barium minerals frequently contain strontium and calcium, and strontium minerals barium and calcium as well. A method of separating these metals is based upon—

1st. The *insolubility* of $\mathbf{BaCl_2}$ in *absolute alcohol* ($\mathbf{SrCl_2}$ and $\mathbf{CaCl_2}$ being soluble).

2nd. The *insolubility* of $\mathbf{N_2O_4}$Bao″, and $\mathbf{N_2O_4}$Sro″ in *absolute alcohol* (calcic nitrate being soluble).

A hydrochloric acid solution of the mineral containing Ba and Sr, or Sr and Ca, or possibly Ba, Sr and Ca, is prepared, and the solution evaporated to dryness and gently ignited. (Strong ignition must be avoided as $\mathbf{CaCl_2}$ is slightly decomposed into an insoluble basic salt.)

Barium is separated from strontium and calcium, by digesting the finely divided residue with absolute alcohol, and separating the undissolved $\mathbf{BaCl_2}$ by filtration.

Strontium is separated from calcium by evaporating or distilling off the absolute alcohol, which contains the $\mathbf{SrCl_2}$ and $\mathbf{CaCl_2}$; precipitating with $\mathbf{CO}$Amo$_2$, filtering, and conversion of the strontic and calcic carbonates into nitrates by means of dilute nitric acid. The solution of the two nitrates is evaporated to dryness on a water-bath and absolute alcohol added, when calcic nitrate is dissolved out, strontic nitrate being insoluble in absolute alcohol.

The presence of these metals may be confirmed by setting fire to the alcoholic solution containing baric, strontic, or calcic chloride (or nitrate); the alcohol is seen to burn with the characteristic colour observed when traces of these salts were heated on a platinum wire.

Several other methods for recognising and separating the metals of Group IV will suggest themselves.

It is often useful to ascertain whether one or two, or all the metals of this group are present in a solution. This can be done by adding to their *neutral* solution a solution of $\mathbf{CrO_2}$Ko$_2$, or 2HF,$\mathbf{SiF_4}$. A yellow or a transparent crystalline precipitate indicates barium. To a portion of the filtrate add $\mathbf{SO_2}$Cao″; a precipitate forms perhaps only after some time, proving the presence of strontium; or the solution remains clear, in which case calcium only need be looked for, the presence of which is indicated by the precipitate which ammonic oxalate produces from another portion of the *largely diluted* solution. If both strontium and calcium are present, separation becomes desirable.

The student will have no difficulty now in drawing up tabular analytical schemes* based upon:—

1st. The *insolubility of* $\mathbf{BaCl_2}$ and $\mathbf{N_2O_4}$Sro″ *in absolute alcohol.*

2nd. The *insolubility of* $\mathbf{BaCl_2}$ *in absolute alcohol* and *that of* $\mathbf{SO_2}$Sro″ *in a concentrated solution of* $\mathbf{SO_2}$Amo$_2$.

3rd. The *insolubility of* $\mathbf{BaF_2,SiF_4}$, or $\mathbf{CrO_2}$Bao″, *as well as of* $\mathbf{SO_2}$Sro″, *in water; calcic sulphate being sufficiently soluble to be readily indicated by ammonic oxalate.*

PRACTICAL EXERCISES† ON GROUPS IV AND V.

You are requested to analyse—

1. A solution of salts of the metals K, Mg, and Ba.

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* Table IV in the analytical tables at the end of the book contains a scheme embodying method 2.

† As a control upon the work done in a laboratory the analytical results should be carefully recorded by the student (as far as possible, in a tabular form), and should be discussed and corrected, if necessary. By these means only it is possible to control and direct the analytical studies of a large class.

2. A mixture (about ·5 grm.) of the solid salts $NaCl$, $SrCl_2$, and *magnesia alba* ($C_3Ho_4Mgo''_4$).
3. A mixture of the solid salts $AmCl$, $BaCl_2$, and $COCao''$.
4. A mixture of the salts $AmCl$ and SO_2Mgo''.
5. A mixture containing finely powdered marble, baric carbonate, and common salt.
6. A solution of $BaCl_2$ and $SrCl_2$, containing ·010 grm. of Ba and ·100 grm. of Sr.
7. A solution of $NaCl$, KCl, and $MgCl_2$, containing ·020 grm. of K, ·200 grm. of Na, and ·050 grm. of Mg.
8. A solution of $SrCl_2$ and $CaCl_2$, containing ·050 grm. of Sr, and ·500 grm. of Ca.

Chapter IV.

REACTIONS OF THE METALS OF GROUP III, OR AMMONIC SULPHIDE GROUP.

Group III comprises the metals Nickel, Cobalt, Manganese, Zinc, Iron, Chromium, Aluminium, likewise the phosphates of these metals, and of Magnesium, Barium, Strontium, and Calcium.

1. Add to a solution* containing N_2O_4Coo'', Fe_2Cl_6, and calcic phosphate, dissolved in a little dilute hydrochloric acid, a concentrated solution of ammonic chloride, and then ammonia. A precipitate is produced. Filter, and add to the filtrate ammonic sulphide. A further precipitation takes place; the precipitate is black.

This shows *that some members of this group are precipitated by AmCl and AmHo; others only on the addition of* SAm_2.

2. Add to a solution of Fe_2Cl_6, Cr_2Cl_6, and Al_2Cl_6, ammonic chloride and ammonia, till it is just distinctly ammoniacal, and boil for a few minutes. A bulky gelatinous precipitate is obtained. Filter. Add to the clear filtrate a few drops of ammonic sulphide: no further precipitation takes place.

Showing *that Iron, Chromium, and Aluminium are precipitated (as hydrates) from their saline solutions by AmCl and AmHo alone, without the aid of* SAm_2. (Ammonic chloride has no share in the precipitation, but counteracts the solubility of the aluminic hydrate in excess of the precipitant, and prevents the precipitation of magnesium as hydrate, if present in a solution.)

3. Dissolve some baric, strontic, calcic, and magnesic phosphates in dilute hydrochloric acid, and cautiously add to the solution ammonia. No precipitate is produced till the free acid has been neutralised (with formation of ammonic chloride), when the phosphates are reprecipitated. Filter and add ammonic sulphide to the filtrate. No further precipitation takes place.

This shows *that the phosphates of the alkaline earthy metals are precipitated by ammonia alone.*

---

* Solutions containing ·005 grm. of the metal in every c.c. are readily prepared, and should be kept for use. 5 c.c. of each solution will be found a convenient quantity.

4. Dissolve some phosphates of Ni, Co, Mn, Zn, and Fe^{iv} in dilute hydrochloric acid.* To one portion of the solution add ammonic chloride and ammonia. A precipitate is formed. The phosphates are reprecipitated. Filter and add ammonic sulphide; a further precipitate is produced.

Showing *that the phosphates of these metals are not entirely precipitated by ammonic chloride and ammonia.*

Thus far we have seen that these two reagents precipitate:—

Nickelous phosphate
Cobaltous ,,
Manganous ,,
Zincic ,,
Ferric ,,
Ferric hydrate
Chromic ,,
Aluminic ,,

Chromic phosphate
Aluminic ,,
Baric ,,
Strontic ,,
Calcic ,,
Magnesic ,,

5. To a solution of $\mathbf{SO_2NiO''}$, $\mathbf{N_2O_4Coo''}$, $\mathbf{SO_2Zno''}$, and $\mathbf{MnCl_2}$ (free from Fe), add AmCl in considerable excess, and then AmHo in slight excess. No precipitate is obtained, the precipitate first produced by AmHo being soluble in the ammonic salt. To one portion of the solution add strong sulphuretted hydrogen water (or pass a current of sulphuretted hydrogen gas); a copious precipitate is produced, consisting of **NiS** and **CoS** (black), **ZnS** (white), and **MnS** (buff coloured).

This *shows that Nickel, Cobalt, Manganese, and Zinc salts are not precipitated by AmCl and AmHo, but by* $\mathbf{S}Am_2$.

On exposing the other portion of the solution for some time to the air, it is seen to turn turbid where it is in contact with the air. Heat and shake the solution and the turbidity increases rapidly.

Showing *that AmCl and AmHo produce, under favourable conditions, a partial precipitation.*

6. To another portion of the solution of the phosphates of Ni, Co, Mn, Zn, and Fe (see 4), add AmCl, AmHo, and $\mathbf{S}Am_2$, without first separating by filtration, the precipitate produced by AmCl and AmHo. THE PHOSPHATES OF Co, Ni, Mn, Zn, AND Fe, which may be present in the hydrochloric acid solution, ARE DECOMPOSED INTO SULPHIDES, AND AMMONIC PHOSPHATE IS LEFT IN SOLUTION.

7. To a solution of $\mathbf{Fe_2Cl_6}$ add AmCl and AmHo. A reddish-brown precipitate of ferric hydrate, $\mathbf{Fe_2Ho_6}$, is produced, which on the addition of $\mathbf{S}Am_2$ turns instantaneously black.

This shows *that iron is first precipitated as hydrate, and is subsequently converted into sulphide.* Chromic and aluminic chlorides are precipitated under the same circumstances as hydrates, but they form no sulphides in the wet way.

We may then sum up by saying that the group-reagents AmCl and AmHo, for reasons stated under 4 and 5, cannot thoroughly separate some of the members of Group III from others, and that

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* This solution may also be prepared by adding hydric disodic phosphate to solutions of the above metals as long as a precipitate forms, and dissolving the precipitate in a little hydrochloric acid.

$\mathbf{S}\mathrm{Am}_2$ should invariably be added as well. The three reagents* precipitate:—

1. SULPHIDES—

$\mathbf{Ni}\mathrm{S}$	black
$\mathbf{Co}\mathrm{S}$	black
$\mathbf{Mn}\mathrm{S}$	buff
$\mathbf{Zn}\mathrm{S}$	white
$\mathbf{Fe}\mathrm{S}$	black.

2. HYDRATES—

$\mathbf{Cr}_2\mathrm{Ho}_6$	green
$\mathbf{Al}_2\mathrm{Ho}_6$	white.

3. PHOSPHATES of Cr, Al, Ba, Sr, Ca, and Mg.

NICKEL, Ni'' and $^{\mathrm{iv}}$. Atomic weight, 58·8.—Occurs in nature as SULPHIDE, $\mathbf{Ni}\mathrm{S}''$, in *capillary pyrites*, *hair nickel*, or *millerite*; as ARSENIDE, in *arsenical nickel*, $\left\{\begin{matrix}{''}\mathbf{As}'\\{''}\mathbf{As}'\end{matrix}\right.\mathrm{Ni}''$, and in *copper nickel*, $\left\{\begin{matrix}{'}\mathbf{As}''\mathrm{Ni}''\\{'}\mathbf{As}''\mathrm{Ni}''\end{matrix}\right.$; as ANTIMONIDE, in $\left\{\begin{matrix}{'}\mathbf{Sb}''\mathrm{Ni}''\\{'}\mathbf{Sb}''\mathrm{Ni}''\end{matrix}\right.$, *antimony nickel*, combined with SULPHIDE, as in *nickel glance* or *grey nickel ore*, $\left\{\begin{matrix}{''}\mathbf{As}'\\{''}\mathbf{As}'\end{matrix}\right.\mathrm{Ni},\mathbf{Ni}^{\mathrm{iv}}\mathrm{S}_2$, as *antimony nickel glance*, $\left\{\begin{matrix}{''}\mathbf{Sb}'\\{''}\mathbf{Sb}'\end{matrix}\right.\mathrm{Ni},\mathbf{Ni}^{\mathrm{iv}}\mathrm{S}_2$; also in the form of minerals, which are the result of the oxidation of other nickel minerals, *e.g.*, as *nickel ochre*, $\mathbf{As}_2\mathrm{O}_2\mathrm{Nio}''_3$, and *emerald nickel*, $\mathbf{C}(\mathrm{ONi}''\mathrm{Ho})_2\mathrm{Nio}'',5\mathbf{O}\mathrm{H}_2$.

REACTIONS IN THE DRY WAY.

When nickel compounds are heated on charcoal with dry sodic carbonate in the *inner* blowpipe flame, they are reduced to a grey metallic powder which is magnetic. Heated on a *borax* bead, in the *outer* flame, nickel compounds yield an intensely coloured glass, which appears **hyacinth-red to violet-brown** when hot, and **yellowish to sherry-red** when cold (according to the quantity of nickel present). On fusing a little nitre in the bead, the colour is changed to blue or dark purple, whereby nickel compounds may be distinguished from iron. Heated in the *reducing* flame the colour disappears, and the bead assumes a turbid grey appearance, owing to finely divided particles of metallic nickel. The reactions with microcosmic salt are similar, but the bead becomes almost colourless when cold.

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* Add AmHo to a solution of baric, strontic, calcic (and magnesic) oxalates in dilute hydrochloric acid, as long as a white precipitate is obtained. The oxalates of the alkaline earths are reprecipitated more or less completely as soon as the hydrochloric acid which (as in the case of the corresponding phosphates) holds them in solution is completely neutralised.

The same applies to the fluorides, borates, tartrates, citrates, &c., of these earthy bases, which are precipitated by AmHo, although in the presence of much AmCl they are to a great extent held in solution.

Silicic acid and silicates, soluble in hydrochloric acid, are likewise acted upon by AmCl and AmHo, gelatinous silica, and silicates, being precipitated.

In order to avoid complicating the qualitative course, it is usually preferred to evaporate the hydrochloric acid filtrate from Group II to complete dryness, with the addition, towards the end of the evaporation, of a little concentrated nitric acid, whenever AmCl and AmHo produce a precipitate. By these means silicic anhydride, $\mathbf{Si}\mathrm{O}_2$, is left behind insoluble in acids; the fluorides and borates are for the most part decomposed; boric and hydrofluoric acid being set free or volatilized. Oxalates are destroyed with evolution of carbonic anhydride by the oxidizing action of the nitric acid; and tartrates, etc., are broken up by gentle ignition into carbon and volatile gaseous products; ferrous salts are converted into ferric salts, and on extracting the ignited residue with a little concentrated hydrochloric acid, the metals are obtained in solution as chlorides, together only with the phosphates of the alkaline earths, earthy and metallic bases.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF NICKELOUS SULPHATE, SO_2Nio'', $= SO_2(O_2Ni)''$.

Solutions of salts of nickel are generally *green*; those of cobalt *red*. A solution of cobaltous chloride turns *blue* on heating. A solution of both a nickel and a cobalt salt is *red*, *green*, or *colourless*, according to the quantities present of each of the metals in solution.

SAm_2 (**group-reagent**) gives a *black* precipitate of **nickelous sulphide**, NiS, slightly soluble in excess of the reagent, especially in the presence of free ammonia or of *yellow* ammonic sulphide, forming a dark brown solution, whence the sulphide is reprecipitated on boiling. The presence of ammonic chloride (or better still, ammonic acetate) assists the precipitation. Nickelous sulphide dissolves with difficulty in dilute hydrochloric acid, readily in nitric acid or aqua regia, and is but slightly soluble in acetic acid.

SH_2 gives no precipitate in an acid solution, and a partial precipitate only from a salt of nickel with a mineral acid; but produces readily a precipitate from a solution of nickelous acetate, or a nickelous salt mixed with an alkaline acetate, especially on heating.

NaHo or KHo precipitates *an apple-green* **hydrate**, $NiHo_2$, insoluble in excess, soluble in ammonic salts to a greenish-blue fluid. Nickelous hydrate leaves on ignition nickelous oxide. It does not absorb oxygen from the air.

AmHo produces a slight *greenish* precipitate, readily soluble to a blue fluid. No precipitate in presence of ammonic chloride.

$CONao_2$ precipitates an *apple-green* **basic carbonate**, varying in composition.

$COAmo_2$, same precipitate, readily soluble in excess, when filtered and washed, to a greenish-blue solution.

KCy (free from cyanate (CyKo) and carbonate*) gives a *yellowish-green* precipitate of **nickelous cyanide**, $NiCy_2$, which dissolves readily in excess of potassic cyanide to a brownish-yellow solution, containing a double cyanide of nickel and potassium, $2KCy,\mathbf{Ni}Cy_2$. On adding a dilute acid (HCl or $\mathbf{S}O_2Ho_2$), $\mathbf{Ni}Cy_2$ is reprecipitated, and KCy is decomposed with evolution of HCy. Boiling with hydrochloric acid decomposes the nickelous cyanide likewise.

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* It is preferable to add hydrocyanic (prussic) acid, HCy, to a neutral solution of a nickelous salt, and then KHo drop by drop, till the yellowish-green precipitate is redissolved. Great caution has to be observed on account of the highly poisonous nature of HCy.

The solution of the double cyanide is not altered by boiling with excess of HCy, but the nickelous salt is oxidized in the cold by chlorine, or on the addition of a *concentrated* solution of sodic hypochlorite, $ClNao$, to *black* **nickelic hydrate**, $'\mathbf{Ni}'''{}_2Ho_6$, which is gradually precipitated, thus:—

$$2\mathbf{Ni}Cy_2 + ClNao + 5\mathbf{O}H_2 = \mathbf{Ni}_2Ho_6 + NaCl + 4HCy.$$

Nickelic hydrate may also be obtained by passing chlorine through water, in which nickelous hydrate is suspended. HCl decomposes the tetrad nickel compound into nickelous chloride and free chlorine. Nickelic oxide, $\mathbf{Ni}_2O_3$, obtained by igniting the hydrate, or by keeping the nitrate at a temperature of about 200° C., is a black substance, scarcely soluble in boiling *acetic acid.*

QUESTIONS AND EXERCISES.

1. Express in symbolic equations the reactions for nickel in the wet way.
2. State which are the principal nickel minerals, and translate into graphic formulæ the constitutional formulæ of *emerald nickel*, *antimony nickel*, nickelous nitrate and arsenate.
3. How many oxides of nickel are there; and how would you prepare them from a solution of nickelous sulphate?
4. How would you recognise the presence of Ni and As in *arsenical nickel?*
5. 50 cubic centimetres of a solution of nickelous sulphate yield on precipitation with KHo and ignition ·370 grm. of $\mathbf{Ni}O$; how much Ni is contained in 1 c.c. of the solution, and how much nickelous sulphate ($\mathbf{S}OHo_2Nio'',6\mathbf{O}H_2$) must be dissolved in a litre of water to obtain a solution of the above strength?
6. Calculate the percentage composition of *capillary pyrites.*

COBALT, Co'' and ^{iv}. Atomic weight, 58·8.—Occurs in nature as SULPHIDE or *cobalt pyrites*, $\mathbf{Co}_2S_3$ or $\left\{\begin{matrix}\mathbf{Co}S'' \\ \mathbf{Co}S''\end{matrix}\right.S''$; as arsenide in $\left\{\begin{matrix}''\mathbf{As}' \\ ''\mathbf{As}'\end{matrix}\right.Co''$, tin-white cobalt or *smaltine* (*speiss cobalt*), as SULPH-ARSENIDE, or *cobalt glance*, $\left\{\begin{matrix}''\mathbf{As}' \\ ''\mathbf{As}'\end{matrix}\right.Co'',\mathbf{Co}^{iv}S_2$; also in the form of products of oxidation, such as *cobalt vitriol*, $\mathbf{S}OHo_2Coo'',6\mathbf{O}H_2$, as *arsenate*, $\mathbf{As}_2O_2Coo''_3,8\mathbf{O}H_2$, in *cobalt bloom*, and generally in small quantity in *nickel* and *iron ores.*

REACTIONS IN THE DRY WAY.

Cobalt is usually detected with comparative facility. Cobalt minerals containing sulphur or arsenic are roasted on charcoal, or in a glass tube, when sulphurous and arsenious anhydride are evolved. The residue is then introduced into a *borax* bead, and heated in the *outer* flame, when a *fine* **blue**, so-called cobalt glass, is obtained.

This colour remains the same both in the outer and inner, or *reducing* flame. In cases where much Mn, Fe, Cu, or Ni are mixed with Co, the blue appears distinctly only after the bead has been heated for some time in the reducing flame. Microcosmic salt gives the same blue bead. Heated on charcoal, with sodic carbonate, in the reducing flame, cobalt separates as a grey metallic powder which is attracted by the magnet.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF COBALTOUS NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Coo''$.

SAm_2 (**group-reagent**) gives a *black* precipitate of **cobaltous sulphide**, CoS, insoluble in excess of the reagent, scarcely soluble in acetic acid, and very difficultly soluble in dilute hydrochloric or sulphuric acid, but readily soluble in aqua regia upon the application of heat. Hence a black residue left, on treating the ammonic sulphide precipitate of Group III with dilute hydrochloric acid, indicates probably the presence of cobaltous or nickelous sulphide.

SH_2 gives no precipitate from an acid solution, but precipitates cobaltous sulphide partially from a neutral solution, and wholly from a solution of cobaltous acetate, or from a solution of a cobaltous salt containing a mineral acid, on the addition of an alkaline acetate, and upon heating.

KHo or NaHo gives a precipitate of a *blue* **basic salt**, which turns *olive-green* on exposure to air, owing to the absorption of oxygen. On heating, a *rose-red* **cobaltous hydrate**, $CoHo_2$, is obtained, which, however, contains mostly a small amount of dark brown cobaltic hydrate. Ammonic carbonate dissolves the precipitate (after filtration and washing) to an intensely violet-red fluid.

By suspending cobaltous hydrate in water, and passing a current of chlorine into it, black cobaltic hydrate is precipitated, whilst cobaltous chloride remains in solution, thus :—

$$3CoHo_2 + Cl_2 = \underset{\substack{\text{Cobaltic}\\\text{hydrate.}}}{Co_2Ho_6} + CoCl_2.$$

In the presence of an alkali (NaHo) the whole of the cobaltous hydrate is converted into cobaltic hydrate.

AmHo produces in neutral solutions a slight precipitate of a **basic salt**, which dissolves readily in excess. The solution is reddish-brown. Ammonic chloride prevents the precipitation altogether. The solution absorbs oxygen from the air, and becomes red on standing.

$CONao_2$ precipitates a *peach coloured* **basic carbonate**

$COAmo_2$, same precipitate; readily soluble, however, in excess, to a red solution.

KCy gives with all normal cobaltous salts a *brownish-white* precipitate of **cobaltous cyanide**, $CoCy_2$, soluble in excess, reprecipitated by dilute hydrochloric or sulphuric acid.

If the cobaltous solution, however, contains free acid, so as to liberate hydrocyanic acid by the action of the latter upon the excess of KCy, and if the solution containing the double cyanide 2KCy,

$CoCy_2$, be heated for some time, dilute hydrochloric or sulphuric acid no longer produces a precipitate, the whole of the cobaltous cyanide having been converted into cobaltic cyanide, $'Co'''_2Cy_6$, which remains combined with 6KCy to form a well defined and stable salt, called **potassic cobalticyanide**, $K_6Co_2Cy_{12}$, hydrogen being evolved, thus :—

$$\begin{aligned} 2CoCy_2 + 2HCy &= Co_2Cy_6 + H_2. \\ 6KCy + Co_2Cy_6 &= \underset{\substack{\text{Potassic} \\ \text{cobalticyanide.}}}{K_6Co_2Cy_{12}}. \end{aligned}$$

This salt is not acted upon by sodic hypochlorite in the cold.

Separation of Nickel from Cobalt.—It is obvious that the hydrocyanic acid reaction enables us to separate nickel from cobalt.—To a *neutral* solution of the two salts add cautiously a small quantity of a strong solution of hydrocyanic acid, and then, drop by drop, KHo (a solution of potassic cyanide may likewise be used) as long as a precipitate forms, and till the precipitate is just redissolved and the yellowish-brown turbid liquid has become clear. Heat gently for some time in a well-ventilated closet, till the odour of hydrocyanic acid has disappeared. Allow to cool, and add a *concentrated* solution of sodic hypochlorite. Ni_2Ho_6 is precipitated in the cold, and cobalt remains in solution, as $K_6Co_2Cy_{12}$. Separate by filtration. Test the residue before the blowpipe for nickel, and evaporate the solution to dryness, and test for cobalt by means of a borax bead.

Instead of separating nickel as Ni_2Ho_6 by means of ClNao, the solution, after digesting with excess of HCy, may also be precipitated whilst hot, with finely divided freshly precipitated **mercuric oxide.** On digesting for a short time at a gentle heat, the whole of the nickel is precipitated, partly as $NiHo_2$, partly as $NiCy_2$, the mercury combining with the liberated cyanogen. Filter off the *greenish* or *yellowish-grey* precipitate, wash, and ignite. Pure NiO is left ; thus :—

$$(1)\quad 2NiCy_2 + xHgO + OH_2 = HgCy_2 + \underset{\substack{\text{Greenish} \\ \text{precipitate.}}}{NiHo_2,NiCy_2} + x-1HgO.$$

$$(2)\quad NiHo_2,NiCy_2 + HgO = 2NiO + \underset{\substack{\text{Volatile} \\ \text{on ignition.}}}{HgCy_2} + OH_2.$$

The cobalt remains in the solution as $K_6Co_2Cy_{12}$. Nearly neutralize with dilute nitric acid, and add a neutral solution of mercurous nitrate, $N_2O_4Hg_2o''$. A white precipitate of **mercurous cobalticyanide**, $(Hg''_2)_3Co_2Cy_{12}$, forms, which contains the whole of the cobalt. Filter, wash, and ignite under a hood with free access of air, when **tricobaltic tetroxide**, Co_3O_4, is left.

Another method of separation consists in adding a concentrated solution of NOKo (**potassic nitrite**) in considerable excess to a concentrated normal solution of a cobaltous salt, then acetic acid in sufficient quantity to freely redissolve the precipitate, which is at first produced by the free KHo and $COKo_2$ contained in the NOKo. On keeping the solution in a moderately warm place, the nickel salt remains in solution, and the whole of the cobalt separates in the form of a crystalline precipitate of a *fine yellow* colour (from a dilute solution only after long standing), the formation of which is expressed by the equation :—

$$2\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Coo'' + 14\mathbf{N}OKo + 4\left\{\begin{matrix}CH_3\\ COHo\end{matrix}\right. + \mathbf{O}H_2 = \underset{\text{Yellow}}{\mathbf{N}_6O_6Co_2o^{vi}},$$

$$\underset{\text{precipitate.}}{6\mathbf{N}OKo,3\mathbf{O}H_2} + 4\mathbf{N}O_2Ko + 4\left\{\begin{matrix}CH_3\\ COKo\end{matrix}\right. + \mathbf{N}_2O_2$$

The precipitate is perceptibly soluble in cold, and more readily still in hot, water ; it is decomposed by hot nitric or hydrochloric acid, or by potassic hydrate ; insoluble in alcohol ; insoluble in the presence of potassic acetate ; and it can therefore be washed by a solution of potassic acetate, and finally with alcohol. This REACTION SEPARATES NICKEL FROM COBALT VERY EFFECTUALLY.

From the filtrate the nickel is best precipitated as an apple-green basic carbonate by a fixed alkaline carbonate.

The presence of Ba, Sr or Ca salts interferes with the reaction, as it gives rise to the precipitation of a triple nitrite of Co, Ni and K.

On igniting a small quantity of $\mathbf{N}_2O_4Nio''$, a dirty greyish powder of $\mathbf{Ni}O$ is left. Ignite next $\mathbf{N}_2O_4Coo''$ gently (200° C.), and black cobaltous dicobaltic tetroxide, $\mathbf{Co}_3O_4 = \left\{\begin{matrix}\mathbf{Co}O\\ \mathbf{Co}O\end{matrix}\right.Coo''$, is left, which is *not* soluble in boiling dilute acetic acid. On treating this oxide with hydrochloric acid, chlorine gas is evolved, according to the equation :—

$$\mathbf{Co}_3O_4 + 8HCl = 3\mathbf{Co}Cl_2 + Cl_2 + 4\mathbf{O}H_2.$$

Both nickel and cobalt are capable of forming compounds in which the metals exist in a **tetrad** condition, viz.,

$$\mathbf{Ni}_2O_3,\ \text{or}\ \underset{\substack{\text{Nickelic}\\ \text{oxide.}}}{\left\{\begin{matrix}\mathbf{Ni}O\\ \mathbf{Ni}O\end{matrix}\right.O},\ \text{and}\ \mathbf{Co}_2O_3,\ \text{or}\ \underset{\substack{\text{Cobaltic}\\ \text{oxide.}}}{\left\{\begin{matrix}\mathbf{Co}O\\ \mathbf{Co}O\end{matrix}\right.O};\ \underset{\substack{\text{Cobaltic}\\ \text{sulphide.}}}{\mathbf{Co}_2S_3}.$$

$\mathbf{Ni}_2O_3$ is, however, mostly obtained in the wet way by the action of oxidizing agents, and cannot exist at a high temperature.

$\mathbf{Co}_3O_4$, on the other hand, is obtained in the dry way, or on gentle ignition of cobaltous salts containing volatile acids, and gives up a portion of its oxygen only on strong ignition.

The same tendency to form a compound in which cobalt exists as a tetrad element, is observed on exposing the freshly-precipitated hydrate to the air, or on passing chlorine or adding bromine or iodine to cobaltous solutions.

Little use is, however, made of these reactions beyond the conversion of $\mathbf{Co}Cy_2$ into $\mathbf{Co}_2Cy_6$, in the presence of potassic cyanide, or of $\mathbf{Co}O$ into $\mathbf{Co}_2O_3$ in the potassic nitrite reaction.

QUESTIONS AND EXERCISES.

1. Translate into graphic formulæ the constitutional formulæ of *cobalt pyrites, cobalt vitriol, cobalt bloom,* cobaltic cyanide.

2. How are $\mathbf{Co}\mathrm{O}$ and $\mathbf{Co}_3\mathrm{O}_4$ prepared?
3. How is Co separated from Ni?
4. 2 grms. of an ore containing Ni and Co yield ·221 grm. of $\mathbf{Ni}\mathrm{O}$ and ·1575 grm. of $\mathbf{Co}_3\mathrm{O}_4$; what is the percentage of Ni and Co in the ore?
5. Explain the formation of a blue glass when cobalt compounds are heated in a borax bead, or a bead of microcosmic salt.
6. How would you prepare potassic cobalticyanide?

MANGANESE, Mn'', $^{\mathrm{iv}}$, and $^{\mathrm{vi}}$. Atomic weight, 55.—Occurs in nature mainly in the state of OXIDES, of which the mineral *pyrolusite*, $\mathbf{Mn}^{\mathrm{iv}}\mathrm{O}_2$, is the most important. It is found in small quantities in many iron ores, and is a frequent constituent of SILICATES: the $\mathbf{Mn}\mathrm{O}$ replacing the isomorphous bases, $\mathbf{Fe}\mathrm{O}$, $\mathbf{Zn}\mathrm{O}$, $\mathbf{Mg}\mathrm{O}$, $\mathbf{Ca}\mathrm{O}$, without altering the crystalline structure of the minerals. It exists both in the dyad and tetrad condition in manganous and manganic oxides. The ANHYDROUS OXIDES known, besides pyrolusite, are *braunite*, $\mathbf{Mn}\mathrm{OMno}''$, or $\mathbf{Mn}^{\mathrm{iv}}{}_2\mathrm{O}_3$, *hausmannite*, $\begin{matrix}\mathbf{Mn}\mathrm{O}\\ \mathbf{Mn}\mathrm{O}\end{matrix}\mathrm{Mno}''$, or $\mathbf{Mn}^{\mathrm{iv}}{}_3\mathrm{O}_4$; the HYDRATES are: *manganite*, $\left\{\begin{matrix}\mathbf{Mn}\mathrm{OHo}\\ \mathbf{Mn}\mathrm{OHo}\end{matrix}\right.$, *psilomelane*, $\begin{matrix}\mathbf{Mn}\mathrm{OHo}\\ \mathbf{Mn}\mathrm{OHo}\end{matrix}\mathrm{Mno}''$, *wad*, $\begin{matrix}\mathbf{Mn}\mathrm{Ho}_3\\ \mathbf{Mn}\mathrm{Ho}_3\end{matrix}\mathrm{Mno}''$, *varvicite*, $\left\{\begin{matrix}'\mathbf{Mn}'''\mathrm{O}\\ \mathrm{Mno}''\,(\mathrm{O}_2\mathrm{Mn}^{\mathrm{iv}}\mathrm{Ho}_2)''\\ '\mathbf{Mn}'''\mathrm{O}\end{matrix}\right]$, *copper mangan*, $\begin{matrix}\mathbf{Mn}\mathrm{Ho}_2\\ \mathrm{O}\\ \mathbf{Mn}\mathrm{Ho}_2\end{matrix}\mathrm{Cuo}''$. Manganese is found in combination with SULPHUR, in *manganese blende*, $\mathbf{Mn}\mathrm{S}$; with CARBONIC ACID, in *diallogite*, $\mathbf{C}\mathrm{OMno}''$; with SILICA, in *red manganese or mangan kiesel* (*rhodonite*), $\mathbf{Si}\mathrm{OMno}''$, and in *tephroite*, $\mathbf{Si}\mathrm{Mno}''_2$; with PHOSPHORIC acid, as *triplite*, $\mathbf{P}_2\mathrm{OMno}''_2\mathrm{Feo}''_2$.

EXAMINATION IN THE DRY WAY.

The presence of manganese is readily detected in minerals which contain no other oxides capable of colouring fluxes, as they dissolve when heated in the *outer* flame, in the *borax* bead, or in a bead of microcosmic salt, to a clear VIOLET-RED pearl which becomes of a fine **amethyst** colour on cooling. The bead becomes **colourless** when heated in the *reducing* flame. If other metallic oxides are present, it is preferable to mix a small trace of the finely powdered manganese compound with two or three times its weight of sodic carbonate (a little nitre may likewise be added), and to fuse on platinum foil (a small platinum spoon or the lid of a platinum crucible) in the oxidising flame, when a **bluish-green mass** is left after cooling, consisting of **sodic manganate,** $\mathbf{Mn}\mathrm{O}_2\mathrm{Nao}_2$. The mass at the same time loses its transparency. THIS FORMS THE MOST CHARACTERISTIC REACTION FOR MANGANESE. Manganous and manganic oxides are converted into a higher oxide, $\mathbf{Mn}^{\mathrm{vi}}\mathrm{O}_3$, in which Mn exists as a hexad.

EXAMINATION IN THE WET WAY.

All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into manganous chloride. The chlorine so evolved becomes the measure of the amount of MnO_2 present in a manganese ore.

We employ A SOLUTION OF MANGANOUS CHLORIDE, $MnCl_2$ (free from Fe).

Solutions of pure manganous salts (free from manganate or permanganate) are colourless.

SAm_2 **(group-reagent)** gives a *flesh-coloured* precipitate of **manganous sulphide,** MnS, readily soluble in dilute acids, even acetic acid. Hence the presence of free acetic acid prevents the precipitation of manganese (METHOD OF DISTINGUISHING Co AND Ni FROM Mn). The manganese may be separated by repeating once or twice the precipitation of cobalt and nickel in the presence of acetic acid.

SH_2 does not precipitate a neutral solution of a manganous salt; the acetate even is precipitated very slowly and imperfectly, and not at all when free acetic acid is present.

KHo or NaHo gives a *white* precipitate of **manganous hydrate,** $MnHo_2$, insoluble in excess. The precipitate absorbs speedily oxygen from the air, and turns dark brown with formation of $\left\{\begin{matrix}MnOHo\\MnOHo\end{matrix}\right.$, when it no longer dissolves completely in ammonic chloride.

AmHo precipitates a *white hydrate* from neutral solutions; insoluble in excess, or in ammonic carbonate.

No precipitate is produced in solutions containing ammonic chloride. On exposing an ammoniacal solution of the soluble double chloride, $2AmCl,MnCl_2$, to the action of the air, the whole of the manganese is gradually precipitated as dark brown **dimanganic dioxydihydrate,** $\left\{\begin{matrix}MnOHo\\MnOHo\end{matrix}\right.$. This reaction is characteristic for manganese compounds.

AmHo conveys in this change oxygen to the manganous salt in a manner similar to the action it has upon cobaltous salts, or upon metallic copper, in the presence of oxygen or air.

Owing to this tendency of manganous salts to become oxidised and precipitated in the presence of AmHo, it is all but impossible to separate manganous from ferric salts by means of AmCl and AmHo. The reddish-brown ferric hydrate, which is precipitated, invariably carries down more or less $\left\{\begin{matrix}MnOHo\\MnOHo\end{matrix}\right.$; and *small quantities of manganese cannot, therefore, be separated from iron by precipitation with AmCl and AmHo.* The separation succeeds best if the excess of ammonia is *immediately* boiled off.

$CONao_2$ or $COKo_2$ precipitates *white* **manganous carbonate,** $COMno''$, insoluble in excess of the reagent, but pretty readily soluble in ammonic chloride. This precipitate absorbs likewise oxygen from the air, and turns to a dirty brownish-white colour, owing to the formation of dimanganic dioxydihydrate. On ignition with free access of air, the white carbonate turns first black, and changes subsequently to brown **trimanganic tetroxide,** Mn_3O_4. All manganese oxides are obtained upon ignition in air in the form of $\mathbf{Mn}_3O_4$.

KCy gives a *whitish* precipitate of **manganous cyanide**, $\mathbf{Mn}Cy_2$, soluble in excess to a brown solution, which is not precipitated by $\mathbf{S}Am_2$.

We have just seen how readily manganous compounds are converted, more or less completely, into higher oxides, in which manganese acts the part of a tetrad element. In the brown hydrated dioxide, obtained when a manganous salt is digested with sodic hypochlorite, according to the equation :—

$$\mathbf{Mn}Cl_2 + ClNao + 2\mathbf{O}H_2 = \mathbf{Mn}^{iv}OHo_2 + NaCl + 2HCl,$$

the manganese exists likewise as a tetrad element. By fusion in the dry way with sodic carbonate, alone or together with nitre, the manganous or manganic compounds are converted into an alkaline manganate, in which the metal manganese acts the part of a hexad element. Manganic acid itself has never been isolated. It is obtained, however, in combination with a few of the stronger metallic bases, forming manganates, of which the alkaline manganates only dissolve in water to *green solutions*.

Manganates are readily decomposed in aqueous solutions. On gently heating a solution of potassic manganate with free access of air, the green colour changes to *purple-red*, owing to the formation of potassic permanganate,* $\mathbf{Mn}_2O_6Ko_2 = \left\{\begin{matrix} '\mathbf{Mn}^{v}O_2(OKo) \\ '\mathbf{Mn}^{v}O_2(OKo) \end{matrix}\right.$, with separation of hydrated dioxide, thus :—

$$3\mathbf{Mn}O_2Ko_2 + 3\mathbf{O}H_2 = \mathbf{Mn}_2O_6Ko_2 + \mathbf{Mn}OHo_2 + 4KHo.$$

The change is accelerated by adding a few drops of a dilute mineral acid, *e.g.*, nitric, hydrochloric, or sulphuric acid, which combines with the liberated alkali. This reaction is extremely delicate.

The metal manganese seems to act here the part of a pseudo-octad element; and it may readily be inferred that the different oxygen atoms perform different functions in such a highly oxygenised compound, and that the metal manganese will part with some more readily than with others.

Manganic dioxide, as well as other native peroxides, already enumerated, also the alkaline manganates and permanganates, act as powerful oxidizers, differing merely in the *intensity* of their oxidizing action.

Manganic dioxide gives off oxygen on the addition of concentrated sulphuric acid, and forms normal manganous sulphate :—

$$\text{(Atomic equation) } \mathbf{Mn}O_2 + \mathbf{S}O_2Ho_2 = \mathbf{O} + \mathbf{S}O_2Mno'' + \mathbf{O}H_2.$$

Sulphuric acid added to sodic manganate, gives off a molecule of oxygen, and forms manganous and sodic sulphates, thus :—

$$\mathbf{Mn}O_2Nao_2 + 2\mathbf{S}O_2Ho_2 = O_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Nao_2 + 2\mathbf{O}H_2.$$

Sulphuric acid added to a solution of potassic permanganate, liberates five atoms of oxygen, and leaves manganous and potassic sulphates in the solution, thus :—

$$\text{(Atomic equation) } \left\{\begin{matrix} \mathbf{Mn}O_2(OKo) \\ \mathbf{Mn}O_2(OKo) \end{matrix}\right. + 3\mathbf{S}O_2Ho_2 = O_5 + 2\mathbf{S}O_2Mno''$$
$$+ \mathbf{S}O_2Ko_2 + 3\mathbf{O}H_2.$$

Hydrochloric acid acts likewise upon the higher oxides of manganese with evolution of chlorine and formation of metallic chlorides and water. The peroxides of manganese, especially the *black oxide*, constitute the principal substances, together with hydrochloric acid, or sodic chloride and oil of vitriol, for evolving chlorine in the laboratory and on a manufacturing scale.

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* Permanganic acid has never been isolated. It exists only in a few metallic salts called *permanganates*, which are soluble in water, forming intensely purple-red solutions. The salts crystallise from an alkaline solution in beautiful large crystals of deep violet lustre.

We know of no other mineral oxidizing agent capable of yielding from one molecular group of elements five atoms of oxygen; and there are but few elementary substances which resist the oxidizing action of potassic permanganate. Hydrogen, freshly-ignited carbon, phosphorus, iodine, sulphuretted hydrogen, carbonic disulphide, are oxidized more or less rapidly. Metals, such as zinc and iron, become oxidized after a few days; lead, copper, mercury and silver after some time. Many lower oxides, chlorides, etc., are converted into higher oxides, etc., especially in the presence of a free acid (hydrochloric or sulphuric acid).

Thus arsenious is converted into arsenic acid, sulphurous into sulphuric, nitrous into nitric, phosphorous into phosphoric acid. Oxalic acid is oxidised into carbonic anhydride and water. Lower, or -ous chlorides, sulphates, etc., are converted into the higher or -ic salts, *e.g.*, ferrous, stannous, antimonious, cuprous, and mercurous chlorides are oxidized ("chlorinized") in the presence of free hydrochloric acid into ferric, stannic, antimonic, cupric, and mercuric chlorides; the manganese and potassium of the permanganate are left in solution as chlorides. Ferrous, cuprous, and other sulphates are converted in the presence of free sulphuric or hydrochloric acid into ferric or cupric sulphates.

Potassic permanganate oxidizes also many organic bodies, such as sugar, gum, cellulose (in paper, cotton), uric acid, etc. The reaction in all these cases is indicated by a change of colour. On adding, for instance, the purple coloured permanganate solution to a solution of sulphurous acid, the colour is instantaneously destroyed as long as any sulphurous acid is left. Permanganate becomes, therefore, the measure for sulphurous acid, and in like manner for other lower oxides, chlorides, etc.

Sulphurous acid requires one atom of oxygen in order to be converted into sulphuric acid, and potassic permanganate can part with five atoms of oxygen. One molecule of the oxidizing agent oxidizes, therefore, five molecules of the reducing agent, *i.e.*, 316 parts by weight of potassic permanganate become the measure for $5 \times 64 = 320$ parts by weight of SO_2.

Two molecules of ferrous sulphate combine with one atom of oxygen and one molecule of sulphuric acid, to form one molecule of ferric sulphate, thus:—

$$2SO_2Feo'' + O + SO_2Ho_2 = S_3O_6Fe_2o^{vi} + OH_2.$$

Hence one molecule of dipotassic permanganate oxidizes ten molecules of SO_2Feo'', ten molecules of FeO, or ten atoms of Fe; and 316 parts by weight of $Mn_2O_6Ko_2$ become the measure for

10×152 parts by weight of SO_2Feo''
or 10×72 „ FeO
or 10×56 „ Fe.

QUESTIONS AND EXERCISES.

1. Which are the most important manganese ores?
2. Which manganese ores can be employed for generating chlorine?
3. Explain the action of concentrated SO_2Ho_2 upon MnO_2, MnO_2Nao_2 and $Mn_2O_6Ko_2$; and express the changes by equations.
4. Translate into graphic formulæ the constitutional formulæ of *pyrolusite, braunite, hausmannite, manganite, psilomelane, wad, varvicite,* and *tephroite.*
5. Describe the most characteristic blowpipe reactions for manganese compounds.
6. How can Mn be separated from Ni and Co?
7. How is Mn separated from calcium or from potassium?
8. What change does a solution of dipotassic manganate undergo when heated in contact with air?
9. Give evidences of the dyad, tetrad, and hexad nature of manganese.
10. Give the graphic formulæ for disodic manganate and dipotassic permanganate.

11. Explain the action of AmHo upon cobaltous and manganous salts, 1st, in the presence of ammonic chloride; 2nd, in the absence of ammonic salts; and 3rd, with free access of air.
12. State why Mn is separated with difficulty from Fe^{iv} by means of AmCl and AmHo.
13. What change does $COMno''$ undergo upon ignition?
14. By precipitating 2·622 grms. of a manganous salt with sodic carbonate and ignition of the precipitate, 1·325 grm. of Mn_3O_4 is left; what is the percentage of manganese in the salt?
15. What is the action of dipotassic permanganate upon HCl, SH_2, SO_2, $\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.$, Cu_2Cl_2, $FeCl_2$, $SnCl_2$? Express the changes by equations.
16. How much sulphurous anhydride by weight and by volume (at 0° C. and 760 mm. barometrical pressure) will be required to decolorise a solution containing ·500 grm. of dipotassic permanganate?
17. Explain the action of sulphurous anhydride upon manganic dioxide.
18. ·125 grm. of dipotassic permanganate had to be added to a given quantity of an acid (SO_2Ho_2) solution of SO_2Feo''. Calculate how much metallic iron the solution contained.
19. ·450 grm. of *spathic iron ore*, $COFeo''$, when dissolved in hydrochloric acid, required ·100 grm. of $Mn_2O_6Ko_2$. What will be the percentage—1st, of carbonate; 2nd, of metallic iron, contained in the ore?
20. 1·240 grm. of CO_2 was evolved when 1·780 grm. of *pyrolusite* was treated with moderately concentrated SO_2Ho_2 and $\left\{\begin{matrix}COKo\\COKo\end{matrix}\right.$. What is the percentage of MnO_2 in the ore, and how much chlorine gas by weight and by volume can be evolved from 100 grms. of the ore when treated with HCl?

ZINC, Zn''. Atomic weight, 65.—Occurs in nature chiefly as SULPHIDE, or *zinc blende*, *black jack*, ZnS; as CARBONATE, or *calamine*, $COZno''$; and as SILICATE, or *zinc glance*, *electric calamine*, $SiZno''_2,OH_2$, *Willemite*, $SiZno''_2$; also as OXIDE—the only oxide known—in *red zinc ore*, ZnO.

REACTIONS IN THE DRY WAY.

The most characteristic blowpipe reaction for zinc consists in the white incrustation of zincic oxide which its compounds yield when heated on charcoal in the reducing flame with sodic carbonate. The zinc compound is reduced to the metallic state, and the metal being volatile, burns, on passing through the outer flame, with a bluish-green flame, and is converted into oxide, which covers the charcoal with an incrustation, **yellow** when hot, **white** when cold, and which assumes a **fine green** colour when treated with a solution of cobaltous nitrate, and on being once more strongly heated in the outer flame. The incrustation is not driven away in the oxidising flame,—zincic oxide being non-volatile.

Zinc compounds give with borax or microcosmic salt in both flames a bead, which is yellowish while hot, and white on cooling; opaque if much zinc salt be present. This applies, however, only to pure zinc compounds, and the detection of zinc in poor ores containing other readily oxidizable metals (such as Pb, Cd, As, Sb, which give likewise incrustations), is a matter of great uncertainty.

Zincic sulphide (*zinc blende*), when roasted in a tube of hard glass, loses part of its sulphur in the form of sulphurous anhydride, and leaves some zincic sulphate, SO_2Zno'' (*white vitriol*), which may be extracted with water.

Calamine leaves on ignition zincic oxide.

REACTIONS IN THE WET WAY.

We employ A SOLUTION of ZINCIC CHLORIDE, $\mathbf{Zn}Cl_2$, OR OF ZINCIC SULPHATE, $\mathbf{SO}_2Zno''$, $= \mathbf{SO}_2(O_2Zn)''$. Both salts yield colourless solutions.

$\mathbf{S}Am_2$ (**group-reagent**) gives a *white* precipitate of **zincic sulphide**, $\mathbf{Zn}S$, insoluble in excess. From dilute solutions the precipitate separates only after some time, more speedily in the presence of ammonic chloride. It is readily decomposed by dilute hydrochloric and sulphuric acids, with evolution of sulphuretted hydrogen; also by nitric acid, but is insoluble in acetic acid.

$\mathbf{S}H_2$ precipitates zinc imperfectly from neutral solutions of zincic salts with mineral acids; but from an acetate or a solution of a zincic salt mixed with an alkaline acetate, the whole of the metal is precipitated by sulphuretted hydrogen as zincic sulphide, even in the presence of much acetic acid (METHOD OF SEPARATION OF ZN FROM MN). Free organic acids prevent the precipitation.

KHo or NaHo precipitates the *white* **hydrate**, $\mathbf{Zn}Ho_2$, readily soluble in excess, and in AmHo, reprecipitated almost entirely on diluting with water and on boiling, soluble also in ammonic chloride. Sulphuretted hydrogen precipitates the whole of the zinc from these solutions. Free organic acids prevent the complete precipitation. In the presence of the hydrates of manganese, nickel and cobalt, KHo or NaHo does not dissolve out the whole of the zincic hydrate.

$\mathbf{CO}Nao_2$ or $\mathbf{CO}Ko_2$ produces a *white* precipitate of **basic carbonate,** consisting of two molecules of zincic carbonate and three molecules of zincic hydrate, according to the equation :—

$$5\mathbf{SO}_2Zno'' + 5\mathbf{CO}Nao_2 + 3\mathbf{O}H_2 = \left\{\begin{array}{l} \mathbf{C}Ho(OZn''Ho)_2 \\ Zno'' \\ \mathbf{C}Ho(OZn''Ho)_2 \end{array}\right. + 5\mathbf{SO}_2Nao_2$$

Dihydric pentazincic dicarbonate tetrahydrate.

$$+ 3\mathbf{CO}_2.$$

A large excess of ammonic salts prevents the precipitation.

This carbonate leaves on ignition $\mathbf{Zn}O$, also known under the name of *zinc white*.

$\mathbf{CO}Amo_2$ produces the same precipitate, soluble, however, in excess.

KCy gives a *white* precipitate of **zincic cyanide,** $\mathbf{Zn}Cy_2$, soluble in excess, not reprecipitated by $\mathbf{S}Am_2$, but completely precipitated by $\mathbf{S}K_2$ as $\mathbf{Zn}S$ (Method for the separation of Zn from Ni).

Zinc precipitates the less electropositive metals from their solutions, viz., As, Sb, Sn, Cd, Cu, Pb, Ag, Bi, Hg : and on dissolving impure metallic zinc in dilute acids (hydrochloric or sulphuric), these metals do not dissolve, as long as any zinc remains undissolved. Hence zinc protects other metals, such as copper, iron (galvanized iron), from the oxidizing action of the air.

Zinc, when placed in contact with platinum, iron, etc., dissolves in alkaline solutions in the cold; when boiled with KHo (NaHo, or even AmHo), it dissolves likewise, with evolution of hydrogen and formation of **dipotassic zincic oxide,** $\mathbf{Zn}Ko_2$.

Zinc vapour decomposes $\mathbf{CO}_2$ at a high temperature, and forms $\mathbf{Zn}O$ and $\mathbf{CO}$;

at a lower temperature, $\mathbf{ZnO}$ yields its oxygen again to carbon (Method of extracting metallic zinc from some of its ores). This forms an interesting instance of reciprocal chemical action.

QUESTIONS AND EXERCISES.

1. Explain the action of HCl, $\mathbf{SO_2Ho_2}$, $\mathbf{NO_2Ho}$, and KHo upon metallic zinc. Express the changes by equations.
2. Give the names and composition of the most important zinc ores, and translate their constitutional into graphic formulæ.
3. Describe the blowpipe reactions for zinc compounds.
4. Express by equations the reactions for zinc in the wet way. Give graphic formulæ for the basic carbonate and dipotassic zincic oxide.
5. 1·5 grm. of *calamine* yielded ·876 grm. of $\mathbf{ZnO}$, what is the percentage of zinc in the ore?
6. How is metallic zinc obtained from *calamine*, or *red zinc ore?*
7. How has $\mathbf{ZnS}$ to be treated in order to extract from it metallic zinc?
8. How is Zn separated from Mn?
9. How can Zn be separated from Ni and Co?
10. How would you remove the zinc from an alloy of Zn and Cu (brass)?
11. How is *white vitriol* prepared, 1st, from *zinc blende*, 2nd, from *calamine?* Give the composition of the crystallized salt.
12. You have given to you *calamine*, *zinc blende*, hydrochloric acid, water, and sodic carbonate. State how you would prepare from these materials zincic oxide or *zinc white*. Express the changes by equations.

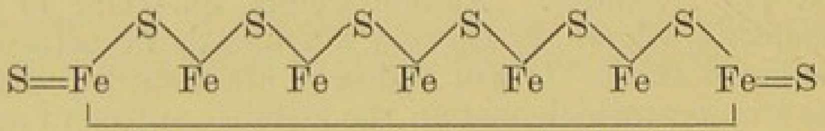
IRON. Fe'', ^{iv}, and ^{vi}. Atomic weight 56.—One of the few metallic elements which occurs very abundantly in nature, mostly in the combined state. It will suffice if we consider more especially those iron ores which contain the metal in sufficient quantities and which are sufficiently free from deleterious substances (such as S, P, As), to render them suitable for the extraction of iron by the usual metallurgical processes. The most important iron ores are:—

1st. ORES CONTAINING FERROUS OXIDE:—*spathic* or *sparry iron ore*, $\mathbf{CO}Feo''$, (*sphaerosiderite*) containing varying quantities of $\mathbf{CO}Mno''$, $\mathbf{CO}Mgo''$, and $\mathbf{CO}Cao''$; *black band* or carbonaceous iron ore, a sphaerosiderite containing from 20 to 25 per cent. of bituminous matter; *clay ironstone* (likewise a siderite) is, as its name indicates, associated with clayey matter. It is from these two ores that the greater part of the iron manufactured in this country is derived. They occur in immediate proximity to the coal measures and limestone beds—the fuel and flux necessary for their reduction to the metallic state.

2nd. ORES CONTAINING FERROUS AND FERRIC OXIDES: *viz.*, *magnetic iron ore*, $\mathbf{Fe_3O_4} = \left\{\begin{matrix}\mathbf{FeO}\\\mathbf{FeO}\end{matrix}\right. Feo''$ (ferrous diferric tetroxide).

3rd. ORES CONTAINING FERRIC OXIDE ONLY: *viz.*, *red hæmatite* (*micaceous iron*, *oligist*, *specular iron* or *iron glance*), $\mathbf{Fe'''_2}O_3 = \left\{\begin{matrix}\mathbf{FeO}\\\mathbf{FeO}\end{matrix}\right. O$ (ferric oxide). This oxide forms different hydrates which, according to the amount of water which they contain, have received different names, *viz.*, *turgite*, $2\mathbf{Fe}_2\mathrm{O}_3,\mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{OHo}\\ \begin{array}{l}\mathbf{Fe}\mathrm{O}\\ \mathbf{Fe}\mathrm{O}\end{array}\mathrm{O}\\ \mathbf{Fe}\mathrm{OHo}\end{array}\right.$ (tetraferric pentoxy-dihydrate); *needle iron ore*, *brown iron ore*, or *pyrrhosiderite*, $\mathbf{Fe}_2\mathrm{O}_3,\mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{OHo}\\ \mathbf{Fe}\mathrm{OHo}\end{array}\right.$ (diferric dioxy-dihydrate); *limonite* or compact *brown iron ore*, *brown hæmatite*, $2\mathbf{Fe}_2\mathrm{O}_3,3\mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{OHo}\\ \mathbf{Fe}\mathrm{Ho}_2\\ \mathrm{O}\\ \mathbf{Fe}\mathrm{Ho}_2\\ \mathbf{Fe}\mathrm{OHo}\end{array}\right.$ (tetraferric trioxy-hexahydrate); (varieties: *oolitic iron ore*, *pea ore*); *yellow iron ore* or *xanthosiderite*, $\mathbf{Fe}_2\mathrm{O}_3,2\mathbf{O}\mathrm{H}_2 = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{Ho}_2\\ \mathbf{Fe}\mathrm{Ho}_2\end{array}\right.\mathrm{O}$ (diferric oxy-tetrahydrate).

A few other iron ores deserve our attention. They are not used for the extraction of iron, but are valuable as a cheap source of sulphur, viz., *iron pyrites*, *martial pyrites* or *mundic*, $\mathbf{Fe}\mathrm{S}_2$, found abundantly in nature; $\mathbf{Fe}_2\mathrm{S}_3$ (diferric trisulphide); *copper pyrites*, $\mathbf{Fe}_2\mathrm{S}_3,\mathbf{Cu}_2\mathrm{S} = \left\{\begin{array}{l}\mathbf{Fe}\mathrm{S}\\ \mathbf{Fe}\mathrm{S}\end{array}\right.\mathrm{Cu}_2\mathrm{s}''$, and *magnetic pyrites*, $5\mathbf{Fe}\mathrm{S},\mathbf{Fe}_2\mathrm{S}_3 = \mathbf{Fe}_7\mathrm{S}_8$, which may be expressed graphically, thus:—



(Pentaferrous diferric octasulphide.)

Besides these ores, iron is found in nature in combination with ARSENIC and SULPHUR, in *mispickel* $\left\{\begin{array}{l}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{array}\right.\mathrm{Fe},\mathbf{Fe}^{\mathrm{iv}}\mathrm{S}_2$; with CHROMIUM as *chrome iron ore* $\left\{\begin{array}{l}{}'\mathbf{Cr}'''\mathrm{O}\\ {}'\mathbf{Cr}'''\mathrm{O}\end{array}\right.\mathrm{Feo}''$; with SILICA as *chloropal*, $\left.\begin{array}{l}\mathbf{Si}\mathrm{O}\\ \mathbf{Si}\mathrm{O}\\ \mathbf{Si}\mathrm{O}\end{array}\right] = \mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}}$, $3\mathbf{O}\mathrm{H}_2$, and many other silicates; as SULPHATE, in *green copperas* or *green vitriol*, $\mathbf{S}\mathrm{OHo}_2\mathrm{Feo}'',6\mathbf{O}\mathrm{H}_2$; as phosphate in *vivianite*,* $\mathbf{P}_2\mathrm{O}_2\mathrm{Feo}''_3,8\mathbf{O}\mathrm{H}_2$ (triferrous phosphate), and others; as ARSENATE, in *scorodite*, $\mathbf{As}_2\mathrm{O}_2\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}},4\mathbf{O}\mathrm{H}_2$, and others.

REACTIONS IN THE DRY WAY.

On heating the different iron compounds on charcoal before the blowpipe, they turn black and become magnetic; when heated in the *outer* flame, on a *borax* bead, iron compounds impart a **dark red** colour to the borax, whilst hot, becoming **light yellow**, when cold. In the *reducing* flame they give an **olive-green** to **bottle-green** bead.

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* Contains also ferric phosphate, $\mathbf{P}_2\mathrm{O}_2\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}},8\mathbf{O}\mathrm{H}_2$, to which the blue colour of the mineral is due.

The reactions with microcosmic salt are similar but less distinct. The presence of Co, Cu, Ni, Cr conceals the colour of the iron bead. Ferric sulphides and arsenides must be roasted, previous to being introduced into the borax bead. When heated with $\mathbf{C}ONao_2$ on charcoal, in the reducing flame, metallic iron is obtained as a magnetic powder.

REACTIONS IN THE WET WAY.

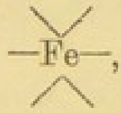
Iron forms two series of salts, viz., FERROUS AND FERRIC SALTS. It dissolves readily in dilute acids, such as HCl, $\mathbf{S}O_2Ho_2$, forming ferrous salts, $\mathbf{Fe}Cl_2$, $\mathbf{S}O_2Feo''$, with evolution of hydrogen. Cold dilute nitric acid dissolves finely divided iron (iron filings) without evolving hydrogen gas, the nitric acid being decomposed, so as to form ferrous nitrate and a small amount of ammonic nitrate; the reaction may be expressed thus:—

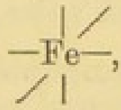
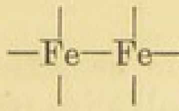
$$4Fe + 10\mathbf{N}O_2Ho = 4\left\{\begin{array}{l}\mathbf{N}O_2\\ \mathbf{N}O_2\end{array}\right.Feo'' + \mathbf{N}O_2Amo + 3\mathbf{O}H_2.$$

The metal iron exists in all these salts in the dyad condition, but exhibits a marked tendency to pass into the tetrad condition. Exposed to the air, $\mathbf{Fe}Cl_2$ and $\mathbf{S}O_2Feo''$ absorb oxygen and are gradually converted into ferric salts. The same change is produced by the action of various oxidising agents, such as Cl_2, Br_2, I_2, ClNao, KO_3Cl in the presence of HCl, $\mathbf{N}O_2Ho$, $\mathbf{N}O_2Ago$, $\mathbf{Au}Cl_3$, $\mathbf{Hg}Cl_2$, $\mathbf{Mn}_2O_6Ko_2$, $\mathbf{Cr}O_2Ko_2$, and others. *We possess therefore in ferrous compounds powerful reducing agents.*

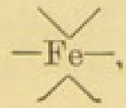
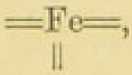
The tetrad condition appears to be the natural state of existence of the metal iron. This is rendered evident, moreover, by the limited number of ferrous compounds which exist in nature. The latter must be viewed as unsatisfied bodies, which, under favourable conditions, deprive other bodies, directly or indirectly, of oxygen, to form ferric compounds. Dyad iron, Fe'' (called *ferrosum*) has two bonds latent, which it is eager to satisfy, so as to become converted into the more stable tetrad iron, Fe^{iv} (or *ferricum*), in which condition it occurs in nature in combination with sulphur only, as $\mathbf{Fe}S_2$, without forming any corresponding oxygen, chlorine, etc., compounds. Two atoms of tetrad iron are invariably linked together in ferric oxide, chloride, etc., whereby iron becomes a pseudo-triad element. It is possible to combine, by artificial means, three atoms of oxygen with one atom of iron, so as to form ferrates, as in potassic ferrate, $\mathbf{Fe}O_2Ko_2$, in which compound the iron exists as a hexad element.

These different combining conditions of the metal iron may be represented graphically, thus:—

Dyad iron , *e.g.*, in $\mathbf{Fe}Cl_2$, $\mathbf{Fe}O$, $\mathbf{Fe}S$.

Tetrad iron , or pseudo-triad iron, , *e.g.*, in

$$\mathbf{Fe}^{iv}S_2,\ \left\{\begin{array}{l}'\mathbf{Fe}'''Cl_3\\ '\mathbf{Fe}'''Cl_3\end{array}\right.,\ \left\{\begin{array}{l}'\mathbf{Fe}'''S\\ '\mathbf{Fe}'''S\end{array}\right.S,\ \left\{\begin{array}{l}'\mathbf{Fe}'''O\\ '\mathbf{Fe}'''O\end{array}\right.O,$$ and lastly as

Hexad iron , or , *e.g.*, in $\mathbf{Fe}^{vi}O_2Ko_2$.

A. **Ferrous compounds.**—We employ A SOLUTION OF FERROUS SULPHATE, SO_2Feo'', $= SO_2(O_2Fe)''$.

SAm_2 (**group-reagent**) gives a *black* precipitate of **ferrous sulphide,** FeS, insoluble in alkalies and alkaline sulphides, easily decomposed and dissolved by dilute hydrochloric acid, with evolution of sulphuretted hydrogen. The moist precipitate absorbs oxygen from the air, and is rapidly converted into ferrous sulphate, and lastly into yellow basic ferric sulphate, with evolution of much heat. (This oxidation constitutes a frequent cause of the spontaneous inflammation of pyritical coal (which contains Fe_7S_8) on board vessels.)

SH_2 does not precipitate neutral or acid solutions of ferrous salts; ferrous acetate even is only partially precipitated.

KHo, $NaHo$, or $AmHo$ precipitates from ferrous salts (free from ferric salts) *white* **ferrous hydrate,** $FeHo_2$, which turns rapidly to a *dirty green* colour, and ultimately becomes *reddish-brown*, owing to absorption of oxygen from the atmosphere. Ammonic salts partially prevent the precipitation by the fixed alkalies, and $AmHo$ gives but a slight precipitate in a ferrous solution, containing a sufficient amount of $AmCl$. The presence of non-volatile organic acids, of sugar, etc., also prevents the precipitation more or less.

$CONao_2$, $COKo_2$, or $COAmo_2$ precipitates *white* **ferrous carbonate,** $COFeo''$, which becomes rapidly oxidized when exposed to air.

K_4FeCy_6 (**potassic ferrocyanide**) produces, by the replacement of K_2 by Fe'', a *bluish-white* precipitate of **dipotassic ferrous ferrocyanide,** $K_2Fe''FeCy_6$, thus:—

$$SO_2Feo'' + K_4FeCy_6 = \underset{\text{Bluish-white precipitate.}}{K_2Fe''FeCy_6} + SO_2Ko_2.$$

insoluble in hydrochloric acid. The light blue precipitate is rapidly converted into a *dark blue* precipitate, or **Prussian blue,** either by exposure to the air, or more speedily by an oxidizing agent, thus:—

$$4K_2Fe''FeCy_6 + 2Cl_2 = \underset{\text{Prussian blue.}}{3FeCy_2,2Fe_2Cy_6} + 4KCl + K_4FeCy_6.$$

$K_6Fe_2Cy_{12}$ (**potassic ferricyanide**) produces a *dark blue* precipitate of **triferrous diferric dodecacyanide,** $Fe''_3{}'Fe'''_2Cy_{12}$ (**Turnbull's blue**), insoluble in hydrochloric acid, thus:—

$$3SO_2Feo'' + K_6Fe_2Cy_{12} = \underset{\text{Turnbull's blue.}}{Fe''_3{}'Fe'''_2Cy_{12}} + 3SO_2Ko_2.$$

$NaHo$ or KHo decomposes both precipitates with formation of soluble alkaline ferro- and ferricyanides, and separation of ferrous and ferric hydrates, thus:—

$$(1)\quad K_2Fe''FeCy_6 + 2KHo = K_4FeCy_6 + FeHo_2.$$
$$(2)\quad 3FeCy_2,2Fe_2Cy_6 + 12NaHo = 3Na_4FeCy_6 + 2Fe_2Ho_6.$$
$$(3)\quad Fe''_3{}'Fe'''_2Cy_{12} + 8NaHo = 2Na_4FeCy_6 + Fe_3O_4,4OH_2.$$

These precipitates cannot form, therefore, in an alkaline solution.

CyKs (**potassic sulphocyanate**) gives no indication, if the ferrous contains no ferric salt.

B. **Ferric compounds**.—We employ A SOLUTION OF FERRIC CHLORIDE, $'\mathbf{Fe}'''_2\mathrm{Cl}_6, = \left\{\begin{matrix} '\mathbf{Fe}'''\mathrm{Cl}_3 \\ '\mathbf{Fe}'''\mathrm{Cl}_3 \end{matrix}\right.$.

$\mathbf{S}\mathrm{Am}_2$ (**group-reagent**) produces a *black* precipitate of **ferrous sulphide**, $\mathbf{Fe}\mathrm{S}$, mixed with sulphur, thus:—$\mathbf{Fe}_2\mathrm{Cl}_6 + 3\mathbf{S}\mathrm{Am}_2 = 2\mathbf{Fe}\mathrm{S} + \mathrm{S} + 6\mathrm{AmCl}$. Dilute solutions of iron give only a greenish coloration.

On dissolving the black precipitate in dilute hydrochloric acid, sulphuretted hydrogen is evolved, and white insoluble sulphur is left. (DISTINCTION BETWEEN FERROUS AND FERRIC SALTS.) Sulphur is not capable of forming a ferric sulphide in the wet way; native sulphides exist, however, viz., $\mathbf{Fe}\mathrm{S}_2$ and $\mathbf{Fe}_2\mathrm{S}_3$, which are insoluble in dilute hydrochloric acid, but dissolve with evolution of $\mathbf{S}\mathrm{H}_2$ in the presence of metallic zinc.

$\mathbf{S}\mathrm{H}_2$ does not precipitate $\mathbf{Fe}_2\mathrm{Cl}_6$; its hydrogen acts as a reducing agent upon the ferric salt, converting it into $2\mathbf{Fe}\mathrm{Cl}_2$ and $2\mathrm{HCl}$, white sulphur being precipitated, which renders the solution of the ferrous salt milky.

KHo, NaHo, or AmHo precipitates the *reddish-brown* **ferric hydrate**, $\mathbf{Fe}_2\mathrm{O}_3,2\mathbf{O}\mathrm{H}_2 = \left\{\begin{matrix} '\mathbf{Fe}'''\mathrm{Ho}_2 \\ '\mathbf{Fe}'''\mathrm{Ho}_2 \end{matrix}\right.\mathrm{O}$, or **diferric oxytetrahydrate**, insoluble in excess and in ammonic salts (except $\mathbf{C}\mathrm{OAmo}_2$). Non-volatile organic bodies (*e.g.*, tartaric or citric acid, sugar, etc.) prevent its precipitation by AmHo, but not by $\mathbf{S}\mathrm{Am}_2$. The precipitate retains with great tenacity small portions of the fixed alkalies.

$\mathbf{C}\mathrm{ONao}_2$, $\mathbf{C}\mathrm{OKo}_2$, and $\mathbf{C}\mathrm{OAmo}_2$ produce the same precipitate with evolution of carbonic anhydride.

$\mathbf{P}\mathrm{OHoNao}_2$ (**hydric disodic phosphate**) produces a *yellowish-white flocculent-gelatinous* precipitate of **ferric phosphate**, $\mathbf{P}_2\mathrm{O}_2\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}}$, $+ 4\mathrm{Aq}$. The precipitation is complete only in the presence of sodic or ammonic acetate, thus:—

$$\mathbf{Fe}_2\mathrm{Cl}_6 + 2\mathbf{P}\mathrm{OHoNao}_2 + 2\left\{\begin{matrix} \mathbf{C}\mathrm{H}_3 \\ \mathbf{C}\mathrm{ONao} \end{matrix}\right. = \mathbf{P}_2\mathrm{O}_2\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}} + 6\mathrm{NaCl} + 2\left\{\begin{matrix} \mathbf{C}\mathrm{H}_3 \\ \mathbf{C}\mathrm{OHo} \end{matrix}\right.$$

On the addition of the first few drops of hydric disodic phosphate, and as long as the ferric salt is largely in excess, the precipitate may disappear again, especially on gently warming, since it is somewhat soluble in ferric acetate. When the precipitation is nearly complete, the ferric phosphate separates more speedily, especially on stirring and gently heating, and allowing to subside after each addition of the phosphate solution. The precipitated ferric phosphate should be filtered hot, and washed by decantation with hot water. It is soluble in dilute mineral acids—hence the addition of an alkaline acetate; insoluble, however, in acetic acid, like the corresponding chromic* and aluminic phosphates.

Phosphates of the alkaline earthy metals (Ba, Sr, Ca, Mg), which are readily soluble in acetic acid, may thus be separated by filtration from the phosphates of Fe^{iv}, Al^{iv}, (and Cr^{iv}). Owing to this property of ferric phosphate, it is also possible to decompose alkaline earthy phosphates, in a sodic acetate and acetic acid solution, by adding, drop by drop, a neutral solution of ferric chloride, according to the equation :—

$$2\mathbf{P}OHoBao'' + 2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. + \left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{Fe}_2Cl_6 = \mathbf{P}_2O_2Fe_2o^{vi}$$
$$+ 2\mathbf{Ba}Cl_2 + 2NaCl + 3\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.,$$

as long as a yellowish-white precipitate comes down, and till the supernatant liquid becomes just red, from the formation of ferric acetate.

Ferric phosphate dissolves in excess of hydric disodic phosphate, in the presence of ammonic hydrate or carbonate, to a brownish-red solution. It is somewhat soluble in ferric, but not in ferrous acetate. Alkalies decompose it with difficulty only. Ammonic hydrate reduces it to a basic phosphate ($\mathbf{P}_4O(Fe_2O_6)^{vi}Fe_2o^{vi}{}_2 + 16$ aq.). Potassic or sodic hydrate removes nearly the whole of the acid. Fusion with caustic fixed alkalies, or with fusion-mixture, or boiling with ammonic sulphide, decomposes ferric phosphate completely, leaving the iron as oxide or sulphide, from which the soluble alkaline phosphate can be separated readily by filtration.

Citric or tartaric acid prevents the precipitation of ferric phosphate.

K_4FeCy_6 gives a *fine blue* precipitate, $3FeCy_2,2Fe_2Cy_6$, known as **Prussian blue,** thus :—$2\mathbf{Fe}_2Cl_6 + 3K_4FeCy_6 = 3FeCy_2,2Fe_2Cy_6 + 12KCl$. Insoluble in hydrochloric acid; decomposed by KHo or NaHo; soluble in oxalic acid ; soluble also in excess of K_4FeCy_6, to a blue solution.

$K_6Fe_2Cy_{12}$ produces no precipitate, but the yellow colour of the ferric solution changes to *reddish-brown*. (DISTINCTION BETWEEN FERROUS AND FERRIC SALTS.)

CyKs (**potassic sulphocyanate**) gives a *dark red* or *blood red* colour, even in the case of very dilute solutions, which is not destroyed by hydrochloric acid. The sensitiveness of the reaction is heightened by shaking a hydrochloric acid solution containing mere traces of a ferric salt with ether. The *blood red* **ferric sulphocyanate,** $Cy_6Fe_2s^{vi}$, being soluble in ether, becomes thus concentrated into a small bulk of liquid. The colour of the liquid is readily destroyed by a solution of mercuric chloride (also by tartaric or phosphoric acid). (Distinction of Fe'' from Fe^{iv}.)

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* Chromic phosphate, especially when freshly precipitated, is dissolved, although with some difficulty, in acetic acid, especially on heating.

This confirmatory test should invariably be applied, because ferric acetate, when heated in presence of acetic acid, gives likewise a deep red coloration, which becomes lighter coloured on cooling.

Excess of **sodic acetate**, added to a solution of a ferric salt, produces a deep red-coloured liquid, owing to the formation of ferric acetate. On diluting and boiling, the whole of the iron is precipitated as **basic ferric acetate** in the form of *brownish-yellow flakes*, which should be filtered hot, and as quickly as possible, as soon as the fluid has become clear. (Method for separating Fe^{iv} from Mn''.)

Ammonic succinate or **benzoate** precipitates ferric, but not ferrous salts' as **ferric succinate** or **benzoate**.* The ferric solution should be perfectly neutral. Salts of **FeO**, **MnO**, **CoO**, **NiO**, **ZnO** are not precipitated. (Method of separation of Fe^{iv} from Fe'', Mn, Ni, Co, Zn.)

Freshly precipitated and well washed **baric** or **calcic carbonate**, suspended in water, precipitates ferric (not ferrous) chloride, as **ferric hydrate**, $\mathrm{Fe_2Ho_6}$, mixed with basic salt, with evolution of carbonic anhydride. The reagent is added to the *neutral* ferric salt *in the cold*, and well shaken up with it, till the *reddish-brown* precipitate acquires a whitish appearance, from excess of the alkaline earthy carbonate.

COBao'' separates in like manner the higher or -ic chlorides of this group from the lower or -ous chlorides. In order to separate ferric from ferrous compounds, or ferric (chromic and aluminic compounds) from ferrous, zincic, manganous, cobaltous, and nickelous salts, it is necessary that these metals should all be obtained in the form of chlorides, when, on the addition of baric carbonate, the respective hydrates, mixed with basic salts, are precipitated from the ferric, etc., chlorides, whilst ferrous chloride and the chlorides of Zn, Mn, Ni, and Co, are not affected. Air has to be excluded as carefully as possible, in order to prevent the oxidation of the ferrous, manganous, and cobaltous oxides; and the reaction should be performed in a small flask, filled nearly to the neck with the liquid, and kept well stoppered, after the evolution of the carbonic anhydride has ceased. The addition of ammonic chloride, previous to the precipitation with baric carbonate, almost entirely prevents any cobaltous and nickelous hydrates from falling out with the baric carbonate precipitate. (Method for separating Fe^{iv}, (also Al and Cr), from Fe'', Zn'', Mn'', Ni'', and Co''.)

The precipitate is filtered off and dissolved in hydrochloric acid; the barium is removed by means of dilute sulphuric acid, and the iron, etc., precipitated by AmHo.

Tannic as well as **gallic acid** (tincture of nut-galls) produces from neutral ferric salts a *bluish-black* precipitate (ink), readily soluble in acids.

A very delicate reaction for Fe^{iv} consists in adding a few drops of a solution of potassic ferricyanide to a dilute solution of a ferric salt, and next a few drops of a very dilute solution of stannous chloride, $\mathbf{Sn}Cl_2$. A blue precipitate indicates the presence of iron, thus:—

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* The formulæ of these compounds will be explained under the respective acids.

(1) $\mathbf{Fe}_2Cl_6 + K_6Fe_2Cy_{12}$ gives no precipitate, but merely a dark-brown coloration.

$$(2)\quad \mathbf{Fe}_2Cl_6 + \mathbf{Sn}Cl_2 = 2\mathbf{Fe}Cl_2 + \mathbf{Sn}Cl_4.$$

$$(3)\quad 3\mathbf{Fe}Cl_2 + K_6Fe_2Cy_{12} = \underset{\text{Turnbull's blue.}}{Fe''_3Fe_2Cy_{12}} + 6KCl.$$

A ferric salt when coming in contact with certain bodies (especially bodies containing some latent bonds) which possess a stronger affinity for oxygen, chlorine, etc., than the ferric compound, acts towards such bodies as an **oxidizing agent.** Thus $\mathbf{S}^{iv}OHo_2$ is converted into $\mathbf{S}^{vi}O_2Ho_2$; KI gives off iodine; $\mathbf{Sn}''Cl_2$ is converted into $\mathbf{Sn}^{iv}Cl_4$; $\mathbf{S}SONao_2$ (sodic hyposulphite) is oxidized to $\mathbf{S}O_2HoNao$. Iron or zinc readily reduce ferric to ferrous salts.

C. **Ferric anhydride,** $\mathbf{Fe}^{vi}O_3$, or ferric acid, $\mathbf{Fe}^{vi}O_2Ho_2$, containing hexad iron, has never been obtained in an uncombined state. The alkali salts only are known and are obtained, like the alkaline manganates, by fusing iron filings with nitre. Ferrates are decomposed far more readily than manganates.

QUESTIONS AND EXERCISES.

1. Mention compounds illustrative of the dyad, tetrad, and hexad nature of iron.
2. Enumerate some of the most important iron ores used for the extraction of iron in this country. Give constitutional and graphic formulæ.
3. Which are the more important sulphides of iron? Give constitutional and graphic formulæ.
4. Give the graphic formulæ of *chloropal*, *chrome iron ore*, *green copperas*, and *vivianite*.
5. How is iron detected in the dry way?
6. What takes place when iron is dissolved in HCl, in $\mathbf{S}O_2Ho_2$, or in dilute $\mathbf{N}O_2Ho$?
7. Explain the change which takes place when $\mathbf{Fe}Cl_2$ is severally acted upon by atmospheric air, by chlorine, KO_3Cl and HCl, $\mathbf{N}O_2Ho$, $\mathbf{Hg}Cl_2$, $\mathbf{Au}Cl_3$, and by $\mathbf{Mn}_2O_6Ko_2$ and HCl. Express the changes by equations.
8. Give graphic formulæ for ferric chloride, ferric hydrate, ferrous sulphide, dipotassic ferrate.
9. Explain the action of $\mathbf{S}H_2$ and $\mathbf{S}Am_2$ upon ferric salts, 1st, in acid solutions; 2nd, in neutral or alkaline solutions.
10. How does K_4FeCy_6 and $K_6Fe_2Cy_{12}$ enable us to distinguish between ferrous and ferric salts?
11. State why $K_6Fe_2Cy_{12}$, in the presence of $\mathbf{Sn}Cl_2$, produces a blue precipitate with ferric salts.
12. Explain the action of CyKs upon ferrous and ferric salts.
13. Explain the action, 1st of $\left\{\begin{matrix} COHo \\ COHo \end{matrix}\right.$, 2nd, of KHo, 3rd, of K_4FeCy_6 upon Prussian blue.
14. What change is produced when $\mathbf{Fe}_2Cl_6$ is brought together, 1st, with $\mathbf{S}O_2$, 2nd, with $\mathbf{Sn}Cl_2$?
15. Explain the action of metallic iron or metallic zinc upon $\mathbf{S}_3O_6Fe_2o^{vi}$.
16. How would you prepare dipotassic ferrate? Explain the action, 1st, of water; 2nd, of HCl upon it.
17. How much hydrogen gas by weight and volume (at 0° C. and 760 mm.) is obtained when 10 grms. of metallic iron are dissolved in dilute hydrochloric acid?

18. How much sulphurous anhydride gas by weight and by volume is required to reduce 1·324 grm. of ferric sulphate to ferrous sulphate?
19. Describe the properties of ferric phosphate. State why an alkaline acetate has to be added, previous to precipitation with hydric disodic phosphate, and explain the decomposition of the phosphates of the alkaline earths by means of ferric chloride in an acetic solution.
20. The value of a ton of Sicilian sulphur (containing 94 per cent. of S) is £5, that of a ton of *iron pyrites*, $\mathbf{FeS_2}$, containing 46·5 per cent. of sulphur, £1 10*s*. 6*d*. Ascertain which can be more profitably worked in the manufacture of sulphuric acid, having regard merely to the respective sources of sulphur.
21. How much metallic iron is required to manufacture one ton of crystallised *green vitriol?*
22. ·432 grm. of *brown hæmatite ore* gave ·350 grm. of $\mathbf{Fe_2O_3}$. What is the percentage of metallic iron in the ore, and what the percentage of *brown hæmatite* present?
23. How is $\mathbf{Fe_2O_3}$ separated from $\mathbf{FeO}$? Describe two methods.
24. How would you separate $\mathbf{Fe_2O_3}$ from Zn'', Mn'', Ni'', and Co''?
25. Why is it preferred to precipitate $\mathbf{Fe_2Cl_6}$ by means of AmHo, instead of KHo?

CHROMIUM, Cr'', ^{iv}, and ^{vi}. Atomic weight, 52·5.—This element is comparatively rare. It occurs in nature chiefly as *chrome iron ore*, $\mathbf{Cr_2O_3,FeO} = \left\{\begin{matrix}\mathrm{CrO}\\ \mathrm{CrO}\end{matrix}\right.\mathrm{Feo}''$, and *crocoisite*, $\mathbf{CrO_2}\mathrm{Pbo}''$. Chromic oxide constitutes the colouring matter in ruby, green serpentine, etc.

REACTIONS IN THE DRY WAY.

Chromium compounds are readily recognized by the very characteristic **green** colour which the oxide imparts to *borax* and microcosmic salt, especially in the *reducing* flame. *Finely powdered* chrome iron ore, when fused in a platinum spoon or crucible with four times its weight of hydric potassic sulphate, and then with the addition of an equal bulk of nitre and $\mathbf{CO}\mathrm{Ko_2}$ (equally mixed), yields a *yellow mass* of **potassic chromate**, $\mathbf{CrO_2}\mathrm{Ko_2}$, which is soluble in water, to a *yellow* solution. If manganese were present the solution would be *green*, owing to the formation of POTASSIC MANGANATE. This latter can be readily removed by adding a few drops of alcohol to the solution, heating, and filtering off the manganic hydrate. The chromate remains unchanged.

REACTIONS IN THE WET WAY.

Chromic salts can be prepared from the yellow $\mathbf{CrO_2}\mathrm{Ko_2}$, or the red dipotassic dichromate, $\mathbf{Cr_2O_5}\mathrm{Ko_2}$, by heating with dilute hydrochloric acid and adding alcohol, drop by drop, when the yellow solution changes to a deep green solution of $\mathbf{Cr_2Cl_6} = \left\{\begin{matrix}'\mathbf{Cr}'''\mathrm{Cl_3}\\ '\mathbf{Cr}'''\mathrm{Cl_3}'\end{matrix}\right.$ in which the Cr exists as a tetrad or pseudotriad element.

A lower chloride, $\mathbf{CrCl_2}$, has been prepared in which Cr acts as a dyad element; but as it has to be carefully kept from the air to prevent its becoming rapidly oxidised, and as it is of no real practical use, a passing notice of it will suffice.

Chromium is capable of forming three series of compounds*

Chromous compounds containing dyad Cr.	Chromic compounds containing tetrad Cr.	Chromates containing hexad Cr.
$Cr''Cl_2$.	$'Cr'''_2Cl_6$.	$Cr^{vi}O_2Ko_2$.
$Cr''O$.	$'Cr'''_2O_3$.	$Cr^{vi}O_2Pbo''$.
$Cr''Ho_2$.	$'Cr'''_2Ho_6$.	

of which we purpose studying only the two latter.

A. **Chromic Compounds.**—We employ a SOLUTION OF CHROMIC CHLORIDE, Cr_2Cl_6.

SAm_2 (**group-reagent**) precipitates *bluish-green* **chromic hydrate,** Cr_2Ho_6, insoluble in excess.

AmHo precipitates the **hydrate,** somewhat soluble in excess, the fluid acquiring a pink tint. The precipitation is complete on boiling.

KHo or NaHo, same precipitate, readily soluble in excess to a green solution; reprecipitated by long-continued boiling or on adding AmCl, whereby the fixed alkali is removed as KCl or NaCl, with substitution of AmHo.

$CONao_2$ and $COAmo_2$ give *greenish* precipitates of **basic carbonates** (varying in composition), somewhat soluble in excess.

$POHoNao_2$ (**hydric disodic phosphate**) precipitates *green* **chromic phosphate,** $P_2O_2Cr_2o^{vi}$, soluble in mineral acids, difficultly soluble in acetic acid.

$COBao''$ precipitates **basic carbonate.** The precipitation takes place in the cold, but is completed only after long digestion.

In the presence of citric, tartaric, and oxalic acid, also of sugar, the precipitation of chromic salts by means of ammonia, sodic, or baric carbonate is more or less incomplete.

Chromic compounds may be recognised also by converting the chromic oxide into chromic acid. This may be accomplished :—

1st. By boiling a solution of Cr_2Cl_6 with PbO_2 and KHo or NaHo. The reaction which takes place, and which is indicated by a change of colour (from *green* to *yellow*), may be expressed thus :—

$$(1)\quad Cr_2Cl_6 + 6KHo = \underset{\substack{\text{Soluble in}\\\text{excess of KHo.}}}{Cr_2Ho_6} + 6KCl.$$

$$(2)\quad Cr_2Ho_6 + 3PbO_2 = \underset{\substack{\text{Soluble in}\\\text{KHo.}}}{2CrO_2Pbo''} + \underset{\substack{\text{Soluble in}\\\text{KHo.}}}{PbO} + 3OH_2.$$

On acidulating the solution with acetic acid, a precipitate of plumbic chromate, CrO_2Pbo'' is obtained.

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[*] The intermediate oxides, $Cr_2O_3,CrO = \left\{\begin{matrix}CrO\\CrO\end{matrix}\right.Cro''$ (chromous dichromic tetroxide), and CrO_2 (chromic dioxide) cannot be considered here.

2nd. By boiling a solution of $\mathbf{Cr}_2Cl_6$ with NaHo and sodic hypochlorite, ClNao, thus :—

$$\mathbf{Cr}_2Ho_6 + 3ClNao + 4NaHo = \underset{\text{Yellow sodic chromate.}}{2\mathbf{Cr}O_2Nao_2} + 3NaCl + 5\mathbf{O}H_2.$$

3rd. By fusion with alkaline carbonates and nitre (or, better still, with potassic chlorate), on platinum foil.

B. **Chromic anhydride,** $\mathbf{Cr}^{vi}O_3$.—Chromic acid, $\mathbf{Cr}O_2Ho_2$, combines with KHo to form two salts, the *normal*, or *yellow chromate*, $\mathbf{Cr}O_2Ko_2$, and the *orange-red dichromate*, $\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right.$, isomorphous with the corresponding sulphate and disulphate. A solution of the neutral (yellow) chromate is changed to an orange-red (acid) dichromate solution on boiling with nitric acid, one half of the alkaline base being removed in the form of potassic nitrate. The two salts are separated by crystallisation.

The anhydride may be prepared by slowly adding to a cold saturated solution of the red dipotassic dichromate $1\frac{1}{2}$ times its bulk of concentrated sulphuric acid, and allowing it to cool slowly. $\mathbf{Cr}O_3$ crystallises out in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed to drain upon a porous tile or slab of unglazed porcelain (biscuit) and kept covered with a bell-jar. They must be preserved in a well-stoppered bottle.

Chromic anhydride is one of the most powerful oxidising agents known. Two molecules of $\mathbf{Cr}O_3$ yield upon ignition chromic oxide and three atoms of oxygen, according to the equation :—

$$2\mathbf{Cr}O_3 = \mathbf{Cr}_2O_3 + O_3.$$

The metal chromium appears to exist in nature mostly in the tetrad and hexad state, as a glance at its natural compounds will show. Chromium differs, however, in a marked manner from iron and manganese, which can likewise exist in the tetrad and hexad state, by forming more stable hexad compounds (chromates), whilst in perchromic acid, on the other hand, the metal chromium appears to hold the oxygen less firmly than manganese holds it in permanganic acid.

REACTIONS OF $\mathbf{Cr}O_3$ BASED UPON ITS OXIDISING ACTION.

A SOLUTION OF DIPOTASSIC DICHROMATE, $\mathbf{Cr}_2O_5Ko_2$, may be employed.

$\mathbf{S}H_2$, in the presence of free hydrochloric acid, reduces the orange-red solution to a green liquid, sulphur only being precipitated, thus :—

$$\mathbf{Cr}_2O_5Ko_2 + 8HCl + 3\mathbf{S}H_2 = \mathbf{Cr}_2Cl_6 + 2KCl + 7\mathbf{O}H_2 + S_3.$$

$\mathbf{S}Am_2$, added in excess to a solution of an alkaline chromate or dichromate, precipitates *dirty green* **hydrated chromic chromate,** On boiling, the whole of the chromium separates as *green* **chromic hydrate**, thus:—

$$Cr_2O_5Ko_2 + 3SAm_2 + 7OH_2 = Cr_2Ho_6 + S_3 + 2KHo + 6AmHo.$$

In the one case the H_2 of the SH_2 acted as the reducing agent; in the other the $(NH_4)_2$ of the SAm_2.

$SOHo_2$, in the presence of a little free SO_2Ho_2, reduces potassic dichromate to chromic sulphate, thus:—

$$Cr_2O_5Ko_2 + 3SOHo_2 + SO_2Ho_2 = S_3O_6Cr_2o^{vi} + SO_2Ko_2 + 4OH_2.$$

Chromic sulphate and potassic sulphate constitute potassium chrome alum, or (dipotassic chromic tetrasulphate) $\left.\begin{matrix}SO_2Ko\\SO_2=\\SO_2=\\SO_2Ko\end{matrix}\right]Cr_2o^{vi}$.

$\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.$ (**oxalic acid**), in the presence of free acid (dilute sulphuric acid), produces the same reaction, carbonic anhydride being evolved. Six molecules of CO_2 become the measure for one molecule of dipotassic dichromate. Tartaric and citric acid act in like manner.

$$Cr_2O_5Ko_2 + 3\left\{\begin{matrix}COHo\\COHo\end{matrix}\right. + 4SO_2Ho_2 = \left.\begin{matrix}SO_2Ko\\SO_2\\SO_2\\SO_2Ko\end{matrix}\right]Cr_2o^{vi} + 6CO_2 + 7OH_2.$$

SO_2Ho_2 (concentrated) reduces the dichromate, on the application of heat, with evolution of oxygen and formation of potassium chrome alum, thus:—

$$\left\{\begin{matrix}CrO_2Ko\\O\\CrO_2Ko\end{matrix}\right. + 4SO_2Ho_2 = \left.\begin{matrix}SO_2Ko\\SO_2\\SO_2\\SO_2Ko\end{matrix}\right]Cr_2o^{vi} + 4OH_2 + O_3.$$

HCl (concentrated) evolves chlorine, and the hydrogen combines with the three available atoms of oxygen in the dichromate, thus:—

$$\left\{\begin{matrix}CrO_2Ko\\O\\CrO_2Ko\end{matrix}\right. + 14HCl = Cr_2Cl_6 + 2KCl + 7OH_2 + 3Cl_2.$$

As_2O_3 (in a hydrochloric acid solution) is converted into $AsOHo_3$, thus:—

$$\left\{\begin{matrix}CrO_2Ko\\O\\CrO_2Ko\end{matrix}\right. + 3AsHo_3 + 8HCl = Cr_2Cl_6 + 2KCl + 3AsOHo_3 + 4OH_2.$$

$SnCl_2$, $SbCl_3$, $FeCl_2$, Zn (Fe, Sn, etc.) in the presence of dilute HCl, reduce likewise chromates or dichromates. The reduction is effected also most readily by numerous organic bodies,—frequently with explosive violence—such as alcohol and HCl, in which case the alcohol is oxidised to aldehyde, ethylic chloride, and other volatile products.

REACTIONS FOR CrO_3 PRODUCED BY DOUBLE DECOMPOSITION.

Chromates of the alkalies and alkaline earthy bases (with the exception of baric chromate), also of iron (Fe^{iv}), zinc, manganese, and copper, are soluble in water; all other chromates are insoluble, but dissolve readily in dilute nitric acid.

$BaCl_2$, added to a solution of a normal chromate (or dichromate), gives a *light lemon-yellow* precipitate of **baric chromate**, CrO_2Bao'', even in very dilute solutions; insoluble in acetic acid, difficultly soluble in *dilute* nitric or hydrochloric acid, and reprecipitated by AmHo.

$\begin{matrix}\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\\\left\{\begin{matrix}CO\\CH_3\end{matrix}\right.\end{matrix}Pbo''$ (**plumbic acetate**) gives a *fine lemon-yellow* precipitate of **plumbic chromate**, CrO_2Pbo'', soluble in KHo, sparingly soluble in dilute nitric, insoluble in acetic acid. The neutral salt is converted upon digestion with alkalies into a basic red chromate, $CrO(PbO_2)''Pbo''$.

NO_2Ago (**argentic nitrate**) gives a *dark purple-red* precipitate of **argentic chromate**, CrO_2Ago_2, soluble in nitric acid and ammonia. From weak acid solutions **argentic dichromate**, $\left\{\begin{matrix}CrO_2Ago\\O\\CrO_2Ago\end{matrix}\right.$, is precipitated.

$\begin{matrix}NO_2\\NO_2\end{matrix}Hg_2o''$ (**mercurous nitrate**) gives a *dark brick-red* basic precipitate of $CrO(Hg_2O_2)''Hg_2o''$, which on ignition is converted into oxygen, mercury vapour, and finely divided green Cr_2O_3. (METHOD OF SEPARATING CHROMIC ACID FROM CHROMIC OXIDE.)

On bringing together a little chromic acid with hydric peroxide, O_2H_2, in an aqueous solution, a deep indigo-blue solution is produced, owing probably to the formation of PERCHROMIC ACID, in which compound chromium plays the part of a pseudo-octad element, analogous to manganese in permanganic acid.

A solution of perchromic acid decomposes, however, rapidly with evolution of oxygen, leaving CrO_2Ho_2, and its constitution is yet doubtful. A solution in ether is far more stable than an aqueous solution. It is obtained by adding ether to a very dilute (acid) solution of O_2H_2, and then a drop of a dilute solution of a chromate. On shaking up gently the ether takes up the whole of the perchromic acid, and acquires an intensely blue colour. Mere traces of CrO_3 can be discovered in this manner, or *vice versâ* the smallest quantities of O_2H_2.

QUESTIONS AND EXERCISES.

1. Which is the most important chromium ore? Give symbolic and graphic formulæ.
2. How is chromium detected in the dry way?
3. What analogy exists there between *chrome iron ore* and chromous dichromic tetroxide?

4. Describe how chromic chloride or sulphate is obtained from an alkaline chromate.
5. Give symbolic and graphic formulæ for dipotassic chromate and dichromate, and trace their analogy with the corresponding sulphates.
6. Describe the reactions by double decomposition which you can produce with chromic compounds. Give equations.
7. How can chromic compounds be converted in the wet way into chromates? Give instances, and express the changes by equations.
8. How is chromic anhydride prepared?
9. Give instances of the oxidizing action of chromic acid. Express the changes by symbolic equations.
10. What is the composition of potassium chrome alum? State shortly by what processes it is prepared from *chrome iron ore.*
11. You have given to you oxalic, hydrochloric, and concentrated sulphuric acids, dipotassic dichromate and water. State how you would prepare CO_2, O, or Cl gas from these materials, and express the changes by equations.
12. What is the action of nascent hydrogen upon alkaline chromates. Give several instances, and express the changes by equations.
13. Describe some of the most characteristic reactions for chromic acid produced by double decomposition. Give equations.
14. How would you distinguish between chromic oxide and chromic acid occurring in one and the same solution?
15. Which chromates are soluble and which are insoluble in water?
16. What evidence is there for the existence of perchromic acid?
17. How can we test for mere traces of hydric peroxide?
18. Calculate the percentage composition of potassium chrome alum containing 24 molecules of water of crystallisation.
19. How can Cr be separated from every other metal of Group III, except Mn?
20. How can Cr_2O_3 be separated from Fe'', Zn'', Mn'', Ni'', Co'' salts?
21. 1·600 grm. of *chrome iron ore* yielded 2·95 grms. of CrO_2Pbo''. What percentage of Cr does the ore contain, and how much dipotassic dichromate can be manufactured from one ton of the ore?
22. 1·2 grm. of a sample of sodic chromate yielded with oxalic acid ·89 grm. of carbonic anhydride. What percentage of chromic anhydride did it contain?

ALUMINIUM, Al'' and ^{iv}. Atomic Weight, 27·5.—One of the metallic elements which occurs most abundantly in nature, both in the form of the OXIDE, and, as an important constituent of many minerals, in combination with SILICA, with SULPHURIC, PHOSPHORIC, and other acids; and in the form of FLUORIDE in *cryolite*, and the rare *topaz*. For a list of some of the more interesting aluminic compounds the student is referred to Frankland's "Lecture Notes," vol. I, page 179.

REACTIONS IN THE DRY WAY.

Alumina, when heated on charcoal, is distinguished from other earths by its property of assuming a beautiful SKY-BLUE colour, after being moistened with a solution of cobaltous nitrate and ignited once more strongly, owing to its forming with the cobalt oxide a quasi-salt—cobaltous aluminate. This test is not always decisive, and becomes inapplicable when coloured oxides, such as Fe_2O_3, MnO, &c., are present, in which case recourse must be had to the examination in the wet way, in order to discover Al_2O_3.

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF AMMONIUM ALUM, $\mathbf{S}_4\mathrm{O}_8\mathrm{Amo}_2\mathrm{Al}_2\mathrm{o}^{vi} = \mathbf{S}_4\mathrm{O}_8(\mathrm{OAm})_2(\mathrm{O}_6\mathrm{Al}_2)^{vi}$, in which Al plays the part of a tetrad (pseudo-triad) element, or of ALUMINIC CHLORIDE, $\left\{\begin{array}{l}'\mathbf{Al}'''\mathrm{Cl}_3 \\ '\mathbf{Al}'''\mathrm{Cl}_3\end{array}\right.$.

$\mathbf{S}\mathrm{Am}_2$ gives a *white gelatinous* precipitate of **aluminic hydrate**, $\mathbf{Al}_2\mathrm{Ho}_6$, sulphuretted hydrogen being evolved, thus :—

$$\mathbf{S}_4\mathrm{O}_8\mathrm{Amo}_2\mathrm{Al}_2\mathrm{o}^{vi} + 3\mathbf{S}\mathrm{Am}_2 + 6\mathbf{O}\mathrm{H}_2 = \mathbf{Al}_2\mathrm{Ho}_6 + 4\mathbf{S}\mathrm{O}_2\mathrm{Amo}_2 + 3\mathbf{S}\mathrm{H}_2.$$

KHo or NaHo* precipitates the **hydrate**, readily soluble in excess, forming a quasi-saline compound, **Sodic Aluminate**, $\mathbf{Al}_2\mathrm{Nao}_6$, which is reprecipitated by excess of AmCl, or by AmHo, after neutralisation of the alkali by hydrochloric acid. The alkaline solution is not precipitated by $\mathbf{S}\mathrm{Am}_2$ (METHOD OF SEPARATION OF AL FROM FE^{iv}).

AmHo precipitates the **hydrate**, somewhat soluble in excess, insoluble in the presence of much ammonic chloride, and on boiling.

$\mathbf{C}\mathrm{ONao}_2$ or $\mathbf{C}\mathrm{OAmo}_2$ precipitates **basic carbonate** of uncertain composition.

$\mathbf{C}\mathrm{OBao}''$ completely, but slowly, precipitates $\mathbf{Al}_2\mathrm{Ho}_6$, even in the cold, mixed with **basic salt**. Carbonic anhydride escapes.

$\mathbf{P}\mathrm{OHoNao}_2$ gives a *bulky white* precipitate of **aluminic phosphate**, $\mathbf{P}_3\mathrm{O}_2\mathrm{Al}_2\mathrm{o}^{vi}$, insoluble in AmHo and AmCl; soluble in KHo or NaHo, like the hydrate (AmCl reprecipitates the phosphate from the soda solution), and in acids, but not in hot acetic acid (DISTINCTION OF $\mathbf{Al}_2\mathrm{O}_3$ FROM ALUMINIC PHOSPHATE). Alkaline acetates precipitate $\mathbf{P}_2\mathrm{O}_2\mathrm{Al}_2\mathrm{o}^{vi}$ from its solution in mineral acids. The presence of citric acid, but not of tartaric acid or of sugar, prevents its precipitation.

In order to decompose aluminic phosphate (*e.g.*, in the mineral *wavellite*, $\mathbf{P}_4\mathrm{O}(\mathrm{Al}_2\mathrm{O}_6)^{vi}\mathrm{Al}_2\mathrm{o}^{vi}{}_2 12\mathbf{O}\mathrm{H}_2$), it is best to fuse the finely powdered mineral with 1½ part of finely divided $\mathbf{Si}\mathrm{O}_2$ and 6 parts of $\mathbf{C}\mathrm{ONao}_2$, in a platinum crucible, for about half an hour. The mass is digested for some time with water, and $\mathbf{C}\mathrm{OHoAmo}$ added in excess; it is then filtered and washed. The residue consists of aluminic and sodic silicate, the solution contains the sodic phosphate. Dissolve the residue in dilute hydrochloric acid, and evaporate to dryness to separate the silica, and filter. The filtrate may be tested for Al in the usual way.

Alumina occurs mostly in minerals which are not soluble in acids. Boiling with concentrated sulphuric acid attacks many; all are, however, decomposed by fusion with $\mathbf{S}\mathrm{O}_2\mathrm{HoKo}$, or with fusion mixture, and become readily soluble in water or in dilute hydrochloric acid.

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* Potassic or sodic hydrate is mostly contaminated with alumina, derived during the manufacture from porcelain vessels, etc., and it is, therefore, absolutely necessary to employ pure NaHo (prepared from sodium) for the separation of Fe and Al. It must likewise be recollected that NaHo acts destructively upon porcelain and glass vessels; the precipitate should, therefore, not be heated longer than is necessary for its complete precipitation.

Powder up some porcelain very finely, and fuse for half an hour in a platinum crucible, with four times it weight of fusion mixture. Extract with water. Transfer both the soluble and insoluble portion—consisting of alkaline aluminate—to a porcelain dish, acidulate with hydrochloric acid, and evaporate to dryness. Take up with a few drops of concentrated hydrochloric acid and hot water, and filter; wash the insoluble $\mathbf{Si}O_2$ well with hot water. The filtrate contains the aluminium as $\mathbf{Al}_2Cl_6$, from which it can be precipitated as usual.

Aluminic silicate is often found in nature associated with potassic or sodic silicate, as in *felspar* (dipotassic aluminic hexasilicate), $\mathbf{Si}_6O_8Ko_2Al_2o^{vi}$, and *albite*, $\mathbf{Si}_6O_8Nao_2Al_2o^{vi}$. In order to test for potassium and sodium, alkali salts must, of course, be carefully avoided. This can be done by making use of hydrofluoric acid.

Introduce a small quantity of finely powdered *felspar* into a platinum crucible or dish; treat with liquid hydrofluoric acid, and evaporate at a gentle heat in a closet which is connected with the chimney. HF attacks the $\mathbf{Si}O_2$, forming silicic fluoride, $\mathbf{Si}F_4$—a volatile compound—and leaves the aluminium and potassium behind as fluorides readily soluble in dilute hydrochloric acid:—

$$\mathbf{Si}_6O_8Ko_2Al_2o^{vi} + 32HF = 6\mathbf{Si}F_4 + 2KF + \mathbf{Al}_2F_6 + 16\mathbf{O}H_2.$$

The decomposition is generally only completed after two or three evaporations with HF.

QUESTIONS AND EXERCISES.

1. Enumerate some of the more important aluminium minerals; give constitutional and graphic formulæ.
2. How is $\mathbf{Al}_2O_3$ detected in the dry way?
3. Give equations for the reactions of aluminium in the wet way.
4. How is *wavellite* examined for alumina?
5. How can insoluble aluminium minerals be rendered soluble in water or acids?
6. Explain the action of HF upon *felspar* and *albite*.
7. How can $\mathbf{Al}_2O_3$ be separated from $\mathbf{Fe}_2O_3$?
8. How is $\mathbf{Al}_2O_3$ separated from Fe'', Zn'', Mn'', Ni'', Co'' compounds?
9. Calculate the percentage composition of *felspar*.
10. How can $\mathbf{Al}_2O_3$ be distinguished from $\mathbf{P}_2O_2Al_2o^{vi}$?

The separation of the metals of Group III is surrounded by some difficulties, on account of the unavoidable complication which arises from the possibly simultaneous precipitation of—

1st. *Sulphides*, viz., **Ni**S, **Co**S, **Mn**S, **Zn**S, **Fe**S.
2nd. *Hydrates*, viz., $\mathbf{Cr}_2Ho_6$, $\mathbf{Al}_2Ho_6$, and
3rd. *Phosphates* of Cr, Al, Ba, Sr, Ca, Mg,

and it is therefore well always to ascertain, by a special experiment, whether phosphoric acid, in combination with the above metals, is present or not in the solution under examination.

This can readily be done by adding AmCl, AmHo, and $\mathbf{S}Am_2$ to a small portion of a solution of metals of this group (or to the filtrate from Group II). On dissolving the precipitate which these reagents produce in a little concentrated nitric acid, and adding a solution of ammonic molybdate,* a yellow precipitate is obtained

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* For the preparation of this reagent see Appendix.

(especially on digesting for some time at a gentle heat), showing the presence of phosphoric acid. If no precipitate is obtained, the solution need only be examined for Ni, Co, Mn, Zn, Fe, Al, and Cr.

I. **Phosphoric acid is absent.**—This is sufficiently indicated if the original substance dissolved readily in water. If insoluble in water, but soluble in dilute acids, phosphoric acid may likewise be absent from the substance, but not necessarily so.

It would appear at first sight that the deportment of the five sulphides and two hydrates with ammonic chloride and ammonic hydrate, sodic or potassic hydrate, or dilute acids (*e.g.*, HCl), would enable us to separate the members of this group, or several of them, from each other. We have seen, for example, that—

1st. *Ni, Co, Mn, Zn are not precipitated by AmHo from a hot solution containing large excess of AmCl; whilst* Fe_2Ho_6,Cr_2Ho_6, *and* Al_2Ho_6 *are precipitated.* It has, however, been found that the mode of separation based upon this solvent property of ammonic chloride, gives but imperfect results, since the Fe_2Ho_6 carries down varying quantities of other oxides, especially on exposure of the solution to the air, when higher oxides of manganese and cobalt are formed, which are not soluble in ammonic chloride. Small quantities of Ni, Co, Mn, and Zn are thus frequently overlooked altogether. It is only by redissolving the precipitate and reprecipitating several times over with AmCl and AmHo, as long as the ammoniacal filtrate gives a precipitate with sulphuretted hydrogen, that iron can be separated from manganese, etc., in this manner.

With these precautions, however, it is mostly possible to separate the metals of this group from each other by first precipitating ferric, chromic, and aluminic hydrates by means of AmCl and AmHo, and then, from the filtrate, the sulphides of Ni, Co, Mn, and Zn by means of SH_2 or SAm_2; and the following method of separation may be consulted with advantage by beginners, as well as the more accurate, but more tedious one, of separation by $COBao''$ (see Table, p. 50).

2nd. *That Zn, Al, and Cr are precipitated by KHo or NaHo, but are soluble in excess, whilst the other metallic hydrates are insoluble.* From this it would appear that these three metals can be separated by means of the fixed alkaline hydrates. But it has been found that Fe_2Ho_6, $NiHo_2$, $CoHo_2$, $MnHo_2$ carry down appreciable quantities of $ZnHo_2$ and—more especially the Fe_2Ho_6 precipitate—of Cr_2Ho_6, and that a complete separation cannot be effected by precipitation with KHo or NaHo.

3rd. *Cold dilute hydrochloric acid does not dissolve* CoS *or* NiS *to any great extent, but dissolves the other sulphides and hydrates.* This method, if practised with care, gives good results, small traces only of CoS and NiS being generally dissolved out. But as it leaves the iron, aluminium, and chromium still to be separated from manganese and zinc, no saving of labour is effected thereby in the separation of these seven metals.

In finely divided freshly precipitated **baric carbonate**, $COBao''$, *we possess a reagent which separates the lower oxides, viz.*, ZnO, MnO, NiO, CoO (this latter not quite so perfectly, except in the presence of much ammonic chloride), *from the higher oxides*, viz., Fe_2O_3, Al_2O_3, and Cr_2O_3. The metals should be first obtained as chlorides.

The examination of the *precipitate* produced by $COBao''$ is based upon—

1st. The *solubility of* Al_2Ho_6 *in NaHo.*

2nd. The *conversion* of Cr_2O_3 *into* CrO_3 *by fusion with sodic carbonate and nitre, or by boiling with ClNao*, or with PbO_2 *in an alkaline solution.*

The examination of the *filtrate* is based upon—

1st. The *solubility* of $\mathbf{ZnHo_2}$ *in sodic hydrate.*
2nd. ,, $\mathbf{MnS}$ *in acetic acid.*
3rd. The *formation of soluble* $K_6Co_2Cy_{12}$ *and the precipitation of* Ni *as black* $\mathbf{Ni_2Ho_6}$ *by* ClNao, *or chlorine.*

Directions for the separation of these seven metals will be found in the analytical tables under Group IIIA.

PRACTICAL EXERCISES* ON GROUPS IIIA, IV and V.

1. A solution of ferric chloride, ammonium alum and manganous chloride, containing ·500 grm. of Fe, ·050 grm. of Mn, and ·050 grm. of Al.
2. A solution of $\mathbf{SO_2}Nio''$ and $\mathbf{N_2O_4}Coo''$, containing ·050 grm. of Ni and ·010 grm. of Co.
3. A mixture of the solid salts: zinc white, green vitriol and potassium alum; both in the dry and in the wet way.
4. A solution of $\mathbf{SO_2}Zno''$ and potassium chrome alum, containing ·500 grm. of Cr and ·050 of Zn.
5. A mixture of potassium chrome alum and green vitriol (about ·050 grm.), in the dry way only.
6. A mixture consisting of ferric oxide, manganic oxide and zincic oxide, containing ·050 grm. of $\mathbf{Fe_2O_3}$ ·010 grm. of $\mathbf{MnO_2}$ and ·100 grm. of $\mathbf{ZnO}$; to be examined in the dry way only.
7. A sample of *dolomite*, for Fe'' (Mn) Ca and Mg.
8. A sample of *calc spar*, for Fe'' and Mg.
9. Samples of iron ores, *e.g.*, *red hæmatite, brown hæmatite, magnetic iron ore, martial pyrites*, to be examined for water and sulphur only.
10. A sample of *calamine*, in the dry way only.
11. A sample of *chrome iron ore* for chromium in the dry way only.
12. A sample of *magnetic iron ore* for Fe'', in the wet way.

Tabulate the reactions produced by AmCl and AmHo, NaHo or $\mathbf{S}Am_2$ with the members of Group IIIA, according to the following scheme:—

Reagent.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	ZnO.	MnO.	NiO.	CoO.
AmCl, and AmHo.	A *white gelatinous* precipitate of $\mathbf{Al_2}Ho_6$, slightly soluble in excess, reprecipitated on boiling.						
NaHo.	Ditto, soluble in excess.						
$\mathbf{S}Am_2$.	A white gelatinous precipitate of $\mathbf{Al_2}Ho_6$, insoluble in excess.						

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* These exercises may of course be varied, and should be looked upon merely as indicative of the course to be pursued.

with the main view of fixing upon the memory the solubility or insolubility of the precipitates in excess of the reagents.

II. **Phosphoric Acid is present.**—The original substance was either insoluble or only partially soluble in water, but soluble in hydrochloric acid. In this case AmCl and AmHo* produce a precipitate, before $\mathbf{S}Am_2$ is added; the precipitate may possibly consist of $\mathbf{Ni}S$, $\mathbf{Co}S$, $\mathbf{Mn}S$, $\mathbf{Zn}S$, $\mathbf{Fe}S$, $\mathbf{Al}_2Ho_6$, $\mathbf{Cr}_2Ho_6$, as well as the phosphates of (Cr), Al, Mg, Ca, Sr, Ba.

It is obvious that ammonic phosphate is formed by the decomposition of the phosphates of the metals Ni, Co, Mn, Zn, Fe (if present) by $\mathbf{S}Am_2$—AmCl and AmHo precipitate these phosphates without decomposition—which, in its turn, would act upon any soluble salts of Mg, Ba, Sr, Ca, and precipitate phosphates of these metals, although none may have been present originally in the saline mixture. An example will make this clear. Let us suppose that the substance under examination consists of $\mathbf{C}OBao''$,$\mathbf{P}_2O_2Cao''_3$ and $\mathbf{P}_2O_2Fe_2o^{vi}$. On dissolving in hydrochloric acid, baric chloride is formed, and the calcic and ferric phosphates are dissolved without decomposition. On adding AmCl and AmHo, a yellowish-white precipitate of $\mathbf{P}_2O_2Fe_2o^{vi}$ and $\mathbf{P}_2O_2Cao''_3$ is obtained, whilst $\mathbf{Ba}Cl_2$ is not precipitated. On adding, however, the AmCl and AmHo, as well as the $\mathbf{S}Am_2$, to the solution, $\mathbf{P}_3O_2Fe_2o^{vi}$ is decomposed into $\mathbf{Fe}S$ and $\mathbf{P}OAmo_3$, which latter, by acting upon the $\mathbf{Ba}Cl_2$, would precipitate baric phosphate.

In order to avoid this, the precipitate produced in Group III by AmCl and AmHo, which contains for the most part the whole of the phosphates, is filtered off and $\mathbf{S}Am_2$ added to the filtrate only. The two precipitates are washed separately, transferred to a porcelain dish and boiled with a little $\mathbf{S}Am_2$, which decomposes the metallic phosphates (possibly also some $\mathbf{Fe}_2Ho_6$), leaving the phosphates of the earths and alkaline earthy bases (if any) as well as the hydrates of Cr and Al, unchanged. The insoluble residue is filtered off and washed with hot water (to which a little $\mathbf{S}Am_2$ has been added to prevent the oxidation of $\mathbf{Fe}S$, etc.); the filtrate is tested for phosphoric acid by means of AmCl, AmHo and $\mathbf{S}O_2Mgo''$. A white crystalline precipitate shows that phosphoric acid was present, *in combination with the metals precipitable as sulphides.*

The residue is dissolved in very little hot hydrochloric acid, with the addition of a little concentrated nitric acid; filtered, if necessary, from the sulphur which separates, and concentrated to a small bulk by evaporation. To a portion of the solution add a little more concentrated nitric acid, and then some ammonic molybdate, and heat gently. In the absence of a yellow precipitate, no phosphates of (Cr), Al, Ba, Sr, Ca, Mg need be looked for, and the solution may be examined at once according to Table IIIA. A yellow precipitate indicates *that phosphates of the earths or alkaline earthy bases*, or of both, are present, in addition to the metallic phosphates already tested for.

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* If AmCl and AmHo should give no precipitate, it is obvious that no phosphates and no Fe, Al and Cr need be looked for.

SEPARATION OF THE METALS OF GROUP IIIA BY

Add AmCl in considerable excess; heat gently, and then add AmHo drop by
the form of Fe^{iv}.) Filter quickly, and wash with hot water. Reserve the
dilute HCl on the filter. Collect the acid solution in another beaker, and
good SH_2 water produces any precipitate in the filtrate. Mix now the

<table>
<tr><td colspan="4">Solution.—Pass a current of SH_2 through the solution, and filter off ZnS, MnS, NiS, CoS. Wash off the filter, and redissolve the precipitate in dilute HCl, with the addition of a few small crystals of $\left\{\begin{matrix}OCl\\OKo\end{matrix}\right.$. Add NaHo in excess, boil, and filter.</td></tr>
<tr><td rowspan="3">The Solution may contain Zn, as $ZnNao_2$. Add SH_2. White precipitate of ZnS.
Presence of Zn.</td><td colspan="3">The Precipitate may contain $MnHo_2$, $CoHo_2$, and $NiHo_2$. Wash, dissolve in a little dilute HCl; nearly neutralize with AmHo; add excess of $\left\{\begin{matrix}CH_3\\COAmo\end{matrix}\right.$; pass a rapid current of SH_2 for several minutes through the solution, and filter.</td></tr>
<tr><td rowspan="2">The Solution contains the manganese as acetate.
Add AmCl, AmHo, and Sulphuretted Hydrogen Water.
Flesh-coloured precipitate of MnS.
Presence of Mn.</td><td colspan="2">Residue. — Dissolve in HCl and $\left\{\begin{matrix}OCl\\OKo\end{matrix}\right.$; nearly neutralize with $CONao_2$; add a weak solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for some time, allow to cool (filter off any slight precipitate), and add a <i>strong</i> solution of ClNao; allow to stand for some time in a warm place, as long as a black precipitate forms, and filter.</td></tr>
<tr><td>Precipitate consists of Ni_2Ho_6. Filter off and confirm by heating a small portion of it on a borax-bead before the blowpipe flame.
A yellowish to sherry-red bead.
Presence of Ni.</td><td>The Solution contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate to dryness, and test a little of the residue before the blowpipe flame on a borax bead.
A blue bead in both flames.
Presence of Co.</td></tr>
</table>

drop as long as a precipitate comes down. (The iron must be present in ammoniacal filtrate. Redissolve the precipitate by treating it with hot repeat in like manner the precipitation with AmCl and AmHo, as long as different ammoniacal filtrates with the main filtrate.

The PRECIPITATE consists of Fe_2Ho_6, Cr_2Ho_6, and Al_2Ho_6. Dissolve in dilute HCl, add a solution of NaHo (free from alumina) in excess, and boil for some time. Filter off.

PRECIPITATE.—Dry and fuse, with fusion mixture and NO_2Ko on platinum foil. Dissolve in hot water, and filter.

RESIDUE.—Dissolve in dilute HCl, and add K_4FeCy_6.
A precipitate of Prussian blue.

Presence of Fe.

Test the original HCl solution specially for Fe'' and Fe^{iv} by means of $Mn_2O_6Ko_2$ in a highly dilute solution, as well as by means of K_4FeCy_6, $K_6Fe_2Cy_{12}$, or CyAms.

SOLUTION, yellow. Confirm by adding $\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.$ and $\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$.
Yellow precipitate of CrO_2Pbo''.

Presence of Cr.

Note.—Traces of manganese—owing to imperfect separation of Mn from Fe by precipitation with AmCl and AmHo—are indicated by the *bluish-green* colour of the fused mass arising from the formation of an alkaline manganate, and after dissolving in water, by the *purplish-red* colour of the alkaline permanganate.

SOLUTION. — Acidulate with dilute HCl, and add AmHo in *slight* excess.
White gelatinous precipitate.

Presence of Al.

Note.—If no sodic hydrate free from alumina can be obtained, it is necessary to test an equal bulk of the reagent by acidulating with HCl and adding a *slight* excess of AmHo, and then comparing the Al_2Ho_6 thus precipitated with the precipitate obtained in testing the solution under examination.

If so, add to the rest of the solution $CONao_2$, till nearly neutral, then an excess of a solution* containing sodic acetate and strong acetic acid: $P_2O_2Fe_2o^{vi}$ (as well as $P_2O_2Cr_2o^{vi}$ and $P_2O_2Al_2o^{vi}$, if present), are precipitated. Any phosphates of the alkaline earths left undecomposed by the ferric chloride already present in the solution, are held in solution by the acetic acid. To the filtrate add Fe_2Cl_6, drop by drop, as long as a precipitate† is obtained, and till the colour of the supernatant liquid becomes distinctly reddish. Digest at a gentle heat; allow to subside and filter. In this manner the whole of the phosphates of the alkaline earthy bases are decomposed, with formation of $P_2O_2Fe_2o^{vi}$, insoluble in acetic acid—(which precipitate may be neglected), and chlorides of Mg, Ba, Sr, Ca which remain in solution, together with the chlorides of Ni, Co, Mn, Zn (and the excess of Fe_2Cl_6 added). The whole of the phosphoric acid having thus been removed, the precipitate produced by AmCl, AmHo and SAm_2 is examined according to Table IIIA. The alkaline earthy metals are separated according to Tables IV and V. It should be borne in mind that these metals can have been present in the original substance only as phosphates, and the filtrate which contains them should on no account be mixed up with the main filtrate from Group III, but should be examined separately.

It may be of interest, occasionally, to ascertain, whether any oxalates of Ba, Sr and Ca (which are destroyed by evaporation with nitric acid and ignition, before proceeding to Group III), were present in the original mixture, in which case the evaporation to dryness and ignition must be omitted.

The precipitate produced in Group III by AmCl and AmHo alone contains the oxalates, as well as the phosphates of the alkaline earthy bases, and possibly also gelatinous silica. The oxalates are decomposed by gently igniting the precipitate, and are converted into carbonates. The ignited mass effervesces strongly on extracting with dilute hydrochloric acid. When the solution is evaporated to dryness and again taken up with dilute HCl, the silica, if present, is rendered insoluble, and may be separated by filtration. To the acid solution, which may possibly contain phosphates of Mg, Ca, Sr and Ba, as well as chlorides of the bases, present before ignition as oxalates, add AmCl and AmHo and filter off. The filtrate contains the chlorides of Ba, Sr and Ca and is tested separately according to Table IV. ALL BASES SO DISCOVERED MUST HAVE BEEN PRESENT ORIGINALLY AS OXALATES.

We may, then, sum by stating that THE SEPARATION OF THE METALS AND SALTS (PHOSPHATES) PRECIPITATED IN GROUP IIIB is based upon:—

1st. *The insolubility of the phosphates of Fe, Al (and Cr) in acetic acid. in the presence of an alkaline acetate.*

2nd. *The separation of the whole of the phosphoric acid which is in combination with the alkaline earthy bases, by means of* Fe_2Cl_6, *in an acetic solution.*

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* For the preparation of this reagent see Appendix.

† If any phosphates of the alkaline earthy bases be left, Fe_2Cl_6 should produce a yellowish-white precipitate when added to *a portion of the acetic acid solution*, if not, no ferric salt need be added to the *main portion of the filtrate.* (The presence of iron, other than phosphate, is generally indicated by the reddish or ferric acetate colour of the filtrate.) In this case Al and Cr, as well as the metals of the alkaline earths, will still have to be looked for in the filtrate.

All other operations are identical with those described in Tables IIIA, IV and V.

A tabular scheme for their examination* will be found in the analytical tables, under Group IIIB.

QUESTIONS AND PRACTICAL EXERCISES ON GROUP IIIB.

1. A hydrochloric acid solution, containing common sodic phosphate, ferric chloride, calcic and magnesic chlorides.
2. A hydrochloric acid solution, containing common sodic phosphate, nickelous sulphate, cobaltous nitrate, zincic sulphate, and ferric chloride.
3. A hydrochloric acid solution of calcic phosphate, chromic chloride, and aluminic phosphate.
4. A mixture of bone-ash and much ferric oxide.
5. A mixture containing little ferric oxide and much *magnesite* (or *magnesia alba*) and *bone-ash*.
6. A hydrochloric acid solution of common alum and hydric disodic phosphate.
7. How would you recognise alumina in the presence of aluminic phosphate?
8. Given a reddish-coloured solution (owing to the presence of ferric salts), which gives a copious precipitate on the addition of sodic acetate and acetic acid in the cold, leaving the solution still coloured. What inference is to be drawn from this observation?
9. A solution contains chromic chloride, chromic phosphate, and dipotassic dichromate. State how you would distinguish these three chromium compounds from each other.
10. An acid solution (HCl) of a mixture, consisting of ferric chloride, baric chloride, and common sodic phosphate, retains its reddish colour, after precipitation with sodic acetate and acetic acid. What inference must be drawn from this, and what would you infer if the filtrate were colourless, but gave no further precipitate on the addition of $\mathbf{Fe}_2\mathrm{Cl}_6$?
11. You have a solution given to you which gives a precipitate with AmCl and AmHo. What inference must you draw if the filtrate gives no further precipitate on the addition of $\mathbf{S}\mathrm{Am}_2$?
12. You have given to you a concentrated solution of ferric chloride. On adding a few drops of a solution of hydric disodic phosphate, a yellowish precipitate appears. Explain what takes place, 1st. When a portion of the solution in which the precipitate is suspended is boiled. 2nd. When acetic acid is added, in the cold, to another portion. 3rd. When the precipitate is filtered and treated with excess of the hydric disodic phosphate, in the presence of ammonia.

CHAPTER V.

REACTIONS OF THE METALS OF GROUP II.

THIS group comprises the metals MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD and PLATINUM), which are precipitated from acid solutions (HCl) by means of sulphuretted hydrogen.

Mix together solutions of $\mathbf{N}_3\mathrm{O}_6\mathrm{Bio}'''$, $\mathbf{Hg}\mathrm{Cl}_2$, $\mathbf{S}\mathrm{O}_2\mathrm{Cuo}''$, $\mathbf{Cd}\mathrm{Cl}_2$, $\mathbf{As}_2\mathrm{O}_3$ (dissolved in HCl), $\mathbf{N}_2\mathrm{O}_4\mathrm{Pbo}''$, $\mathbf{Sb}\mathrm{Cl}_3$, $\mathbf{Sn}\mathrm{Cl}_2$, and $\mathbf{Sn}\mathrm{Cl}_4$, and pass a current of

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* The examination of Group IIIB, containing phosphates, may be deferred until the student has become acquainted with the reactions for acids.

SH_2, without first filtering off the white precipitate which is produced. Filter; pass the gas again through the clear filtrate, to make sure that the metals have been entirely precipitated. Wash the precipitate with hot water; remove a portion from the filter; boil with a little yellow ammonic sulphide, and filter off. A black residue is left, consisting of **HgS**, **PbS**, Bi_2S_3, **CuS**, **CdS**. The solution contains As_2S_3, Sb_2S_3, **SnS** and SnS_2. This can be shown by acidulating with dilute hydrochloric acid, when a yellow precipitate comes down—because yellow ammonic sulphide converts **SnS** into SnS_2—consisting of the sulphides of As, Sb, Sn.

This shows that *we can divide Group II by means of ammonic sulphide, into two portions.*

The name *sulphide*, in its widest sense, is given to all compounds into which sulphur enters as the electronegative element. A remarkable analogy is observable between oxides and sulphides. There is a certain class of sulphides which resemble metallic oxides or bases; another class which plays the part of oxy-acids. Sulphides are therefore divided into *sulpho-bases* and *sulpho-acids*. To the latter belong the sulphides of H, As, Sn, Sb (Pt, Au); to the former the sulphides of many metals, especially such of the metals as constitute powerful bases (K, Na, Am, Ba, Ca, etc.). An electropositive element, which forms with oxygen an oxide, combines generally also with the same number of sulphur atoms, to form a corresponding *sulphide*, in which the sulphur is almost invariably a dyad.

The resemblance in the constitution of these oxygen and sulphur compounds is further borne out by the analogy in their solubility and alkaline reaction. Thus we have—

	Oxy-bases.		*Sulpho-bases.*
OK_2	Potassa, alkaline and soluble.	SK_2	Potassic sulphide, alkaline and soluble.
OAm_2	Ammonia " "	SAm_2	Ammonic " "
ONa_2	Soda " "	SNa_2	Sodic " "
BaO	Baryta " "	BaS	Baric " "
CaO	Lime " "	CaS	Calcic " "
FeO	Ferrous oxide, no reaction, insoluble.	FeS	Ferrous " no reaction, insoluble.
ZnO	Zincic " "	ZnS	Zincic " "
	Oxy-anhydrides.		*Sulpho-anhydrides.*
As_2O_3	Arsenious anhydride.	As_2S_3	Arsenious sulphide, or sulpharsenious anhydride.
As_2O_5	Arsenic "	As_2S_5	Arsenic sulphide, or sulpharsenic anhydride.
Sb_2O_3	Antimonious "	Sb_2S_3	Antimonious sulphide, or sulphantimonious anhydride.
Sb_2O_5	Antimonic "	Sb_2S_5	Antimonic sulphide, or sulphantimonic anhydride.
SnO_2	Stannic "	SnS_2	Stannic sulphide, or sulphostannic anhydride.
	Oxy-acids.		*Sulpho-acids.*
$AsHo_3$	Arsenious acid.	$AsHs_3$	Sulpharsenious acid.
$AsOHo_3$	Arsenic acid.	$AsSHs_3$	Sulpharsenic acid.
$SbHo_3$	Antimonious acid.	$SbHs_3$	Sulphantimonious acid.

	Oxy-acids.		*Sulpho-acids.*
$SbOHo_3$	Antimonic acid.	$SbSHs_3$	Sulphantimonic acid.
SbO_2Ho	Metantimonic acid.	SbS_2Hs	Sulphometantimonic acid.
$SnHo_4$	Stannic acid.	$SnHs_4$	Sulphostannic acid.

Sulpho-salts are obtained by the mutual action of a sulpho-acid and a sulpho-base upon each other.

Sulphides soluble in water, comprising the sulphides of the alkalies and alkaline earthy metals, are divided into *normal sulphides*, such as SK_2, SAm_2, SNa_2, BaS; into *sulphhydrates* (acid sulphides), such as SKH, $SAmH$, $BaHs_2$; and *polysulphides*, such as S_2H_2, S_5K_2, S_5Am_2. The aqueous solutions of the normal and acid sulphides are colourless, and give off SH_2 when treated with dilute hydrochloric acid, *without separation of sulphur*. Solutions of the polysulphides are yellow, or yellowish-brown, and when treated with hydrochloric acid, give off sulphuretted hydrogen, with separation of white (or precipitated) sulphur. The number of sulpho-salts is small compared with the salts of oxy-acids, and they are far less stable than ordinary oxy-salts. This arises from the fact that sulphur is comparatively indifferent to chlorine, phosphorus, nitrogen, carbon, silicon—non-metallic elements, which are endowed with a powerful chemical affinity for oxygen, with which they form in the presence of water energetic oxy-acids—and that there are either no sulphides corresponding to the oxygen compounds of these elements, or sulphides of a very indifferent nature. The number of sulpho-acids is principally restricted to the acids enumerated above, and these again combine mostly only with the soluble sulphides possessed of an *alkaline reaction;* or, if combined with the sulphides of the heavy metals, as in certain minerals, they are readily decomposed by chemical agencies.

The following is a list of some of the more important sulpho-salts compared with the corresponding oxy-salts :—

	Oxy-salts.		*Sulpho-salts.*
$SnNao_2$	Disodic stannite.	$SnNas_2$	Disulphosodic sulphostannite.
$SnONao_2$	Disodic stannate.	$SnSNas_2$	Disulphosodic sulphostannate.
$AsKo_3$	Tripotassic arsenite.	$AsKs_3$	Trisulphopotassic sulpharsenite.
$AsONao_3$	Trisodic arsenate.	$AsSNas_3$	Trisulphosodic sulpharsenate.
$SbOKo$	Potassic metantimonite.	$SbSKs$	Sulphopotassic metasulphantimonite.
SbO_2Ko	Potassic metantimonate.	SbS_2Ks	Sulphopotassic metasulphantimonate.

In these sulphur compounds the radical Nas, sodiumsulphyl, occupies the place of the compound radical Nao, sodoxyl. In like manner

Ks Potassiumsulphyl occupies the place of Ko Potassoxyl.
Ams Ammoniumsulphyl ,, Amo Ammonoxyl.
Bas'' Bariumsulphyl ,, Bao'' Baroxyl.
Cas'' Calciumsulphyl ,, Cao'' Calciumoxyl,

in the analogous sulpho-salts.

Instances of some interesting natural sulpho-salts, to be considered more fully under silver and lead, are :—

$AsAgs_3$ trisulphargentic sulpharsenite (*proustite*).

$SbAgs_3$ trisulphargentic orthosulphantimonite (*pyrargyrite* or *dark red silver ore*).

$Sb_2S''(Cu_2FeS''_3)''_2$ sulphocuproso ferrous pyrosulphantimonite (*fahl ore*).

$Sb_2Pbs''_3$ trisulphoplumbic orthosulphantimonite (*boulangerite*).

$Sb_2Pbs''_2(Cu_2S''_2)''$ disulphoplumbic sulphocuprous orthosulphantimonite (*bournonite*).

$Sb_4S_3Pbs''Pbs''_2$ trisulphoplumbic metasulphantimonite* (*jamesonite*).

Treat another portion of the above SH_2 precipitate with NaHo or KHo and filter off. A black residue is likewise left, and on adding dilute HCl to the filtrate, As_2S_3, Sb_2S_3, SnS and SnS_2 are reprecipitated.

This shows that the *hydrates of the alkali metals dissolve a portion of the sulphides precipitated by* SH_2 *in Group II.* The following equations explain the action of the alkaline hydrates :—

Sb_2S_3	$+ \; 6KHo$	$=$	$SbKs_3$	$+$	$SbKo_3$	$+ \; 3OH_2.$		
Antimonious sulphide.			Trisulphopotassic sulphantimonite.		Tripotassic antimonite.			

As_2S_3	$+ \; 4KHo$	$=$	$AsHsKs_2$	$+$	$AsHoKo_2$	$+ \; OH_2.$		
Arsenious sulphide.			Sulphhydric disulphopotassic sulpharsenite.		Hydric dipotassic arsenite.			

$2SnS$	$+ \; 4KHo$	$=$	$SnKs_2$	$+$	$SnKo_2$	$+ \; 2OH_2.$		
Stannous sulphide.			Disulphopotassic sulphostannite.		Dipotassic stannite.			

$2SnS_2$	$+ \; 4NaHo$	$=$	$SnSNas_2$	$+$	$SnONao_2$	$+ \; OH_2$	$+$	$SH_2.$
Stannic sulphide.			Disulphosodic sulphostannate		Disodic stannate.			

Addition of hydrochloric acid reprecipitates the sulphides, thus :—

$$SbKs_3 + SbKo_3 + 6HCl = Sb_2S_3 + 6KCl + 3OH_2.$$

Hence the metals which are precipitated by SH_2 in Group II can be subdivided by means of SAm_2 or NaHo into—

A. *Metals whose sulphides act as sulpho-bases*, viz., the sulphides of Hg, Pb, Bi, Cu, and Cd. These are insoluble in ammonic sulphide (HgS dissolves to some extent in potassic or sodic sulphide; CuS is somewhat soluble in ammonic sulphide).

B. *Metals whose sulphides act as sulpho-acids*, viz., the sulphides of As, Sb, Sn (Au, Pt).

GROUP II. SUBDIVISION A.

1. Mercury. Hg''. Atomic weight, 200.—Occurs native, but is chiefly obtained from *cinnabar* or mercuric sulphide, HgS.

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* This compound may also be viewed as Sb_2S_2Pbs'' (sulphoplumbic metasulphantimonite) and $Sb_2SPbs''_2$ (sulphoplumbic pyrosulphantimonite).

EXAMINATION IN THE DRY WAY.

Add a little finely-divided lead or zinc to a few globules of mercury on a watch-glass. The liquid metal mercury becomes thick and pasty by the combination with the solid metal lead or zinc. It enters into combination with the lead, in the cold, to form an *amalgam*. Other metals combine with mercury only when heated.

The term amalgam is applied to the combinations into which mercury enters with other metals. Combinations between metals, other than mercury, are called *alloys*. This property of mercury has received an important application in the extraction of gold and silver from poor ores by the so-called *amalgamation process*. Mercury can be separated again by distillation, gold and silver being left behind.

The combination of the metal mercury with other metals is obviously due to its liquid condition at the ordinary temperature, which facilitates its being brought into intimate contact with other metals. This contact action is materially increased, if the solid metals are offered to the mercury in a finely-divided condition, or in the form of foil—an amalgam of 4 parts of tin and 1 part of mercury is employed for covering looking-glasses—and by rubbing the two metals together in a mortar.

Heat some *cinnabar* in a small flask with narrow neck, loosely closed with a piece of charcoal. HgS sublimes without undergoing any chemical change.

Heat a little *cinnabar* in a piece of glass tube open at both ends, and allow a current of air to pass over it. Hg is seen to condense in the form of a metallic mirror towards the further end of the tube, and SO_2 makes itself perceptible by its odour.

Heat about two parts of yellow mercuric oxide and one part of mercuric sulphide in a test-tube. Metallic mercury sublimes and sulphurous anhydride is given off, according to the equation :—

$$HgS + 2HgO = Hg_3 + SO_2.$$

Introduce some *cinnabar* into a small tubulated retort connected with a two-necked receiver and gas delivery-tube, and pass through the tubulus of the retort a current of air or oxygen from a gas-holder, and heat gently. A blue flame playing over the HgS indicates that combustion takes place. Mercury distils and condenses partly in the neck of the retort and partly in the receiver. Sulphurous anhydride issues from the delivery-tube and is readily recognised by its pungent odour; or it may be passed into water, and the solution tested with litmus-paper.

This illustrates the mode of extraction of mercury from its principal ore. *Cinnabar* is roasted in a reverberatory furnace, and proper provision is made for the condensation of the vapour of mercury in chambers and flues. The sulphurous anhydride is allowed to escape.

HgS (as well as SAg_2, Au_2S_3, PtS_2) parts with its sulphur when roasted in the air, and yields the metal: *it is in fact reduced to the metallic state by oxygen*, owing to the weak affinity which exists between the metal mercury and the non-metal sulphur, and owing likewise to its weak affinity for oxygen, on account of which the HgO (and OAg_2) first formed gives up its oxygen again to a fresh quantity of HgS (or SAg_2).

Hydrogen and carbon, copper, tin, zinc, etc., reduce HgS at a high temperature, forming with the sulphur SH_2, CS_2 (carbon disulphide), CuS, etc. The native HgS is, however, best reduced by the action of strong bases, such as lime or soda.

Mix a little cinnabar with dry $CONao_2$, and heat in a little tube, sealed up at one end, or blown into a small bulb. Metallic mercury sublimes and forms a mirror in the cold part of the tube; the sulphur is fixed by the alkali metal.

Mercury salts, when heated by themselves, out of contact with the air, **volatilise** or **sublime**, either without decomposition, such as $HgBr_2$, $HgCl_2$, Hg_2Cl_2 (without undergoing previous fusion), HgI_2, HgS; or they are decomposed into oxide or metal. Salts of mercury with fixed acids (P_2O_5, CrO_3, etc.), leave fixed residues of acid or oxide (Cr_2O_3).

REACTIONS IN THE WET WAY.

Mercury forms two series of salts : **mercurous and mercuric salts**. It dissolves readily in nitric acid, even in the cold, forming mercurous nitrate, if the mercury be in excess, and mercuric nitrate, if the acid be in excess. These salts have the composition—

$$\begin{matrix}NO_2\\NO_2\end{matrix}Hg_2o'' \quad \text{and} \quad \begin{matrix}NO_2\\NO_2\end{matrix}Hgo''.$$

Mercurous nitrate. Mercuric nitrate.

Mercurous salts contain Hg_2O (Mercurous oxide.) mercuric salts, HgO (Mercuric oxide.)

The oxygen atom being in the one case linked to two atoms of the dyad mercury, thus, $\left\{\begin{matrix}Hg\\Hg\end{matrix}\right\rangle O$, the mercury atoms being held together by one of their bonds, as well as by the bonds of the oxygen atom; in the other to one atom, thus :— $Hg{=}O$.

Mercurous oxide exhibits a tendency to combine with another atom of oxygen, or when exposed to heat, to part with one atom of mercury and to become converted into mercuric oxide. Hence we possess in mercurous salts powerful *reducing* agents.

On account of the *insoluble chloride* which 'Hg_2' forms, we shall consider its reactions in connection with the reactions for silver and lead in Group I.

In order to study the reactions of mercuric salts, we can either employ A SOLUTION of MERCURIC NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Hgo''$, or MERCURIC CHLORIDE, $HgCl_2$ (*corrosive sublimate*).

SH_2 (**group-reagent**) added to $HgCl_2$ gives a *black* precipitate of **mercuric sulphide**, HgS. The precipitation is marked by characteristic changes of colour. Accordingly as sulphuretted hydrogen water is added in small quantities, or the gas passed slowly through the solution, it produces at first a perfectly *white* precipitate, and on the addition of more SH_2, a *yellow* precipitate which passes through *dirty yellow* to *brown*, and becomes *black* only when excess of SH_2 has been added to the mercuric salt. The white, yellow, or brown precipitate consists of varying quantities of HgS and $HgCl_2$. It may be represented by the formula $\begin{cases} HgCl \\ S'' \\ HgCl \end{cases}$ (**dimercuric sulphodichloride**). HgS is insoluble in nitric or hydrochloric acid and in yellow ammonic sulphide, potassic hydrate, or potassic cyanide; soluble, however, in aqua regia and in potassic or sodic sulphide in the presence of sodic hydrate, but insoluble in their sulphhydrates. Long digestion with concentrated nitric acid converts the black HgS into a white body consisting of $2HgS + N_2O_4Hgo''$.

SAm_2 gives the same precipitate.

$NaHo$ or KHo added in excess produces a *yellow* precipitate of **mercuric oxide**, HgO, insoluble in excess.

$AmHo$ produces a *white* precipitate of **mercuric salt** and **mercuramide**, known as "the *white precipitate*."

$$N'''_2H_4Hg'' + HgCl_2 = 2(NH_2Hg''Cl).$$

Mercurammonic chloride.

$CONao_2$ or $COKo_2$ gives a *reddish-brown* basic precipitate.

KI gives a *bright red* precipitate of **mercuric iodide**, HgI_2, soluble either in excess of potassic iodide or of the mercuric salt.

KCy gives with mercuric nitrate (not the chloride) a *white* precipitate of **mercuric cyanide**, $HgCy_2$, soluble in excess; not decomposed by boiling with alkalies or alkaline carbonates, but only by SH_2.

Mercuric salts are readily reduced to mercurous salts:—

$SnCl_2$ (**stannous chloride**) gives with mercuric salts a *white* precipitate of **mercurous chloride**, Hg_2Cl_2, which when boiled with excess of the reagent, is reduced to grey metallic mercury. On pouring off the solution and boiling the grey precipitate with HCl, the mercury is obtained in little globules.

SO_2Feo'' (**ferrous sulphate**) reduces $\begin{matrix} NO_2 \\ NO_2 \end{matrix}Hgo''$, but not $HgCl_2$, to the metallic state.

Cu, Zn, Fe precipitate metallic mercury from mercuric solutions, provided they are not too acid.

If a strip of bright metallic copper be employed, a silvery-white deposit of metallic Hg is obtained, which, when gently rubbed, shows a bright metallic lustre, and gives, after drying and heating in a dry and narrow test-tube, a sublimate of *metallic* mercury.

Mercuric salts act the part of *oxidizing agents;* they are first reduced to mercurous salts, and finally to metallic mercury.

QUESTIONS AND EXERCISES.

1. What is understood by the terms *sulpho-base*, *sulpho-acid*, *sulpho-salt*?
2. Define normal sulphides, sulphhydrates, and polysulphides, and state how they can be distinguished by treatment with HCl?

3. Give instances of sulpho-salts together with the corresponding oxy-salts.
4. Write out the graphic formulæ of a few sulpho-salts and of the minerals *boulangerite*, *jamesonite*, *fahl ore*.
5. Which metals form sulphides capable of acting as sulpho-acids, and which form sulphides capable of playing the part of bases?
6. Write out the formulæ, both symbolic and graphic, for the persulphides of the metals K, Na, Ba, Ca, Fe.
7. What changes take place when the sulphides of As, Sb, and Sn are boiled, 1st, with $\mathbf{S}\mathrm{Am}_2$, 2nd with NaHo? Express the changes by equations.
8. Give the graphic formulæ of cinnabar, dimercuric sulpho-dichloride, of *white precipitate* and of mercuric nitrate.
9. Write out the symbolic equations for the reactions which mercuric nitrate gives with the group and special reagents.
10. Calculate the percentage composition of *white precipitate*.
11. How much metallic copper will have to be dissolved, in order to precipitate 2 grms. of Hg from a solution of mercuric chloride?
12. Explain why the dyad condition appertains to one atom of mercury and to the double atom. Give proofs of the atomicity of mercury in mercurous and mercuric compounds.
13. How is *corrosive sublimate* manufactured, and whence does it derive its name?
14. 1·5 grm. of $\mathbf{Hg}\mathrm{Cl}_2$ is precipitated as $\mathbf{Hg}\mathrm{S}$ and collected on a weighed filter. How much by weight of $\mathbf{Hg}\mathrm{S}$ should there be obtained?
15. *Cinnabar* is sometimes found adulterated with red-lead, red oxide of iron, brick-dust. State how you would discover the adulteration. (No separation of the impurities from each other is required.)
16. What reaction takes place when mercury is acted upon by concentrated sulphuric acid? and by what consecutive stages is the product of this reaction converted into *white precipitate*?
17. How much metallic mercury will 100 lb. of *cinnabar* yield when distilled with lime?
18. What is the percentage composition of an amalgam containing $\mathrm{Sn}_4\mathrm{Hg}$?

2. **LEAD,** Pb'' and $^{\mathrm{iv}}$. Atomic weight, 207.—Only a slight precipitate of $\mathbf{Pb}\mathrm{S}$ is for the most part obtained in Group II, since the greater part of the lead is removed in Group I as $\mathbf{Pb}\mathrm{Cl}_2$. It happens frequently that this small quantity of lead is not precipitated by $\mathbf{S}\mathrm{H}_2$, on account of the solution being too acid (HCl), or too concentrated, in which case a little lead is found in Group III, and is often mistaken for some other metal. It is necessary, therefore, to dilute a portion of the filtrate from Group II considerably and to pass a current of $\mathbf{S}\mathrm{H}_2$ through, in order to make sure of the presence of lead, especially so, when lead has been discovered in Group I; and, if a precipitate be obtained, to pass the gas once more through the whole of the filtrate, after having diluted it considerably with distilled water.

3. **BISMUTH,** Bi''' and $^{\mathrm{v}}$. Atomic weight, 208.—This metal is principally found native; also in combination with oxygen and sulphur, as *bismuth ochre*, $\mathbf{Bi}_2\mathrm{O}_3$, from the decomposition of *bismuth glance*, $\mathbf{Bi}_2\mathrm{S}_3$, and in the form of sulpho-salts, as *kobellite*, $\mathbf{Bi}_2\mathrm{Pbs}''_3$ (trisulphoplumbic orthosulpho-bismuthite), and as *needle ore*, $\mathbf{Bi}_2\mathrm{Pbs}''_2({}'\mathrm{Cu}'_2\mathrm{S}_2)''$, disulphoplumbo-cuprous orthosulpho-bismuthite.

EXAMINATION IN THE DRY WAY.

The metal bismuth fuses with ease, both in the reducing and oxidizing flame of the blowpipe, covering the charcoal with an incrustation of oxide, **orange-yellow**, *while hot*, **lemon-yellow**, *when cold*, passing at the edges into a **bluish-white**. The incrustation can be driven from place to place by either flame, *without colouring* the outer flame. (DISTINCTION FROM LEAD.) Heated with borax or microcosmic salt, Bi_2O_3 gives beads which are *yellowish*, when hot, and *colourless*, when cold. All bismuth compounds can be reduced to the metallic state by heating on charcoal with $CONao_2$, in the inner or reducing flame. The metallic bead is brittle. (DISTINCTION FROM LEAD AND SILVER BEADS.) The incrustation is *yellow*.

EXAMINATION IN THE WET WAY.

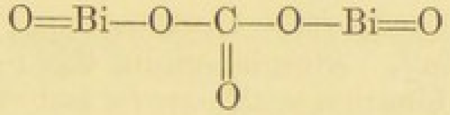
Bismuth dissolves readily in nitric acid, forming N_3O_6Bio'''. A SOLUTION OF THIS SALT IS CONVENIENTLY EMPLOYED.

SH_2 (**group-reagent**) gives a *brownish-black* precipitate of **bismuthous sulphide**, Bi_2S_3, insoluble in dilute acids, in alkalies and in alkaline sulphides; soluble in concentrated nitric acid.

Alkaline sulphides give the same precipitate.

KHo, NaHo and AmHo produce a *white* precipitate of **bismuthous hydrate**, $BiHo_3$, insoluble in excess; on boiling it turns yellow, *i.e.*, it becomes anhydrous (Bi_2O_3).

$COAmo_2$ or $CONao_2$ throws down a *white bulky* precipitate of **basic carbonate** (*bismuthylic carbonate*) (consisting of one mol. of carbonate and two of the oxide, $C_3O_3Bio'''_2, 2Bi_2O_3) = CO(BiO_2)'_2$, graphic formula :—



$$O{=}Bi{-}O{-}\underset{\overset{\|}{O}}{C}{-}O{-}Bi{=}O$$

in which the compound radical **bismuthyl**, BiO, acts the part of H in Ho. The precipitate is insoluble in excess.

$Cr_2O_5Ko_2$ gives a *yellow* precipitate of **basic chromate** (consisting of one mol. of bismuthous hexachromate, $Cr_6O_{15}Bio'''_2$, and two mol. of bismuthous oxide, $2Bi_2O_3) = \left\{\begin{array}{l} CrO_2(BiO_2)' \\ O \\ CrO_2(BiO_2)' \end{array}\right.$ readily soluble in dilute nitric acid, insoluble in potassic hydrate. (DISTINCTION FROM PLUMBIC CHROMATE.)

SO_2Ho_2 gives no precipitate. (DISTINCTION FROM LEAD.)

KI produces a *brown* precipitate of **bismuthous iodide**, BiI_3, soluble in excess.

KCy produces a *white* precipitate, insoluble in excess, soluble in acids.

Bismuthous salts are partially decomposed by *water*, a basic salt being precipitated. The addition of an acid redissolves the precipitate. This constitutes the most characteristic reaction for bismuthous salts. The salt most readily precipitated is the chloride

($\mathbf{Bi}Cl_3$). It can be prepared from the nitrate by precipitating the oxide first, and then filtering and dissolving the precipitate off the filter with dilute hydrochloric acid. Excess of acid should be avoided.

$\mathbf{O}H_2$ gives with $\mathbf{Bi}Cl_3$ a *white* precipitate of **bismuthous oxychloride** (consisting of one mol. of $\mathbf{Bi}_2O_3$ and one of $\mathbf{Bi}Cl_3$), $\mathbf{Bi}OCl$, which is almost absolutely insoluble in water, but soluble in hydrochloric acid, from which it is reprecipitated on the addition of ammonic or sodic chloride. $\mathbf{Bi}OCl$ is insoluble in tartaric acid. (DISTINCTION FROM ANTIMONY.)

Metallic zinc precipitates bismuth from its salts.

Bismuthous salts exhibit a tendency to form basic salts, showing that $\mathbf{Bi}_2O_3$ is a very indifferent and weak base.

There are several other oxides known, *e.g.*, **bismuthic oxide** or **anhydride**, $\mathbf{Bi}_2O_5$, which parts readily with two atoms of oxygen, when heated or acted upon by reducing agents.

QUESTIONS AND EXERCISES.

1. How can Bi be separated from Ag, Pb, or Hg?
2. Express in symbolic equations the reactions which a bismuthous salt gives with different reagents in the wet way.
3. Give the graphic formulæ for bismuthous nitrate, bismuthous oxide, *bismuth glance*, bismuthous oxychloride.
4. Calculate the percentage composition of an alloy of 1 atom of Pb, 1 atom of Sn, and 3 atoms of Bi.
5. 1·245 grm. of $\mathbf{Bi}_2O_3$ are obtained from 10 c.c. of a solution of normal bismuthous nitrate. How much metallic bismuth does a litre of the bismuth solution contain?

4. **COPPER**, Cu''. Atomic weight, 63·5.—This metal is found native; also in combination with OXYGEN and SULPHUR, as *red copper ore* or *ruby ore*, $\mathbf{Cu}_2O$, as *vitreous copper* or *copper glance*, $\mathbf{Cu}_2S$, and *indigo copper* or *blue copper*, $\mathbf{Cu}S$; more frequently as *copper pyrites*, $\mathbf{Fe}_2S_3,\mathbf{Cu}_2S = \left\{\begin{matrix}\mathbf{Fe}S\\ \mathbf{Fe}S\end{matrix}\right.(Cu_2S_2)''$, (diferric cuprous tetrasulphide), and *variegated copper* or *horseflesh ore*, $\mathbf{Fe}_2S_3,3\mathbf{Cu}_2S = \left\{\begin{matrix}\mathbf{Fe}\\ \mathbf{Fe}\end{matrix}\right.(Cu_2S_2)''_3$, (diferric tricuprous hexasulphide); also as *fahl ore*, *bournonite*, etc.; in combination with CARBONIC ACID, as basic carbonate, *malachite*, $\mathbf{C}O(O\mathbf{Cu}Ho)'_2$, and *azurite*, *mountain blue*, or *copper azure*, $\begin{matrix}\mathbf{C}HoCuo''\\ \mathbf{C}HoCuo''\end{matrix}Cuo''$; with SULPHURIC ACID, as *blue vitriol*, $\mathbf{S}O_2Cuo'',5\mathbf{O}H_2$; with PHOSPHORIC ACID, as *phosphorocalcite*, *libethenite*; with ARSENIOUS ACID, as *tennantite*; SILICIC ACID, as *dioptase*, and others.

EXAMINATION IN THE DRY WAY.

Copper minerals form a very numerous class of ores; and as many of them exhibit precisely similar blowpipe reactions, a knowledge of their physical character is indispensable to enable the student to distinguish readily between them. It is advisable to examine the doubtful ores in the wet way also.

The most characteristic reaction in the dry way is that which copper compounds give, when heated in a bead of borax or microcosmic salt before the blowpipe flame. The bead is **green** *whilst hot*, **blue** *on cooling*. Most copper compounds, when heated on platinum wire in the inner flame, impart an **intense green** colour to the outer flame. All copper compounds are reduced when heated in the inner flame on charcoal, together with $CONao_2$ and KCy, yielding red metallic scales. Sulphides give off SO_2, when roasted in an open tube, and leave CuO behind. *Malachite* or *azurite* gives off water and carbonic anhydride when gently heated in a tube. Blue vitriol loses water, sulphurous anhydride and oxygen, and leaves cupric oxide. Cupric phosphate, arsenate, and silicate fuse to coloured glasses.

Metallic copper is not affected in dry air at the ordinary temperature, but is readily oxidized when heated in air or oxygen and converted into black cupric oxide. Hydrochloric acid in the presence of air dissolves copper but slightly, forming Cu_2Cl_2; nitric acid is the most active solvent for copper (as it is for Ag, Hg, Pb and Bi), forming cupric nitrate. Sulphuric acid (concentrated) dissolves copper, on heating, with evolution of SO_2, and formation of SO_2Cuo''.

SO_2Ho_2 acts here the part of an oxidizing agent. This method of preparing sulphurous anhydride gas is frequently employed in the laboratory in preference to other methods.

EXAMINATION IN THE WET WAY.

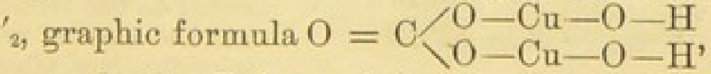
A SOLUTION OF CUPRIC SULPHATE, SO_2Cuo'', OF CUPRIC NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Cuo''$, may conveniently be employed.

SH_2 (**group-reagent**) gives a *brownish-black* precipitate of **cupric sulphide**, CuS, insoluble in dilute acids; slightly soluble in yellow ammonic sulphide; soluble with decomposition in nitric acid; completely soluble in potassic cyanide; insoluble in potassic and sodic sulphides, or caustic alkalies. CuS is rapidly oxidized to SO_2Cuo' by exposure to the air; it is insoluble in hot dilute sulphuric acid.

SAm_2 produces the same precipitate, somewhat soluble in excess, especially in yellow ammonic sulphide (S_5Am_2).

$NaHo$ or KHo gives a *light-blue* precipitate of **cupric hydrate**, $CuHo_2$. The precipitate turns black on boiling and becomes denser. Three molecules of $CuHo_2$ lose two molecules of OH_2 and leave $3CuO,OH_2$ (graphic formula $H—O—Cu—O—Cu—O—Cu—O—H$). In the presence of many organic substances, such as grape sugar, etc., the precipitate dissolves to a deep blue solution, whence the whole of the copper is reprecipitated on boiling in the form of *bright red* **cuprous oxide**, Cu_2O.

$CONao_2$ produces a *greenish-blue* **basic carbonate**, of the composition $CO(OCu''Ho)'_2$, graphic formula



$$O = C\begin{cases}O—Cu—O—H\\O—Cu—O—H\end{cases}$$

carbonic anhydride being evolved. This precipitate is converted on boiling into the black precipitate of $3CuO,OH_2$. It is soluble in ammonic hydrate to an azure-blue and in potassic cyanide to a colourless fluid forming a soluble double cyanide.

AmHo or $\mathbf{CO}Amo_2$, when added in small quantities, produces a *greenish-blue* precipitate of a **basic salt**, which dissolves readily in excess of the reagents, and forms a magnificent *azure-blue* liquid,—a blue which is perceptible, if a solution contains small traces of copper only. The blue solution contains a double compound of **cuprammonic hydrate**, $\mathbf{N}^{v}{}_2H_6Cu''Ho_2$, and **ammonic sulphate**, or ammonio-cupric sulphate, symbolic formula, $\mathbf{S}Ho_2Amo_2\left[\begin{matrix}NH_3\\NH_3\end{matrix}CuO\right]''$, whence the black cupric oxide separates on boiling with sodic hydrate.

This tendency of ammonia to combine with cupric hydrate and to form cuprammonic hydrate induces metallic copper to combine with oxygen even at the *ordinary temperature.*

KCy gives a *greenish-yellow* precipitate of **cupric cyanide**, $\mathbf{Cu}Cy_2$, soluble in excess. $\mathbf{S}H_2$ produces no precipitate from this solution.

K_4FeCy_6 gives a *reddish-brown* precipitate of **cupric ferrocyanide**, Cu_2FeCy_6, insoluble in dilute acids, decomposed by potassic or sodic hydrate, with separation of $3\mathbf{Cu}O,\mathbf{O}H_2$. Even in very dilute solutions of copper salts a brownish colour is produced,—best seen when the reaction is performed on a watch glass, placed on a sheet of white paper or in a little porcelain dish. Hence K_4FeCy_6 supplies one of the most delicate reactions for copper salts.

Metallic zinc or iron precipitates metallic copper, especially in the presence of a little free hydrochloric acid. If a few drops of a slightly acidulated dilute copper solution are placed on platinum foil (the lid of a platinum crucible), together with a small piece of sheet zinc, the platinum becomes rapidly coated with a reddish film of metallic copper, visible even in the case of very dilute solutions, an equivalent quantity of the metal zinc being dissolved.

This simple experiment requires some explanation. Bright copper is not attacked by dilute hydrochloric or sulphuric acid. Metals such as Pb, Hg, Ag, Au, Pt are also indifferent to dilute hydrochloric or sulphuric acid, whilst zinc and iron are readily dissolved with evolution of hydrogen, the metals taking the place of the hydrogen in two molecules of hydrochloric acid.

By the aid of voltaic electricity, however, we are enabled to dissolve metals in dilute hydrochloric or sulphuric acid, which are either not dissolved at all, such as copper, or dissolve only with difficulty, such as the metal tin. This is done by connecting the positive pole of a voltaic battery with a piece of the metal to be dissolved, and the negative pole with a platinum wire ending in a piece of platinum foil. Both electrodes dip into the dilute hydrochloric or sulphuric acid solutions.

Connect the positive pole, *a*, with a piece of sheet copper or a coil of copper wire, placed in dilute sulphuric acid, contained in a glass basin, as seen in Fig. 7. The negative pole, *b*, consisting of a platinum wire fused to a strip of platinum foil, dips likewise into the dilute acid, without touching, however, the copper. The solution turns blue, owing to the formation of a blue cupric-salt, and the sheet of metallic copper or the copper wire dissolves after some time. Hydrogen is evolved at the negative pole.

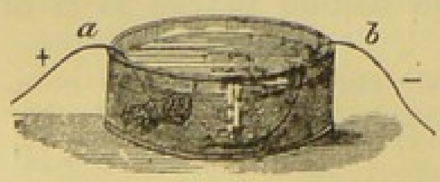


Fig. 7.

This shows that the action of dilute acids upon copper which is nil at the ordinary temperature is very energetic when we call voltaic electricity to our aid.

The reaction will be readily understood, if it be remembered what takes place when water is decomposed by voltaic electricity. Hydrogen is obtained at the negative and oxygen at the positive electrode, because the latter consists likewise of platinum, a metal which has no affinity for oxygen. Hence both constituents of water, hydrogen and oxygen, are evolved at the respective poles. Now, if instead of water, hydrochloric acid be decomposed in like manner, chlorine is evolved at the positive electrode. If the positive electrode consists, however, of a metal, such as Zn, Cu, Fe, for which chlorine possesses a strong affinity, the latter combines with these metals, the moment it is liberated on the positive electrode, or as it is termed in its nascent state (*in statu nascendi*), and hydrogen alone is evolved at the negative pole.

If in the place of hydrochloric or sulphuric acid, we employ a dilute solution of a metallic chloride or sulphate, *e.g.*, cupric sulphate, $\mathbf{S}O_2Cuo''$, and dip the two electrodes into it, we observe at the negative (platinum) electrode instantaneously a red film or deposit of metallic copper, whilst, at the positive electrode, consisting of metallic zinc, no evolution of gas is visible, since the zinc is acted upon by the acid liberated from the copper, and is converted thereby into $\mathbf{S}O_2Zno''$. An equivalent quantity (65 parts by weight) of zinc remains dissolved in the acid for the 63·5 parts by weight of copper, precipitated on the platinum foil or crucible-lid. In this manner the amount of copper present in a solution may be determined quantitatively. The undissolved zinc and zincic salt are removed and the platinum with its deposit of copper dried and weighed. The total weight, minus the previous weight of the platinum, gives the weight of the metallic copper.

It will be readily perceived that this and other similar experiments furnish valuable illustrations of the theory of constant combining weights, and they acquire on this account additional interest.

Great interest attaches, moreover, to these chemical changes, on account of the important practical application which they have found, of late, in covering metals—mostly the common metals—with a thin coating of noble metals (electroplating, silvering, platinizing), or in producing solid metallic deposits on properly prepared matrices, generally consisting of some plastic material, such as plaster of Paris, gutta-percha, &c. (*electrotype process*).

Pass a voltaic current through a solution of cupric chloride, $\mathbf{Cu}Cl_2$, by means of copper electrodes. No chlorine gas is evolved at the positive pole, for it is immediately again fixed by its dissolving an equivalent quantity of copper off the positive copper electrode. The movement of the molecules of chlorine and copper in the solution of cupric chloride cannot be perceived; it is nevertheless proved by the decrease in weight of the positive copper electrode and the increase in weight of the negative copper electrode, and we infer from this that the copper is transferred from the positive to the negative pole, although we cannot see the change. The deposition of metallic copper continues as long as the positive electrode lasts, and the saline solution in the decomposing vessel retains its original strength thus far unaltered.

If a properly prepared mould or matrix of some object be hung in the metallic solution and connected with the negative pole of a voltaic battery, copper will be slowly but steadily deposited on the mould, as long as the positive pole is connected with a sheet of copper, acting as the positive electrode in the bath. The copper thus precipitated is immediately restored to the bath by the dissolution of a fresh quantity of copper. This mode of depositing copper on moulds or matrices by the aid of voltaic electricity is termed the *electrotype process*.

Employ a solution of argentic nitrate instead of the solution of cupric chloride, and introduce the two copper electrodes into the bath. The negative electrode is speedily covered with silver, and an equivalent quantity of copper, *i.e.*, 63·5 parts by weight, is dissolved from the positive copper electrode, and 216 parts by weight of silver (2 × 108, silver being a monad element) are deposited on the negative copper electrode; and it results from this, that in the place of the silver solution, there must ultimately be left a solution of cupric nitrate. This has found a practical application in the *silvering* (electro-plating) of artistic articles made of an inferior metal.

Copper, like mercury, forms a *lower* or *cuprous oxide*, Cu_2O, in which two atoms of Cu are joined by one of their bonds, and are also linked to one atom of oxygen; it is analogous in constitution to the important copper ore, Cu_2S, thus:—

$$\left\{\begin{matrix}'Hg' \\ 'Hg'\end{matrix}\right.O \qquad \left\{\begin{matrix}'Cu' \\ 'Cu'\end{matrix}\right.O \qquad \left\{\begin{matrix}'Cu' \\ 'Cu'\end{matrix}\right.S.$$

Mercurous oxide. Cuprous oxide (*red copper ore*). Cuprous sulphide (*copper glance*).

Cuprous oxide is a feeble base; it forms with concentrated hydrochloric acid cuprous chloride, Cu_2Cl_2, which is colourless when pure. Other acids decompose it into metallic copper and cupric oxide, which latter remains dissolved in the acid as a cupric salt. Cuprous chloride attracts oxygen very rapidly, and is, therefore, a powerful reducing agent. It is used for absorbing carbonic oxide.

To A SOLUTION OF CUPROUS CHLORIDE, Cu_2Cl_2, in concentrated hydrochloric acid, add

OH_2, a *white* precipitate of Cu_2Cl_2 is produced.

KHo gives a *yellow* precipitate of **cuprous hydrate**, Cu_2Ho_2, insoluble in excess; it attracts oxygen very rapidly, being converted into cupric hydrate.

KI, in the presence of $SOHo_2$, or SO_2Feo'', precipitates from cupric salts *greenish-white* **cuprous iodide**, Cu_2I_2, soluble in excess. Both sulphurous acid and ferrous sulphate are reducing agents, which, by the absorption of oxygen from the cupric salt, are converted into SO_2Ho_2 and $S_3O_6Fe_2o^{vi}$, thus:—

$$(1)\quad \underset{\text{Cupric sulphate.}}{2SO_2Cuo''} + 2SO_2Feo'' = \underset{\text{Cuprous sulphate.}}{SO_2Cu_2o''} + S_3O_6Fe_2o^{vi}.$$

$$(2)\quad SO_2Cu_2o'' + 2KI = \underset{\text{Cuprous iodide.}}{Cu_2I_2} + SO_2Ko_2.$$

QUESTIONS AND EXERCISES.

1. How does copper occur in nature?
2. Express in symbolic equations the reactions of copper in the wet way.
3. Write out the graphic formulæ for *malachite*, *copper glance*, *azurite*, and *blue vitriol*, ammonio-cupric sulphate, cuprous iodide.
4. Explain what takes place—

   1st. When copper is treated with concentrated NO_2Ho.
   2nd. " " " SO_2Ho_2.
   3rd. " " " HCl.
   Give equations.

5. Give instances of the oxidizing action of cupric salts.
6. What action takes place when the polished blade of a knife is plunged into a solution of a cupric salt?
7. How much metallic zinc is required to precipitate 1·5 grm. of copper from a cupric solution?
8. A sample of iron pyrites which has been used for manufacturing sulphuric acid is found on analysis to contain 4·56 per cent. of copper. How much metallic iron is required to precipitate the copper from a hydrochloric acid solution of a ton of the spent pyrites?
9. Explain the electrotype process.
10. What is understood by nascent hydrogen?
11. What is the percentage of the metallic copper in *malachite*?
12. How is Cu separated from Ag and Pb?
13. How can copper in **CuS** be separated from bismuth in Bi_2S_3?
14. What change takes place when metallic copper is heated in air?
15. How much hydrogen gas (at 0° and 760 mm. pressure) is required to deprive 10 grms. of ignited cupric oxide of its oxygen, and how much water will be obtained?

5. **CADMIUM**, Cd''. Atomic weight, 112.—This metal is found in nature, associated with zinc, in certain zinc ores, *e.g.*, *zinc blende* **ZnS**. It is of comparatively rare occurrence; only one mineral of cadmium being known at present, viz., the extremely rare *greenockite*, **CdS**. It can be distilled like mercury or zinc. Being more volatile than metallic zinc, its vapour distils over first, and burns with a brown flame (*brown blaze*), *i.e.*, it is converted into cadmic oxide.

Cadmium dissolves readily in acids with evolution of hydrogen. It also resembles the metal zinc in being dissolved by boiling potassic hydrate, hydrogen being given off—

$$Cd + 2KHo = \mathbf{CdKo_2} + H_2.$$

EXAMINATION IN THE DRY WAY.

Cadmium compounds, mixed with sodic carbonate, when heated on charcoal in the inner flame, give a characteristic brown incrustation, *i.e.*, they are readily reduced to the metallic state; the metal being highly volatile, is reoxidised on its passage through the outer flame. Cadmium is recognized with more difficulty when it is in combination with zinc, as for instance in *cadmiferous blende*. By heating, however, a mixture of blende and sodic carbonate and potassic cyanide for a few moments only, on charcoal, a slight *brown* incrustation is generally obtainable, before the zinc is volatilized. Cadmic oxide turns the bead of borax or microcosmic salt *yellowish*, whilst hot, *colourless* when cold.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF CADMIC CHLORIDE, $\mathbf{CdCl_2}$, or SULPHATE, $\mathbf{SO_2Cdo''}$.

SH_2 (**group-reagent**) gives from dilute solutions a *fine yellow* precipitate of **cadmic sulphide**, **CdS**, insoluble in alkaline sulphides, caustic alkalies, or potassic cyanide; insoluble in cold, but soluble in hot dilute nitric and hydrochloric acids; soluble also in dilute sulphuric acid. (DISTINCTION FROM COPPER.)

Hence the separation of cadmium by means of SH_2, especially from acid solutions, is frequently left either incomplete, or is not effected at all, in Group II, unless the precaution be taken of nearly neutralising the free acid with ammonia, before passing SH_2, as well as neutralizing the mineral acid as fast as it is liberated by the SH_2.

SAm_2, same precipitate.

KHo, a *white* precipitate of **cadmic hydrate**, $CdHo_2$, insoluble in excess.

AmHo, same precipitate, soluble in excess.

$COAmo_2$ (free from AmHo) a *white* precipitate of **cadmic carbonate**, $COCdo''$, insoluble in excess.

$CONao_2$, same precipitate.

KCy gives a *white* precipitate of **cadmic cyanide**, $CdCy_2$, soluble in excess. Sulphuretted hydrogen precipitates from this solution CdS. (DISTINCTION FROM COPPER.)

Metallic zinc precipitates cadmium from its solutions.

QUESTIONS AND EXERCISES.

1. Describe three methods of separation of Cd from Cu.
2. How is Cd separated from Zn?
3. How is Cd separated from Pb, Ag, and Bi?
4. How much cadmic sulphide can be prepared from 10 grms. of crystallised cadmic sulphate, $SO_2Cdo'',4OH_2$?
5. What takes place when *greenockite* is roasted in a glass tube open at both ends?
6. How is the metal cadmium converted 1st into oxide, 2nd into chloride, 3rd into sulphate?
7. How can we extract cadmium from its oxide or sulphide?
8. You are requested to convert 10 grms. of cadmic sulphate into cadmic bromide; how would you proceed, and how much $CdBr_2$ should there be obtained?

SEPARATION OF THE METALS OF SUBDIVISION A, GROUP II,* viz., MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, WHOSE SULPHIDES ARE INSOLUBLE IN AMMONIC SULPHIDE OR SODIC HYDRATE.

The precipitate produced by the group-reagent SH_2, which is insoluble in ammonic sulphide or sodic hydrate, may consist of all the five sulphides, or only of one, two, etc. A precipitate of a bright yellow colour, *e.g.*, would be indicative of cadmic sulphide only. If the precipitate be black, it is necessary to examine for all the five metals.

We have already seen that the sulphides of the metals of this subdivision are—

1st. Insoluble in alkalies and alkaline sulphides, and

2nd. Insoluble in dilute acids, or nearly so; but soluble in concentrated acids.

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[*] The student may, with advantage, tabulate the reactions produced by the principal reagents employed in Group II, according to the scheme given on page 52.

Concentrated nitric acid (free from chlorine), diluted with its own bulk of water, dissolves four out of the five sulphides, viz., **PbS**, **Bi_2S_3**, **CuS**, and **CdS**, with separation of sulphur; mercuric sulphide being soluble only in aqua regia. Hence by boiling with moderately concentrated nitric acid (in the absence of HCl), we can separate mercury from the other metals of subdivison A. Concentrated nitric acid converts **PbS** partially into SO_2Pbo'', by the simultaneous oxidation of the sulphur. We should, therefore, obtain in the residue **HgS**, as well as SO_2Pbo'' and sulphur. But as the whole of the **PbS** can be converted into SO_2Pbo'' only by boiling with fuming nitric acid, and as SO_2Pbo'' is slightly soluble in concentrated nitric acid, we should not succeed in removing the lead entirely as sulphate. This difficulty is overcome by boiling the whole of the sulphides with moderately concentrated nitric acid, then diluting with water and adding dilute sulphuric acid (SO_2Pbo'' being less soluble in dilute sulphuric acid than in water), and lastly, when cold, adding to the solution its own bulk of alcohol (methylated spirit). A *residue* is left which may be white, indicative of the presence of SO_2Pbo'', or black, from the presence of **HgS** and sulphur. The *solution* contains the metals Bi, Cu, Cd.

EXAMINATION OF THE RESIDUE.—SO_2Pbo'' dissolves readily in certain salts, such as ammonic acetate or tartrate. By treating the residue, therefore, with a concentrated solution of ammonic acetate, we are able to dissolve out the SO_2Pbo''. The absence of mercury compounds may be inferred, if no black but only a yellow residue of sulphur, is left, and if no mercury has been indicated by the reactions in the dry way. The presence of both lead and mercury should, however, invariably be confirmed by special tests; viz., the lead by means of CrO_2Ko_2, and the mercury, by heating the dry residue in a bulb tube with dry sodic carbonate.

EXAMINATION OF THE SOLUTION.—We have seen that AmHo precipitates $BiHo_3$, which is insoluble in excess, whilst $CuHo_2$ and $CdHo_2$ are likewise precipitated, but are soluble in excess. If a white precipitate be obtained on adding AmHo, we infer that bismuth is present. (Should the lead not have been removed entirely, some $PbHo_2$ would be likewise precipitated.) The precipitate is filtered off and well washed, then redissolved in a *little* hydrochloric acid, and precipitated by the addition of water. The ammoniacal filtrate is of a fine *azure-blue* colour, when copper—even in small quantities—is present. If colourless, and if, by the addition of SH_2 a fine yellow precipitate comes down, we infer that no copper is present, but only cadmium. If a black precipitate comes down, on passing the gas through the *slightly* acidulated (HCl) solution, we infer the presence of copper and possibly of cadmium. These two metals can be separated either by means of KCy (**CdS** being insoluble in potassic cyanide), or dilute sulphuric acid (**CuS** being insoluble in hot dilute sulphuric acid). Filter again; in the one case copper is left in solution, in the other cadmium. It is not difficult to identify these two metals by special tests.

The separation of the metals mercury, lead, bismuth, copper and cadmium, is therefore based upon :—

1st. *The insolubility of* HgS *in nitric acid.*

2nd. *The formation of* SO_2Pbo'', *and its solubility in ammonic acetate.*

3rd. *The insolubility of* $BiHo_3$ *in excess of ammonic hydrate.*

4th. *The insolubility of* CuS *in dilute sulphuric acid, or its solubility in potassic cyanide.*

A tabular scheme for their separation is given in the Analytical Tables, Table II.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP II, SUBDIVISION A, AND THE PREVIOUS GROUPS.

1. A sample of *galena*, to be analysed in the dry way only.
2. A hydrochloric acid solution, containing much mercuric and little plumbic chloride.
3. A mixture of the solid salts, blue vitriol, corrosive sublimate, and white vitriol, in the dry and wet way.
4. A mixture of the solid salts, plumbic and bismuthous nitrate, in the dry and wet way.
5. A solution containing much baric chloride and little plumbic chloride.
6. A solution containing cupric, ferrous, and zincic sulphates.
7. A solution of cupric, cadmic, and zincic sulphates, containing ·500 grm. of Cu, ·020 grm. of Cd, and ·500 grm. of Zn.
8. An alloy of zinc and copper (brass).
9. A solution of mercuric, plumbic, and bismuthous nitrates, containing ·050 grm. of Hg, ·500 grm. of Pb, and ·100 grm. of Bi.
10. A sample of *copper glance*, in the dry way only.
11. A sample of *malachite*, in the dry way.
12. A solution of plumbic and bismuthous nitrates (to be distinguished by means of CrO_2Ko_2 and NaHo).
13. A solution of plumbic and cupric nitrates.
14. What takes place when an ore, containing PbS, CdS, and ZnS, is roasted in a current of air?
15. You have given to you a solution of cupric sulphate, dipotassic tartrate, sodic hydrate, and grape sugar: what changes can you produce with these materials?

Group II. Subdivision B.

I. **TIN**, Sn'' and ^{iv}, atomic weight, 118.—This metal is found in nature mainly in the form of *tinstone* or *cassiterite*, SnO_2, sometimes combined with sulphur, as *tin pyrites*, SnS_2 (*bell-metal ore*).

EXAMINATION IN THE DRY WAY.

When tin minerals are fused on charcoal, with $CONao_2$ and KCy, in a strongly reducing flame, they yield small globules of tin which are malleable, and the charcoal becomes covered with a *white* coating of SnO_2. If this white incrustation be treated with a solution of cobaltous nitrate, and strongly heated, it assumes a *bluish-green* colour, which is characteristic of tin. Insoluble stannic oxide, SnO_2, or the native oxide, may also be fused with caustic potash in a silver crucible, and thus converted into potassic stannate, soluble in water; or it may be rendered soluble by fusion on charcoal with 3 parts of $CONao_2$ and 3 of sulphur, when sodic sulphostannate is formed, which is soluble in water, but is decomposed and precipitated as SnS_2 by means of hydrochloric acid.

By introducing into a borax bead—in which sufficient cupric oxide has been diffused to render the bead faintly blue—*traces* of a tin compound and heating in the reducing flame, the bead turns *reddish-brown* or forms a *ruby-red* glass.

EXAMINATION IN THE WET WAY.

Tinstone being insoluble in acids, must be fused with alkaline carbonates and a reducing agent, such as potassic cyanide, charcoal, or black flux (ignited *Rochelle salt*), when metallic tin is obtained. Tin dissolves slowly in hot hydrochloric acid with evolution of hydrogen and formation of $SnCl_2$, readily in aqua regia with formation of $SnCl_4$. Nitric acid converts tin into metastannic acid, $Sn_5O_5Ho_{10}$, which by evaporation and ignition is converted into SnO_2. 100 parts by weight of metallic tin when thus oxidized, are found to increase to 127·6 by weight (atomic weight of $Sn = 118$).

Tin is capable of combining either with two, or four atoms of chlorine, etc. In stannous chloride, $SnCl_2$, the metal exists as a dyad, and in stannic chloride, $SnCl_4$, as a tetrad element. It is capable of forming *two series of salts*, *of oxides*, *sulphides*, etc., viz. :—

Stannous compounds.		*Stannic compounds.*	
$Sn''Cl_2$	Stannous chloride.	$Sn^{iv}Cl_4$	Stannic chloride.
$Sn''O$	,, oxide.	$Sn^{iv}O_2$	,, oxide (anhydride).
SO_2Sno''	,, sulphate.	$Sn^{iv}S_2$	,, sulphide.
$\begin{matrix}NO_2\\NO_2\end{matrix}Sno''$	,, nitrate.		
$Sn''S$	,, sulphide.		

Stannic acid, $SnOHo_2$, combines not only with the strong alkali bases, OK_2, ONa_2, but even with stannous oxide, SnO, to form stannates, *e.g.*, $SnOKo_2$, dipotassic stannate, $SnOSno''$, stannous stannate. Finely divided tin acts, therefore, like Zn and Cd, upon a strong boiling solution of caustic potash or soda, with evolution of hydrogen and formation of potassic or sodic stannate.

A. **Stannous compounds.**—A SOLUTION OF STANNOUS CHLORIDE, $SnCl_2$, is employed.

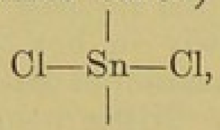
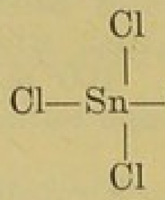
SH_2 (**group-reagent**) gives a *dark brown* precipitate of **stannous sulphide**, SnS, insoluble in ammonia; nearly insoluble in normal ammonic sulphide, but readily dissolved in the presence of sulphur or by the yellow sulphide: from this latter solution it is reprecipitated as yellow stannic sulphide, SnS_2, on the addition of hydrochloric acid; it is also soluble in potassic or sodic hydrate, from which hydrochloric acid precipitates SnS unchanged. Soluble in boiling hydrochloric acid.

SAm_2 gives the same precipitate. Soluble in excess.

KHo or NaHo gives a *white bulky* precipitate of **stannous**

hydrate, $2SnO,OH_2$, or $\begin{matrix}SnHo\\SnHo\end{matrix}O$, readily soluble in excess to $SnKo_2$ (dipotassic stannite).

AmHo or $COAmo_2$, same precipitate, insoluble in excess.

By far the most interesting reactions are based, however, upon the tendency of stannous salts to become converted into stannic salts. $SnCl_2$ combines with two more atoms of chlorine to become converted into $SnCl_4$, whereby the chemical affinities of tin for chlorine become satisfied; and stannous compounds may be viewed as unfinished bodies, which can deprive certain other bodies of chlorine, oxygen, etc. Expressed graphically, dyad tin (or *stannosum*, as it is sometimes called) has two bonds left unsatisfied or latent, thus:—  $\begin{matrix} & | & \\ Cl— & Sn & —Cl \\ & | & \end{matrix}$, whilst in tetrad tin (*stannicum*) all the bonds are satisfied, thus:—  $\begin{matrix} & Cl & \\ & | & \\ Cl— & Sn & —Cl \\ & | & \\ & Cl & \end{matrix}$, or O=Sn=O.

$HgCl_2$ added to a solution of $SnCl_2$, produces first a *white* precipitate of **mercurous chloride**, Hg_2Cl_2, and when boiled with excess of $SnCl_2$, yields a greyish powder of **metallic mercury.**

NO_2Ago gives with excess of $SnCl_2$ a finely divided *black* precipitate of **metallic silver**—

$$2SnCl_2 + 2NO_2Ago = Ag_2 + \begin{matrix}NO_2\\NO_2\end{matrix}Sno'' + SnCl_4.$$

$CuCl_2$ is reduced by $SnCl_2$ to **cuprous chloride**, Cu_2Cl_2, with formation of $SnCl_4$.

Fe_2Cl_6 yields two atoms of chlorine to $SnCl_2$, forming $SnCl_4$, and leaving two molecules of $FeCl_2$. The yellowish solution turns green.

$AuCl_3$ gives with $SnCl_2$ a *purple* precipitate (*purple of cassius*), to which the formula $SnOAu_2o'' + SnOSno'' + 4Aq$ (sometimes viewed also as $Au_2 + 3SnO_2$), has been assigned. The change may be expressed thus:—

$$2AuCl_3 + 3SnCl_2 + 6OH_2 = Au_2 + 3SnO_2 + 12HCl.$$

This is a most delicate reaction.

B. **Stannic compounds.**—A SOLUTION OF STANNIC CHLORIDE, $SnCl_4$, is employed in studying the reactions of Sn^{iv} in the wet way.

SH_2 (**group-reagent**) gives a *yellow* precipitate of **stannic sulphide**, SnS_2, readily soluble in alkaline sulphides, potassic hydrate, boiling concentrated hydrochloric acid, and aqua regia; soluble, although somewhat difficultly, in ammonic hydrate (DISTINCTION FROM SnS), and nearly insoluble in ammonic (sesqui-) carbonate.

SAm_2, same precipitate, soluble in excess.

KHo or NaHo produces a *white* precipitate of **stannic hydrate**, $SnOHo_2$, or **stannic acid**, which is completely soluble in excess, forming dipotassic or disodic stannate, soluble in hydrochloric acid.

AmHo precipitates likewise the **hydrate**; excess redissolves it but slightly. Tartaric acid prevents the precipitation.

$\mathbf{CO}\mathrm{Amo}_2$ or $\mathbf{CO}\mathrm{Nao}_2$ precipitates *white* **stannic acid,** $\mathbf{Sn}\mathrm{OHo}_2$, soluble in caustic alkalies.

Stannic chloride furnishes us, moreover, with an interesting process of precipitation, viz., by means of neutral salts, such as sodic sulphate, ammonic nitrate (in fact, most neutral salts). Metastannic acid ($\mathbf{Sn}_5\mathrm{O}_5\mathrm{Ho}_{10}$) is precipitated on heating, provided the solution of stannic chloride be not too acid, thus :—

$$5\mathbf{Sn}\mathrm{Cl}_4 + 20\mathbf{SO}_2\mathrm{Nao}_2 + 15\mathbf{O}\mathrm{H}_2 = \mathbf{Sn}_5\mathrm{O}_5\mathrm{Ho}_{10} + 20\mathrm{NaCl} + 20\mathbf{SO}_2\mathrm{HoNao}.$$

$$5\mathbf{Sn}\mathrm{Cl}_4 + 20\mathbf{NO}_2\mathrm{Amo} + 15\mathbf{O}\mathrm{H}_2 = \mathbf{Sn}_5\mathrm{O}_5\mathrm{Ho}_{10} + 20\mathrm{AmCl} + 20\mathbf{NO}_2\mathrm{Ho}.$$

Metallic zinc precipitates from acid solutions of stannous or stannic chloride metallic tin in the form of grey laminæ, or of a spongy mass which can be readily dissolved in hydrochloric acid, especially by the aid of a piece of platinum foil. Metallic iron produces *no* precipitate.

Metallic tin or copper reduces stannic to stannous chloride, thus :—

$$\mathbf{Sn}\mathrm{Cl}_4 + \mathrm{Sn} = 2\mathbf{Sn}\mathrm{Cl}_2.$$

A solution of stannous chloride (containing hydrochloric acid) cannot be kept, when exposed to air, without changing rapidly to stannic chloride, as well as insoluble stannous oxychloride, $\mathbf{Sn}_2\mathrm{OCl}_2$, on account of the great attraction which stannous salts possess for oxygen, thus :—

$$(1)\ 2\mathbf{Sn}\mathrm{Cl}_2 + \mathrm{O} = \mathbf{Sn}_2\mathrm{OCl}_2 + \mathrm{Cl}_2.$$
$$(2)\ \mathbf{Sn}\mathrm{Cl}_2 + \mathrm{Cl}_2 = \mathbf{Sn}\mathrm{Cl}_4.$$

Hence granulated metallic tin or pure tinfoil is usually put into stannous solutions in order to prevent the formation of a bulky white precipitate of stannous oxychloride.

QUESTIONS AND EXERCISES.

1. How do you detect a stannic salt in the presence of a stannous salt?
2. Give the constitutional and graphic formulæ for metastannic and stannic acids, stannous and stannic chlorides, and stannous oxychloride.

3 How can the correctness of the atomic weight assigned to tin be shown experimentally?

4. Why does a chemical change take place when $\mathbf{Sn}\mathrm{Cl}_2$ and $\mathbf{Hg}\mathrm{Cl}_2$ are heated together?
5. Explain the action of chlorine, nitric acid, and air upon stannous salts.
6. How is Sn separated from Ag?
7. How would you analyse an alloy consisting of Pb, Cu, Bi, Sn?
8. A *tinstone* yielded on analysis 77·5 per cent. of metallic tin; how much $\mathbf{Sn}\mathrm{O}_2$ did it contain?
9. How much chlorine gas by weight and by volume (at 0° and 760 mm.) will be absorbed by 10 grms. of $\mathbf{Sn}\mathrm{Cl}_2$?
10. Express in symbolic formulæ the equations for the reactions, in the wet way, of stannous and stannic chlorides.

2. **ANTIMONY,** Sb''' and ^{v}. Atomic weight, 122.—This metal is found *native;* also in combination with oxygen as *white antimony*, Sb_2O_3, but more frequently as sulphide, Sb_2S_3 (*grey antimony*), and in combination with other metallic sulphides (Ag_2S, PbS, $'Cu'_2S$), as sulphantimonite and sulphantimonate.

EXAMINATION IN THE DRY WAY.

On heating metallic antimony or an antimony mineral, *e.g.*, *grey antimony*, with free access of air, either on charcoal or in a glass tube open at both ends, dense white fumes of antimonious and antimonic oxides are given off, which condense on the colder part of the charcoal or glass tube, thus :—

$$Sb_2S_3 + O_9 = \underset{\text{Sublimed.}}{Sb_2O_3} + 3SO_2$$

All compounds of antimony can be reduced to the metallic state when heated on charcoal in the reducing flame, together with $CONao_2$ and KCy. A brittle globule of metallic antimony is obtained, giving off dense white fumes of Sb_2O_3 (even after the withdrawal of the metal from the flame), which thickly incrust the metallic globule with a network of brilliant acicular crystals.

EXAMINATION IN THE WET WAY.

Chlorine attacks antimony violently, forming with it $SbCl_3$ or $SbCl_5$, according to the proportions of chlorine employed, and according to the temperature at which the combination takes place. Hydrochloric acid has scarcely any action upon the metal; aqua regia dissolves it readily to $SbCl_5$. Nitric acid converts it into a compound containing Sb_2O_3 and Sb_2O_5, insoluble in nitric acid, *soluble in tartaric acid. Grey antimony*, Sb_2S_3, as well as Sb_2S_5, dissolve in concentrated hydrochloric acid with evolution of sulphuretted hydrogen, the latter sulphide with separation of sulphur.

Antimony forms two series of compounds by combining either with three or five atoms of chlorine, etc., viz. :—

Antimonious compounds.		*Antimonic compounds.*	
$Sb'''Cl_3$,	Antimonious chloride.	$Sb^{v}Cl_5$,	Antimonic chloride.
Sb'''_2O_3,	,, oxide.	$Sb^{v}_2O_5$,	,, oxide.
Sb'''_2S_3,	,, sulphide.	$Sb^{v}_2S_5$,	,, sulphide.
$Sb'''OHo$,	Metantimonious acid.	$Sb^{v}O_2Ho$,	Metantimonic acid.*

Both these acids can enter into combination with strong bases, such as potassa, or soda, to form weak salts,—metantimonites and metantimonates, viz. :—

$Sb'''OKo$,	Potassic metantimonite.
$Sb^{v}O_2Ko$,	Potassic metantimonate.
$Sb^{v}O_2Nao$,	Sodic metantimonate.

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* Orthantimonic acid, $SbOHo_3$, and pyrantimonic acid, $Sb_2O_3Ho_4$ (said to be formed when antimonic chloride is decomposed by water), are little known.

$\mathbf{Sb}^{v}O_2(Sb'''O_2)'$, antimonylic metantimonate, or $\left\{\begin{matrix}'\mathbf{Sb}^{iv}O_2\\ '\mathbf{Sb}^{iv}O_2\end{matrix}\right.$, diantimonic tetroxide, is formed when antimonic oxide (obtained by dissolving antimony in nitric acid) is ignited. This compound is of some importance, as it serves for the quantitative estimation of antimony.

A. **Antimonious compounds.**—A SOLUTION OF ANTIMONIOUS CHLORIDE, $\mathbf{Sb}_2Cl_3$, is employed for the reactions in the wet way.

$\mathbf{S}H_2$ (**group-reagent**) gives an *orange-red* precipitate of hydrated **antimonious sulphide**, $\mathbf{Sb}_2S_3$, soluble in alkaline sulphides and in potassic or sodic hydrate; reprecipitated by hydrochloric acid; slightly soluble in ammonic hydrate, all but insoluble in hydric ammonic carbonate and in hydric ammonic or hydric potassic sulphites. It dissolves in boiling concentrated hydrochloric acid.

Temperature and concentration of the reagents produce *reciprocal* effects. In a dilute hydrochloric acid solution the $\mathbf{Sb}Cl_3$ exchanges its chlorine in the cold for sulphur, with precipitation of $\mathbf{Sb}_2S_3$, whilst boiling concentrated hydrochloric acid dissolves $\mathbf{Sb}_2S_3$ readily with evolution of $\mathbf{S}H_2$.

$\mathbf{S}Am_2$ produces the same precipitate as $\mathbf{S}H_2$, soluble in excess.

KHo or NaHo precipitate *antimonious oxide*, $\mathbf{Sb}_2O_3$, readily soluble in excess, with formation of potassic antimonite.

AmHo, same precipitate, almost insoluble in excess.

$\mathbf{C}OAmo_2$, $\mathbf{C}OKo_2$, or $\mathbf{C}ONao_2$, same precipitate.

$\mathbf{O}H_2$ decomposes $\mathbf{Sb}Cl_3$, forming a *white insoluble basic salt*, **antimonious oxychloride**, $\mathbf{Sb}OCl$, soluble in tartaric acid. (DISTINCTION FROM BISMUTHOUS OXYCHLORIDE, $\mathbf{Bi}OCl$). Water, therefore, gives no precipitate with a solution of potassic antimonylic tartrate (*tartar emetic*) $\left\{\begin{matrix}\mathbf{C}O(Sb'''O_2)'\\ \mathbf{C}HHo\\ \mathbf{C}HHo\\ \mathbf{C}OKo\end{matrix}\right.$; and alkalies and alkaline carbonates produce a partial precipitation only after some time.

Metallic Zn, Cu, Cd, Fe, Co, Sn, and Pb precipitate the metal in the absence of free nitric acid as a black powder.

An exceedingly delicate reaction for antimony consists in precipitating the metal from a dilute hydrochloric acid solution on platinum foil or on the lid of a platinum crucible, by means of a small strip of metallic zinc. H and $\mathbf{Sb}H_3$ (antimonietted hydrogen*) are evolved, and the platinum is stained brown or black by the deposited metal. Mere traces of antimony can thus be discovered. The stain is not affected by hot dilute hydrochloric acid, but disappears on heating with nitric acid. Tin cannot be precipitated on platinum. It is precipitated by zinc, and is readily soluble in hot dilute hydrochloric acid.

Compounds containing triad antimony exhibit a tendency (less marked, however, than in stannous compounds) to combine with more chlorine, etc., and to pass into pentad or antimonic compounds. Expressed graphically—

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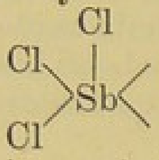
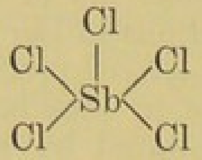
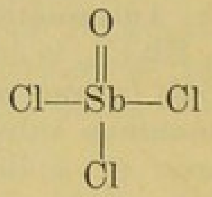
* Of this gas more at page 89.

Antimonious chloride  has two bonds left unsatisfied or latent,

whilst pentad antimony in $Sb^{v}Cl_5$ or $Sb^{v}OCl_3$ (oxy-trichloride), has all its bonds satisfied, thus :—

Antimonic chloride. 

Antimonic oxy-tri-chloride. 

The following are some of the reactions naturally arising from this condition of antimonious compounds :—

When a current of chlorine gas is passed over solid $SbCl_3$, a molecule of chlorine is absorbed, and the chloride liquefies, thus :—

$$SbCl_3 + Cl_2 = SbCl_5.$$

Solid antimonious chloride. Liquid antimonic chloride.

Sodic metantimonite, $SbONao$, is oxidised, in the presence of sodic hydrate, by free iodine, with formation of sodic metantimonate, SbO_2Nao, and NaI, thus :—

$$SbONao + I_2 + 2NaHo = SbO_2Nao + 2NaI + OH_2.$$

A hydrochloric acid solution of $SbCl_3$ reduces $AuCl_3$ to metallic gold (frequently with separation of SbO_2Ho), thus :—

$$3SbCl_3 + 2AuCl_3 = 3SbCl_5 + Au_2.$$

Sodic metantimonite is oxidised in an alkaline solution by argentic oxide, OAg_2, to sodic metantimonate, argentous oxide, OAg_4, being formed, which is insoluble in ammonic hydrate, OAg_2, being readily soluble. (DISTINCTION BETWEEN Sb_2O_3 AND Sb_2O_5.)

The several reactions may be expressed as follows :

$$(1)\quad SbCl_3 + 4NaHo = SbONao + 3NaCl + 2OH_2.$$

Sodic metantimonite.

$$(2)\quad 2NO_2Ago + 2NaHo = OAg_2 + 2NO_2Nao + OH_2.$$

Argentic oxide (insoluble in NaHo, soluble in AmHo).

$$(3)\quad SbONao + 2OAg_2 = SbO_2Nao + OAg_4.$$

Black argentous oxide, insoluble in AmHo.

$SSONao_2$ (**sodic hyposulphite**) reduces antimonious compounds to metallic antimony, which combines with sulphur and forms Sb_2S_3, thus :—

$$3SSONao_2 + Sb_2O_3 = Sb_2S_3 + 3SO_2Nao_2.$$

B. **Antimonic compounds.**—A SOLUTION OF POTASSIC METANTIMONATE, SbO_2Ko, may conveniently be employed for studying the reactions in the wet way.

This salt is prepared by fusing metantimonic acid, SbO_2Ho, with a large excess of KHo, in a silver crucible, and dissolving the mass in cold water. Fused with caustic soda, a sodic metantimonate is obtained, which is insoluble in water.

SbO_2Ko is readily decomposed by concentrated acids (hydrochloric or nitric), metantimonic acid being precipitated.

SH_2 gives from a solution of SbO_2Ho in excess of hydrochloric acid, an orange precipitate of antimonic sulphide, Sb_2S_5, mixed with Sb_2S_3 and S; soluble in alkaline sulphides, readily soluble in ammonic or potassic hydrate; also soluble in boiling concentrated hydrochloric acid, with evolution of SH_2 and deposition of S; only very sparingly soluble in cold hydric ammonic carbonate.

SAm_2, same precipitate, soluble in excess.

SO_2Feo'' does not reduce antimonic compounds.

NO_2Ago, added to an alkaline solution of SbO_2Ko, yields, for obvious reasons, only OAg_2, readily soluble in ammonic hydrate.

Antimonic compounds, like stannic salts, *can, under certain conditions, also act as oxidizing agents, e.g.*:—

On igniting antimonic anhydride, it splits up into Sb_2O_4 and oxygen.

$SnCl_2$ precipitates $SbOHo$ from a hydrochloric acid solution of SbO_2Ho, the $SnCl_2$ being converted into $SnCl_4$.

On boiling a solution of SbO_2Ho in hydrochloric acid with potassic iodide, iodine is liberated, colouring the solution brown. ($SbCl_5$ is in fact frequently employed for the purpose of conveying chlorine to other bodies, both mineral and organic.) Iodine is set free, because $SbCl_5$, on being heated, together with 2KI, forms $SbCl_3 + I_2 + 2KCl$. The liberated iodine is readily recognized by means of starch paste, when the highly delicate and characteristic blue iodide of starch reaction is obtained. (DISTINCTION BETWEEN ANTIMONIOUS AND ANTIMONIC COMPOUNDS.)

QUESTIONS AND EXERCISES.

1. How is antimonious chloride prepared? What change does it undergo when water is added to it?
2. How can the metal antimony be obtained from *grey antimony ore?*
3. By what characteristic reaction can antimony compounds be recognized when examined in the dry way?
4. What is the action of concentrated nitric acid upon metallic antimony? Explain the change by an equation.
5. How can you distinguish between antimonious and antimonic compounds?
6. Explain the action of Zn or Fe upon a solution of $SbCl_3$.
7. What evidence have we to show the triad and pentad nature of Sb?
8. Give illustrations of the reducing action of antimonious compounds, *e.g.*, antimonious chloride.
9. Give instances of the oxidising action of antimonic compounds, *e.g.*, metantimonic acid.
10. State how you would separate Sb from Sn, in the wet way.
11. How can Sb be separated from Bi?
12. Express by symbolic equations the reactions for antimony in the wet way.
13. Calculate the percentage composition of *white antimony* and antimonious oxychloride.
14. 1 grm. of a sample of *grey antimony* yielded on analysis ·854 grm. of Sb_2O_4; what percentage of antimony does the ore contain?

15. How would you separate Sn from Sb, in the dry way?
16. How much $\mathbf{Sb}_2O_4$ by weight will 1·32 grm. of metallic antimony yield?
17. How much chlorine by weight and by volume (at 0° C. and 760 mm.) is required to convert 10 grms. of $\mathbf{Sb}Cl_3$ into $\mathbf{Sb}Cl_5$?
18. How much oxygen gas by weight and by volume (at 0° C. and 760 mm.) can be obtained by igniting 5 grms. of $\mathbf{Sb}_2O_5$?
19. Describe the preparation of potassic metantimonate.
20. How much Pb and Sb have to be employed to prepare 50 lb. of type metal, an alloy having the composition Pb_4Sb?

3. **ARSENIC**, As''' and ^{v}. Atomic weight, 75.—This body constitutes one of the most widely diffused elements in nature. It is found *native*, but exists most frequently in combination with sulphur as *realgar*, $\left\{\begin{matrix}\mathbf{As}S''\\ \mathbf{As}S''\end{matrix}\right.$, or diarsenious disulphide, and as *orpiment*, $\mathbf{As}_2S''_3$, or arsenious sulphide (sulpharsenious anhydride); in combination with metals it exists in *arsenical nickel*, $\left\{\begin{matrix}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{matrix}\right.\mathrm{Ni}$, *copper nickel*, $\left\{\begin{matrix}{}'\mathbf{As}''\mathrm{Ni}\\ {}'\mathbf{As}''\mathrm{Ni}\end{matrix}\right.$, and in *smaltine*, $\left\{\begin{matrix}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{matrix}\right.\mathrm{Co}$. Arsenic acts in some of these mineral bodies more like a metalloïd than a metal. Metallic *arsenides* are frequently found in combination with metallic sulphides, such as the sulphides of Ag, Fe, Ni, Co, Cu, etc., as in the common mineral *mispickel*, or *arsenical pyrites*, $\left\{\begin{matrix}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{matrix}\right.\mathrm{Fe}'',\mathbf{Fe}^{iv}S_2$, in *nickel glance* or *grey nickel ore*, $\left\{\begin{matrix}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{matrix}\right.\mathrm{Ni}'',\mathbf{Ni}^{iv}S_2$, and in *cobalt glance* $\left\{\begin{matrix}{}''\mathbf{As}'\\ {}''\mathbf{As}'\end{matrix}\right.\mathrm{Co}'',\mathbf{Co}^{iv}S_2$. Arsenic occurs also in the form of metallic *arsenates*, such as calcic, magnesic, nickelous, cobaltous, plumbic arsenates; for example, in the mineral *pharmacolite*, $\mathbf{As}_2O_3Cao''_2, 6\mathbf{O}H_2$ (calcic pyrarsenate), in *nickel ochre*, $\mathbf{As}_2O_2Nio''_3, 9\mathbf{O}H_2$, in *cobalt bloom*, $\mathbf{As}_2O_2Coo''_3, 8\mathbf{O}H_2$, and in *mimetesite*, $3(\mathbf{As}_2O_2Pbo''_3)$, $\mathbf{Pb}Cl_2$.

Traces of arsenic are almost invariably found in commercial sulphur, iron, copper, tin, and antimony. On account of the solubility of its oxides, arsenic is sometimes found in mineral springs and in the ochreous deposits from mineral waters.

EXAMINATION IN THE DRY WAY.

Arsenic can be completely *volatilized*. When heated in contact with air, either on charcoal or in an open tube, it burns and forms arsenious anhydride, $\mathbf{As}_2O_3$, giving off at the same time a peculiar and most characteristic garlic odour. Arsenical compounds give the same indications when heated by themselves, on charcoal in the reducing flame, and on the addition of sodic carbonate and potassic cyanide, whether the arsenic be present as arsenite or arsenate. The blowpipe experiments should be performed with great precaution, since arsenical fumes are poisonous. The reaction being so very delicate, small quantities only of the substance should be operated upon.

When arsenical compounds are heated in a bulb-tube, Fig. 8, *a*, mixed with a proper reducing agent (such as sodic carbonate and charcoal powder or black-flux), metallic arsenic sublimes and is deposited in the shape of a lustrous steel grey mirror, *b*, in the upper part of the tube.

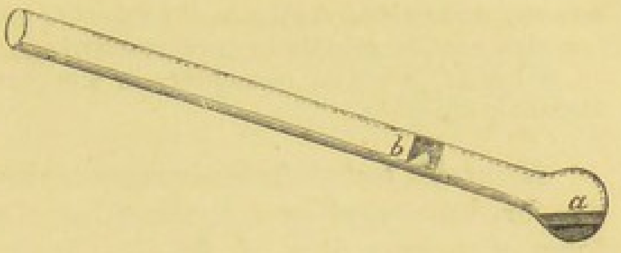


FIG. 8.

EXAMINATION IN THE WET WAY.

Chlorine attacks arsenic violently, forming a highly poisonous liquid, arsenious chloride, $AsCl_3$. Hydrochloric acid does not act upon arsenic; nitric acid oxidizes it to arsenious and arsenic acids, according to the concentration of the acid.

Arsenic forms *two oxides*, *sulphides*, etc., and *two well characterized series of salts*, *arsenites*, and *arsenates*.

A. **Arsenious compounds.**—We may employ either a SOLUTION OF ARSENIOUS ANHYDRIDE, As_2O_3, in dilute hydrochloric acid, or AN AQUEOUS SOLUTION OF AN ARSENITE, $AsKo_3$ (tripotassic arsenite).

SH_2 (**group-reagent**) produces in an acid solution of As_2O_3, especially on gently heating, a *lemon-yellow* precipitate of **arsenious sulphide**, As_2S_3, readily soluble in caustic alkalies, in alkaline carbonates and sulphides forming alkaline arsenites and sulpharsenites; it is reprecipitated from any of these solutions on the addition of dilute hydrochloric or nitric acid. It is nearly insoluble in concentrated hydrochloric acid, even on boiling; but soluble in nitric acid. On digesting freshly precipitated arsenious sulphide in a solution of hydric potassic sulphite, $SOHoKo$, and excess of sulphurous acid, the yellow precipitate is dissolved, and the solution contains potassic metarsenite and potassic hyposulphite, after driving off the excess of sulphurous acid by evaporation, thus :—

$$2As_2S_3 + 16SOHoKo = 4AsOKo + 6SSOKo_2 + S_3 + 7SO_2 + 8OH_2.$$

SAm_2, same precipitate soluble in excess.

NO_2Ago produces from a solution of a neutral arsenite, or from a solution of As_2O_3 in water, rendered neutral by cautiously adding ammonic hydrate, a *yellow* precipitate of **triargentic arsenite**, $AsAgo_3$, readily soluble in ammonic hydrate, ammonic chloride, or nitric acid. The ammoniacal solution of $AsAgo_3$ and OAg_2 is decomposed on boiling, with separation of metallic silver and formation of **triargentic arsenate**, $AsOAgo_3$, thus :—

$$AsAgo_3 + OAg_2 = AsOAgo_3 + Ag_7.$$

Soluble in AmHo.	Soluble in AmHo.	Soluble in AmHo.	Black precipitate.

SO_2Cuo'' produces a characteristic *yellowish-green* precipitate of **hydric**

cupric arsenite, $AsHoCuo''$ (*Scheele's green*), from a solution of tripotassic arsenite, readily soluble in ammonic hydrate, ammonic chloride, or nitric acid.

SO_2Mgo'' gives no precipitate in the presence of free ammonic hydrate and ammonic chloride.

Reinsch's test.—Arsenic is precipitated on a strip of clean metallic copper, immersed in a hydrochloric acid solution of As_2O_3, in the form of a grey film of As_2Cu_5, from highly dilute solutions, especially on heating. The film peels off in black scales if the solution contain sufficient arsenic. The presence of the metal should be confirmed in the dry way, especially as antimony is also precipitated by metallic copper under similar conditions.

Arsenious compounds exert a powerful *reducing action*, when brought together with bodies that are capable of parting with oxygen, chlorine, etc. This property is even more marked in arsenious than in antimonious compounds. Triad arsenic compounds, containing two unsatisfied bonds, give rise to numerous interesting reactions, thus :—

$AuCl_3$ (**auric chloride**) produces from an acid solution of As_2O_3 a precipitate of metallic gold, and the reaction is so accurate that the amount of arsenic can be determined quantitatively from the weight of the precipitated gold.

Two atoms of Au $(2 \times 196{\cdot}7)$ = three atoms of As (3×75).

$$4AuCl_3 + 3As_2O_3 + 15OH_2 = 6AsOHo_3 + Au_4 + 12HCl.$$

Chlorine water, or compounds capable of yielding chlorine, such as a solution of bleaching powder, or of sodic hypochlorite, $ClNao$ (*Eau de Javelle*), oxidize As_2O_3 rapidly, thus :—

$$As_2O_3 + 2Cl_2 + 5OH_2 = 2AsOHo_3 + 4HCl.$$

Iodine, dissolved in a solution of potassic iodide, likewise converts a solution of As_2O_3, dissolved in excess of hydric sodic carbonate, into As_2O_5, with formation of an alkaline iodide, thus : —

$$AsHoNao_2 + 2COHoNao + I_2 = AsOHoNao_2 + 2NaI + OH_2 + 2CO_2.$$

Chlorine, iodine, and bromine act as *oxidizing* agents by decomposing water or a metallic oxide. They form, with the hydrogen, HCl, HI, HBr, or with a metal the corresponding haloïd salt, and the oxygen is transferred to the As_2O_3.

The oxidizing action of OAg_2 upon $AsAgo_3$ in an ammoniacal solution has already been noticed.

An analogous change is produced by cupric oxide in the presence of potassic hydrate. On adding to a strongly alkaline solution of tripotassic arsenite a few drops of cupric sulphate, and applying a gentle heat, the blue solution deposits a red precipitate of cuprous oxide, Cu_2O, and leaves tripotassic arsenate, $AsOKo_3$, in solution. (DISTINCTION BETWEEN As_2O_3 AND As_2O_5.)

The deoxidizing action which arsenious compounds exert upon the higher oxides of chromium (chromates) and manganese (manganates and permanganates), has already been described, pages 46 and 32.

B. **Arsenic Compounds.**—We employ AN AQUEOUS SOLUTION OF TRIPOTASSIC ARSENATE, $AsOKo_3$.

SH_2 gives scarcely any precipitate from an acidulated solution of $AsOKo_3$, until the solution is heated, and a current of gas passed through for some time. It is difficult to effect complete precipitation even then. The precipitate consists of arsenious sulphide and sulphur. It is preferable to reduce the As_2O_5 first to As_2O_3, by a more powerful reducing agent than SH_2, for example, by sulphurous acid, or an acid sulphite, such as $SOHoKo$ or $SOHoAmo$—

$$AsOKo_3 + SOHo_2 = AsKo_3 + SO_2Ho_2,$$

whence sulphuretted hydrogen precipitates the arsenic readily as arsenious sulphide.

NO_2Ago gives a *reddish-brown* precipitate of **triargentic arsenate**, $AsOAgo_3$, soluble in ammonic hydrate and in nitric acid.

SO_2Cuo'' produces a *pale greenish-blue* precipitate of **hydric cupric arsenate**, $AsOHoCuo''$, soluble in ammonic hydrate and nitric acid.

SO_2Mgo'', in the presence of ammonic chloride and ammonic hydrate, gives a *white crystalline* precipitate of **ammonic magnesic arsenate**, $AsOAmoMgo''$ (DISTINCTION OF As_2O_3 FROM As_2O_5).

Fe_2Cl_6 gives a *yellowish-white* precipitate of **ferric arsenate**, $As_2O_2Fe_2o^{vi}$.

$\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$ (**plumbic acetate**) gives a *white* precipitate of **triplumbic arsenate**, $As_2O_2Pbo''_3$.

MO_2Amo_2 (**ammonic molybdate**), dissolved in nitric acid, gives a *yellow* precipitate of **arsenio-ammonic molybdate.**

Metallic copper does not precipitate metallic arsenic from dilute acid solutions of As_2O_5; but on adding concentrated hydrochloric acid, and heating, a grey film of As_2Cu_5 is obtained (DISTINCTION BETWEEN As_2O_3 AND As_2O_5).

Arsenic as well as arsenious compounds are capable of oxidizing other bodies, and become themselves reduced either to a lower oxide (sulphide), or to the metallic state.

Sulphurous acid reduces arsenic to arsenious acid.

$SSONao_2$ (**sodic hyposulphite**) deprives arsenious acid of its oxygen, and converts it into As_2S_3, thus:—

$$2AsHo_3 + 3SSONao_2 = As_2S_3 + 3SO_2Nao_2 + 3OH_2.$$

Carbon reduces both Oxides of Arsenic to Metallic Arsenic.—A fragment of arsenious anhydride (*white arsenic*) is placed in the pointed end, *a*, of a hard glass tube drawn out before the blowpipe, as seen in Fig. 9. A splinter of well ignited charcoal is next placed in the narrow part of the tube at *b*, somewhat above the fragment of the arsenical compound. This charcoal is heated over a gas flame or the flame of a spirit lamp. When the charcoal is well ignited a second flame is applied to the lower

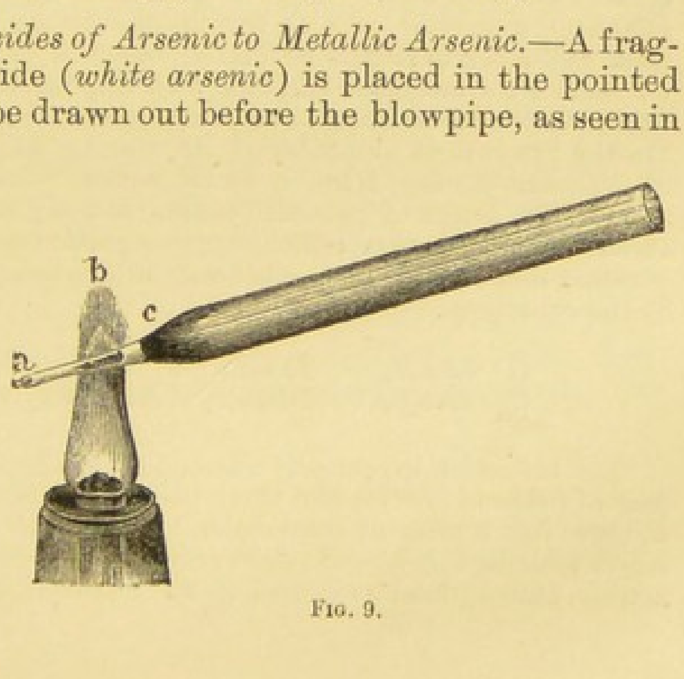


Fig. 9.

end of the tube in order to volatilize the arsenical compound, the vapour of which, on passing over the glowing charcoal, is deprived of its oxygen, and metallic arsenic is deposited in the form of a shining black mirror on the inside of the tube, above the charcoal at *c*. The reaction takes place according to the equation :—

$$2\mathbf{As}_2O_3 + 3C = \mathbf{As}_4 + 3\mathbf{C}O_2.$$

This test is very delicate. Arsenic, in the form of an arsenite or arsenate, is liberated by mixing perfectly dry charcoal powder, or black-flux, with the dry substance, previous to its introduction into the drawn out portion of the tube, which for this purpose has a small bulb blown at its lower end. The sublimation of metallic arsenic is accompanied by the characteristic *garlic odour*.

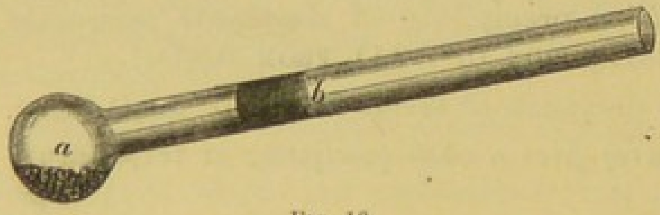


Fig. 10.

KCy reduces arsenical compounds—oxides as well as sulphides—with formation of potassic cyanate or sulphocyanate. A mixture of potassic cyanide with the arsenical compound is heated in a bulb tube, *a* (Fig. 10). Metallic arsenic is deposited at *b*.

The changes are expressed as follows :—

$$2\mathbf{As}_2O_3 + 6KCy = \underset{\text{Potassic cyanate.}}{6CyKo} + As_4.$$

$$2\mathbf{As}_2S_3 + 6KCy = \underset{\text{Potassic sulphocyanate.}}{6CyKs} + As_4.$$

But since potassic cyanide contains potassic cyanate, as well as potassic carbonate (its composition may be expressed by the formula $5KCy + CyKo + x\mathbf{CO}Ko_2$), a *portion* only of the arsenic in $\mathbf{As}_2S_3$ is obtained in the metallic form, and a sulpharsenate is formed which is not reduced by potassic cyanide. On mixing the arsenious sulphide with sulphur, the whole of the arsenic remains behind in the fused mass, as sulpharsenate, and no metallic deposit is obtained. (In the presence of sulphides of Pb, Cu, Ag, Au, Ni, Co, Fe—as, *e.g.*, of $\mathbf{Fe}S_2$, in *arsenical pyrites*, $\mathbf{Ni}S_2$, in *nickel glance*—which are reduced to the metallic state by the action of potassic cyanide, scarcely any arsenical mirror is obtained, because the liberated metallic arsenic—a portion only of the arsenic being liberated—would immediately alloy itself with the metals.) These changes are expressed by the equations :—

$$(1)\ 5\mathbf{As}_2S_3 = 3\mathbf{As}_2S_5 + As_4.$$
$$(2)\ 4\mathbf{As}_2S_5 + 12\mathbf{CO}Ko_2 = 5\mathbf{As}SKs_3 + 3\mathbf{As}OKo_3 + 12\mathbf{CO}_2.$$

The reduction is generally effected by mixing dry arsenious sulphide with one part of potassic cyanide and three parts of sodic carbonate, and introducing the mixture into a piece of combustion tube, C, drawn out to a point, as seen on a larger scale in Fig. 11. A slow current of carbonic anhydride generated from marble and hydrochloric acid in the flask A, Fig. 12, and dried by passing through *b* into the flask B, containing concentrated sulphuric acid, and out through the delivery tube *c*, is passed over the mixture in tube C, heated at

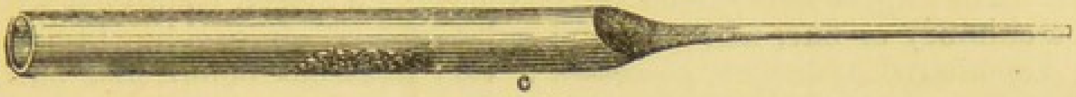


FIG. 11.

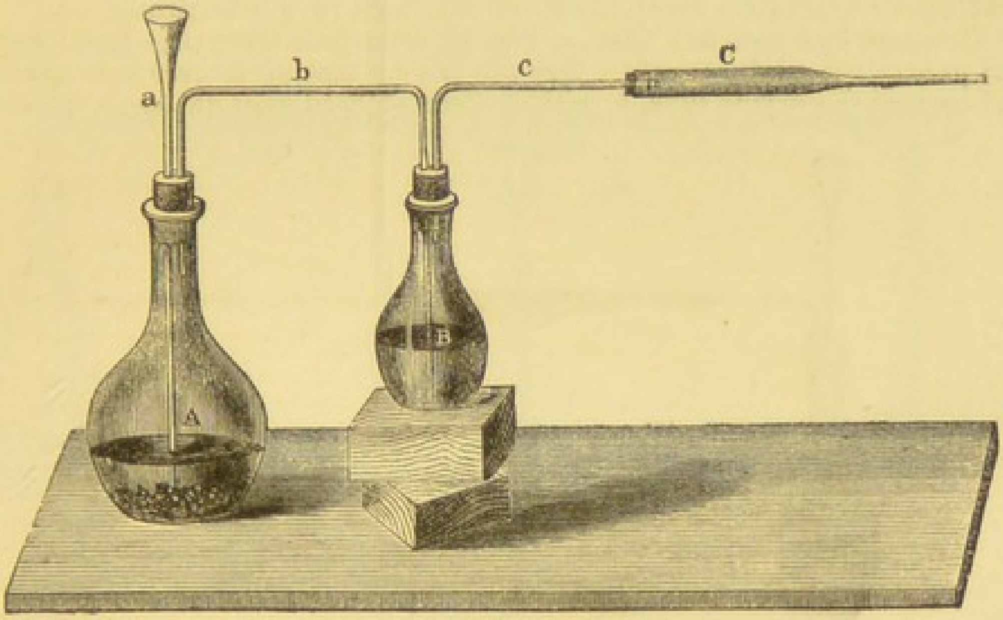


FIG. 12.

first gently, till all the moisture has been driven out, and then strongly to fusion, —when a mirror of metallic arsenic collects in the neck of the drawn-out tube.

The reaction has this advantage, that no antimony mirror is obtained in the same way.

In order, however, to avoid missing the arsenic, either altogether or obtaining only a portion of it, as stated above, it is preferable to treat the arsenious sulphide with a few drops of concentrated nitric acid, and to evaporate with a little sulphuric acid (in order to decompose any metallic nitrates, if present). The sulphuric acid is next neutralised with sodic carbonate, and the mass thoroughly dried, before mixing it with potassic cyanide and reducing it as described. The fused mass retains the antimony, and a good arsenical mirror is obtained, provided no lead, copper, or other reducible metals were present.

Arsenious and arsenic acids are both reduced by nascent hydrogen, which combines with the oxygen of the arsenical oxides to form water, whilst the arsenic in its nascent state, or the very moment it is liberated from the oxygen, combines likewise with hydrogen to form a gaseous compound of arsenic, called *arsenietted hydrogen* (arsenious hydride)—$\mathbf{As}'''H_3$. This gas is obtained pure by acting with dilute sulphuric acid upon an alloy of zinc and arsenic. The zinc takes the place of the hydrogen in the acid, and arsenietted hydrogen is liberated, thus:—

$$\mathbf{As}_2\mathrm{Zn}_3 + 3\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 = 3\mathbf{S}\mathrm{O}_2\mathrm{Zno}'' + 2\mathbf{As}\mathrm{H}_3.$$

Arsenietted hydrogen is an exceedingly poisonous gas, and the student should on no account attempt to prepare it pure. Its properties may be studied equally well in a mixture of the gas with much hydrogen.

The experiment should be conducted in a closet, connected with a chimney or flue, where a good indraught of air can be obtained. Arseniettted hydrogen possesses a very nauseous odour, and burns with a peculiarly livid bluish flame, when the jet of hydrogen and arseniettted hydrogen gas is lighted, owing to the combustion of arsenic to arsenious anhydride which rises in white fumes.

Generate hydrogen in a flask, *a*, Fig. 13, from pure zinc (free from arsenic) and pure dilute sulphuric acid. Dry the gas by passing it over calcic chloride and connect the drying tube, *b*, with a piece of hard glass tubing, *c*, drawn out to a jet. The hydrogen gas may be ignited at the jet, *as soon as it has displaced the air in the generating flask, a, and drying tube, b.* It burns with an almost colourless flame if the zinc and acid are pure. On introducing a few drops of an arsenious or arsenic acid solution* through the funnel-tube, the flame is seen to change to blue, and on holding a piece of porcelain (*e.g.*, a dish, or the lid of a porcelain crucible) into the flame, a black mirror or deposit of metallic arsenic is obtained. Or the metal may be collected—by heating the glass tube through which the arseniettted hydrogen passes—in the form of a metallic ring, *d*, which deposits within the tube immediately behind the spot where the glass is heated. The hydrogen should not be generated too rapidly, if a good ring is to be obtained. The mirror may be driven on to *e* by gradually moving the flame from *c* towards *d*.

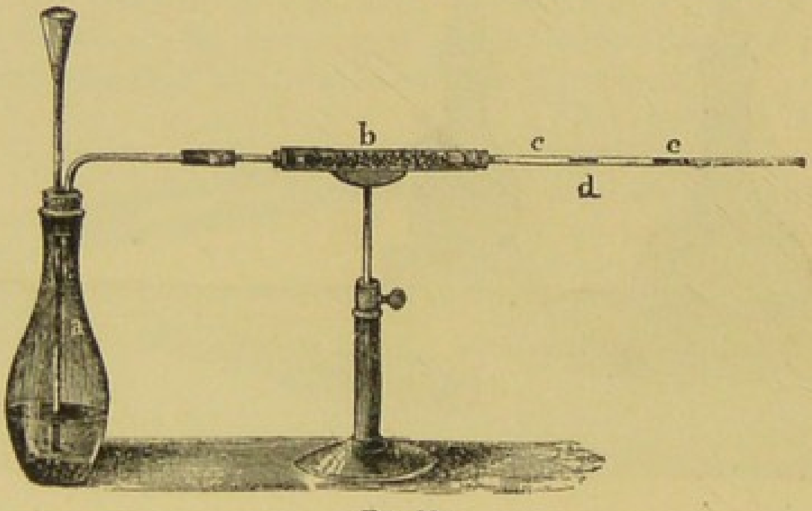


FIG. 13.

Several arsenical mirrors may be obtained if a long piece of narrow combustion tube, Fig. 14, be employed, which has been contracted in several places by drawing it out in the flame of a blowpipe. Arseniettted hydrogen is generated in the flask, *a*, and passing through *b*, the drying tube, *c*, and combustion tube, *d*, issues from the drawn-out jet, where it can be burnt. The tube, *d*, is heated in one or in several places, just before the several drawn-out narrow parts. An arsenical mirror is obtained a little behind the heated part of the tube, as seen in Fig. 14. Little or no arseniettted hydrogen need thus escape from the jet, especially if a slow current of hydrogen be generated.

The deposition of arsenic in the tube or on the cold porcelain arises from the decomposition of the arseniettted hydrogen, which, at a high temperature, is broken up into arsenic, which is deposited, and hydrogen, which passes on and burns at the jet. The decomposition which takes place when a cold piece of porcelain is lowered into the flame, is readily explained, if we remember what takes place when some cold porcelain is held in a candle or gas flame. We obtain a deposit of soot (finely-divided carbon from the hydrocarbons), because the combustion is disturbed, and the temperature of the flame suddenly lowered. The flame can only burn where it is in contact with air, *i.e.*, on the outside. The arseniietted hydrogen on passing through the inner portion of the flame, is decomposed by the heat into arsenic vapour and hydrogen gas; the latter escapes through the outer portion of the flame, and is burnt, arsenic being deposited on the cold porcelain surface. The decomposition of arseniietted hydrogen takes place, even if very little of the gas be mixed with much hydrogen gas, and *this test*—known as *Marsh's test*—*is therefore extremely delicate.*

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* It should be borne in mind, that only *acid* solutions of the *oxides* of arsenic can be employed. Any considerable excess of oxidizing agents, such as nitric, chloric, etc., acids, should also be avoided. The same holds good for the preparation of $\mathbf{SbH_3}$.

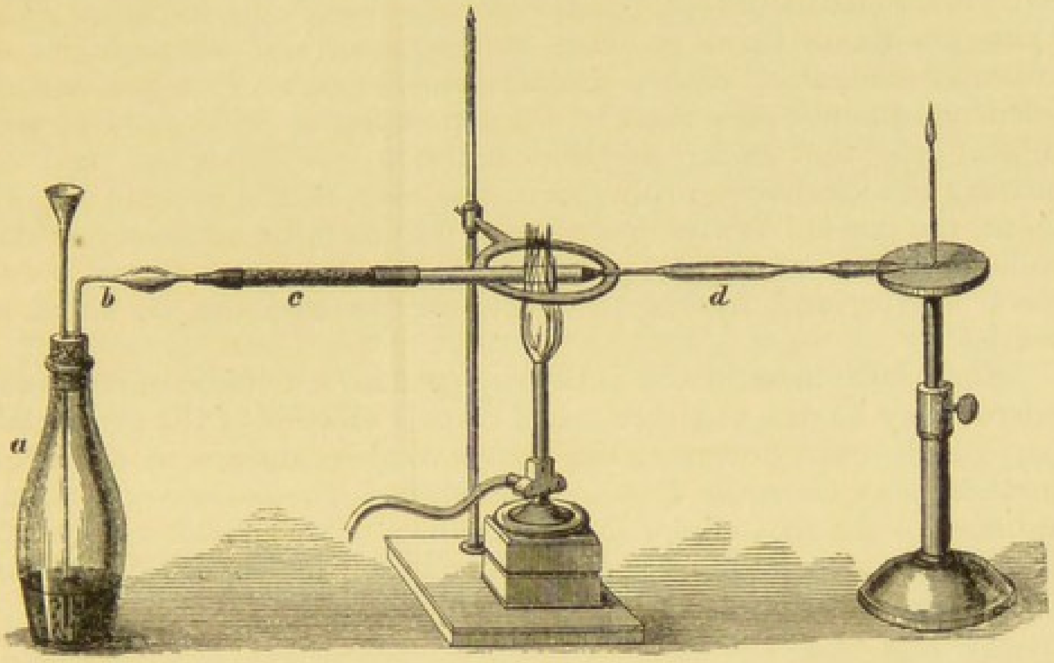

FIG. 14.

It is of paramount importance that both zinc and sulphuric acid should be tested first. This is done by generating hydrogen, and allowing the gas to escape by itself for some time, through the combustion tube ignited in several places.

Care should also be taken to avoid introducing nitric acid, since arseniietted hydrogen is readily decomposed by this acid. It is therefore preferable to dissolve arsenical compounds in hydrochloric acid, with the addition of a few small crystals of potassic chlorate, and to heat gently till no more chlorous odour is observable.

The metal antimony forms with nascent hydrogen a combustible gas analogous to arseniietted hydrogen, called *antimonietted hydrogen* (antimonious hydride), $\mathbf{Sb}\mathrm{H}_3$. It is prepared by acting with dilute sulphuric or hydrochloric acid upon an alloy of three atoms of zinc and two atoms of antimony, thus :—

$$\mathbf{Sb}_2\mathrm{Zn}_3 + 3\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 = 3\mathbf{S}\mathrm{O}_2\mathrm{Zno}'' + 2\mathbf{Sb}\mathrm{H}_3.$$

Mixed with hydrogen gas it is obtained by introducing into a hydrogen apparatus a few drops of an antimony solution ($\mathbf{Sb}Cl_3$, $\mathbf{Sb}O_2Ko$, or tartar emetic). The greater part of the antimony, however, remains behind, precipitated as metal on the zinc. The hydrogen flame turns at once bluish-green, and white fumes of antimonious oxide, $\mathbf{Sb}_2O_3$, ascend into the air. The gas has no odour, and is not poisonous.* On depressing a cold piece of porcelain into the flame, metallic antimony is deposited, and on heating the combustion tube, as in the case of the arsenic experiment, the gas is likewise decomposed into metallic antimony, which collects in the narrowed portions of the tube and forms a *dull black mirror*, and hydrogen, which escapes and can be burnt at the jet.

Since both arsenic and antimony produce a metallic mirror, such mirror may be due to either metal or to a mixture of the two metals (in which case, however, the more volatile arsenic is deposited further away from the flame, and a part of the antimony is found anterior to the spot where the glass tube is heated), and it is obvious that we must make further experiments in order to *distinguish* the *arsenic* from the *antimony in the mirror* itself.

This can be done very readily—

1st. By adding to the mirror obtained on cold porcelain a concentrated solution of bleaching powder, or of sodic hypochlorite (*Eau de Javelle*); or by simply exposing the mirror to chlorine gas, evolved by treating a little bleaching powder with dilute hydrochloric acid: the arsenical mirror is speedily dissolved; antimony only after some lengthened exposure, thus:—

$$As_2 + 5ClNao = \mathbf{As}_2O_5 + 5NaCl.$$

2nd. By passing a very slow current of dry sulphuretted hydrogen through the glass tube containing the arsenic and antimony mirror, and applying a gentle heat. The metals are converted into sulphides—arsenic into lemon-yellow arsenious sulphide, and antimony into a black or partly orange-red antimonious sulphide; and, if both metals are present, the two sulphides appear side by side; the former somewhat in front of the latter, arsenious sulphide being the more volatile of the two sulphides. On passing next a current of dry hydrochloric acid gas without the application of heat, antimonious sulphide disappears entirely, being converted into antimonious chloride, which volatilizes in the current of hydrochloric acid gas, and may be passed into water and tested by means of sulphuretted hydrogen. Arsenious sulphide remains unaffected, even if the hydrochloric acid gas be passed over it for some time. The residuary arsenious sulphide *dissolves readily in hydric ammonic carbonate*, $\mathbf{C}OHoAmo$.

Antimonietted and arsenietted hydrogen can moreover be distinguished from each other by passing a slow current of the mixed gases into a solution of argentic nitrate; argentic oxide, acting the part of an oxidizing agent, converts arsenietted hydrogen into arsenious acid, thus:—

$$\mathbf{As}H_3 + 6\mathbf{N}O_2Ago + 3OH_2 = Ag_6 + \mathbf{As}Ho_3 + 6\mathbf{N}O_2Ho.$$

Antimonietted hydrogen is not acted upon in like manner. The oxidation extends only to the hydrogen and not to the antimony, the metallic silver taking the place of the hydrogen, thus:—

$$\mathbf{Sb}H_3 + 3\mathbf{N}O_2Ago = \mathbf{Sb}Ag_3 + 3\mathbf{N}O_2Ho.$$

---

* The evidence on this point appears to be doubtful.

The arsenious acid is separated by filtration from the insoluble $SbAg_3$, and Ag. On cautiously adding to the filtrate a dilute solution of ammonic hydrate, a *yellow* precipitate of **triargentic arsenite** is obtained, where the two layers of the ammonic hydrate and acid solution meet.

The residue is boiled with a solution of tartaric acid, when the antimonious argentide is acted upon with formation of soluble antimonious tartrate (?), silver being left behind. Filter; acidulate the filtrate with dilute hydrochloric acid, and pass sulphuretted hydrogen. An *orange* precipitate indicates antimony. Another method of detecting the antimony consists in digesting the $SbAg_3$ with yellow ammonic sulphide, when the Sb is dissolved out as sulphantimonite, and can be separated from the filtered solution by HCl as Sb_2S_3.

QUESTIONS AND EXERCISES.

1. Which are the most important natural compounds of arsenic?
2. Translate into graphic formulæ the symbolic formulæ of *realgar, orpiment, copper nickel, smaltine, nickel ochre.*
3. Adduce evidences of the triad and pentad nature of arsenic.
4. What changes does metallic arsenic undergo when heated, 1st, by itself, in a current of a neutral gas (CO_2 or H); 2ndly, in contact with air; 3rdly, in contact with chlorine?
5. How is metallic arsenic obtained from white arsenic?
6. How can arsenious compounds be distinguished in the presence of arsenic compounds? Give several methods.
7. What action has sulphuretted hydrogen upon an acid solution of arsenious and upon a solution of arsenic acid?
8. Express by an equation the reaction which takes place when arsenious sulphide is dissolved; 1st, in NaHo; 2ndly, in SAm_2; 3rdly, in COHoAmo.
9. What precipitates are produced when argentic nitrate is added to a neutral solution of an arsenite or arsenate?
10. Why is triargentic arsenite, in an ammoniacal solution, converted on boiling into triargentic arsenate. Express the change by equations.
11. What is the action of magnesic sulphate in an ammoniacal solution (so-called *magnesia mixture*) upon arsenious and arsenic solutions?
12. Give a few instances of the reducing action of arsenious compounds. Express the changes by equations.
13. Explain the oxidizing action of chlorine, bromine, and iodine upon arsenious compounds.
14. What takes place when metallic copper is introduced into a dilute hydrochloric acid solution: 1st, of As_2O_3; 2ndly, of As_2O_5 (Reinsch's test)?
15. Explain under what conditions arsenic, as well as arsenious compounds, act as oxidizing agents. Give examples, and express the changes by equations.
16. Explain why a portion of the arsenic only is liberated, when an arsenical sulphide is heated with potassic cyanide. Give equations.
17. Explain how the presence of free sulphur, or the presence of certain metallic sulphides influences the reduction of arsenical compounds by potassic cyanide. Give equations.
18. Explain the reduction of arsenical compounds by nascent hydrogen (Marsh's test), and show by equations the formation of arsenietted hydrogen.
19. What change does arsenietted hydrogen undergo: 1st, when burnt in the air; 2ndly, when passed through a tube heated in one or more places; 3rdly, when passed into a solution of argentic nitrate; 4thly, when passed through concentrated nitric acid?
20. Explain the formation of antimonietted hydrogen, and state—1st, what properties arsenietted hydrogen has in common with antimonietted hydrogen; and, 2ndly, how it differs from the latter in its chemical deportment with argentic nitrate.

21. How would you distinguish between an arsenic and antimony mirror?
22. State how arsenic can be separated—1st, from antimony, 2ndly, from tin.
23. 1·2 grm. of finely divided gold has been obtained by boiling a solution of arsenious acid with auric chloride: how much $\mathbf{As}_2O_3$ by weight did the solution contain?
24. Calculate the percentage composition of ammonic magnesic arsenate, $(\mathbf{As}OAmoMgo'' + 6Aq.)$

4. **GOLD**, Au′ and ‴. Atomic weight, 196·7.—Gold is generally found native and is then readily recognised by its colour, malleability, and physical character generally. Gold occurs in anything like considerable quantities in combination only with the rare element tellurium. In small quantities it occasionally accompanies metallic sulphides.

EXAMINATION IN THE DRY WAY.

When heated on charcoal with sodic carbonate and borax in the reducing flame, gold compounds yield a yellow, very malleable globule of metallic gold.

To detect gold in argentiferous minerals in which it is present only in minute quantities, and associated with large quantities of other non-volatile metals, the powdered mineral is fused with borax and metallic lead, and the metallic button cupelled, as will be described under silver. The globule of white metal which is left on the cupel is beaten out, and the silver dissolved by digesting with a little nitric acid in a small porcelain dish. The argentic nitrate is poured off, and the gold washed with distilled water. The black insoluble residue is once more fused on charcoal before the blowpipe, when it assumes the well-known appearance of fine gold.

Old silver coins frequently contain a small quantity of gold, which, on dissolving in nitric acid, is left as a black powder.

When an insufficient quantity of silver is present in the button (which may be inferred from its pale-yellow colour), from two to four times its own weight of silver should be fused up with it, and the button so obtained beaten out and then treated with nitric acid in order to separate or "*part*" the gold.—*Method of assaying gold.*

EXAMINATION IN THE WET WAY.

Gold when unalloyed is soluble in *aqua regia* only, forming a SOLUTION OF AURIC CHLORIDE, $\mathbf{Au}Cl_3$, which may be employed for studying the reactions in the wet way.

$\mathbf{S}H_2$ (**group-reagent**) gives from a cold solution a *black* precipitate of **auric sulphide**, $\mathbf{Au}_2S_3$, from a boiling solution a *brownish* precipitate of **aurous sulphide**, $\mathbf{Au}_2S = \left\{\begin{matrix} ''\mathbf{Au}' \\ ''\mathbf{Au}' \end{matrix}\right. S''$. These precipitates are insoluble in hydrochloric and nitric acids, but dissolve in aqua regia. They are likewise insoluble in normal ammonic sulphide, but soluble, although with difficulty, in yellow sulphide, more readily in yellow sodic sulphide, with which they form a sulpho-salt, $\mathbf{Au}Nas_3$.

$\mathbf{S}Am_2$ and $\mathbf{S}SONao_2$, same precipitate.

KHo or NaHo produces no precipitate.

AmHo produces from a concentrated solution of auric chloride a *reddish-yellow* precipitate of **ammonic aurate** or **fulminating gold,** $(NH_3)_2Au_2O_3, = \begin{matrix}N^vH_2HoAu\\N^vH_2HoAu\end{matrix}O$, thus:—

$$2AuCl_3 + 8AmHo = (NH_3)_2Au_2O_3 + 6AmCl + 5OH_2.$$

The detection of gold is attended with no difficulty, owing to the facility with which auric chloride is reduced to the metallic state. Gold has little affinity for non-metallic elements; the compounds which it forms with them are readily broken up by heat alone, or on being brought in contact with bodies which have more affinity for the metalloïds, leaving metallic gold in a finely-divided condition, as a brown powder, which acquires metallic lustre when dried and rubbed in a mortar. Hence in auric chloride we possess a powerful *oxidizing* agent, as we have already seen under tin, antimony, and arsenic. The same oxidizing action is called into play, when $AuCl_3$ comes together with solutions of sulphurous and oxalic acids, ferrous sulphate, or chloride, cuprous chloride, dissolved in hydrochloric acid, mercurous nitrate, potassic nitrite, sugar in an alkaline liquid, and many other organic substances (*e.g.*, the epidermis); arsenietted, antimonietted, and phosphoretted hydrogen decompose $AuCl_3$ likewise.

The following equations express these changes:—

(1) $2AuCl_3$, when ignited splits up into $Au_2 + 3Cl_2$.

(2) Au_2S_3, ” ” ” $Au_2 + S_3$.

(3) $2AuCl_3 + 3SOHo_2 + 3OH_2 = Au_2 + 3SO_2Ho_2 + 6HCl$.

(4) $2AuCl_3 + 3\left\{\begin{matrix}COHo\\COHo\end{matrix}\right. = Au_2 + 6CO_2 + 6HCl$.

(5) $2AuCl_3 + 6FeCl_2 = Au_2 + 3Fe_2Cl_6$

(6) $2AuCl_3 + 6SO_2Feo'' = Au_2 + Fe_2Cl_6 + 2S_3O_6Fe_2o^{vi}$.

(7) $2AuCl_3 + 3Cu_2Cl_2 = Au_2 + 6CuCl_2$.

(8) $2AuCl_3 + 3\begin{matrix}NO_2\\NO_2\end{matrix}Hg_2o'' = Au_2 + 3\begin{matrix}NO_2\\NO_2\end{matrix}Hgo'' + 3HgCl_2$.

(9) $2AuCl_3 + 3NOKo + 3OH_2 = Au_2 + 3NO_2Ko + 6HCl$.

(10) $2AuCl_3 + 2AsH_3 + 3OH_2 = Au_2 + 2AsHo_3 + 6HCl$.

(11) $2AuCl_3 + SbH_3 = Au_2 + SbCl_3 + 3HCl$.

In the analysis of a solution containing gold, as well as some other metals of Group II, precipitable by SH_2, it is usual to first remove the gold in the metallic state, by boiling with oxalic and hydrochloric acids, before passing SH_2. The precipitated gold is collected on a filter and fused to a button on charcoal.

Gold is precipitated from a hydrochloric acid solution of $AuCl_3$ by most metals, even by Pt, Ag, and Hg.

QUESTIONS AND EXERCISES.

1. How would you treat a silver coin containing a small quantity of gold, in order to extract this latter metal from it?
2. How is $AuCl_3$ prepared?

3. Describe how pure metallic gold is prepared from $\mathbf{AuCl_3}$, in the wet way.
4. Explain the change which $\mathbf{Au_2S_3}$ undergoes, 1st, when gently heated in a bulb tube; 2ndly, when heated in a tube open at both ends.
5. What reaction takes place when $\mathbf{AuCl_3}$ is brought together with bodies which have any latent bonds left? Give instances of such reactions and express the changes by equations.
6. How can gold be separated from an alloy of Au, Ag, and Cu?
7. 9·37 grms. of a gold mineral, when treated with aqua regia and reduced by $\mathbf{FeCl_2}$, yield ·53 grm. of metallic gold; what is the percentage of gold in the mineral?
8. How much chlorine gas, by weight and by volume, can be obtained by the ignition of 1·25 grm. of $\mathbf{AuCl_3}$?
9. What action takes place when a piece of gold is suspended from the positive electrode in a bath of $\mathbf{AuCl_3}$, metallic copper forming the negative electrode? Explain the process of electro-gilding.

5. **PLATINUM**, Pt'' and ^{iv}. Atomic weight, 197·4.—This metal is found native, but more frequently alloyed with other metals. It is characterized by its infusibility before the blowpipe, and is not acted upon by the usual fluxes. It can, therefore, only be examined *in the wet way*.

Unalloyed platinum is not attacked by either nitric, hydrochloric, or sulphuric acid, but by *aqua regia*, with formation of platinic chloride, $\mathbf{Pt}Cl_4$. A SOLUTION OF THIS SALT is employed for studying the reactions of platinum.

SH_2 (**group-reagent**) produces slowly a *dark brown* precipitate of **platinic disulphide**, $\mathbf{Pt}S_2$. On heating, the precipitate forms quickly. It is insoluble in nitric or hydrochloric acid, soluble in aqua regia; difficultly soluble in normal ammonic sulphide, more speedily in yellow sulphide, with which it forms a sulpho-salt, $\mathbf{Pt}SAms_2$. Heated out of contact with air, it is decomposed into $''\mathbf{Pt}''S$ and S.

$\mathbf{S}Am_2$, same precipitate.

$\mathbf{Pt}Cl_4$ is interesting on account of the compounds which it forms with the chlorides of the alkali metals (and with the chlorides of many organic bodies, *e.g.*, the so-called alkaloïds, such as quinine, nicotine, etc.).

AmCl produces a *light yellow crystalline* precipitate of **ammonic platinic chloride**, $2AmCl,\mathbf{Pt}Cl_4$. From dilute solutions a precipitate is obtained only after evaporation to dryness on a water-bath. The precipitate is somewhat soluble in water, insoluble in alcohol.

KCl produces a *yellow crystalline* precipitate of **potassic platinic chloride**, $2KCl,\mathbf{Pt}Cl_4$, analogous in its appearance and properties to the precipitate just described.

NaCl forms with platinic chloride a double chloride, which is, however, soluble in water, and is obtained in needle-shaped crystals only after considerable evaporation.

The precipitate produced by platinic chloride with AmCl and KCl serves for the detection and isolation of platinum, and *vice versâ*, for the detection of ammonium or potassium compounds. (Comp. Chapter II.)

Platinum is capable of forming a lower chloride, viz., platinous chloride, $''\mathbf{Pt}''Cl_2$, in which the platinum acts as a dyad. This salt is obtained by heating the platinic chloride for some time in an air- or oil-bath up to 204° C., as long as any chlorine is evolved; or by acting with sulphurous acid upon a solution of platinic chloride, until the latter ceases to give a precipitate with ammonic chloride, $\mathbf{Pt}Cl_2$ is a greenish-grey powder, *insoluble* in water, but soluble in hydrochloric acid.

Several reactions in the wet way for platinum are based upon the power, which its salts possess, of oxidizing other bodies which have some bonds left unsatisfied; but as platinic salts are not so easily reduced as gold salts, a solution of the latter metal is generally preferred. After what has been stated under gold, the following reactions will be readily understood:—

$\mathbf{Pt}Cl_4$ produces with $\mathbf{Sn}Cl_2$ only a dark brownish-red colour, owing to the reduction of the platinic to platinous chloride.

$\mathbf{Pt}Cl_4$ is reduced by $\mathbf{S}O_2Feo''$ only after long-continued boiling.

$\mathbf{Pt}Cl_4$ is reduced to platinum by formic acid, $\left\{\begin{array}{l}H\\ \mathbf{C}OHo\end{array}\right.$, on heating, if the free acid be neutralized with sodic carbonate.

Metallic zinc precipitates metallic platinum.

It is obvious that platinous chloride could act as a reducing agent, but it is rarely employed for this purpose.

Whenever platinum and gold are contained in a solution, together with other metals of Group II, precipitable by sulphuretted hydrogen, it is preferable to remove the gold, by means of oxalic acid (which does not reduce platinic chloride), before removing the platinum by evaporation with ammonic chloride.

QUESTIONS AND EXERCISES.

1. How is platinic chloride prepared? Give an equation.
2. How much metallic platinum is left when two grms. of $\mathbf{Pt}S_2$ are strongly ignited in a porcelain crucible?
3. How much Pt will be left, when 1·5 grm. of $2AmCl,\mathbf{Pt}Cl_4$ is ignited?
4. Calculate how much potassic platinic chloride ought to be obtained from ·521 grm. of KCl.
5. How is platinous chloride prepared?

Separation of the metals arsenic, antimony, and tin, whose sulphides are soluble in yellow ammonic sulphide, or in sodic hydrate.

The precipitate produced by the group-reagent is soluble in *yellow* ammonic sulphide, or in sodic hydrate, and may consist of three sulphides. If the precipitate be of a dark brown colour, it may be inferred that stannous sulphide is present. If it be of a fine lemon-yellow colour, the presence of arsenious or stannic sulphide may be inferred, if orange-coloured, antimony should be looked for.

The three sulphides are unequally soluble in hydric ammonic carbonate. $\mathbf{As}_2S_3$ dissolves freely, $\mathbf{Sn}S_2$ very slightly, and $\mathbf{Sb}_2S_3$

is all but insoluble. On digesting, therefore, the precipitate with $\mathrm{COHoAmo}$, and filtering, arsenic is obtained in the filtrate, and antimony and tin are left in the residue. In order to separate the remaining two metals, the antimony is, for the most part, converted into antimonietted hydrogen,—tin does not form a gaseous compound with hydrogen. For this purpose the two sulphides are dissolved in hot hydrochloric acid, and the solution of the mixed chlorides introduced into a Marsh's apparatus. Antimony is detected by the metallic deposit which antimonietted hydrogen gives on porcelain, insoluble in ClNao. Tin (antimony) is found in the generating flask deposited on the strips of zinc as a powder. The greyish-black metal is removed from the undissolved zinc, dissolved in hot hydrochloric acid (by the aid of a little platinum foil), and the solution tested with mercuric chloride. A white precipitate of mercurous chloride, Hg_2Cl_2, indicates the presence of tin.

The separation of arsenic, antimony, and tin, may thus be based upon—

1. *The solubility of* As_2S_3 *in hydric ammonic carbonate.*
2. *The formation of antimonietted hydrogen.*
3. *The precipitation of tin by metallic zinc.*

A tabular scheme, embodying this method of separation, will be found in Table II in the Analytical Tables at the end of the book.

Several other methods of recognizing and separating the metals tin, antimony, and arsenic, will readily suggest themselves, such as the one which is based upon:—

1st. The oxidation of As_2S_3, Sb_2S_3, and SnS by concentrated nitric acid; and the conversion of the three oxides (by fusion with caustic soda in a silver crucible) into sodic metantimonate, arsenate, and stannate.

2nd. The insolubility of SbO_2Nao in cold water and alcohol ($AsONao_3$ and $SnONao_2$ being soluble).

3rd. The conversion of $AsONao_3$ and $SnONao_2$ into As_2S_3 and SnS, by means of sulphurous acid and sulphuretted hydrogen.

4th. The volatility of As_2S_3, when heated in a current of dry SH_2 gas, SnS being non-volatile.

5th. The absorption of the volatilized As_2S_3 in a solution of sodic hydrate, oxidation by chlorine and precipitation as $AsOAmoMgo''$.

6th. The conversion of the non-volatile SnS into SnO_2 by ignition in air.

Another method is based upon:—

1st. The precipitation of arsenic and antimony in the form of sulphides, by boiling a hydrochloric acid solution of the three metals with sodic hyposulphite, tin remaining in solution.

2nd. By boiling the precipitated As_2S_3 and Sb_2S_3 with hydric potassic sulphite and sulphurous acid; As_2S_3 is converted into potassic metarsenite, Sb_2S_3 remains undissolved.

A third method consists in:—

1st. Removing the As_2S_3, by boiling with hydric sodic sulphite and sulphurous acid; the other two sulphides are not dissolved.

2nd. The oxidation of the undissolved Sb_2S_3 and SnS_2 with concentrated nitric acid and boiling with tartaric acid; Sb_2O_4 is soluble, SnO_2 remains undissolved.

A fourth method of recognizing arsenic, antimony, and tin is based upon:—

1st. The introduction of a solution (in HCl and KO_3Cl) of the three sulphides into a hydrogen apparatus, and passing the evolved arsenietted and antimonietted hydrogen through a solution of argentic nitrate; the tin remains behind precipitated on the zinc.

2nd. The solubility of the precipitated $SbAg_3$ in tartaric acid, and precipitation of the antimony by means of sulphuretted hydrogen from a hydrochloric acid solution.

3rd. The precipitation of the $AsAgo_3$ from the argentic nitrate solution by means of ammonia.

A fifth method of recognizing the metals of Group IIB, depends upon:—

1st. The insolubility of As_2S_3 in strong hydrochloric acid, Sb_2S_3 and SnS_2 being dissolved. The presence of arsenic is confirmed by fusion with potassic cyanide and sodic carbonate

2nd. The precipitation of the antimony on platinum by means of a strip of metallic zinc; a black stain indicates antimony.

3rd. Dissolving the tin precipitated on the zinc in warm dilute hydrochloric acid, confirming it by means of mercuric chloride.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP IIB.

1. Sulphuretted hydrogen produces a fine yellow precipitate, a portion of which is soluble in yellow ammonic sulphide. What inference would you draw from this, and how would you examine both the solution and the residuary yellow sulphide?
2. Describe several methods for separating As from Sb.
3. Examine some green paper-hangings for As (Scheele's green).
4. Test a sample of commercial hydrochloric acid for As and Fe.
5. Separate As from Sn in a solution of $SnCl_2$ and As_2O_3, containing ·500 grm. of Sn, and ·020 grm. of As.
6. Analyse a solution containing ·010 grm. of As and ·100 grm. of Sb, by converting the two metals into the respective hydrogen compounds.
7. You have given to you a hydrochloric acid solution containing ·200 grm. of Sn and ·020 grm. of Sb; also a strip of zinc and a piece of platinum foil. Describe how you would separate the two metals.
8. Test a sample of *iron pyrites*, FeS_2, for arsenic, in the dry and in the wet way.
9. A precipitate consists of Sb_2S_3 and As_2S_3. Describe different methods of analysis, and state the possible causes of error inherent upon each method.
10. Analyse a mixture of SnO_2 and Sb_2O_4, both in the dry and wet way.
11. You have given to you a solution containing potassic arsenite and arsenate. State how you would identify the two oxides of arsenic in the presence of each other.

12. Test a solution of stannic chloride for stannous chloride.
13. How can you detect traces of antimonic chloride in a solution of antimonious chloride?
14. What are the changes which As_2S_3, Sb_2S_3, and SnS_2 undergo when they are treated with concentrated nitric acid and when the products of the oxidation are fused with caustic soda?

CHAPTER VI.

REACTIONS OF THE METALS OF GROUP I.

This group comprises the metals SILVER, LEAD, and MERCURY in the form of mercurous compounds, which are precipitated by dilute hydrochloric acid.

1. **SILVER**, Ag'. Atomic weight, 108.—This metal occurs *native;* also as sulphide in *silver glance*, SAg_2, and in combination with antimony, as sulpho-salt in trisulphargentic orthosulphantimonite, or *dark red silver ore* (*pyrargyrite*), $SbAgs_3$; with arsenic as trisulphargentic sulpharsenite, in *proustite*, $AsAgs_3$; as CHLORIDE, $AgCl$, in *horn silver*, and other ores.

EXAMINATION IN THE DRY WAY.

Place a small quantity of powdered *silver glance* towards the middle of a hard glass tube (combustion tubing of about $\frac{1}{4}$ inch internal diameter, cut with a sharp file into lengths of 5 to 6 inches, answers best). Heat the powder gradually by moving the tube about in a Bunsen gas flame, and lastly, heat it strongly towards the centre. By holding the tube in a slightly slanting position, a current of air is made to pass over the ignited sulphide; the sulphur becomes oxidized and is carried off as sulphurous anhydride, readily recognizable by its pungent odour. Metallic silver is left, together with a little argentic sulphate.

Other volatile bodies, such as antimony, arsenic (selenium and tellurium), which are frequently present in pyritical silver ores, are likewise oxidized, but are, to a great extent, deposited as As_2O_3 and Sb_2O_3, in the cool part of the tube.

Mix a little of the finely-powdered *silver glance* (or of the roasted ore) with sodic carbonate, and heat upon charcoal under the reducing flame of the blowpipe. A globule of bright metallic silver is left, which is, however, almost invariably contaminated with a little carbon.

Silver ores which contain no other fixed element but silver, are reduced on charcoal to the metallic state by a simple fusion with sodic carbonate. Antimony and arsenic, if present, are readily volatilized as metals, before the reducing flame. The sulphur combines with the alkali metal.

Silver ores which contain non-volatile metals, such as copper, iron, etc., as in *argentiferous fahl ore*, and from which the metal silver could not be eliminated before the blowpipe flame, are treated in the following manner:—

Mix ·100 grm. of the finely-powdered ore with its own bulk of pounded borax glass; wrap it up in a small piece of assay lead;* introduce it into a cavity, made in a good piece of charcoal, and fuse under the reducing flame of the blowpipe, at first gently, and afterwards more strongly. The heat is kept up till the whole mass has resolved itself into a metallic button and a clear glassy borax bead, which does not adhere to the charcoal. Should the metallic button, on cooling, present a dull grey surface, indicative of the presence of antimony, it is next heated in the oxidizing flame, until, on cooling, it shows a bright, somewhat prismatic surface. It is then detached from the borax, cleaned by a blow with a hammer and carefully cupelled on some bone-ash (tricalcic phosphate, $P_2O_2Cao''_3$), pressed into a shallow cavity in a piece of charcoal, the surface being made smooth and thoroughly concave with the round end of a pestle. The button is thoroughly freed from borax, placed in the cupel and heated in the oxidizing flame. The lead is oxidized and absorbed by the porous bone-ash, forming a mass of fused litharge around the metallic bead. If one cupellation does not yield a brilliant white globule of silver, *i.e.*, if the copper has not been entirely removed—a fact which is indicated by a black colour, instead of the pale yellow colour of the litharge, in the cupel—the cupellation of the button must be repeated in a fresh cupel, and the button, if necessary, re-melted with a small quantity of assay lead. The silver not being an oxidizable metal, is obtained in the metallic state.

Small quantities of silver must be separated from lead (as well as from other metals), *by cupellation.*

Fuse some finely-powdered *argentiferous galena*, PbS,SAg_2 (or $PbAgs_2$), on charcoal before the reducing flame of the blowpipe, either alone or with sodic carbonate. A bead of an alloy of much lead and very little silver is left. Expose this bead on a small cupel (Fig. 15) to the oxidizing action of the blowpipe flame. The lead is oxidized and absorbed by the cupel, metallic silver being left.

FIG. 15.

Dried AgCl is mixed with dry $CONao_2$, in a small mortar, transferred to the charcoal and heated in the reducing flame of the blowpipe. A button of metallic silver is left thus:—

$$2AgCl + CONao_2 = 2NaCl + CO_2 + O + Ag_2.$$

REACTIONS IN THE WET WAY.

For the reactions of silver in the wet way we employ a SOLUTION OF ARGENTIC NITRATE, NO_2Ago.

HCl (**group-reagent**), and **soluble chlorides** (NaCl, etc.), give a *white curdy* precipitate of **argentic chloride**, AgCl, which turns *violet* on exposure to light. The precipitate is insoluble in water and dilute acids; slightly soluble in concentrated nitric and hydrochloric acids; readily soluble in ammonic hydrate, potassic cyanide and sodic hyposulphite; soluble also to a perceptible extent in concentrated hydrochloric acid and in saturated solutions of alkaline chlorides, more particularly when heated, whence the dissolved argentic chloride is, however, reprecipitated on dilution with water.

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* Lead free from silver, prepared from plumbic acetate.

Collect the precipitated AgCl on a filter and dry over a sand-bath. Fuse a portion of the dried salt in a porcelain crucible over a small gas-flame. The white powder fuses; it undergoes a mere physical change, and leaves on cooling a hard mass, called *horn silver*.

Place a small piece of zinc on the fused *horn silver*, and add a drop of dilute hydrochloric acid and a little water. A voltaic action is set up between the metallic zinc and silver. The zinc removes the chlorine and leaves the metallic silver. The same action takes place when the white curdy precipitate of argentic chloride is brought in contact with strips of metallic zinc.

This forms a convenient method of recovering silver from silver residues.

NaHo or KHo precipitates **argentic oxide**, OAg_2, in the form of a *brown powder*, which, on strong ignition, gives off oxygen, and is converted into metallic silver.

AmHo, when gradually added, precipitates argentic oxide, readily soluble in excess.

SH_2 precipitates *black* **argentic sulphide**, SAg_2, from acid solutions; insoluble in dilute acids, in alkalies, alkaline sulphides, and potassic cyanide; readily soluble in dilute boiling nitric acid, with separation of sulphur.

SAm_2 (or any **soluble sulphide**) precipitates from neutral solutions *black* **argentic sulphide**.

HI or KI gives a *yellowish* precipitate of **argentic iodide**, AgI, insoluble in dilute nitric acid; almost insoluble in ammonic hydrate (DISTINCTION BETWEEN AgCl and AgI).

HBr or KBr gives a *yellowish-white curdy* precipitate of **argentic bromide**, AgBr, insoluble in dilute nitric acid; difficultly soluble in ammonic hydrate; readily soluble in potassic cyanide, or sodic hyposulphite; decomposed by concentrated hydrochloric acid, with evolution of bromine vapour and conversion into AgCl.

HCy or KCy gives a *white curdy* precipitate of **argentic cyanide**, AgCy, soluble in excess of the reagent; insoluble in dilute nitric acid; soluble in ammonic hydrate, but reprecipitated by dilute nitric acid; soluble in sodic hyposulphite. The precipitate is decomposed by concentrated boiling nitric acid; it is decomposed also when heated by itself in a porcelain crucible, to *paracyanide*, metallic silver, and cyanogen gas (DISTINCTION FROM AgCl, AgI, AND AgBr).

Place a bright and clean strip of copper into a solution of argentic nitrate. The copper becomes rapidly covered with a lustrous coating of metallic silver, and the solution, after a time, gives no more precipitate with hydrochloric acid. The silver is deposited on the copper in the metallic state, and the solution contains now N_2O_4Cuo'': an equivalent quantity of copper (63·5 by weight of copper for every 216 of silver) having been dissolved.

Place a small globule of mercury into a concentrated solution of argentic nitrate on a watch-glass. The globule of mercury becomes rapidly covered with a crystalline mass, resembling some vegetable growth, termed *arborescence*. After a time the whole of the silver becomes removed from the solution, and the solution contains in the place of the argentic nitrate, mercuric nitrate, $\mathbf{N}_2O_4Hgo''$. Metallic silver is precipitated and forms with the mercury an amalgam which is crystalline. This crystalline mass is termed a *silver tree* (*arbor Dianæ*).

Strips of the metals Zn, Fe, Sn, Sb, Pb may likewise be employed for the precipitation of metallic silver.

These changes illustrate the action of the more electropositive metals upon solutions of less electropositive metals, induced by voltaic electricity. They come under the third class of chemical changes, viz., *displacement of one element by another element*.

Take a clear solution of one part of grape sugar and 6—8 parts of distilled water, and a somewhat dilute solution of argentic nitrate. Heat the latter in a test-tube, nearly to boiling, and add the grape sugar solution. The liquid becomes at once turbid, and a greyish-white powder of metallic silver falls to the bottom; or a yellowish-white metallic deposit forms on the sides of the test-tube which, on rubbing with a glass rod, shows bright streaks of metallic silver. The metallic silver can be filtered off and fused on charcoal, before the blowpipe, to a brilliant globule.

The cause of the reduction of argentic salt must evidently be sought for in the grape sugar. We have seen that argentic oxide loses its oxygen readily on ignition. Certain organic substances, such as grape sugar, formic acid, and aldehyde, are known to combine eagerly with oxygen, and the $\mathbf{O}Ag_2$ (in two molecules of $\mathbf{N}O_2Ago$) parts with its oxygen and yields a deposit of metallic silver.

This reaction has found an important practical application in the manufacture of looking-glasses, etc.

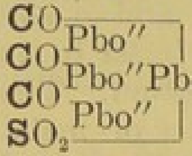
The silver in the argentic nitrate is displaced by hydrogen from the organic bodies, nitric acid being left in solution, carbonic anhydride and water—the two ultimate products of oxidation of organic matter—being formed by the oxidation of the organic substances.

Ignite a few crystals of argentic acetate, $\left\{\begin{array}{l}\mathbf{C}H_3\\ \mathbf{C}OAgo\end{array}\right.$, in a covered porcelain crucible. Heat gently at first, and strongly, as soon as no more fumes are given off. A mass of frosted silver is left, having the shape of the original crystals.

QUESTIONS AND EXERCISES.

1. How is argentic nitrate prepared?
2. Why do HCl, HI, etc., precipitate silver from its solutions?
3. What change takes place when *silver glance* is roasted in a tube?
4. How is Ag separated from Pb in the dry way?
5. Write out the equations for the reactions of silver in the wet way.
6. Give the graphic formulæ for *silver glance, dark red silver ore, proustite,* and *fahl ore.*
7. How much NaCl will be required to convert 1·5 grm. of $\mathbf{N}O_2Ago$ into AgCl?

8. A dilute solution of hydrochloric acid (containing ·00365 grm. of the acid in one cubic centimetre of the solution) is precipitated with NO_2Ago. How much AgCl by weight do we get from 150 c.c. of the acid solution?
9. How much metallic copper is required to precipitate 1 grm. of argentic nitrate?
10. What is the percentage composition of argentic acetate, $\left\{\begin{array}{l}CH_3\\COAgo,\end{array}\right.$ and how much silver will be left, when ·451 grm. of acetate is ignited?
11. How is argentic nitrate converted into sulphate, and how much of the latter salt can be prepared from 10 grms. of argentic nitrate?
12. What change does AgCy undergo upon ignition?

2. **LEAD,** Pb'' and ^{iv}. Atomic weight, 107.—Occurs in nature chiefly in combination with SULPHUR, as PbS'', in *galena;* also as CARBONATE, in *lead spar* or *white lead ore*, $COPbo''$; as SULPHATE, in *lead vitriol*, SO_2Pbo'', in *leadhillite*, 
$\begin{array}{l}CO\\CO\\CO\\SO_2\end{array}\begin{array}{l}Pbo''\\Pbo''Pbo''\\Pbo''\end{array}$, and in *lanarkite*, $\begin{array}{l}CO\\SO_2\end{array}Pbo''_2$; as OXYCHLORIDE in *mendipite*, $PbCl_2,2PbO$, graphic formula:— Cl—Pb—O—Pb—O—Pb—Cl; as PHOSPHATE and OXYCHLORIDE, in *pyromorphite*, $P_3O_3Pbo''_4\left(\begin{array}{l}O\\Cl\end{array}Pb''\right)$.

EXAMINATION IN THE DRY WAY.

The principal blowpipe reaction consists in reducing lead compounds on charcoal to metallic lead, either by themselves, or in conjunction with sodic carbonate, or potassic cyanide, and in the *yellow* incrustation of oxide which they yield, which disappears when heated in the oxidizing flame, imparting a *blue* colour to the flame. The change which takes place when *galena* is heated with sodic carbonate in a crucible, out of contact with air, is expressed by the equation:—

$$7PbS + 4CONao_2 = 4Pb + \underset{\text{Fusible slag.}}{3PbNas_2} + SO_2Nao_2 + 4CO_2;$$

but when heated in contact with air, or in the presence of an oxidizing agent, such as saltpetre, the loss of lead in the slag is avoided, thus:—

$$PbNas_2 + 7O + CONao_2 = Pb + 2SO_2Nao_2 + CO_2.$$

When *galena* is roasted in a glass tube open at both ends, it is converted into SO_2Pbo'', PbO and SO_2, thus:—

$$(1)\ PbS + O_4 = SO_2Pbo''.$$
$$(2)\ PbS + O_3 = PbO + SO_2.$$

With borax and microcosmic salt, lead compounds give in the outer flame a clear *yellowish* glass (owing to the combination of the

PbO with the boric or phosphoric acid, and formation of a sodic plumbic borate or phosphate), which is *colourless* when cold.

All lead minerals, especially the antimonial sulpho-salts, *boulangerite*, Sb_2Pbs_3, *bournonite*, $Sb_2Pbs''_2(Cu_2S''_2)$,'' *jamesonite*, $Sb_4S_3Pbs''Pbs''_2$, and *argentiferous galena*, contain more or less silver, as may be ascertained by carefully cupelling the metallic button on charcoal (comp. silver, page 99).

The presence of antimony, arsenic, and sulphur reveals itself, when these ores are heated on charcoal (garlic odour and fumes of As_2O_3, or Sb_2O_3), or in a glass tube open at both ends (white sublimate, fumes, and odour of SO_2).

REACTIONS IN THE WET WAY.

For the reactions of lead in the wet way we employ either A SOLUTION OF PLUMBIC NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Pbo''$, or acetate $\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$; most other plumbic salts being insoluble in water.

HCl (**group-reagent**), or **soluble chlorides** give, with a not too dilute solution of plumbic salts, a *heavy white* precipitate of **plumbic chloride**, $PbCl_2$, soluble in much cold water, readily in boiling water, from which the plumbic chloride crystallizes out, on cooling, in fine needles; less soluble in solutions containing dilute hydrochloric or nitric acid. Ammonia converts it into a **basic salt**, of the composition, $PbHoCl$ (*plumbic chlorohydrate*),—a white powder almost insoluble in water.

$NaHo$ or KHo precipitates **plumbic hydrate**, $PbHo_2$, soluble in excess of the reagent, especially on heating. The $PbHo_2$ must be viewed as acting the part of a weak acid, on combining with the strong alkali base.

$AmHo$ precipitates a *white* **basic salt**, insoluble in excess. The precipitate forms only slowly in a solution of plumbic acetate.

SH_2 precipitates *black* **plumbic sulphide**, PbS, from acid solutions. If a large excess of hydrochloric acid be present, the precipitate is *reddish-brown*, consisting of $\left\{\begin{matrix}PbCl\\S\\PbCl\end{matrix}\right.$, (*diplumbic sulphodichloride*). On diluting considerably with water, a *black* precipitate is obtained.

SAm_2, or **soluble sulphides**, precipitate likewise *black* PbS, insoluble in dilute acids, alkalies, and alkaline sulphides. Plumbic sulphide is soluble in hot dilute nitric acid, plumbic nitrate being formed, with separation of sulphur. Concentrated nitric acid converts it into SO_2Pbo''; the oxidation extends to the sulphur, as well as to the lead.

SO_2Ho_2, and **soluble sulphates**, precipitate *white* **plumbic sulphate**, SO_2Pbo'', almost insoluble in water, especially in the presence of excess of dilute sulphuric acid; insoluble also in cold dilute acids, soluble in boiling hydrochloric acid, from which plumbic chloride crystallizes out on cooling; soluble in potassic hydrate, and, lastly, readily soluble in concentrated solutions of certain salts, such as sodic hyposulphite, ammonic acetate or tartrate, in the presence of excess of ammonic hydrate, from which solutions SO_2Ho_2, SAm_2, or CrO_2Ko_2, precipitate the lead again. Boiling with sodic carbonate converts SO_2Pbo'' into insoluble $COPbo''$. Plumbic sulphate separates from dilute aqueous solutions only on the addition of alcohol (methylated spirit).

CrO_2Ko_2 precipitates *yellow* **plumbic chromate**, CrO_2Pbo'' (*chrome yellow*), readily soluble in potassic or sodic hydrate; difficultly soluble in dilute nitric acid, insoluble in acetic acid.

$CONao_2$, as well as $COKo_2$ and $COAmo_2$, give a *white* precipitate of a **basic carbonate** (*white lead*), of varying composition, usually considered to contain two molecules of plumbic carbonate and one molecule of plumbic hydrate, viz., $\begin{matrix}CO(OPbHo)\\CO(OPbHo)\end{matrix}Pbo''$ (*triplumbic dihydrate dicarbonate*), insoluble in water and in potassic cyanide.

KI gives a *yellow* precipitate of **plumbic iodide**, PbI_2, soluble in excess of the reagent; also soluble in much hot water, from which it separates on cooling in beautiful golden-yellow scales.

KCy precipitates *white* **plumbic cyanide**, $PbCy_2$, insoluble in excess, soluble in dilute nitric acid.

Soluble *phosphates, arsenites* and *arsenates, silicates, borates, oxalates, tartrates, citrates, ferro-* and *ferricyanides* give precipitates with plumbic salts, which are insoluble in water, but soluble in dilute nitric acid. These precipitates possess, however, only a secondary interest.

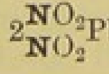
Metallic iron or zinc precipitates lead from its salts. This is seen very strikingly on dissolving a few ounces of plumbic acetate (*sugar of lead*) in distilled water, with the addition of a little acetic acid, and suspending in the solution a piece of zinc from a thread. The zinc becomes covered with a beautiful crystalline deposit of metallic lead, which increases rapidly, if the solution be left undisturbed, and acquires the appearance of a branch of a tree (*arbor Saturni*). The metallic structure can be preserved for days in unaltered beauty. On removing the precipitated lead from the piece of zinc, the latter is found much corroded and considerably diminished in size and weight. The lead may be collected on a filter and washed with water, dried and fused in a crucible, under a covering of borax, to a bright metallic button. A quantity of zinc, atomically equivalent in weight to the precipitated lead (*i.e.*, 65 parts by weight of zinc for every 207 of lead) must have dissolved, and is found in the solution, in the form of zincic acetate. The atomic weights of Zn (65) and Pb (207) can be determined roughly, by weighing the metallic zinc, before and after immersion, as well as the precipitated lead.

Heat a little *red lead*, Pb_3O_4,* in a small porcelain crucible or in a test-tube, to which a delivery-tube is attached. Oxygen gas is given off, which may be collected in the usual manner over water. The residue is dark yellow, and on cooling turns bright yellow. It consists of plumbic oxide, PbO (*litharge*), according to the equation:—$Pb_3O_4 = 3PbO + O$.

Treat a little Pb_3O_4 with dilute hydrochloric acid in a test-tube, and heat gently. A greenish-yellow gas comes off, and the *red lead* dissolves to plumbic chloride. The gas is readily recognized, by its odour, as chlorine:—

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4OH_2.$$

Treat another portion of *red lead* with dilute nitric acid. The red colour changes to brown—the colour of plumbic dioxide, PbO_2. The reaction is expressed by the equation:—



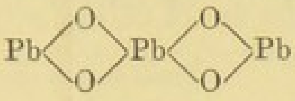
$$Pb_3O_4 + 4NO_2Ho = 2\begin{matrix}NO_2\\NO_2\end{matrix}Pbo'' + PbO_2 + 2OH_2.$$

---

* The composition of commercial *red lead* is more correctly expressed by the formula Pb_4O_5.

Lead can thus combine either with one or two atoms of oxygen to form $\mathbf{Pb}O$ or $\mathbf{Pb}O_2$; it can exist in the dyad or tetrad condition (Pb'' and Pb^{iv}) and *red lead* is obviously composed of two oxides, of $\mathbf{Pb}^{iv}O_2 + 2\mathbf{Pb}''O$. The plumbic dioxide in *red lead* yields the oxygen. It is written graphically :—

$\mathbf{Pb}^{iv}Pbo''_2$ =



(Triplumbic tetroxide).

The minerals *plattnerite*, $\mathbf{Pb}O_2$, and *minium*, $\mathbf{Pb}_3O_4$, represent the corresponding natural oxides.

It is evident from the above experiments, that lead occurs more frequently in the dyad than in the tetrad condition.

$\mathbf{S}O_2Ho_2$ forms with $\mathbf{Pb}O_2$ a sulphate, oxygen being given off.

$\mathbf{Pb}O_2$ absorbs sulphurous anhydride abundantly, forming $\mathbf{S}O_2Pbo''$.

HCl liberates chlorine from plumbic dioxide.

Minium or *red lead*, and the brown plumbic dioxide are powerful *oxidizing* agents. They furnish us likewise with ready means for preparing chlorine gas.

QUESTIONS AND EXERCISES.

1. Calculate the percentage composition of plumbic acetate.
2. How much oxygen by weight and by volume (at 0° C. and 760 mm.) can be obtained from 30 grms. of *red lead ?*
3. Write out the symbolic equations for the reactions of lead in the wet way.
4. How can Pb be separated from Ag, in the wet way?—1st, by using hydrochloric acid ; 2nd, potassic cyanide ; 3rd, sulphuric acid, as a precipitant.
5. Give graphic formulæ for *white lead*, *red lead*, plumbic acetate, *mendipite*, plumbic chlorohydrate, plumbic nitrate and chromate, diplumbic sulphodichloride.
6. How much HCl by weight will be required to decompose 10 grms. of *red lead ;* and how much chlorine gas will be evolved—1st, by weight ; 2nd, by volume at 0° C. and 750 mm. pressure ?
7. How would you separate Pb and Sb in type metal ?
8. Describe how you would analyse an alloy of 5 parts of lead, 3 parts of tin, and 8 parts of bismuth, a so-called *fusible alloy* melting at 98° C.
9. Calculate the percentage composition of Pb_4Sb (type-metal).

3. **MERCURY.**—(Mercurosum) $'Hg'_2$. Atomic weight 2 × 200.—

We employ A SOLUTION OF MERCUROUS NITRATE, $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o''$.

HCl (**group-reagent**), or **soluble chlorides**, give a *white* precipitate of **mercurous chloride**, $'\mathbf{Hg}'_2Cl_2$ (*calomel*), which is insoluble in dilute acids and is blackened by KHo or AmHo, the latter converts it into $'\mathbf{Hg}'_2O$ and *mercurosammonic chloride*, $\mathbf{N}H_2'Hg'_2Cl$. Mercurous is converted into mercuric chloride by the addition of chlorine water. Concentrated hydrochloric acid converts it, upon long-continued boiling, into $\mathbf{Hg}Cl_2$ and grey metallic mercury. Nitric acid oxidizes it readily into $\mathbf{Hg}Cl_2$ and $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$, with evolution of nitrous fumes. Dry $'\mathbf{Hg}'_2Cl_2$ sublimes unchanged.

NaHo or KHo gives a *black* precipitate of **mercurous oxide**, $'\mathbf{Hg}'_2O$, insoluble in excess.

AmHo produces a *black* precipitate of **basic dimercurosammonic nitrate** by the substitution of 'Hg'$_2$ for 2 atoms of hydrogen in two of Amo, thus:—

$$2\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' + 4AmHo = \mathbf{N}_2O_3'Hg'_2o''\left[\begin{matrix}NH_3'\\ NH_3\end{matrix}Hg'_2O_2\right]''$$

Basic dimercurosammonic nitrate.

$$+ 2\mathbf{N}O_2Amo + 3\mathbf{O}H_2.$$

The precipitate is insoluble in excess.

$\mathbf{S}H_2$ precipitates *black* **mercurous sulphide**, $'\mathbf{Hg}'_2S$,* insoluble in excess or in dilute acids; soluble in aqua regia or in yellow potassic sulphide. When boiled with concentrated nitric acid, the second atom of mercury in $'\mathbf{Hg}'_2S$ is converted into $\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hgo''$, and a white compound of mercuric nitrate and sulphide, $\begin{matrix}\mathbf{N}O_2OHg\\ \mathbf{N}O_2OHg\end{matrix}\!\!>\!S$, is formed.

$\mathbf{S}Am_2$ produces the same black precipitate.

A clean strip of metallic copper precipitates from mercurous solutions metallic mercury, cupric nitrate being left in solution. On gently rubbing the greyish deposit with a piece of wash-leather, the surface becomes bright and shining like silver. *The more electro-positive metals*, Cu, Cd, Zn, Fe, Pb, Bi, *precipitate the less electro-positive metal* Hg.

$\mathbf{S}OHo_2$, $\mathbf{S}O_2Feo''$, or $\mathbf{Sn}Cl_2$ produces a grey precipitate of metallic mercury. On decanting the liquid and boiling the grey deposit with hydrochloric acid, distinct metallic globules are obtained. The changes may be expressed thus:—

$$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' + \mathbf{S}OHo_2 + \mathbf{O}H_2 = 2Hg + 2\mathbf{N}O_2Ho + \mathbf{S}O_2Ho_2.$$

$$3\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' + 6\mathbf{S}O_2Feo'' = 6Hg + 2(\mathbf{S}O_2)_3Fe_2o^{vi} + (\mathbf{N}O_2)_6Fe_2o^{vi}.$$

$$\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}Hg_2o'' + \mathbf{Sn}Cl_2 + 2HCl = 2Hg + \mathbf{Sn}Cl_4 + 2\mathbf{N}O_2Ho.$$

Mercurous salts act thus the part of *oxidizing agents*, when coming in contact with more powerful reducing agents: a property which in conjunction with the *reducing action* which they exert under favourable circumstances, proves clearly that the double atom 'Hg'$_2$ possesses but little chemical affinity for other elements, and *that the compounds which it forms are rather unstable.*

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* This compound appears to be a mixture of mercuric sulphide and mercury, as is shown by the ready action which concentrated nitric acid has upon it.

QUESTIONS AND EXERCISES.

1. Write out the graphic formulæ of *calomel*, mercurous nitrate, mercurous oxide, mercurosammonic chloride, basic dimercurosammonic nitrate.
2. Write out equations for the reactions which mercurous compounds give in the wet way.
3. How can mercurous chloride be converted into mercuric chloride? Give equations.
4. How much *calomel* can be manufactured from 20 lb. of metallic mercury; and how much $\mathbf{S}O_2Ho_2$ and NaCl by weight will be required?
5. Explain the action of metallic mercury upon mercurous nitrate.
6. What is the action of boiling nitric acid upon mercurous sulphide?
7. In what manner can mercuric and mercurous chlorides be distinguished from each other by the reactions in the dry way?
8. State under what conditions mercurous salts play the part of oxidizing, or that of reducing agents.

A method of separating the metals of Group I will readily suggest itself, and a tabular analytical scheme may be drawn up without much difficulty, if we bear in mind:—

1st. The *solubility of* $\mathbf{Pb}Cl_2$ *in boiling water.*

2nd. The *solubility of* AgCl *in* AmHo.

3rd. The *conversion of the* $\mathbf{Hg}_2Cl_2$ *into black* $\mathbf{N}H_2'Hg_2'Cl$ *by the action of* AmHo.

Table I in the Analytical Tables at the end of the book embodies this method of separation.

Before proceeding to the study of the reactions for acids, the student will do well to tabulate according to some such scheme as the one given on p. 52, the knowledge gained of all the metallic *oxides* and *hydrates*, *sulphides*, *carbonates*, neutral as well as basic, etc., and to commit the reactions to memory.

He will also gain much precise information by working out in a tabular form and illustrated by equations:—

(1.) The solubility of all the metals hitherto treated of—

(*a.*) In dilute and concentrated hydrochloric acid.
(*b.*) In dilute and concentrated nitric acid.
(*c.*) In dilute and concentrated sulphuric acid.
(*d.*) In *aqua Regia*.

The information given in my *Introduction to Inorganic Chemistry*, III Ed., pp. 96, 101 and 102, 117, 118, 119 and 120, should be consulted, as well as that found in this work under each metal.

(2.) The solubility of the metallic oxides and sulphides obtained by double decomposition in the wet way, in the different acids, in caustic alkalies, and in alkaline sulphides.

PRACTICAL EXERCISES AND QUESTIONS ON GROUP I.

1. Test a sample of *galena* for silver in the dry way.
2. Analyse a sample of *ruby silver* in the dry and in the wet way.

3. You have given to you some precipitated argentic chloride, dilute HCl, and a strip of metallic zinc. How would you prepare pure metallic silver?
4. Analyse a solution, containing ·010 grm. of Ag, as $\mathbf{N}O_2Ago$, ·100 grm. of Hg, as $\mathbf{N}_2O_4Hg_2o''$ and ·010 grm. of Pb, as $\mathbf{N}_2O_4Pbo''$.
5. Describe what takes place when a solution of argentic nitrate, containing about ·010 grm. of Ag, is added to a hot saturated solution of KCl.
6. You have given to you a mixture of *red lead* and *calomel*. What takes place when the mixture is treated with HCl?
7. Analyse a mixture (about ·050 grm.) of *white arsenic* and *corrosive sublimate*, both in the dry and wet way.
8. Test a commercial sample of baric chloride for lead.
9. Test a sample of *white lead* paint for impurities, insoluble in dilute nitric acid, and examine the acid filtrate by the respective group-reagents.
10. Prepare some pure $\mathbf{N}O_2Ago$ from an alloy of copper and silver.

CHAPTER VII.

REACTIONS OF THE ACIDS.

A. INORGANIC ACIDS.

CARBONIC ANHYDRIDE, CO_2.—Occurs in the atmosphere and in mineral waters. In the combined state it forms a constituent of many minerals, called *carbonates*, which have for the most part been enumerated, in speaking of the natural compounds in which the different metals occur.

REACTIONS IN THE DRY WAY.

On ignition some carbonates undergo changes, others remain unchanged. The carbonates of the fixed alkali metals are not decomposed by the strongest heat. At very high temperatures they are somewhat volatilized. The acid carbonates of the alkalies are reduced by heat to normal carbonates, with evolution of CO_2. The carbonates of all other metals are decomposed more or less readily into oxides (or metals), carbonic anhydride (and oxygen) being given off. Baric and strontic carbonates require the strongest white heat for their decomposition; calcic carbonate requires a strong red heat. All the others are readily decomposed on heating. The evolved carbonic anhydride is a colourless and almost odourless gas, heavier than air, and can be poured from one vessel into another. When poured or passed into a test-tube containing lime- or baryta-water, a white precipitate is obtained, owing to the combination of the carbonic anhydride with the caustic alkaline earthy bases.

REACTIONS IN THE WET WAY.

All normal carbonates may be divided into—

1st. *Carbonates which are soluble in water*, consisting of the carbonates and bicarbonates of the alkali metals and possessing an alkaline reaction.

2nd. *Carbonates which are insoluble in water*, a few of which are, however, soluble in carbonic anhydride, with formation of acid carbonates, such as the carbonates of Ba, Sr, Ca, Mg, Fe'', Mn'', but are reprecipitated on boiling.

All carbonates are *decomposed* by dilute acids,—organic or mineral (with the exception of HCy and SH_2). The decomposition is marked by strong effervescence and evolution of CO_2. (A few native carbonates, such as *spathose iron ore*, and *dolomite*, require the application of heat.) On passing the evolved gas into a solution of caustic lime or baryta, the carbonic anhydride becomes once more fixed, and the formation of a white precipitate (soluble in excess of the gas with formation of acid carbonates) confirms the presence of CO_2.

Metallic sulphites, sulphides, and nitrites are likewise decomposed by dilute acids with evolution of a gas; but the evolved SO_2, SH_2, or N_2O_3 gases are readily recognized by their characteristic odour or colour. In order to recognize CO_2 in the presence of SO_2 or SH_2, the gaseous mixture is first passed into a solution of an alkaline chromate mixed with an acid, or into bromine water, or a solution of a cupric or ferric salt, and then through lime- or baryta-water.

QUESTIONS AND EXERCISES.

1. How would you prove experimentally the presence of carbonic anhydride, 1st, in spring water; 2nd, in atmospheric air; 3rd, in white lead; 4th, in coal gas?
2. Classify all metallic carbonates according to their respective deportment, 1st, on ignition; 2nd, on treatment with water; 3rd, in contact with excess of CO_2. Give examples.
3. What change takes place when tartaric acid and hydric potassic carbonate are mixed together?
4. Which is the most characteristic reaction for CO_2?
5. How would you recognize the presence of CO_2 in a gaseous mixture, containing SO_2 and CO_2, or SH_2 and CO_2?
6. How much CO_2, by weight and by volume, can be obtained from 1·235 grm. of $COCao''$?
7. What change takes place, 1st, when a current of CO_2 is passed through cold water in which finely divided chalk is suspended; and 2nd, when the liquid is heated to boiling, subsequent to the passing of the gas?
8. Explain the occurrence of CO_2 in mineral waters and in atmospheric air.
9. Explain the effect of boiling upon most spring waters.
10. What is the usual composition of boiler deposits, and how would you propose to prevent them? (Comp. p. 19.)

SULPHURIC ACID, SO_2Ho_2.—This is one of the most powerful acids, for it is capable of displacing, in the wet way (with few exceptions), all other acids from saline compounds. It forms with bases a series of very important salts,—the sulphates, most of which have already been enumerated in treating of the natural compounds of the various metals.

REACTIONS IN THE DRY WAY.

On heating a sulphate on charcoal, in the reducing flame, together with $CONao_2$ (free from sulphate), sodic sulphide is formed thus:—

$$SO_2Mgo'' + 2C + CONao_2 = SNa_2 + MgO + 3CO_2.$$

The fused mass gives off SH_2, when treated with a strong acid (HCl), readily recognized by its odour. When placed on a bright silver coin and moistened with a drop of water, it produces a black stain of argentic sulphide. This reaction applies, however, to all sulphur acids, without exception, and it is impossible to prove thereby the presence of SO_2Ho_2 any more than that of some other (lower) oxide of sulphur.

Heated by themselves, the sulphates of the fixed alkalies and alkaline earthy metals, as well as of lead, are not decomposed. Acid sulphates (SO_2HoKo, etc.) are converted at a bright red heat into normal sulphates, with evolution of strong sulphuric acid. Other metallic sulphates become decomposed more or less speedily on ignition, giving off sulphuric or sulphurous anhydride and oxygen, according to the nature of the metal, *e.g.* :—

$$2SO_2Feo'' = Fe_2O_3 + SO_3 + SO_2.$$
$$SO_2Cuo'' = CuO + SO_2 + O.$$

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC SULPHATE, SO_2Ko_2, may be employed.

Sulphuric acid forms normal and acid sulphates, which are mostly soluble in water, the exceptions being baric, strontic, calcic, and plumbic sulphates. (A few basic sulphates are insoluble in water, but soluble in acids.)

$BaCl_2$ or N_2O_4Bao'' gives a *white* finely divided precipitate of **baric sulphate**, SO_2Bao'', insoluble in dilute acids. Care must be taken not to have too much free hydrochloric or nitric acid present, lest any of the baric salts be precipitated: baric chloride and nitrate being much less soluble in strong acids than in water. If a very dilute solution of a sulphate has to be precipitated, the solution should be heated to boiling, and allowed to stand for some time after the addition of the baric salt.

This reaction distinguishes SO_2Ho_2 from all other acids, except hydrofluosilicic acid, $2HF,SiF_4$, and selenic acid, SeO_2Ho_2, which also form baric salts, insoluble in acids.

Soluble salts of strontium, calcium, and lead produce *white* precipitates of **strontic, calcic**, and **plumbic sulphates**, which are more or less soluble in large quantities of water: SO_2Cao'' being the most soluble (in about 500 parts of water), SO_2Sro'' dissolving in 7,000 parts of cold water, and SO_2Pbo'' in 22,000 parts of water only.

Since barric salts answer every purpose, recourse is rarely had to these reactions in order to detect sulphuric acid. The addition of alcohol (methylated spirit), ensures the complete precipitation of strontic, calcic, and plumbic sulphates. Most soluble sulphates can, in fact, be precipitated from their aqueous solutions by the addition of strong alcohol.

In order to detect free sulphuric acid, by itself, or in the presence of a sulphate, the solution is evaporated to dryness on a water-bath, together with a little cane sugar. A blackened or charred residue indicates *free* sulphuric acid, as no other acid is capable of decomposing cane sugar in like manner.

An *insoluble sulphate* can be decomposed by continued boiling with a concentrated solution of an alkaline carbonate: more readily, however, by fusion with alkaline carbonates (fusion mixture), into a soluble alkaline sulphate, and an insoluble carbonate or oxide of the metal, thus:—

$$\mathbf{S}O_2Bao'' + \mathbf{C}ONaoKo = \mathbf{S}O_2NaoKo + \mathbf{C}OBao''.$$
$$\mathbf{S}O_2Pbo'' + \mathbf{C}ONaoKo = \mathbf{S}O_2NaoKo + \mathbf{Pb}O + \mathbf{C}O_2.$$

The fused mass is extracted with boiling water, and the insoluble carbonate or oxide separated by filtration from the soluble alkaline sulphate. The residue is examined as usual for base, and the solution for sulphuric acid, by acidulating with dilute hydrochloric acid (in order to destroy the excess of alkaline carbonates), and adding baric chloride. Calcic sulphate dissolves in ammonic sulphate and a little AmHo; plumbic sulphate in ammonic acetate or tartrate, or in sodic hyposulphite.

QUESTIONS AND EXERCISES.

1. Classify all metallic sulphates according to their solubility in water.
2. How are metallic sulphates detected in the dry way?
3. Explain the action of heat upon the different metallic sulphates.
4. How is free sulphuric acid detected?
5. Describe shortly in what manner $\mathbf{S}O_2Bao''$, $\mathbf{S}O_2Sro''$, $\mathbf{S}O_2Cao''$, and $\mathbf{S}O_2Pbo''$ differ from each other with regard to their solubility in water, and their respective deportment with various other solvents.
6. How are insoluble sulphates examined qualitatively?
7. 1·648 grm. of a sample of *soda-ash* yielded ·234 grm. of $\mathbf{S}O_2Bao''$; what is the percentage of sodic sulphate in the ash?

SULPHUROUS ACID, $\mathbf{S}OHo_2$.—Obtained as gaseous anhydride, $\mathbf{S}O_2$, whenever sulphur is burnt in air or oxygen, or when metallic sulphides (*pyrites*, *blende*, *galena*, etc.), are roasted with free access of air; also by the partial deoxidation of sulphuric acid by means of metals, such as Cu, Hg, Ag, of charcoal and various organic bodies, of sulphur, etc. The gas is readily soluble in water, forming sulphurous acid, which combines with bases, and forms a series of salts, normal or acid, termed sulphites: compounds strongly characterized by the tendency which they exhibit to absorb oxygen and to become converted into sulphates. This property causes sulphurous acid, or metallic sulphites, to be of considerable interest.

REACTIONS IN THE DRY WAY.

Sulphurous anhydride is recognized by its characteristic odour, the odour of burning sulphur. It combines readily with metallic peroxides, such as $\mathbf{Mn}O_2$, $\mathbf{Pb}O_2$ with formation of manganous and plumbic sulphates. In order, therefore, to remove $\mathbf{S}O_2$ from a gaseous mixture, the latter is usually passed over $\mathbf{Pb}O_2$.

Many solid sulphites are decomposed by heat into sulphates and sulphides, thus:—

$$4SONao_2 = 3SO_2Nao_2 + SNa_2.$$

The earthy sulphites break up, on heating, into oxides and sulphurous anhydride.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC SULPHITE, $SONao_2$, may be employed.

Sulphites are examined by liberating sulphurous anhydride by means of strong sulphuric or hydrochloric acid, the gas being readily recognized by its characteristic pungent odour.

The only sulphites soluble in water are the alkaline sulphites. Normal baric, strontic, calcic, and magnesic sulphites are insoluble in water, but are dissolved to a great extent, by a solution of sulphurous acid, with formation of acid sulphites, from which the normal salts are reprecipitated on boiling. They are also soluble in dilute hydrochloric acid (with partial decomposition); but on the addition of an oxidizing agent, such as chlorine water, free iodine, sodic hypochlorite, nitric acid, etc., they are immediately precipitated as insoluble sulphates (SO_2Mgo'' excepted).

Sulphites generally contain sulphates. A precipitate consisting of baric sulphate is, therefore, frequently obtained on adding baric chloride to an acidulated solution of a soluble, or to a dilute hydrochloric acid solution of an insoluble sulphite.

On filtering off the precipitate, and adding chlorine water to the filtrate, a further precipitate is obtained, showing the presence of a sulphite.

Traces of sulphurous acid are distinguished with difficulty by the odour alone, and it is preferable, therefore, to make use of the deoxidizing, as well as oxidizing action which the acid can exert.

1. *Sulphurous acid acts as a powerful reducing agent.*

NO_2Ago gives with sodic sulphite a *white* precipitate of **argentic sulphite,** $SOAgo_2$, soluble in excess of the alkaline sulphite. The precipitate blackens on heating, owing to the separation of metallic silver, and conversion of the $SOHo_2$ into SO_2Ho_2, according to the equation:—

$$SOAgo_2 + OH_2 = Ag_2 + SO_2Ho_2.$$

$N_2O_4Hg_2o''$ produces a *grey* precipitate of **metallic mercury,** thus:—

$$SOHg_2o'' + OH_2 = Hg_2 + SO_2Ho_2.$$

The instances of the reducing action of sulphurous acid are very numerous; we need only refer here to its action upon solutions of $AuCl_3$, CrO_2Ho_2, Fe_2Cl_6, and others, already noticed under the respective metals.

2. Under favourable circumstances *sulphurous acid acts as an oxidizing agent,* especially when brought in contact with other *more powerful* reducing agents, such as nascent hydrogen, SH_2, $SnCl_2$, etc. Thus, by introducing the least trace of $SOHo_2$, or a sulphite, into a flask, in which hydrogen is generated from zinc and hydrochloric acid, SH_2 is immediately evolved, together with the hydrogen, and may be recognized by its odour and action upon lead paper. The change is expressed as follows:—

$$SO_2 + 3H_2 = SH_2 + 2OH_2.$$

SO_2 and SH_2 give rise to the formation of pentathionic acid, with precipitation of *white* sulphur, according to the equation :—

$$5SO_2 + 5SH_2 = \left\{\begin{array}{l} SO_2Ho \\ S_3 \\ SO_2Ho \end{array}\right. + S_5 + 4OH_2.$$

Pentathionic
acid.

Sulphurous acid added to stannous chloride in the presence of hydrochloric acid, gradually precipitates yellow SnS_2. The hydrogen of the hydrochloric acid acts as the reducing agent, and is detached from the chlorine by the simultaneous action of the $SnCl_2$ and SO_2, the one eager to combine with chlorine, the other capable of yielding oxygen to the hydrogen, to form water, and ultimately sulphur, to form SH_2, which in its turn acts upon the stannic chloride, $SnCl_4$, (or $SnCl_2$), to form yellow stannic sulphide, SnS_2 (or brown SnS). The following equations express the changes :—

$$(1)\quad SOHo_2 + 3SnCl_2 + 6HCl = 3SnCl_4 + SH_2 + 3OH_2.$$

$$(2)\quad SnCl_4 + 2SH_2 = SnS_2 + 4HCl.$$

Yellow
stannic sulphide.

QUESTIONS AND EXERCISES.

1. Describe different methods of preparing sulphurous anhydride.
2. How would you prepare normal and acid potassic sulphite ?
3. What is the action of heat upon sulphites ?
4. Which sulphites are soluble and which are insoluble in water ?
5. Give illustrations of the reducing action of sulphurous acid or of soluble sulphites.
6. Explain under what circumstances sulphurous acid can act as an oxidizing agent ; give instances of such action.
7. How would you distinguish sulphurous in the presence of sulphuric acid ?
8. What changes take place when a mixture of dipotassic dichromate and sodic sulphite is treated with concentrated HCl ? Give equations.
9. How would you fix the sulphurous acid produced by the combustion of carbon disulphide contained in coal gas ?

HYPOSULPHUROUS ACID, $SSOHo_2$ (*sulpho-sulphuric acid.*)—This acid has never been obtained in the free state. Combined with soda it forms an important salt, viz., sodic hyposulphite (the *hypo.* of the photographer), obtained by boiling a solution of sodic sulphite with sulphur, or by the oxidation of an alkaline persulphide in contact with the air.

REACTIONS IN THE DRY WAY.

All hyposulphites are decomposed on ignition. Alkaline hyposulphites leave a polysulphide and a sulphate, thus :—

$$4(SSONao_2) = S_5Na_2 + 3SO_2Nao_2.$$

Others yield sulphites or sulphates, with evolution of sulphurous anhydride, owing to the oxidation of a portion of the sulphur.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC HYPOSULPHITE, $SSONao_2$, is employed.

Most hyposulphites are soluble in water (baric hyposulphite is difficultly soluble in cold water), and their solutions may, with few exceptions, be boiled without decomposition. Calcic hyposulphite is gradually decomposed on boiling, the precipitate consisting of calcic sulphate and sulphur. The same decomposition takes place more speedily when hyposulphites are treated with sulphuric or hydrochloric acid. Sulphurous anhydride is evolved with separation of sulphur. The precipitated sulphur is yellow, and not white, as is usually the case when sulphur separates in chemical reactions. *This change characterizes hyposulphites.*

The same instability of the sulphur atom, occupying the place of an atom of oxygen in sulphuric acid,* is observed, when hyposulphites come in contact with salts, whose metals form with sulphur insoluble sulphides.

NO_2Ago gives a *white* precipitate of **argentic hyposulphite,** $SSOAgo_2$, soluble in sodic hyposulphite, which speedily turns yellow, then brown, and lastly black (SAg_2), especially on the application of heat, thus :—$SSOAgo_2 + OH_2 = SAg_2 + SO_2Ho_2$.

Mercurous nitrate and plumbic acetate give similar precipitates, which are decomposed by heat into Hg_2S or PbS, and sulphuric acid.

$SnCl_2$ gives a *brown* precipitate of SnS.

Hyposulphites, like sulphites, *are readily oxidized*, but yield under certain conditions oxygen to more powerful reducing agents, and become thus *oxidizing* agents.

Free chlorine, sodic hypochlorite, ferric chloride, etc., oxidize hyposulphites completely to sulphates, even in the cold, thus :—

$$\begin{aligned} SSONao_2 + 4Cl_2 \quad + 5OH_2 &= 2SO_2HoNao + 8HCl. \\ SSONao_2 + 4ClNao + OH_2 &= 2SO_2HoNao + 4NaCl. \end{aligned}$$

$SSONao_2$ gives with Fe_2Cl_6 at first a reddish-violet coloration (DIFFERENCE BETWEEN SULPHITES AND HYPOSULPHITES), but on standing, the solution is slowly decolorized (more rapidly on heating), with formation of $FeCl_2$, thus :—

$$SSONao_2 + 4Fe_2Cl_6 + 5OH_2 = 2SO_2HoNao + 8FeCl_2 + 8HCl.$$

Nascent hydrogen *reduces* hyposulphites to sulphides, which evolve with the acid sulphuretted hydrogen :—

$$SSONao_2 + 4H_2 + 2HCl = 2SH_2 + 3OH_2 + 2NaCl.$$

Sodic hyposulphite is a useful solvent for $AgCl$ (hence its application in photography), Hg_2Cl_2 and SO_2Pbo''. Calcic hyposulphite, $SSOCao''$, has also found an interesting application, as an agent for removing the last traces of chlorine in the bleaching of paper pulp, and from fabrics bleached by means of *bleaching powder*, to prevent their deterioration by the traces of chlorine which they are apt to retain. It has on that account received the name of *antichlor*. The free hydrochloric acid which is formed in the reaction is neutralized by passing the fabrics through a weak alkaline bath.

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* Recent investigations (Deut. Chem. Ges. Ber., vii, p. 646) render it probable that the composition of hyposulphites is not $SSORo_2$, but SO_2Rs,Ro ($R =$ monad metal).

The property of sodic hyposulphite of dissolving AgCl has found an important metallurgical application in the removal of silver from poor argentiferous ores, after they have undergone the process of roasting with common salt, which converts the silver into AgCl, insoluble in water.

Besides the three oxygen acids of sulphur just described, there are others, such as *dithionic*, $\left\{\begin{matrix}SO_2Ho\\SO_2Ho\end{matrix}\right.$, *trithionic*, $\left\{\begin{matrix}SO_2Ho\\S\\SO_2Ho\end{matrix}\right.$, *tetrathionic*, $\left\{\begin{matrix}SO_2Ho\\S_2\\SO_2Ho\end{matrix}\right.$ and *pentathionic acids*, $\left\{\begin{matrix}SO_2Ho\\S_3\\SO_2Ho\end{matrix}\right.$, which occur but rarely, and resemble one another considerably in their reactions. Their consideration must be reserved for a more extensive course of study.

QUESTIONS AND EXERCISES.

1. How is sodic hyposulphite prepared ?
2. How would you prepare ferrous, aluminic, chromic, and manganous hyposulphites ?
3. How are hyposulphites affected by ignition ?
4. What change takes place, when a solution of calcic hyposulphite is boiled, 1st, by itself, 2nd, when it is treated with HCl ?
5. Explain the action of sodic hyposulphite upon plumbic, argentic, mercurous and stannous salts.
6. Give instances, 1st, of the reducing action, and 2nd, of the oxidizing action of hyposulphites.
7. Explain the term *antichlor*.
8. State what application sodic hyposulphite has found in photography and in metallurgy.
9. Give graphic formulæ for sulphosulphuric, dithionic, trithionic, tetrathionic and pentathionic acids.
10. How would you separate baric hyposulphite from baric sulphate ?

HYDROSULPHURIC ACID, SH_2.—Obtained as a colourless gas by the decomposition of certain metallic sulphides, such as $\mathbf{Fe}S$, $\mathbf{Zn}S$, $\mathbf{Sb}_2S_3$, by means of sulphuric or hydrochloric acid. It is characterized by a most fœtid odour, resembling that of rotten eggs. It is absorbed by cold water, forming sulphuretted hydrogen water or hydrosulphuric acid, which reddens blue litmus-paper feebly. Hydrosulphuric acid exchanges its sulphur for the oxygen of most metallic oxides, both in the dry and wet way, forming water and metallic sulphides. It is on this account a most valuable reagent. Many of the native sulphides, *e.g.*, *iron pyrites*, *galena*, *cinnabar*, *zinc blende*, are met with in vast masses.

REACTIONS IN THE DRY WAY.

Metallic sulphides are acted upon in various ways, when submitted to heat. Some are decomposed, when heated in a close vessel, into metal and sulphur, *e.g.*, $\mathbf{Au}_2S_3$; some sulphides, such as PtS_2, FeS_2, Sb_2S_5, SnS_2, PbS yield up a portion of their sulphur and are reduced to PtS, Fe_3S_4, Sb_2S_3, SnS, Pb_2S; others sublime without decomposition, such as As_2S_3 (*orpiment*), HgS (*cinnabar*). The greater number of metallic sulphides remain, however, undecomposed, when heated out of contact with atmospheric air.

Most sulphides undergo a change, when roasted in a tube open at both ends. SAg_2 leaves metallic silver (usually also a little SO_2Ago_2), the sulphur by combining with oxygen, passes off as SO_2; some sulphides leave a metallic oxide, *e.g.*, SnS, Sb_2S_3, Bi_2S_3; others again, such as the sulphides of the alkalies and alkaline earthy metals, are converted into sulphates. Plumbic sulphide (*galena*) is converted into a mixture of oxide and sulphate; cupric sulphide, when roasted at a high temperature, yields SO_2 and CuO; at a lower temperature SO_2Cuo''. FeS and other sulphides of the iron group are partially converted into sulphates, which on the application of a stronger heat, lose their acid, leaving metallic oxides. Many native metallic sulphides are distinguished for their metallic lustre, such as *iron* and *copper pyrites*, *galena*, *grey antimony*. The presence of a metallic sulphide cannot, however, be inferred conclusively from the evolution of SO_2, since earthy sulphites are broken up, on ignition, into oxides and sulphurous anhydride.

REACTIONS IN THE WET WAY.

Alkaline and alkaline earthy sulphides are soluble in water (CaS and MgS are only sparingly soluble). Dilute hydrochloric acid decomposes them readily into metallic chlorides and SH_2. *All other sulphides are insoluble in water.* Several of the latter, such as FeS, MnS, ZnS are decomposed by dilute hydrochloric acid with evolution of sulphuretted hydrogen. Others require concentrated hydrochloric acid, such as NiS, CoS (difficultly soluble), Sb_2S_3, SnS_2, PbS. Sulphides which are insoluble, or difficultly soluble, in concentrated hydrochloric acid, such as Bi_2S_3, CuS, SAg_2, PbS, As_2S_3, are decomposed by concentrated nitric acid; they are generally oxidized into sulphates—at first with separation of sulphur which, by prolonged digestion, is for the most part converted into sulphuric acid. Others, such as HgS, PtS_2, Au_2S_3. (As_2S_3) dissolve in aqua regia, or hydrochloric acid and potassic chlorate, with separation of sulphur and formation of SO_2Ho_2, and of a metallic chloride. On dissolving PbS, SnS_2, Sb_2S_3, As_2S_3, in concentrated nitric, instead of hydrochloric acid, they are converted principally into SO_2Pbo'', SnO_2, Sb_2O_4, As_2O_5.

To detect SH_2 (*in an aqueous solution*) *or a soluble sulphide* (a solution of SAm_2 may be conveniently employed), add a solution of a salt of cadmium, lead, or silver, which gives by double decomposition a characteristic precipitate of a metallic sulphide: fine yellow for cadmium, black for plumbic or argentic salts.

To analyse *a sulphide decomposable by hydrochloric acid*, the evolved sulphuretted hydrogen gas is made to act upon lead paper or is passed through a solution of a plumbic salt. (*Iron pyrites*, FeS_2, and *copper pyrites*, Cu_2S,Fe_2S_3, give off SH_2 only in the presence of hydrochloric acid and zinc).

Sulphides which are not decomposed by hydrochloric acid, yield sulphur on treatment with nitric acid or aqua regia, and must be recognized by this and the products of decomposition, such as SnO_2, SO_2Pbo'', as well as the reactions which they give, when examined in the dry way.

Many native sulphides, such as fahl ore, etc., are expeditiously examined by heating the finely-powdered mineral in a hard glass tube, in a current of dry chlorine gas, when the metals are converted into chlorides and the sulphur into volatile chloride of sulphur, which is decomposed on being passed into water.

To detect a *soluble alkaline sulphide in the presence of free* SH_2, add a few drops of a solution of sodic nitroprusside. This reagent does not affect free SH_2, but gives a fine purple colour with the merest traces of soluble sulphides. The colour disappears only after some time. It does not show in the presence of free caustic alkalies.

A mixture containing *a soluble alkaline sulphide, hyposulphite, sulphite*, or *sulphate* may be examined by adding $COCdo''$ to the aqueous solution. Filter, dissolve the excess of $COCdo''$ in the precipitate by means of dilute acetic acid; a residue of yellow CdS indicates the presence of an alkaline sulphide. Add to the filtrate $BaCl_2$; a precipitate is obtained, consisting of SO_2Bao'' and $SOBao''$. Filter off; digest the precipitate with dilute hydrochloric acid, and filter. A white residue shows the presence of an alkaline sulphate. Add chlorine water to the filtrate; a precipitate of SO_2Bao'' indicates the presence of an alkaline sulphite. The filtrate from the $BaCl_2$ precipitate is searched for $SSOHo_2$ by the addition of HCl and boiling. A precipitate of *yellow* sulphur and the odour of SO_2 indicates the presence of a hyposulphite.

To remove SH_2 from a gaseous mixture of CO_2 and SH_2, add a solution of cupric chloride and shake up with the gases.

QUESTIONS AND EXERCISES.

1. Explain the changes which take place when hydrosulphuric acid is passed through saline solutions, the metals of which form insoluble sulphides. Give instances.
2. Explain the action of heat upon the different metallic sulphides.
3. Which sulphides are soluble and which are insoluble in water?
4. Explain how certain sulphides are affected by dilute hydrochloric acid, and how by concentrated hydrochloric acid. Give characteristic instances, and express the changes by equations.
5. Describe the most delicate reaction for gaseous SH_2.
6. What is the action of nitric acid upon ZnS, PbS, CuS, SnS, Sb_2S_3?
7. How would you prove the presence of an alkaline sulphide, hyposulphite, sulphite, and sulphate in an aqueous solution?
8. State how you would separate SH_2 and CO_2 contained in a gaseous mixture.
9. How can you prove the presence of SH_2 in coal gas?
10. 10 litres of unpurified coal gas yielded ·235 grm. of CdS. What is the percentage of SH_2 in the gas?
11. ·650 grm. of *galena* gave ·532 grm. of SO_2Pbo''. What is the percentage of Pb and of S in the galena?
12. What change takes place when PtS_2, Sb_2S_5, FeS_2, As_2S_3, and HgS are heated with exclusion of air?
13. How would you test for SH_2 in sewer gases?
14. How would you detect sulphur in pig iron?
15. Explain the action of chlorine, bromine, and iodine upon SH_2?
16. How is sulphur detected in organic compounds, such as coal?

NITRIC ACID, $\mathbf{N}O_2Ho$.—Obtained as a colourless, highly corrosive, volatile liquid, of a deep yellow colour when it is mixed with nitrous acid. It is characterized by the facility with which it parts with its oxygen, and it is this property of which we avail ourselves invariably, when nitric acid or a nitrate has to be detected.

REACTIONS IN THE DRY WAY.

Most nitrates fuse readily when heated. All are decomposed when exposed by themselves to a high temperature. The decomposition varies with the nature of the base: a lower oxide of nitrogen and oxygen being generally given off. Thus ammonic nitrate, $\mathbf{N}O_2Amo$, breaks up into $\mathbf{O}N_2$ and $\mathbf{O}H_2$; potassic or sodic nitrate into nitrite (always contaminated, however, with nitrate and caustic alkali) with liberation of oxygen, and ultimately, on the application of a stronger heat, into oxide or peroxide—nitrogen and oxygen being given off; others, such as plumbic nitrate, into O and $\mathbf{N}_2O_4$, leaving the oxide of the metal. When heated together with bodies eager to take up oxygen, such as carbon (charcoal, alkaline cyanides, etc.), sulphur or phosphorus, the decomposition becomes explosively violent, and nitrogen gas only is left as the remnant of the molecule $\mathbf{N}_2O_5$. (Chlorates explode in like manner, but leave metallic chlorides.)

REACTIONS IN THE WET WAY.

With the exception of a few basic salts, nitrates are readily soluble in water; hence nitric acid cannot be tested in the usual way, by producing precipitates by way of double decomposition. When acted upon by various reducing agents, the deoxidation of the acid may be *partial* (accompanied by the evolution of lower oxides of nitrogen) or *complete* (nitrogen only being left); in which case the nascent nitrogen is capable of combining with hydrogen in the nascent state to form ammonia.

1st. *Reactions in which nitric acid is reduced to lower oxides of nitrogen.*

A SOLUTION OF NITRIC ACID OR OF POTASSIC NITRATE, $\mathbf{N}O_2Ko$, may be employed.

$\mathbf{N}O_2Ho$ (or $\mathbf{N}O_2Ko$) is decomposed when heated with concentrated hydrochloric acid (or a chloride when heated with nitric acid). Chloronitric gas,* $\mathbf{N}_2O_2Cl_4$, is evolved, and the liquid acquires the power of dissolving gold-leaf or platinum foil, which are not soluble in single acids. (Chlorates, bromates, iodates, chromates, and permanganates evolve chlorine when treated with hydrochloric acid; they dissolve gold or platinum, but give off no $\mathbf{N}_2O_2$.)

Add to a dilute solution of ferrous sulphate cautiously its own volume of concentrated sulphuric acid (free from nitric acid), and allow the mixture to cool; then add gradually a solution containing a nitrate. A ring is seen to form at the point of contact of the two layers, of a violet, red, or dark brown colour, according to the quantity of the nitrate present. The coloration is increased by carefully shaking up the fluid, but it disappears on heating. This is owing to the formation of a transient compound of the ferrous salt with $\mathbf{N}_2\mathrm{O}_2$, consisting of four molecules of the salt with one molecule of nitric oxide ($4\mathbf{S}\mathrm{O}_2\mathrm{Feo}'',\mathbf{N}_2\mathrm{O}_2$). The other three atoms of oxygen from two molecules of nitric acid oxidize six molecules of ferrous into three molecules of ferric sulphate, $\mathbf{S}_3\mathrm{O}_6\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}}$. This constitutes one of the most delicate reactions for nitric acid. The change may be expressed thus :—

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* From the recent investigations of *Tilden* (Chem. Soc. Journ., July, 1874, p. 634) it appears that *Gay-Lassac's* $\mathbf{N}_2O_2Cl_4$ gas is a mixture of nitrosyl monochloride, $\mathbf{N}OCl$, with varying quantities of chlorine.

$$10\mathbf{S}\mathrm{O}_2\mathrm{Feo}'' + 3\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 + 2\mathbf{N}\mathrm{O}_2\mathrm{Ho} = 3\mathbf{S}_3\mathrm{O}_6\mathrm{Fe}_2\mathrm{o}^{\mathrm{vi}} + 4\mathbf{S}\mathrm{O}_2\mathrm{Feo}'',\mathbf{N}_2\mathrm{O}_2 + 4\mathbf{O}\mathrm{H}_2.$$

A solution of a nitrate, when added to a solution of indigo in sulphuric acid (sulphindigotic acid), changes the blue colour of the indigo to yellow. (Free chlorine and other oxidizing agents bleach indigo likewise).

Metallic copper (Ag, Zn, Pb, or Hg) is dissolved by nitric acid with evolution of ruddy fumes, and by potassic nitrate on the addition of sulphuric acid.

A similar reaction takes place, when copper filings are mixed with a nitrate and hydric potassic sulphate and fused in a test-tube or crucible.

Minute quantities of nitrates found in mineral waters, in rain water, or water draining from arable land, may be detected by first reducing the nitrate to nitrite. This is effected by heating the solution for some time with a little zinc amalgam. On filtering and adding to the filtrate a solution of ferrous salt, a dark brown coloration is obtained; or by adding a drop of a solution of potassic iodide, some freshly prepared cold starch solution, and a little acetic (or very dilute sulphuric) acid, a fine blue precipitate of iodide of starch is produced, thus :—

$$2\mathbf{N}\mathrm{OKo} + 2\mathrm{KI} + 2\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 = \mathbf{N}_2\mathrm{O}_2 + 2\mathbf{S}\mathrm{O}_2\mathrm{Ko}_2 + \mathrm{I}_2 + 2\mathbf{O}\mathrm{H}_2.$$

This reaction is exceedingly delicate.

2nd. *Reactions in which nitric acid is entirely reduced, and its nitrogen converted into ammonia.*

All nitrates when fused with caustic potassa, lime, or soda-lime, and some non-nitrogenous organic substance, such as sugar or starch, evolve ammonia, thus :—

$$6\mathbf{N}\mathrm{O}_2\mathrm{Ko} + 18\mathrm{KHo} + \underset{\text{Sugar.}}{\mathbf{C}_{12}\mathrm{H}_{22}\mathrm{O}_{11}} = 12\mathbf{C}\mathrm{OKo}_2 + 6\mathbf{N}\mathrm{H}_3 + 11\mathbf{O}\mathrm{H}_2.$$

The gas may be readily recognized by its odour, or action upon red litmus paper.

Nascent hydrogen, produced by the action of KHo upon metallic zinc, iron, or aluminium, gives rise, in the presence of a nitrate, to the formation of ammonia, thus :—

$$\begin{array}{llcll}
(1) & \mathrm{Zn} + 2\mathrm{KHo} & = & \mathbf{Zn}\mathrm{Ko}_2 + \mathrm{H}_2. \\
(2) & \mathbf{N}\mathrm{O}_2\mathrm{Ko} + 4\mathrm{H}_2 & = & \mathbf{N}\mathrm{H}_3 + \mathrm{KHo} + 2\mathbf{O}\mathrm{H}_2.
\end{array}$$

When stannous chloride, hydrochloric acid, and a nitrate are heated together, the tendency of the stannous chloride to combine with two more atoms of chlorine to form stannic chloride, aided by the oxidizing action of nitric acid upon the hydrogen, breaks up hydrochloric acid, with formation of stannic chloride and ammonia, thus:—

$$4\mathbf{Sn}Cl_2 + \mathbf{N}O_2Ko + 10HCl = 4\mathbf{Sn}Cl_4 + \mathbf{N}H_4Cl + KCl + 3\mathbf{O}H_2.$$

To detect *free* nitric acid in the presence of a nitrate, evaporate the solution on a water-bath with quill cuttings or white woollen fabrics. Nitric acid colours these substances yellow. Or digest the solution at a gentle heat with $\mathbf{CO}Bao''$, filter off and test the filtrate for barium by means of sulphuric acid.

QUESTIONS AND EXERCISES.

1. Explain what changes take place when nitrates are heated by themselves.
2. State what action takes place when ferrous, cuprous, and mercurous chlorides are heated with nitric acid.
3. Why can the metals Cu, Pb, Ag, be employed for the detection of nitric acid or a nitrate?
4. Explain what changes take place when a solution of potassic nitrite, potassic iodide, starch, and dilute sulphuric acid are mixed together.
5. How can ammonia be obtained from a nitrate? Describe several processes.
6. How would you test for nitrates in a soil, in sewage water, in mineral waters?
7. How much ferrous sulphate ($\mathbf{SO}Ho_2Feo'' + 6aq.$) is required for the complete decomposition of 1 grm. of pure potassic nitrate?
8. Calculate how much nitre is required to deflagrate, 1st, 1·5 grm. of sugar, and 2nd, ·5 grm. of sulphur.
9. How is free nitric acid detected in the presence of a nitrate?

NITROUS ACID, $\mathbf{N}OHo$.—Both the acid and anhydride are marked by their proneness to undergo decomposition in the presence of water, into nitric acid and nitric oxide.

REACTIONS IN THE DRY WAY.

Nitrites fuse and are decomposed on ignition into oxides, with evolution of nitrogen and oxygen. Ammonic nitrite ($\mathbf{N}OAmo$) breaks up when heated, into nitrogen and water. Mixed with carbon, potassic cyanide, sulphur, and other oxidizable bodies, nitrites deflagrate like nitrates, with which they have, in fact, most of the dry reactions in common.

REACTIONS IN THE WET WAY.

All nitrites are soluble in water; argentic nitrite, $\mathbf{N}OAgo$, although readily soluble in hot water, is difficultly soluble in cold water (300 parts), and serves for the preparation of pure nitrites, by double decomposition with neutral soluble chlorides. Dilute acids liberate $\mathbf{N}_2O_2$ and convert a portion of the nitrite into nitrate, thus:—

$$3\mathbf{N}OKo + \mathbf{S}O_2Ho_2 = \mathbf{N}_2O_2 + \mathbf{N}O_2Ko + \mathbf{S}O_2Ko_2 + \mathbf{O}H_2.$$

The reactions by which the presence of nitrous acid can be readily recognized, may be divided into two classes :—

1st. *Reactions in which the acid acts as an oxidizing agent :—*

SH_2 decomposes aqueous solutions of alkaline nitrites, with formation of N_2O_2 (of NH_3 when the reaction goes on for some time) and alkaline sulphides, thus :—

$$2NOKo + 2SH_2 = N_2O_2 + 2OH_2 + S_2K_2.$$

In acid solutions the decomposition is accompanied by a copious separation of sulphur.

$FeCl_2$, on the addition of a little hydrochloric acid, is turned dark brown, if a nitrite be present, owing to the absorption of N_2O_2 gas by a portion of the unoxidized ferrous salt. On the application of heat N_2O_2 is evolved, thus :—

$$2FeCl_2 + 4HCl + 2NOKo = Fe_2Cl_6 + 2KCl + N_2O_2 + 2OH_2.$$

$NO(NH_4O)$ breaks up, on the application of heat, into N and OH_2, the hydrogen of the NH_4 acting as the reducing agent. Nitrites containing fixed bases are decomposed in like manner, on the addition of ammonic chloride (or some other ammonic salt), thus :—

$$COAmo_2 + 2NOKo = N_4 + 4OH_2 + COKo_2.$$

KI and starch solution give in the presence of a nitrite and a dilute acid blue iodide of starch. (See under HI, p. 133).

When a dilute solution of a nitrite—say a polluted well-water—is added to a cold saturated solution of *sulphate of diamidobenzoic acid* and the nitrous acid liberated with a few drops of dilute acid (SO_2Ho_2), the solution acquires an intense *yellow* colour. As little as $\frac{1}{5}$ mgr. of N_2O_3 diffused in one litre of water can thus readily be discovered.

2nd. *Reactions in which the acid acts as a reducing agent, and is converted into nitric acid*, thus :—

$$2NOHo + O_2 = 2NO_2Ho,$$

$AuCl_3$ and Hg_2Cl_2 give metallic gold and grey metallic mercury.

$\left\{\begin{matrix} MnO_2(OKo) \\ MnO_2(OKo) \end{matrix}\right.$ oxidizes nitrites into nitrates in the presence of a mineral acid (SO_2Ho_2, HCl), and the permanganate solution is rapidly decolorized.

$Cr_2O_5Ko_2$ is reduced under similar conditions to a chromic salt. Nitrates are not affected by potassic permanganate or alkaline chromates.

PbO_2 converts NOHo into NO_2Ho ; but does not act upon dilute NO_2Ho (DISTINCTION BETWEEN NITROUS AND NITRIC ACID).

QUESTIONS AND EXERCISES.

1. Explain the changes which take place when N_2O_4 is acted upon by KHo.
2. Explain what takes place when nitrites are heated, 1st, by themselves ; 2nd, in contact with carbon or sulphur.
3. How can NOKo be separated from NO_2Ko ?
4. What is the action of dilute sulphuric acid upon NOKo ?
5. Give instances, 1st, of the oxidizing, and 2nd, of the reducing action of NOHo ; and express the changes by equations.
6. What are the products of decomposition of strongly ignited N_2O_4Pbo'', $NO(NH_4O)$, and NOKo ?
7. How can a trace of a nitrite be detected in the presence of a nitrate ?
8. Explain the action of concentrated NO_2Ho, 1st, upon starch, 2nd, upon As_2O_3.

9. How would you prepare pure $\substack{NO\\NO}Cao''$?

10. Explain the action of heat upon a solution of $\substack{NO\\NO}Cao''$ and AmCl.

HYDROCHLORIC ACID, HCl.—Gaseous hydrochloric acid is readily absorbed by water, and forms then one of the most useful acids. *Chlorides* are among the most important chemical compounds. They differ considerably in their physical properties.

REACTIONS IN THE DRY WAY.

Some chlorides are liquid and can be distilled without decomposition, such as $SnCl_4$, $SbCl_5$; $SbCl_3$ is a soft grey crystalline fusible solid which distils at 225° C.; others are solid, fusible and non-volatile at a moderate heat, such as AgCl, $PbCl_2$, $BaCl_2$, KCl, NaCl. Upon ignition certain chlorides, such as $AuCl_3$, $PtCl_4$, are decomposed with evolution of chlorine gas, first into AuCl, and $PtCl_2$, which are almost insoluble in water, and finally into Au and Pt. Magnesic chloride is decomposed by heat, in the presence of water, into magnesic oxy-chloride, Mg_2OCl_2, with elimination of 2HCl. Anhydrous ferric chloride, when heated in contact with air, is decomposed into Fe_2O_3 and $3Cl_2$.

Heated in a bead of microcosmic salt, saturated with cupric oxide, chlorides impart a *blue* colour to the *outer flame*, owing to the formation of volatile $CuCl_2$.

When a *dry* chloride is mixed with dipotassic dichromate and concentrated sulphuric acid, and gently heated in a small retort, a *deep brownish-red* gas, called **chlorochromic acid**, CrO_2Cl_2, comes off, which condenses to a like-coloured liquid, and can be collected in a receiver. The reaction which takes place is expressed by the equation:—

$$4NaCl + Cr_2O_5Ko_2 + 3SO_2Ho_2 = \underset{\text{Chlorochromic acid.}}{2CrO_2Cl_2} + 2SO_2Nao_2$$

$$+ SO_2Ko_2 + 3OH_2.$$

This liquid is speedily decomposed, on dilution with water, into chromic and hydrochloric acids, thus:—

$$CrO_2Cl_2 + 2OH_2 = CrO_2Ho_2 + 2HCl;$$

or by aqueous ammonia or potassic hydrate into the corresponding salts. The presence of chromic acid, and indirectly of hydrochloric acid, is inferred from the yellow precipitate which a plumbic salt produces with their solutions. This reaction is employed *for recognizing a chloride in the presence of a bromide.* The latter yields bromine when treated similarly, and a colourless solution of NH_4Br.

The presence of an iodide, yielding free iodine, would give rise to the formation of explosive black insoluble *iodide of nitrogen,* on the addition of $\mathbf{N}H_3$; the reaction can, therefore, only be performed after the previous removal of the iodide.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC CHLORIDE is employed.

All chlorides may be divided into:—

1st. *Chlorides insoluble in water*, such as $AgCl$ and $\mathbf{Hg}_2Cl_2$, which are quite insoluble; $\mathbf{Pb}Cl_2$, soluble in 135 parts of cold water, readily soluble in boiling water; and $\mathbf{Cu}_2Cl_2$, almost insoluble in water and in dilute sulphuric acid; soluble in ammonia, HCl and $NaCl$ solutions. $\mathbf{Au}Cl$ and $\mathbf{Pt}Cl_2$, are almost insoluble in water.

2nd. *Chlorides which are soluble in water*, comprising all other chlorides. The majority of the chlorides of the most powerfully basilous metals, as K, Na, Ba, etc., are less soluble in aqueous HCl, than in $\mathbf{O}H_2$.

The chlorides of the less basilous metals (with the exception of Hg and Ag) are decomposed by water, with formation of free acid and metallic oxides, *ex. gr.* $\mathbf{As}Cl_3$, or of some insoluble oxychloride ($\mathbf{Sb}Cl_3$, $\mathbf{Bi}Cl_3$), soluble, however, in excess of HCl.

In order to ascertain the presence of a soluble chloride, or of hydrochloric acid, we have merely to add a soluble argentic, mercurous or plumbic salt, when a white precipitate is produced. The first of these salts answers every purpose, and is therefore invariably employed to detect hydrochloric acid or a metallic chloride.

$\mathbf{N}O_2Ago$ gives a *white curdy* precipitate of **argentic chloride**, $AgCl$, especially from a solution acidulated with dilute nitric acid. The precipitate turns *violet* on exposure to light. It is insoluble in dilute nitric acid; soluble in ammonic hydrate, but is reprecipitated unchanged, on the addition of nitric acid; it is likewise soluble in potassic cyanide and sodic hyposulphite; soluble to a considerable extent in alkaline chlorides, from which $AgCl$ is reprecipitated on dilution. Argentic chloride fuses without undergoing decomposition, to a horn-like mass, called *hornsilver*, when gently heated.

Chlorides are detected also by heating with a little black manganic oxide and concentrated sulphuric acid, when chlorine is evolved according to the equation:—

$$\mathbf{Mn}O_2 + 2NaCl + 2\mathbf{S}O_2Ho_2 = Cl_2 + \mathbf{S}O_2Mno'' + \mathbf{S}O_2Nao_2 + 2\mathbf{O}H_2.$$

This gas is readily recognized by its characteristic odour and bleaching properties, its yellowish-green colour, and its action upon iodized starch paper, or upon a dilute solution of potassic iodide and *freshly prepared* starch solution, giving rise to the formation of *blue iodide of starch.*

Concentrated sulphuric acid liberates gaseous hydrochloric acid from chlorides, thus:—

$$2NaCl + \mathbf{S}O_2Ho_2 = \mathbf{S}O_2Nao_2 + 2HCl.$$

$\mathbf{Hg}Cl_2$, $\mathbf{Hg}_2Cl_2$, $AgCl$, $\mathbf{Pb}Cl_2$, $\mathbf{Sn}Cl_2$, and $\mathbf{Sn}Cl_4$, are decomposed, with difficulty only, or not at all, by concentrated sulphuric acid.

In order to effect the decomposition of insoluble chlorides, such as AgCl, Hg_2Cl_2, and $PbCl_2$, they are mixed with fusion mixture, perfectly free from alkaline chlorides, and heated in a porcelain crucible. The chlorine is thereby transferred to the alkali metals, and may be readily detected by means of argentic nitrate in the aqueous extract, after acidulating with dilute nitric acid. The same may be effected also by galvanic action, by bringing the solid chlorides into contact with metallic zinc, when soluble $ZnCl_2$ is formed.

Traces of *free* HCl, in the presence of a soluble chloride, are best detected by gently heating with MnO_2 or PbO_2, and passing the evolved chlorine into a solution of potassic iodide and starch. The chlorine liberates iodine ($2KI + Cl_2 = 2KCl + I_2$), which forms with the starch blue iodide of starch.

QUESTIONS AND EXERCISES.

1. How are the several solid chlorides acted upon by heat?
2. How is chlorochromic acid prepared?
3. Classify all chlorides according to their solubility in water.
4. Describe the most characteristic tests for chlorine, as well as for hydrochloric acid or chlorides.
5. How are insoluble chlorides examined?
6. How would you detect free HCl in the presence of a metallic chloride?
7. Explain the action of distilled water, of chlorine water, ammonic hydrate, potassic cyanide, sodic hyposulphite, and sulphuric acid upon AgCl, Hg_2Cl_2, and $PbCl_2$.
8. You have given to you 100 c.c. of a liquid containing free HCl and a solution of sodic chloride. 50 c.c. of the liquid gave 2·345 grms. of AgCl. After evaporation and ignition of the other 50 c.c. the residue yielded on precipitation with argentic nitrate 1·596 grm. of AgCl. What is the percentage of HCl and of sodic chloride in the liquid?

CHLORIC ACID, $\left\{\begin{matrix} OCl \\ OHo \end{matrix}\right.$.—Obtained in combination with calcium, by passing chlorine through a solution of calcic hydrate and potassic carbonate to complete saturation. To a concentrated solution of the calcic chlorate, formed according to the equation:—

$$6CaHo_2 + 6Cl_2 = \left\{\begin{matrix} OCl \\ O \\ \end{matrix}\right. \!\! \begin{matrix} \\ Cao'' \\ \end{matrix} \!\! \left\{\begin{matrix} O \\ OCl \end{matrix}\right. + 5CaCl_2 + 6OH_2,$$

add a solution of potassic chloride, when calcic chloride and potassic chlorate, $\left\{\begin{matrix} OCl \\ OKo \end{matrix}\right.$, are formed by double decomposition. Potassic chlorate, being little soluble in cold water, and still less so in a solution of calcic chloride, crystallizes out, and is washed with cold water and purified by recrystallization.

REACTIONS IN THE DRY WAY.

All chlorates are decomposed by heat; they fuse and evolve oxygen, or a mixture of chlorine and oxygen, according to the greater or less affinity of the metal for oxygen or chlorine, leaving a residue, consisting of a metallic chloride, oxychloride, or oxide.

On heating a few crystals of potassic chlorate in a test-tube, the presence of oxygen can be shown by introducing a glowing splinter of wood into the test-tube. On dissolving the fused mass in water, and adding a drop of argentic nitrate, a white curdy precipitate is obtained, whilst a solution of a pure chlorate (unignited) gives no precipitate.

Chlorates part with their oxygen far more readily, upon ignition, than nitrates. When mixed with oxidizable substances, such as C, S, P, or KCy, they explode violently, even when gently rubbed together in a mortar, or when moistened with a drop of concentrated sulphuric acid. Care should, therefore, be taken to powder, or heat together, only very small quantities of a chlorate and organic substances.

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC CHLORATE may be employed.

All chlorates are soluble in water. In order, therefore, to detect chlorates, we avail ourselves of their powerful oxidizing action, and their leaving for the most part a chloride on ignition. Strong hydrochloric and sulphuric acids decompose chlorates, with evolution of chlorine and formation of lower oxides of chlorine.

Concentrated sulphuric acid decomposes potassic chlorate even in the cold, a *greenish-yellow gas*, called **chloric peroxide**, $\mathbf{O}_4Cl_2$, comes off, which is recognized by its suffocating odour. On the application of heat (especially on operating with somewhat large quantities) violent explosions occur. A few small crystals only of the chlorate should, therefore, be employed, and the test-tube should be held with its mouth turned away from the operator. The change may be expressed by the equation :—

$$3\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right. + 2SO_2Ho_2 = 2SO_2HoKo + \underset{\text{Potassic perchlorate.}}{\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}Ko\end{matrix}\right.} + \underset{\text{Chloric peroxide.}}{\left\{\begin{matrix}\mathbf{O}Cl\\ O_2\\ \mathbf{O}Cl\end{matrix}\right.} + \mathbf{O}H_2.$$

HCl, especially when heated, decomposes potassic chlorate, giving off a mixture of chloric peroxide and free chlorine, called *euchlorine*, thus :—

$$8\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right. + 24HCl = 3\left\{\begin{matrix}\mathbf{O}Cl\\ O_2\\ \mathbf{O}Cl\end{matrix}\right. + 9Cl_2 + 8KCl + 12\mathbf{O}H_2.$$

A solution of indigo (sulphindigotic acid) is decolorized on the addition of a solution of a chlorate and a little sulphuric acid, by a reaction analogous to that produced by free nitric acid.

Perchlorates are more stable than chlorates. Concentrated sulphuric acid fails to decompose perchloric acid in the cold and with difficulty only on heating. (DISTINCTION FROM CHLORIC ACID.) Hydrochloric, nitric, and sulphurous acids do not decompose aqueous solutions of perchlorates, nor is indigo solution decolorized. All perchlorates are soluble in water, most of them freely. Potassic perchlorate is sparingly soluble in water, insoluble in alcohol.

In order *to distinguish a nitrate from a chlorate*, dissolve a small portion of the two salts in water, and add a few drops of argentic nitrate to make sure that no chloride is present. Ignite another portion strongly till the evolution of oxygen ceases; allow to cool, and dissolve out with hot water. To one portion of the solution add a few drops of dilute nitric acid, and then argentic nitrate. A white curdy precipitate indicates the presence of a chloride, and, indirectly, of a chlorate. To the other portion of the solution add potassic iodide and starch solution, and then a few drops of acetic acid; a blue coloration of iodide of starch proves the presence of a nitrite, derived from the potassic nitrate.

If a *chloride be present*, as *well as a chlorate and nitrate*, a solution of argentic sulphate must be added to the solution, as long as a precipitate comes down. The $AgCl$ is filtered off, and the filtrate evaporated to dryness, with the addition of a little pure sodic carbonate, and the residue strongly ignited. The dry mass is extracted with a little boiling water, filtered, and argentic nitrate added to a portion of the acidulated (NO_2Ho) solution, as long as a precipitate comes down. The remaining portion is tested for nitric acid, either by the iodide of starch reaction, or by means of a ferrous salt and sulphuric acid.

QUESTIONS AND EXERCISES.

1. State briefly how potassic chlorate is prepared.
2. Describe the changes which potassic chlorate undergoes on ignition.
3. Explain the action—1st, of concentrated sulphuric acid; 2nd, of concentrated hydrochloric acid upon potassic chlorate. Give equations.
4. How can a chlorate be detected in the presence of a chloride?
5. How can a nitrate and a chloride be recognized in the presence of a chlorate?
6. Introduce some strips of metallic copper into a mixture of potassic chlorate, arsenious acid and hydrochloric acid, and explain why no precipitate of metallic arsenic is obtained on the copper.

HYPOCHLOROUS ACID, $ClHo$.—The salts which this acid forms possess considerable interest, on account of the powerful bleaching action which they exert in the presence of acids. Of importance are the sodic and calcic hypochlorites, which are obtained along with the corresponding chlorides,[*] by passing chlorine *in the cold* through a solution of the carbonates or hydrates. An important compound closely related to the hypochlorites is the calcic chlorohypochlorite (a constituent of chloride of lime or *bleaching powder*[†]), which appears to be formed according to the equation:—

$$CaHo_2 + Cl_2 = Ca(OCl)Cl + OH_2.$$

---

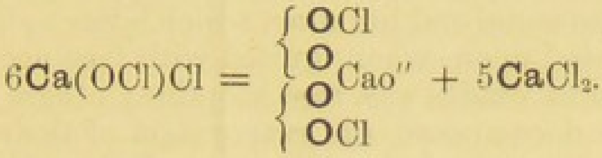
[*] In the case of the monad metals the body R'_2OCl_2 is a mere mixture of $ClRo$ and RCl, whilst the calcic compound seems to be a definite compound of Cl_2Cao'' and $CaCl_2 = 2Ca(OCl)Cl$.

[†] The actual composition of this important body is usually expressed by the formula:—$Ca(OCl)Cl,CaO,2OH_2$, requiring 32·42 p.c. of chlorine, more accurately, however, by that of $Ca(OCl)Cl,CaHo_2$, which requires 35·32 p.c. of chlorine.

Hypochlorites are gradually decomposed on exposure to air (owing probably to the action of the carbonic anhydride contained in air). Dilute acids liberate chlorine, and it is on this account that hypochlorites are of such great value as *disinfectants* and *bleaching agents.*

REACTIONS IN THE DRY WAY.

Hypochlorites are converted into chlorates (which give off oxygen when ignited), and chlorides, thus :—



$$6\mathbf{Ca}(\mathrm{OCl})\mathrm{Cl} = \begin{array}{l}\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\end{array}\right.\\ \left\{\begin{array}{l}\mathbf{O}\\ \mathbf{O}\mathrm{Cl}\end{array}\right.\end{array}\mathrm{Cao}'' + 5\mathbf{Ca}\mathrm{Cl}_2.$$

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF CALCIC OR SODIC HYPOCHLORITE, ClNao.

All hypochlorites are soluble in water. Their aqueous solutions bleach vegetable colours. On heating or evaporating dilute solutions of hypochlorites, they are decomposed into chlorides and chlorates, concentrated solutions into chlorides and oxygen. Dilute hydrochloric acid decomposes them with evolution of chlorine. (DISTINCTION BETWEEN HYPOCHLORITES AND CHLORATES.) Hypochlorites yield oxygen to readily oxidizable substances, and become converted into chlorides; the detection of hypochlorous acid is based upon the various processes of oxidation to which its salts can give rise, thus :—

$\mathbf{As}_2\mathrm{O}_3$ is oxidized to $\mathbf{As}_2\mathrm{O}_5$.
$\mathbf{Mn}\mathrm{Cl}_2$ „ „ $\mathbf{Mn}\mathrm{O}_2$.
$\mathbf{Pb}\mathrm{O}$ „ „ $\mathbf{Pb}\mathrm{O}_2$.
$\mathbf{Pb}\mathrm{S}$ „ „ $\mathbf{S}\mathrm{O}_2\mathrm{Pbo}''$.
$\left\{\begin{array}{l}\mathbf{C}\mathrm{OHo}\\ \mathbf{C}\mathrm{OHo}\end{array}\right.$ „ „ $2\mathbf{C}\mathrm{O}_2 + \mathbf{O}\mathrm{H}_2$.

Indigo or litmus is readily decolorized.

QUESTIONS AND EXERCISES.

1. Give the graphic formula for calcic chlorohypochlorite.
2. Give illustrations of the oxidizing action of hypochlorites. Express the changes by equations.
3. How is *bleaching powder* prepared ?
4. Explain the bleaching action of an aqueous solution of a hypochlorite.
5. What change takes place—1st, when a hypochlorite is ignited by itself ; 2ndly, when a concentrated solution of a hypochlorite is boiled ?
6. Explain the deodorizing action of hypochlorites when brought in contact with $\mathbf{S}\mathrm{H}_2$, $\mathbf{S}\mathrm{Am}_2$, $\mathbf{P}\mathrm{H}_3$, $\mathbf{N}\mathrm{H}_3$.
7. How can a hypochlorite be distinguished in the presence of a chloride ?
8. A sample of *bleaching powder* contains 26·5 per cent. of chlorine. How much $\mathbf{As}_2\mathrm{O}_3$ by weight will be required to deoxidize (" dechlorinize ") 1·235 grm. of the bleaching powder ?

HYDROBROMIC ACID, HBr.—The element bromine occurs in nature mainly in combination with the fixed alkalies and the metals of the alkaline earths (calcium, magnesium), forming salts, called bromides, which resemble the chlorides of the same metals very closely, and from which we derive both bromine and hydrobromic acid.

REACTIONS IN THE DRY WAY.

Most bromides remain unaltered when ignited; others are volatilized without decomposition. **$AuBr_3$** and **$PtBr_4$** are decomposed upon ignition into metal and bromine, which latter volatilizes. Many bromides are acted upon, when ignited with free access of air, and are converted into oxides and free bromine; others again, such as **Al_2Br_6**, etc., are decomposed, on evaporation of their aqueous solutions, into oxides and hydrobromic acid. KBr and NaBr are converted, to a great extent, into KCl and NaCl, on repeated ignition with ammonic chloride. When fused with hydric potassic sulphate, bromides are decomposed into sulphates, with evolution of sulphurous anhydride and bromine. The few insoluble bromides of the heavy metals are converted into soluble alkaline bromides by fusion with alkaline carbonates.

Heated before the inner flame of the blow-pipe on a bead of microcosmic salt, in which a little cupric oxide has been diffused, bromides impart a *blue* colour to the flame, which passes into *green*, especially at the edges. This distinction between chlorides and bromides is, however, not very marked.

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC BROMIDE, KBr, may be employed.

All metallic bromides can be divided into:—

1st. *Bromides which are insoluble in water*, such as AgBr, **$'Hg'_2Br_2$**, **$PbBr_2$** (less soluble in water than **$PbCl_2$**), and—

2nd. *Bromides which are soluble in water*, comprising all other bromides.

Certain bromides, *e.g.*, **$SbBr_3$**, **$BiBr_3$**, are decomposed by water into insoluble oxybromides and hydrobromic acid. They resemble in this respect the corresponding chlorides.

In order to detect hydrobromic acid or a soluble bromide, add a solution of an argentic (mercurous or plumbic) salt to the solution, when a *yellowish-white* precipitate of **argentic bromide**, AgBr, is formed, which is insoluble in dilute nitric acid, somewhat soluble in concentrated ammonic hydrate, readily soluble in potassic cyanide or sodic hyposulphite. By decanting the supernatant liquid, washing with a little water, and treating the precipitated argentic bromide with strong hydrochloric acid, reddish-brown fumes of bromine are evolved which colour starch paste *yellowish*. (DISTINCTION BETWEEN AgBr AND AgCl.)

Insoluble bromides, such as AgBr, **Hg_2Br_2**, **$PbBr_2$**, are best decomposed by heating in an ignition-tube with alkaline carbonates (free from chlorides). The aqueous extract is tested for hydrobromic acid, and the insoluble residue for silver or lead. **Hg_2Br_2** gives a sublimate of metallic mercury.

In the absence of any well-marked distinguishing features in the argentic bromide precipitate, it is preferable to liberate bromine from soluble bromides, and to cause the *reddish-brown* vapour to act upon starch paste with formation of yellowish *bromide of starch.*

Nitrous acid (or a nitrite and dilute sulphuric acid) does not liberate any bromine from pure soluble bromides. (DISTINCTION BETWEEN BROMIDES AND IODIDES.) All bromides are, however, decomposed by chlorine, with evolution of bromine, which remains dissolved in the aqueous solution. On shaking with a little ether, the bromine is taken up by the ether, forming a yellowish-red liquid, which floats on the top of the saline aqueous solution. This ethereal liquid may be removed by means of a small pipette, and on being treated with potassic hydrate is converted, on evaporation, into potassic bromide and potassic bromate, thus:—

$$3Br_2 + 6KHo = 5KBr + \left\{\begin{matrix}OBr\\OKo\end{matrix}\right. + 3OH_2.$$

Bromine is obtained from natural bromides, such as potassic, magnesic, and calcic bromides, by reactions analogous to those employed for the preparation of chlorine from common salt (page 123); for instance, on distilling with manganic oxide and concentrated sulphuric acid, thus:—

$$2KBr + MnO_2 + 2SO_2Ho_2 = Br_2 + SO_2Ko_2 + SO_2Mno'' + 2OH_2,$$

or by distilling a bromide with dipotassic dichromate and sulphuric acid, thus:—

$$6KBr + Cr_2O_5Ko_2 + 7SO_2Ho_2 = 3Br_2 + S_3O_6Cr_2o^{vi} + 4SO_2Ko_2 + 7OH_2.$$

A mixture of a bromide and manganic oxide, or dipotassic dichromate is introduced into a tubulated retort (Fig. 16), with concentrated sulphuric acid, diluted with its own weight of water, and gently heated over a gas flame. The reddish-brown vapour of bromine passes over, and condenses in a flask (which should be kept cold by a stream of water, or better still, in a vessel surrounded with ice) to a reddish-brown heavy liquid.

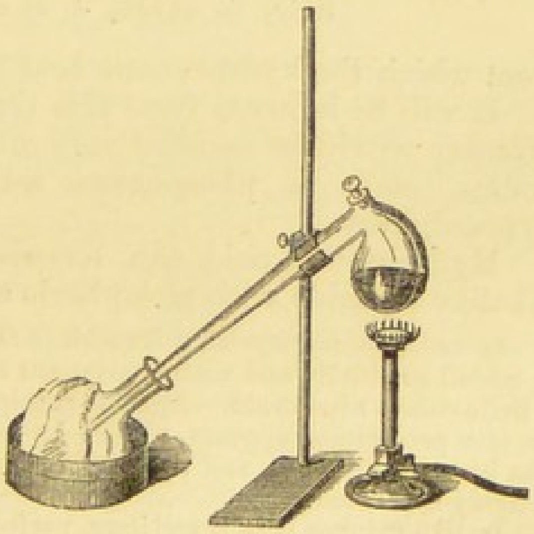


FIG. 16.

Concentrated sulphuric acid alone evolves hydrobromic acid, together with bromine and sulphurous anhydride, thus:—

$$4KBr + 3SO_2Ho_2 = Br_2 + 2HBr + 2SO_2Ko_2 + 2OH_2 + SO_2.$$

Concentrated nitric acid evolves bromine, together with nitrous fumes, thus:—

$$2KBr + 4\mathbf{N}O_2Ho = Br_2 + 2\mathbf{N}O_2Ko + \mathbf{N}_2O_4 + 2\mathbf{O}H_2.$$

In the two last reactions the sulphuric and nitric acids act as oxidizing agents, performing in fact the functions of the manganic oxide and dipotassic dichromate in the former reactions.

It is obvious that the hydrogen may also be removed from hydrobromic acid (or the metal from a metallic bromide) by other oxidizing agents, such as permanganates and metallic peroxides, in the presence of an acid.

Bromine is a heavy reddish-brown liquid, of disagreeable odour, resembling the odour of chlorine. It boils at 63° C., and volatilizes at the ordinary temperature. Bromine vapour bleaches vegetable colours like chlorine gas. It is difficultly soluble in water, somewhat more soluble in alcohol, and readily soluble in ether to a yellowish-red liquid.

Bromine (like chlorine) is an oxidizing agent, *i.e.*, it is eager to combine with hydrogen, and is capable of decomposing water, sulphuretted hydrogen, etc., under favourable circumstances (*e.g.*, sunlight), with liberation of oxygen, sulphur, etc. We avail ourselves of this tendency to prepare hydrobromic acid, which cannot be obtained pure by distilling a bromide with sulphuric acid. By passing sulphuretted hydrogen through bromine suspended in water, a colourless solution of hydrobromic acid is obtained, and sulphur separates, thus:—

$$Br_2 + \mathbf{S}H_2 = 2HBr + S.$$

This solution always contains some sulphuric acid, owing to a secondary reaction of the bromine upon water, in the presence of nascent sulphur:—

$$3Br_2 + 4\mathbf{O}H_2 + S = 6HBr + \mathbf{S}O_2Ho_2,$$

from which the hydrobromic acid is separated by distillation.

It will be inferred from this that the decomposition of water by bromine would be assisted very much by the presence of deoxidizing bodies, such as phosphorus, metallic hypophosphites, sulphites, hyposulphites.

Hydrobromic acid can likewise be prepared by distilling an alkaline bromide with phosphoric acid.

In order *to distinguish a bromide in the presence of a chloride,* argentic nitrate is added gradually and with continuous agitation to the solution, acidulated with a little dilute nitric acid. AgBr is precipitated first, and by filtering off, as soon as the precipitate appears white—an indication that the whole of the bromide has been precipitated, and that AgCl begins to fall out—the two acids may be roughly separated.

In like manner it is sometimes useful to separate, or practically to concentrate, small quantities of bromides and also iodides, for in a mixed solution of chlorides, bromides and iodides, the iodine falls out first as yellow AgI, the bromine next as yellowish-white AgBr, and the chlorine last, as white AgCl. With care and patience, a fair *approximate* fractional separation may be effected.

It is, however, preferable to employ the reaction described at page 122, viz., of distilling a mixture of a dry chloride and bromide with dipotassic dichromate and concentrated sulphuric acid, and of obtaining chlorochromic acid and bromine, the former being decomposed by water into $\mathbf{CrO_2Ho_2}$ and HCl. The bromine remaining unchanged, can be removed by ether. On adding AmHo to the bromine solution a colourless liquid containing ammonic bromide and bromate is obtained.

QUESTIONS AND EXERCISES.

1. Describe a method by which bromine can be obtained from a soluble bromide.
2. How would you prepare HBr from a soluble bromide?
3. Explain the action of heat upon solid soluble bromides.
4. Classify all bromides according to their solubility in water.
5. Describe the most characteristic tests for bromine, and for HBr.
6. Explain the action of chlorine, dilute HCl, concentrated $\mathbf{SO_2Ho_2}$, concentrated $\mathbf{NO_2Ho}$, and of $\mathbf{POHo_3}$ upon potassic bromide.
7. How is HBr distinguished from HCl?
8. What takes place when bromine, phosphorus, and water are brought together?
9. Explain the action of $\mathbf{SH_2}$, $\mathbf{SONao_2}$, and $\mathbf{SSONao_2}$ upon bromine suspended in water.
10. Give the atomic and volume weights of bromine and of hydrobromic acid.
11. 1·56 grm. of argentic bromide is heated in a current of chlorine; what will be the weight of the silver salt left?

BROMIC ACID, $\left\{\begin{matrix}\mathrm{OBr}\\ \mathrm{OHo}\end{matrix}\right.$.—Obtained in combination with potassium by adding bromine to a moderately concentrated solution of potassic hydrate. Potassic bromate crystallizes out from the slightly yellowish coloured liquid, and is purified from potassic bromide by washing with water and recrystallization. The reaction takes place according to the equation :—

$$3Br_2 + 6KHo = 5KBr + \left\{\begin{matrix}\mathrm{OBr}\\ \mathrm{OKo}\end{matrix}\right. + 3OH_2.$$

The free acid is obtained by decomposing baric bromate with dilute sulphuric acid.

REACTIONS IN THE DRY WAY.

All bromates are decomposed by heat. Some, *e.g.*, the alkaline bromates, fuse and evolve oxygen, leaving a bromide; others, such as zincic and magnesic bromates, leave an oxide and give off oxygen and bromine; others, again, leave an oxide and a bromide, *e.g.*, plumbic and cupric bromates. When mixed with readily oxidizable substances, such as carbon, sulphur, etc., bromates deflagrate.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC BROMATE, $\left\{\begin{matrix}\mathrm{OBr}\\ \mathrm{OKo}\end{matrix}\right.$.

All bromates are soluble in water. Argentic and mercurous bromates are difficultly soluble.

Dilute sulphuric, nitric, or phosphoric acid liberates bromic acid from its salts, which, however, exhibits great instability and breaks up into bromine, oxygen, and water.

Bromates are readily broken up by deoxidizing substances, such as sulphurous and phosphorous acids, sulphuretted hydrogen, etc., with formation of sulphuric and phosphoric acids, sulphur and water, and liberation of bromine. A mixture of potassic bromide and bromate, when acted upon by dilute acids, is decomposed into bromine and water, thus :—

$$5KBr + \left\{\begin{matrix}\mathrm{OBr}\\ \mathrm{OKo}\end{matrix}\right. + 6HCl = 3Br_2 + 3OH_2 + 6KCl.$$

The weak affinity of bromine for oxygen is, moreover, rendered apparent on boiling bromine with such powerful oxidizing agents as nitric acid, potassic chlorate or manganate, which are without action upon it.

A bromate in the presence of a chlorate is readily distinguished by precipitation with NO_2Ago; the *white* **argentic bromate**, $\left\{\begin{matrix}OBr\\OAgo\end{matrix}\right.$, gives off bromine on being treated with HCl. The residue which bromates and chlorates leave on ignition may also be tested by any of the methods described under hydrochloric and hydrobromic acids.

QUESTIONS AND EXERCISES.

1. State how potassic and baric bromates are prepared.
2. Describe the changes which metallic bromates undergo when submitted to heat.
3. Explain the action of dilute acids upon potassic bromate.
4. What is the action of $\mathbf{SH_2}$, $\mathbf{SO_2}$, or $\mathbf{P_2O_3}$ upon potassic bromate?
5. How can a bromate be distinguished in the presence of a bromide?
6. How can a bromate be distinguished from a chlorate or nitrate?
7. How is free bromic acid obtained?
8. How much potassic bromate should there be obtained from 50 grms. of bromine?

HYDRIODIC ACID, HI.—Occurs in nature in the form of soluble iodides (KI, NaI, $\mathbf{MgI_2}$, $\mathbf{CaI_2}$), in sea water, in the ashes of marine plants, in some mineral springs, from which bodies iodine is obtained, by processes similar to those employed for the extraction of bromine from bromides.

REACTIONS IN THE DRY WAY.

Most iodides undergo decomposition when heated by themselves, either with or without exclusion of air. $\mathbf{AuI_3}$ and $\mathbf{PtI_4}$ give off iodine, and leave the metals; others are partially decomposed, giving off iodine, and leaving an oxide of the metal. The alkaline iodides, however, can be heated to fusion, without undergoing any decomposition. Ignition with ammonic chloride converts iodides only partially into chlorides. On fusing cupric oxide in a bead of microcosmic salt, and introducing a little potassic iodide into the bead and heating in the inner blowpipe flame, the outer flame becomes of a *fine emerald-green colour.*

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF POTASSIC IODIDE, KI.

All metallic iodides may be divided into—

1st. *Iodides insoluble in water*, such as AgI, $\mathbf{Hg_2I_2}$, $\mathbf{HgI_2}$, $\mathbf{PbI_2}$, $\mathbf{Cu_2I_2}$ ($\mathbf{BiI_3}$, $\mathbf{AuI_3}$, $\mathbf{PtI_4}$), and $\mathbf{PdI_2}$, and—

2nd. *Iodides soluble in water*, comprising all others. The iodides of the heavy metals are less soluble than the corresponding bromides or chlorides.

Soluble iodides may be examined in two ways—

1st. *By precipitation or conversion of the soluble into insoluble iodides.*

NO_2Ago gives a *yellowish-white* precipitate of **argentic iodide,** AgI, insoluble in dilute nitric acid, almost entirely insoluble in ammonic hydrate (DISTINCTION BETWEEN HI AND HCl, OR HBr); soluble in potassic cyanide.

$N_2O_4Hg_2o''$ gives a *yellowish-green* precipitate of **mercurous iodide,** Hg_2I_2, very slightly soluble in water, insoluble in dilute nitric acid, soluble in potassic iodide.

$HgCl_2$ gives a beautiful *vermillion-red* precipitate of **mercuric iodide,** HgI_2, little soluble in water, soluble in alcohol, and soluble also in excess either of mercuric chloride or of potassic iodide.

$\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$ gives a *bright yellow* precipitate of **plumbic iodide,** PbI_2, soluble, like the chloride, in hot water (120 parts), from which it crystallizes out, on cooling, in beautiful shining yellow scales; soluble in dilute nitric acid.

SO_2Cu_2o'' (**cuprous sulphate**), obtained by treating SO_2Cuo'' with $SOHo_2$, produces a *dirty white* precipitate of **cuprous iodide,** Cu_2I_2, insoluble in water, sparingly soluble in HCl, soluble in ammonic salts and free NH_3. This precipitate is of particular interest, because *chlorides and bromides cannot be precipitated in like manner*, and because it serves frequently for removing iodides from dilute solutions containing chlorides and bromides.

2nd. *By liberating iodine*, and causing the iodine vapour to act upon starch paste. This may be effected in several ways.

On mixing a dilute solution of potassic iodide with a few drops of hydrochloric acid, and then adding a drop or two of a solution of potassic nitrite, iodine is instantly liberated, and may be detected by the yellowish-brown tint it imparts to the solution, or better still by allowing it to act upon a *freshly-prepared* solution of starch, to which it imparts a *fine blue colour*, owing to the formation of *iodide of starch.* This is one of the most delicate tests. The reaction serves equally well for the detection of $NOHo$ (comp. page 121), or NO_2Ho, after reducing to $NOHo$ (see page 119), thus :—

$$2KI + 2NOKo + 4HCl = I_2 + 4KCl + N_2O_2 + 2OH_2.$$

A solution containing free iodine may also be shaken up with a few drops of carbon disulphide, which dissolves the iodine, assuming a fine violet colour. Ether dissolves iodine, but the colour which is produced resembles ether coloured by bromine.

Nitric acid containing a lower oxide of nitrogen, acts like a nitrite.

Bromine or chlorine (or what amounts to the same, ClNao and HCl, or metallic peroxides or perchlorides, *e.g.*, BaO_2, PbO_2, MnO_2 and HCl, or Fe_2Cl_6 and HCl), liberates iodine from iodides. According to the quantity of iodide employed, iodine separates either as a bluish-black powder, forming a brown liquid, or in the form of deep violet fumes, which condense to beautiful fern-leaf shaped crystals.

The methods adopted for the extraction of iodine from metallic iodides are all based upon the expulsion of iodine by oxygen (or its equivalent of chlorine or bromine). Iodine is obtained by distilling an iodide with an oxidizing agent and sulphuric acid, *e.g.*:—

$$2KI + MnO_2 + 2SO_2Ho_2 = I_2 + SO_2Mno'' + SO_2Ko_2 + 2OH_2, \text{ or}$$

$$6KI + Cr_2O_5Ko_2 + 7SO_2Ho_2 = 3I_2 + S_3O_6Cr_2o^{vi} + 4SO_2Ko_2 + 7OH_2.$$

Concentrated acids, such as SO_2Ho_2, or NO_2Ho, decompose iodides with separation of bluish-black scales of iodine and evolution of SO_2 or lower oxides of nitrogen, thus:—

$$2KI + 2SO_2Ho_2 = I_2 + SO_2Ko_2 + SO_2 + 2OH_2.$$
$$2KI + 4NO_2Ho = I_2 + 2NO_2Ko + N_2O_4 + 2OH_2.$$

On fusing an iodide with SO_2HoKo, iodine is likewise liberated, thus:—

$$2KI + 4SO_2HoKo = 3SO_2Ko_2 + SO_2 + I_2 + 2OH_2.$$

On examining for *traces* of iodine by acting upon an iodide with chlorine, excess should be carefully avoided, as the iodine is oxidized by the chlorine to colourless *iodic acid*, which does *not* yield the blue colour of iodide of starch, or the violet colour of the carbon disulphide solution. The blue colour of iodide of starch is destroyed by various reducing agents, such as SO_2, SH_2, As_2O_3, $SnCl_2$, and Hg_2Cl_2, or by any organic reducing body. Alkalies destroy the colour, dilute acids (even acetic acid) restore it again. On heating iodide of starch the colour disappears, but reappears on cooling.

The destruction of the blue colour of iodide of starch by various reducing agents is due to the decomposition of water by the iodine, with formation of HI, the oxygen being transferred to the reducing agent, thus:—

$$SOHo_2 \text{ (a dilute solution) } + I_2 + OH_2 = SO_2Ho_2 + 2HI.$$
$$SH_2 + I_2 = 2HI + S.$$
$$AsHo_3 + I_2 + OH_2 = 2HI + AsOHo_3.$$

Hydriodic acid is usually prepared by acting upon iodine suspended in water (or dissolved in hydriodic acid), with a current of SH_2. Sulphur separates and is removed by filtration, and the solution of hydriodic acid concentrated by distillation. Its aqueous solution absorbs oxygen from the air, water being formed and iodine liberated, which dissolves in the undecomposed hydriodic acid, and imparts a brown colour to the liquid.

Insoluble iodides may be fused with alkaline carbonates, or decomposed galvanically by means of metallic zinc. The aqueous extract is examined for iodine, and the residue for the metal.

QUESTIONS AND EXERCISES.

1. How would you extract iodine from MgI_2? Give several methods, and express the changes by equations.
2. Explain the action of heat upon solid iodides.
3. Classify all iodides according to their solubility in water.

4. Explain how you would distinguish HCl, HBr, and HI, when occurring in one and the same substance.
5. Explain the action of iodine vapour upon starch.
6. Why is it preferable to liberate iodine by means of N_2O_3, instead of by bromine or chlorine?
7. How would you prepare a solution of hydriodic acid?
8. How much iodine can be obtained from 100 lb. of NaI?
9. Give graphic formulæ for cuprous and mercurous iodides.
10. Explain how you would distinguish free iodine in the presence of an iodide.
11. What action takes place when a dilute solution of SO_2 acts upon iodine, and how can iodine be made the measure for SO_2 and *vice versâ?*
12. 10 litres of a mineral water yield ·134 grm. of AgI; how much iodine is there in 100,000 parts of the water?

IODIC ACID, $\left\{\begin{array}{l}OI\\OHo\end{array}\right.$.—Potassic iodate is obtained, like the corresponding chlorate and bromate, by dissolving iodine in potassic hydrate. The iodate crystallizes out first, being much less soluble than KI. The free acid can be prepared by decomposing baric iodate with sulphuric acid, thus:—

$$\begin{array}{l}\left\{\begin{array}{l}OI\\O\end{array}\right.\\\left\{\begin{array}{l}O\\OI\end{array}\right.\end{array} Bao'' + SO_2Ho_2 = 2\left\{\begin{array}{l}OI\\OHo\end{array}\right. + SO_2Bao''.$$

Iodic acid is also obtained by the action of strong boiling nitric acid upon iodine, or by passing chlorine through iodine suspended in water.

REACTIONS IN THE DRY WAY.

All iodates are decomposed upon ignition, some breaking up into an iodide, with evolution of oxygen; others into metallic oxides, iodine and oxygen being expelled. When heated with charcoal they explode less violently than chlorates or bromates.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC IODATE, $\left\{\begin{array}{l}OI\\OKo\end{array}\right.$.

Alkaline iodates alone are soluble in water.

$BaCl_2$ gives a *white* precipitate of **baric iodate**, nearly insoluble in water and difficultly soluble in dilute nitric acid.

NO_2Ago produces a *white* crystalline precipitate of **argentic iodate**, sparingly soluble in water and in dilute nitric acid, readily soluble in ammonic hydrate (DISTINCTION FROM HI). On the addition of a reducing agent, *e.g.*, $SOHo_2$, to the clear ammoniacal solution of argentic iodate, a precipitate of AgI is obtained, thus:—

$$\left\{\begin{array}{l}OI\\OAgo\end{array}\right. + 3SOHo_2 = AgI + 3SO_2Ho_2.$$

Potassic iodate is decomposed by SH_2, with formation of potassic iodide and sulphuric acid, and precipitation of sulphur; by $SOHo_2$, with separation of iodine, which (by the decomposition of water) is converted into hydriodic acid.

A mixture of an iodate and iodide is decomposed by weak acids (*e.g.*, acetic acid), with liberation of iodine. Traces of an iodate in potassic iodide can, therefore, be detected by means of the delicate iodide of starch reaction.

Iodates which give off iodine when they come in contact with various reducing agents, *e.g.*, SO_2, $SSONao_2$, $SnCl_2$, differ, however, in a marked manner from chlorates and bromates by remaining unacted upon by concentrated sulphuric acid, unless the action be assisted by deoxidizing agents, such as ferrous salts, etc. Instead of acquiring a less stable character by the interposition of the atoms of oxygen between the iodine and potassium, potassic iodate,* and still more so *periodate* (obtained by passing chlorine through an alkaline solution of potassic iodate), is capable of resisting the action of sulphuric acid far more readily than potassic iodide. Periodates are, in fact, not reduced by the ordinary reducing agents by which iodic acid is reduced, except by $\mathbf{S}H_2$.

QUESTIONS AND EXERCISES.

1. How are potassic iodate and periodate obtained? Give equations.
2. Explain the changes which iodates and periodates undergo upon ignition.
3. Explain the change which takes place when potassic iodate is acted upon—1st, by reducing agents, *e.g.*, $\mathbf{S}O_2$, $\mathbf{S}H_2$, $\mathbf{Fe}Cl_2$; 2ndly, by concentrated sulphuric acid.
4. A precipitate contains AgI and $\left\{\begin{matrix}\mathbf{O}I \\ \mathbf{O}Ago\end{matrix}\right.$. State how you would separate the two salts from each other.
5. Explain the action of HI upon a mixture of KI and $\left\{\begin{matrix}\mathbf{O}I \\ \mathbf{O}Ko\end{matrix}\right.$.

HYDROFLUORIC ACID, HF.

—Occurs in nature in combination chiefly with calcium in the mineral called *fluorspar* (*Derbyshire spar*), $\mathbf{Ca}F_2$; also as double fluoride of aluminium and sodium in *cryolite*, $6NaF,\mathbf{Al}_2F_6$. It is, moreover, met with in certain *natural phosphates*, *e.g.*, *coprolite*, *fossil bones*, *wavellite*, and in a few *silicates*, *e.g.*, *topaz*, *mica*, *hornblende*.

REACTIONS IN THE DRY WAY.

Heated out of contact with the air, most fluorides remain unchanged. Volatile fluorides can be distilled; but when heated in a moist atmosphere, or if water be added, they are decomposed into oxides (oxyfluorides) and hydrofluoric acid. The changes which fluorides undergo in the dry way are of two kinds.

1st. *The fluoride gives off hydrofluoric acid gas, which corrodes glass.*—By heating a fluoride containing water in a piece of combustion tubing, open at both ends, before the blowpipe, the glass around the fluoride is attacked. The experiment may be carried out also by mixing a little microcosmic salt with the fluoride, and holding the tube in a slightly slanting position.

By heating a mixture of a fluoride with hydric potassic sulphate in a test-tube, HF is disengaged, thus:—

$$\mathbf{Ca}F_2 + 2\mathbf{S}O_2HoKo = \mathbf{S}O_2Cao'' + \mathbf{S}O_2Ko_2 + 2HF.$$

The gas corrodes the upper part of the tube on account of its action upon the silica of the glass, with which it forms a gaseous compound, silicic fluoride, $\mathbf{Si}F_4$, thus:—

$$4HF + \mathbf{Si}O_2 = \mathbf{Si}F_4 + 2\mathbf{O}H_2.$$

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* J. Thomson (Deut. Chem. Ges. Ber., vii, p. 112) deduces from the differences observed in the solubility of chlorates and bromates, compared with that of iodates, also the formation, by preference, of acid salts with the alkali bases, and the facility with which iodic anhydride can be prepared directly, by heating the hydrated acid, that iodic acid must be viewed as a dibasic acid, and he assigns to it the formula:—$I_2O_6H_2$, or $I'''I'O_4(OH)_2$, and he derives periodic acid, $H_3IO_6H_2$, or $H_3IO_4(OH)_2$, by replacing the triatomic iodine atom by H_3.

2nd. *The fluoride is decomposed by hydric potassic sulphate in the presence of a borate, with formation of volatile boric fluoride,* $\mathbf{B}F_3$.—By heating a mixture* of powdered hydric potassic sulphate and fused borax with the finely powdered fluoride, on the loop of a platinum wire, in a clear flame of a Bunsen gas lamp, boric fluoride is disengaged, imparting a beautiful *yellowish-green* colour to the flame, which is highly characteristic, although very evanescent.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC FLUORIDE, NaF.

Most metallic fluorides are solid; others, again, such as the fluorides of the metals whose higher oxides possess acid properties, form volatile, fuming, highly corrosive liquids, or are gaseous at the ordinary temperature.

Fluorides are either soluble in water and more or less crystalline, such as KF, NaF, AmF, AgF, $\mathbf{Sn}F_2$, $\mathbf{Fe}_2F_6$, $\mathbf{Hg}F_2$, $\mathbf{Al}_2F_6$, or *insoluble or very sparingly soluble in water*, and amorphous when obtained by precipitation, *e.g.*, $\mathbf{Ca}F_2$, $\mathbf{Ba}F_2$, $\mathbf{Pb}F_2$, $\mathbf{Zn}F_2$, $\mathbf{Cu}F_2$.

The reactions which a soluble fluoride gives by *double decomposition* with solutions of salts, whose metals form insoluble fluorides, are not very characteristic.

$\mathbf{Ba}Cl_2$ produces a *bulky white* precipitate of **baric fluoride**, $\mathbf{Ba}F_2$, soluble in hydrochloric acid and in much ammonic chloride.

$\mathbf{Ca}Cl_2$ (or $\mathbf{Ca}Ho_2$) gives a *gelatinous translucent* precipitate of **calcic fluoride**, $\mathbf{Ca}F_2$, which becomes visible by the addition of ammonic hydrate. $\mathbf{Ca}F_2$ is slightly soluble in cold hydrochloric or nitric acid, difficultly soluble in boiling hydrochloric acid, less soluble in acetic acid, insoluble in free hydrofluoric acid, soluble to some extent in ammonic chloride.

$\mathbf{N}O_2Ago$ produces no precipitate. (DISTINCTION BETWEEN HF AND HCl.)

It is preferable to test for HF by the reactions based upon the formation of gaseous $\mathbf{Si}F_4$ or $\mathbf{B}F_3$.

All fluorides (soluble or insoluble) are decomposed on heating with concentrated sulphuric acid, with disengagement of HF, a metallic sulphate being left, thus:—

$$\mathbf{Ca}F_2 + \mathbf{S}O_2Ho_2 = 2HF + \mathbf{S}O_2Cao''.$$

The experiment is best performed by treating the fluoride with sulphuric acid in a small leaden cup heated over a water-bath (Fig. 17), and connected with a leaden still and U-tube, surrounded with ice, for the condensation of the acid.

Hydrofluoric acid gas is highly corrosive, and should not be inhaled. If it comes in contact with silica (*e.g.*, in glass), $\mathbf{Si}F_4$ is formed. The glass becomes *corroded or etched*.

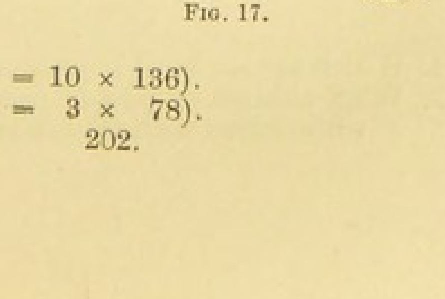

FIG. 17.

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* 10 mol. of $\mathbf{S}O_2HoKo$ (= 10 × 136).
3 mol. of $\mathbf{Ca}F_2$ (= 3 × 78).
1 mol. of $\mathbf{B}_4O_5Nao_2$ 202.

Its action upon glass may be shown also by covering a platinum crucible containing a little finely powdered fluoride and concentrated sulphuric acid, with a piece of glass, *e.g.*, a watch-glass. The vapour of the evolved hydrofluoric acid corrodes the glass. The action of the hydrofluoric acid becomes apparent when the glass is covered with a thin layer of melted wax, and some design scratched on the waxed side with a pointed instrument. The gas acts upon the unprotected portion of the glass. To prevent the melting of the wax, a little cold water is kept on the watch-glass. The design will be found etched more or less deeply into the glass, after the removal of the wax. Mere traces of a fluoride are thus detected, and as no other substance attacks glass similarly, the reaction is perfectly characteristic for hydrofluoric acid. It should be remembered, however, that the softer kinds of glass are liable to be corroded by the vapour of ordinary acids alone. In doubtful cases, therefore, it is preferable to employ a glass-bulb blown out of combustion glass, or also a plate of rock-crystal.

If the fluoride contain much silica, sulphuric acid disengages silicic fluoride instead of hydrofluoric acid, which does not attack glass; but when passed into water—best by letting the delivery-tube dip into a little mercury—it is decomposed into hydrofluosilicic acid and into $\mathrm{SiHo_4}$, thus :—

$$3\mathrm{SiF_4} + 4\mathrm{OH_2} = \mathrm{SiHo_4} + 2(2\mathrm{HF},\mathrm{SiF_4}).$$

This reaction is employed for detecting fluorine in silicates, or if applied to fluorides which are free from silica, some finely powdered quartz or glass is first mixed with the fluoride, before treating with sulphuric acid, and passing the silicic fluoride into water.

The experiment may be performed in a glass flask or small stone-ware bottle, provided with a wide delivery-tube, which dips under mercury contained in a small porcelain cup at the bottom of a beaker or glass cylinder. Care should be taken that the inside of the delivery-tube remains perfectly dry, when the receiving vessel is filled with water. A mixture of one part by weight of finely powdered fluorspar, and one by weight of fine sand is introduced into the glass or stone-ware vessel. Seven to eight parts by weight of oil of vitriol are added, and the whole shaken up together and gently heated upon a sand- (or water-) bath. Each bubble of the evolved $\mathrm{SiF_4}$, on passing through the water, is decomposed, with separation of gelatinous silica, which after a time fills the whole glass vessel in the form of a dense jelly. The silica is separated by straining through a cloth from the hydrofluosilicic acid, which may be returned to the glass cylinder, and a fresh quantity of $\mathrm{SiF_4}$ passed through, till the acid solution has become sufficiently concentrated.

Silicates containing fluorides which are not decomposed by sulphuric acid, are fused with four parts of fusion mixture. The fused mass is extracted with water and filtered. The filtrate contains the fluorine in the form of alkaline fluorides together with alkaline silicates. On slightly acidulating with dilute hydrochloric acid to decompose the excess of alkaline carbonates, and then digesting with ammonic hydrate, $\mathrm{SiHo_4}$ is precipitated, which can be filtered off, leaving the alkaline fluoride. On adding $\mathrm{CaHo_2}$ or $\mathrm{CaCl_2}$, and digesting at a gentle heat, a gelatinous precipitate of $\mathrm{CaF_2}$ is obtained, which is filtered off, dried, and examined. If phosphoric acid be present, the precipitate contains $\mathrm{P_2O_2Cao''_2}$, as well as $\mathrm{CaF_2}$, which does not, however, interfere with the disengagement of hydrofluoric acid gas.

Insoluble fluorides, *e.g.*, $\mathrm{CaF_2}$, are not completely decomposed by fusion with alkaline carbonates, unless $\mathrm{SiO_2}$ be present.

QUESTIONS AND EXERCISES.

1. Which are the most important natural compounds of fluorine ?
2. What changes do solid fluorides undergo when heated by themselves ; 2ndly, when mixed with microcosmic salt or hydric potassic sulphate ?

3. How is BF_3 formed, and why does it furnish us with a characteristic reaction for fluorine, or *vice versâ* for boron?
4. Classify fluorides according to their solubility in water.
5. Describe some characteristic reactions for fluorine in the wet way.
6. How would you distinguish gaseous HCl from HF?
7. How is hydrofluoric acid gas prepared? Explain its action upon glass.
8. How would you test for small quantities of a fluoride?
9. Explain the action of concentrated sulphuric acid upon a fluoride containing much SiO_2.
10. How is fluorine detected in silicates decomposable by SO_2Ho_2, containing traces of a fluoride?
11. How can fluorine be detected in a mineral containing a silicate which is not decomposed by sulphuric acid, some phosphate, and traces of a fluoride?
12. How would you prepare KF, AmF, and liquid HF?

HYDROFLUOSILICIC ACID, $2HF,SiF_4$.—Obtained by passing silicic fluoride into water and separating the precipitated silica by filtration.

It forms salts, called silicofluorides, or fluosilicates, on acting upon metallic oxides, hydrates, or metals, such as Fe or Zn (these latter with evolution of hydrogen), of which the potassic and baric silicofluorides are the most interesting.

REACTIONS IN THE DRY WAY.

Silicofluorides are decomposed by heat into fluorides, with disengagement of silicic fluoride.

REACTIONS IN THE WET WAY.

A CONCENTRATED SOLUTION OF THE ACID may be employed.

On evaporating a solution of hydrofluosilicic acid in a platinum vessel, it volatilizes, and is decomposed into SiF_4 and $2HF$. The acid ought not, therefore, to be heated in a glass vessel.

A few silicofluorides, e.g., $2KF,SiF_4$, $2NaF,SiF_4$, BaF_2,SiF_4, *are difficultly soluble in water, and are rendered quite insoluble by the addition of alcohol.* Most other metallic silicofluorides are readily soluble in water.

$BaCl_2$ precipitates *translucent* crystalline **baric silicofluoride,** BaF_2,SiF_4, which falls out very readily. The precipitation is complete on the addition of an equal volume of alcohol. Strontium is not precipitated from concentrated solutions. (DISTINCTION BETWEEN BARIUM AND STRONTIUM.)

KCl gives a *translucent gelatinous* precipitate of **dipotassic silicofluoride,** $2KF,SiF_4$.

$AmHo$ separates $SiHo_4$ and forms AmF.

On heating a metallic silicofluoride with concentrated sulphuric acid in a platinum crucible, covered with a watch-glass, the glass becomes corroded or etched.

QUESTIONS AND EXERCISES.

1. How is $2HF,SiF_4$ prepared?
2. State how $2HF,SiF_4$ acts upon KHo, OH_2, Fe, CuO.
3. What decomposition takes place when silicofluorides are heated—1st, by themselves; 2ndly, with concentrated SO_2Ho_2?
4. How is BaF_2, SiF_4 obtained?
5. What proportions by weight of CaF_2, SiO_2, and SO_2Ho_2, are required for the preparation of $2HF,SiF_4$?

PHOSPHORIC ACID, $POHo_3$.—This acid is never met with in the free state in nature, but invariably in combination with bases, such as CaO, MgO, Al_2O_3, FeO, Fe_2O_3, PbO, as *bone-*

ash, *sombrerite*, *coprolite*, *apatite*, *wagnerite*, *wavellite*, *vivianite*, *pyromorphite*, etc.

REACTIONS IN THE DRY WAY.

Most anhydrous metallic phosphates, when mixed with dry $\mathbf{C}ONao_2$ and lamp-black, and heated together with metallic sodium or magnesium in a narrow ignition-tube, yield phosphides of these metals, recognisable by the smell of $\mathbf{P}H_3$ which is given off when they are moistened with water.

Normal phosphates of fixed bases are not decomposed upon ignition. Mono- and di-hydric normal phosphates lose water, and are converted into pyro- and metaphosphates, thus:—

$$(1)\ 2\mathbf{P}OHoNao_2 = \underset{\text{Sodic pyrophosphate.}}{\mathbf{P}_2O_3Nao_4} + \mathbf{O}H_2.$$

$$(2)\ \mathbf{P}OHo_2Nao = \underset{\text{Sodic metaphosphate.}}{\mathbf{P}O_2Nao} + \mathbf{O}H_2.$$

Fusion with caustic or carbonated alkalies converts pyro- and metaphosphates into normal or orthophosphates. Boiling with concentrated acids ($\mathbf{N}O_2Ho$) effects this conversion likewise.

Alkaline earthy phosphates are only partially decomposed by fusion with alkaline carbonates; most others, *e.g.*, magnesic, ferric, zincic, nickelous, manganous, cupric phosphates are completely decomposed. The solution contains trisodic and tripotassic phosphates. $\mathbf{P}_2O_2Al_2o^{vi}$ can only be decomposed by fusion with silicic anhydride or sodic silicate (water-glass) and fusion mixture,* being converted into sodic aluminic silicate and trisodic phosphate. (Comp. p. 49.)

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF HYDRIC DISODIC PHOSPHATE, $\mathbf{P}OHoNao_2$. All phosphates may be divided into—

1st. *Phosphates which are soluble in water*, comprising the alkaline phosphates only; their solutions react alkaline; and

2nd. *Phosphates which are insoluble in water*, *but soluble in mineral acids* (some also in acetic acid), comprising all other metallic phosphates.

The following are some of the more important reactions by double decomposition:—

$\mathbf{Ba}Cl_2$ yields a *white* precipitate of **hydric baric phosphate**, $\mathbf{P}OHoBao''$, difficultly soluble in ammonic chloride, soluble in nitric or hydrochloric acid.

$\mathbf{Ca}Cl_2$, or $\mathbf{S}O_2Cao''$ produces a *white* precipitate of **hydric calcic** (or tricalcic) **phosphate**, $\mathbf{P}OHoCao''$, readily soluble in mineral acids;* soluble in acetic acid, after being freshly precipitated; slightly soluble in ammonic chloride.

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* One part of $\mathbf{Si}O_2$, together with six parts of fusion mixture.

SO_2Mgo'' (or better still **$MgCl_2$**) in the presence of AmCl and AmHo produces a *white crystalline*, quickly subsiding precipitate of **ammonic magnesic phosphate**, $POAmoMgo'' + 6$ aq., insoluble in ammonic hydrate, readily soluble in acids, even acetic acid. A highly dilute solution of sodic phosphate is only precipitated after some time. The precipitation is promoted by stirring and allowing the liquid to stand in a warm place, when the precipitate is seen to adhere, in the form of white streaks, to those parts of the glass vessel which have been touched by the glass rod. Arsenic acid gives an analogous precipitate.

This is the most important reaction for **$POHo_3$**; it is almost invariably resorted to, both for the recognition of magnesia and phosphoric acid.

NO_2Ago gives a *light yellow* precipitate of **triargentic phosphate**, **$POAgo_3$**, soluble in ammonic hydrate and in nitric acid.

$\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$, **plumbic acetate**, produces a *white* precipitate of **plumbic phosphate**, $P_2O_2Pbo''_3$, readily soluble in nitric acid, almost insoluble in acetic acid, as well as ammonic hydrate. If the precipitate is fused before the blowpipe on charcoal, the bead appears *crystalline* on cooling; *no reduction to the metallic state* takes place.

Fe_2Cl_6 gives a *yellowish-white gelatinous* precipitate of **ferric phosphate**, $P_2O_2Fe_2o^{vi}$, soluble in hydrochloric acid. The ferric salt should be added drop by drop, sufficient to just impart a red tinge to the supernatant solution, since the precipitate is somewhat soluble in excess of ferric chloride. Sodic acetate must be added to remove the two molecules of free hydrochloric acid resulting from the reaction, which would otherwise dissolve some of the precipitate.

When phosphoric acid has to be removed from a phosphate dissolved in hydrochloric acid, *e.g.*, from the alkaline earthy phosphate, $P_2O_2Cao''_3$, the free acid is nearly neutralized with ammonic hydrate or ammonic carbonate, and then sodic acetate added, which, by double decomposition with the free hydrochloric acid, forms sodic chloride and free acetic acid, in which the precipitate, produced by a *slight excess* of ferric chloride, is absolutely insoluble. The mixture is heated nearly to boiling; a reddish-brown precipitate is obtained, which contains the whole of the phosphoric acid, together with some basic ferric acetate. It must be filtered hot, and washed with hot water; the filtrate contains the alkaline earthy bases as chlorides.—(Comp. also p. 39 and 40).

Small quantities of *phosphoric acid*, in the presence of *large amounts of a ferric salt*, such as we meet with in solutions of iron ores, of pig iron, steel, etc., are best removed by first reducing the ferric to ferrous salt by boiling with **$SOHoAmo$**, neutralizing with **$CONao_2$**, and lastly with sodic acetate and precipitation with *a few drops* of ferric chloride (or by reoxidizing a small portion of the ferrous salt by the addition of a little chlorine water, or a drop or two of bromine). The whole of the phosphoric acid is usually precipitated in this

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* $$P_2O_2Cao''_3 + 4NO_2Ho = P_2O_2Ho_4Cao'' + 2\,\begin{matrix}NO_2\\NO_2\end{matrix}Cao''.$$

Soluble tetrahydric
calcic diphosphate, reprecipitated by AmHo.

manner. Loss arising from the solvent action of ferric acetate is avoided, as ferrous acetate does not dissolve ferric phosphate.

This method is employed with advantage in the examination of iron ores, etc. The precipitate is filtered hot, redissolved in dilute HCl, and the phosphoric acid precipitated in the presence of citric or tartaric acid, AmCl and AmHo, by means of magnesic sulphate.

$AsOHo_3$ exhibits with ferric chloride a similar reaction, and has, therefore, to be separated from an acid solution, by boiling with SOHoAmo and precipitation by a current of SH_2 gas.

Small *traces of phosphorus* (phosphoric acid), usually found in soils, iron ores, in pig iron, steel, sheet copper, etc., may also be precipitated after dissolving the ore or metal in hydrochloric and nitric acids, whereby the phosphorus is converted into $POHo_3$, and after driving off the excess of acids by evaporation and taking up of the residue with concentrated nitric acid, by adding a solution of ammonic molybdate and concentrated nitric acid; the silicic acid is separated by the evaporation to dryness, and arsenic acid, if present, should be first removed by sulphuretted hydrogen. On digesting the solution at a gentle heat (60° C.) for some time (hours if necessary), and stirring with a glass rod, a *bright yellow* precipitate of **ammonic phospho-molybdate** is obtained.

The constitution of this precipitate is not well understood; we know merely that it contains molybdic acid, ammonia, and phosphoric acid* (about 3 per cent.). By washing the yellow precipitate with a solution of ammonic molybdate, and lastly with a solution of ammonic nitrate, and then dissolving it in ammonic hydrate, filtering, and adding SO_2Mgo'', AmCl, and AmHo, the phosphoric acid is obtained as $POAmoMgo''$.

White of egg (albumen) is not coagulated by tribasic phosphoric acid, nor by a solution of an orthophosphate acidulated with acetic acid.

PYROPHOSPHORIC ACID, $P_2O_3Ho_4$.—Pyrophosphates are obtained by heating monohydric phosphates. They are of little importance, however, since they are not usually met with in natural compounds, and as they are speedily converted, by the action of acids or alkalies, into tribasic phosphates.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC PYROPHOSPHATE, $P_2O_3Nao_4$.

Alkaline pyrophosphates are soluble in water.

All others are insoluble in water, but soluble in dilute acids.

The presence of a soluble pyrophosphate is indicated on adding NO_2Ago, which gives a *white* precipitate of **argentic pyrophosphate**, $P_2O_3Ago_4$, soluble in nitric acid and ammonic hydrate.

Albumen is not coagulated by the free acid, nor by an acetic solution of a pyrophosphate.

MO_2Amo_2 (**ammonic molybdate**) does not give a precipitate, until by the action of mineral acids the pyrophosphate has been converted into tribasic phosphate.

METAPHOSPHORIC ACID, PO_2Ho, is distinguished from the tetra- and tribasic acid as follows :—

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* MoO_3, 90·7 P.C.; P_2O_5, 3·1 P.C.; OAm_2, 3·6 P.C., and OH_2, 2·6 P.C.

Albumen gives an abundant *white* precipitate with the free acid, and with soluble metaphosphates, on the addition of acetic acid.

SO_2Mgo'', AmCl and AmHo fail to precipitate soluble metaphosphates.

NO_2Ago produces a *white* precipitate of **argentic metaphosphate.**

In the ordinary course of analysis both pyro- and metaphosphates are converted into tribasic phosphates, and their tetrabasic and monobasic nature is lost sight of. They can, therefore, only be detected by special experiments.

PHOSPHOROUS ACID, PHo_3 (tribasic).—Phosphorous anhydride is obtained by the slow oxidation of phosphorus on exposure to dry air at the ordinary temperature. By combining with water it forms a very weak acid, and with hydrated alkalies alkaline phosphites.

REACTIONS IN THE DRY WAY.

Heated by themselves on platinum foil, *phosphites* are decomposed, burning with a bright flame. Heated in a retort they evolve hydrogen, mixed towards the end of the decomposition with PH_3, and are converted into phosphates.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC PHOSPHITE, $PHoNao_2$, may be employed.

Alkaline phosphites are soluble in water.

All other phosphites are, for the most part, difficultly soluble or insoluble in water, but soluble in acetic acid (plumbic phosphite excepted). Phosphites (as well as hypophosphites) are of interest mainly on account of the powerful reducing action which they exert upon salts of various metallic oxides, capable of forming lower oxides, or of being reduced to the metallic state, as well as upon the lower oxides, etc., of metalloïds, *e.g.*, SO_2.

NO_2Ago is reduced thereby to metallic silver, especially in the presence of ammonia and on the application of a gentle heat.

$HgCl_2$ and $N_2O_4Hg_2o''$, are reduced to Hg_2Cl_2 and metallic mercury.

SO_2 forms a phosphate with liberation of sulphur and evolution of SH_2.

Nascent hydrogen yields a mixture of H_2 and PH_3 which fumes in the air and burns with an emerald-green colour. When passed into a solution of argentic nitrate, the gaseous mixture precipitates PAg_3 and metallic silver.

The difficultly soluble phosphites of Ba, Ca, Pb, etc., are obtained by double decomposition, the latter salt being insoluble in acetic acid.

HYPOPHOSPHOROUS ACID, POH_2Ho (monobasic).—Obtained by the action of alkalies or hydrates of the alkaline earthy bases upon phosphorus and water.

$$P_4 + 3OH_2 + 3KHo = 3POH_2Ko + PH_3.$$

REACTIONS IN THE DRY WAY.

Hypophosphites are decomposed upon ignition into pyrophosphates and PH_3.

$$4POH_2Ko = P_2O_3Ko_4 + 2PH_3 + OH_2.$$

REACTIONS IN THE WET WAY.

A SOLUTION OF POTASSIC HYPOPHOSPHITE may be employed.

All hypophosphites are soluble in water. They constitute even more powerful reducing agents than the phosphites.

Nitric acid or chlorine water changes them into phosphates.

SO_2Ho_2 is reduced to $SOHo_2$, partly even to sulphur.

SO_2Cuo'' is reduced to metallic copper (cupric hydride).

$HgCl_2$ is reduced to Hg_2Cl_2, and then to mercury.

$AuCl_3$ and NO_2Ago yield the pure metals.

Zn + SO_2Ho_2 (nascent hydrogen) yield H_2 and PH_3.

In the ordinary course of analysis, both phosphorous and hypophosphorous acids are converted into phosphoric acid, and they must therefore be identified by the special reactions just described.

QUESTIONS AND EXERCISES.

1. How does phosphoric acid occur in nature?
2. Explain the action of heat upon $\mathrm{POHo_2Nao}$, $\mathrm{POAmoMgo''}$, and $\mathrm{POHoAmoNao}$.
3. How are meta- and pyrophosphates converted into tribasic phosphates?
4. Explain the action of potassic hydrate or carbonate upon $\mathrm{P_2O_2Fe_2o^{vi}}$, $\mathrm{P_2O_2Cao''_3}$, $\mathrm{P_2O_2Cuo''_3}$, $\mathrm{POHoBao''}$, in the wet and dry way.
5. How can $\mathrm{P_2O_2Al_2o^{vi}}$ be decomposed?
6. Classify all phosphates, pyrophosphates, phosphites, and hypophosphites according to their solubility in water.
7. Explain the solvent action of HCl or $\mathrm{NO_2Ho}$ upon the alkaline earthy phosphates.
8. How is phosphoric acid removed from alkaline earthy phosphates?
9. State how you would detect phosphoric acid in a soil or iron ore; or phosphorus in metallic copper or cast iron.
10. What is the approximate composition of ammonic phospho-molybdate?
11. Which reactions enable us to distinguish between tribasic, tetrabasic, and monobasic phosphates?
12. How would you prove the presence of magnesic, as well as of potassic phosphates, in wheat flour, pale ale, and in cheese?
13. How would you prepare $\mathrm{POH_2Ho}$ and $\mathrm{(POH_2)_2Cao''}$?
14. How are calcic phosphite and potassic hypophosphite acted upon by heat?
15. What are the products of oxidation obtained on burning $\mathrm{PH_3}$ in air?
16. Explain the deoxidizing action of phosphites and hypophosphites.
17. How can potassic hypophosphite be detected in the presence of potassic phosphite and phosphate?
18. How would you prepare gaseous $\mathrm{PH_3}$? What is its action upon solutions of cupric sulphate and argentic nitrate?
19. Give symbolic and graphic formulæ for gaseous phosphoretted hydrogen, calcic hypophosphite, cupric phosphide.
20. Express by a symbolic equation the change which $\mathrm{POH_2Ho}$ undergoes when it is acted upon by $\mathrm{SO_2Ho_2}$, by $\mathrm{SO_2Cuo''}$, or by $\mathrm{AuCl_3}$.
21. How would you convert bone-ash into a soluble calcic phosphate (into $\mathrm{P_2O_2Ho_4Cao''}$—a constituent of calcic superphosphate)?
22. 5·4 grms. of cast iron yielded ·046 of $\mathrm{P_2O_3Mgo''_2}$; what is the percentage of phosphorus in the iron?

SILICIC ACID, $\mathrm{SiHo_4}$.—*Silicic anhydride or silica*, $\mathrm{SiO_2}$, occurs in nature both in a *crystalline* and *amorphous* condition, either in the free or combined state. *Quartz* and *rock crystal* are composed of almost pure crystalline silica. *Opal*, *hyalite*, and some other minerals consist of amorphous silica, and are probably derived from silicic hydrate by a process of slow dehydration. Other silicious bodies, such as *chalcedony*, *agate*, *flint*, are principally composed of amorphous silica, or of a mixture of the two.

The compounds of silica with bases, especially with $\mathrm{OK_2}$, $\mathrm{ONa_2}$, CaO, MgO, $\mathrm{Al_2O_3}$, FeO, MnO, are exceedingly numerous, and vary to a very great extent in their constitution and properties.

REACTIONS IN THE DRY WAY.

Both varieties of silica are characterized by their infusibility when heated by themselves before the blowpipe, or in a bead of microcosmic salt. Pure silica fuses with sodic carbonate to a clear glass, which, if sufficient silica has been used, remains transparent on cooling. Silicates rich in silica behave like pure silica. If a silicate be heated in like manner with microcosmic salt, its base or bases are dissolved, while the silica is seen to float about in the liquid phosphate bead as a *silica skeleton.* Silicates containing coloured oxides give rise to opalescent beads, in which the $\mathbf{Si}O_2$ can be distinguished only with difficulty.

When silica, or a silicate rich in silica, is heated on platinum wire before the blowpipe with sodic carbonate, the $\mathbf{Si}O_2$ displaces the $\mathbf{C}O_2$, and forms a clear glass of sodic silicate. The alkaline carbonate should not be employed in excess. Calcic and magnesic silicates do not dissolve to a clear bead as a rule.

Beyond identifying silica and obtaining a general knowledge of the nature of any silicate under examination, respecting its fusibility, state of hydration, etc., the blowpipe reactions fail to supply distinguishing tests regarding the chemical composition of these bodies, since a very large number of silicates differ from each other merely in the relative proportions of their component metallic elements.

REACTIONS IN THE WET WAY.

All silicates may be divided into—

1. *Silicates* which are *soluble in water*, including only potassic and sodic silicates ; and
2. *Silicates insoluble in water*, including all others.

These latter silicates are either *soluble* in concentrated hydrochloric or sulphuric acid, or *partly soluble* and *partly insoluble*, or lastly, *insoluble in these acids.*

All insoluble silicates are attacked by hydrofluoric acid, with disengagement of silicic fluoride, or by fusion mixture (or caustic baryta) at a high temperature.

By treating an aqueous solution of sodic silicate, $\mathbf{Si}Nao_4$, with dilute hydrochloric acid, it is decomposed into NaCl and $\mathbf{Si}Ho_4$. The latter remains either dissolved in the acid, or is partially separated as a flaky or gelatinous mass. On evaporating in a porcelain dish over a water-bath, the gelatinous mass becomes firmer, and can be broken up, by means of a glass rod, into lumps, which speedily lose their water, leaving *anhydrous* silica, especially on being ignited on a sand-bath, as long as acid fumes are evolved. The dried mass is treated with a little concentrated hydrochloric acid and hot water, when NaCl is dissolved out (together with small quantities of Al and Fe—impurities in the sodic silicate). The impalpable powder of amorphous silica is thrown on a filter and washed with hot water, dried and ignited.

AmCl or $\mathbf{C}OAmo_2$ precipitates $\mathbf{Si}Ho_4$ from a solution of sodic silicate. Salts of most of the heavy metals, as well as of the alkaline earthy metals, form by double decomposition with a soluble silicate, white or yellowish-white silicates, soluble in dilute hydrochloric or nitric acid, which, however, possess no characteristic properties. It is, therefore, necessary to remove the silica in order to detect bases, by evaporating to dryness with hydrochloric acid. On digesting the dry mass with a little hydrochloric acid, the metallic oxides are dissolved, and can be separated by filtration from the silicic anhydride. $\mathbf{SiO}_2$, *like* $\mathbf{P}_2\mathbf{O}_5$, *is detected whilst testing for bases.*

Most natural and artificial silicates are insoluble in water. Many, *e.g.*, zeolites, as well as certain artificial silicates, such as slags from blast furnaces, etc., are decomposed on digesting the finely powdered silicate with concentrated hydrochloric acid. The gelatinous mass is evaporated to dryness on a water-bath, when amorphous silica separates.

Silicates, such as kaolin and clays, *which are not dissolved by hydrochloric acid, can frequently be decomposed, either partly or wholly, by hot concentrated sulphuric acid diluted with about one-third of its weight of water;* many natural silicates yield more or less silica, on treatment with hydrochloric acid, which silica may be taken to represent the soluble silica or the decomposable silicates, leaving the greater portion of the mineral behind in an insoluble condition.

Silica, or silicates insoluble in acids, forming by far the greater number, *are readily attacked by gaseous hydrofluoric acid*, or by fluorspar and $\mathbf{SO}_2\mathbf{Ho}_2$, *gaseous* $\mathbf{Si}F_4$ *being given off.* This method is invariably resorted to whenever alkalies are present in a silicate, as *e.g.*, in felspar, $\mathbf{Si}_6O_8Ko_2Al_2o^{vi}$. A little of the finely powdered silicate is moistened with strong ammonia, put into a platinum crucible or small platinum capsule, and exposed to the action of gaseous HF. This gas should be generated in a leaden or platinum vessel. The platinum crucible is to this end placed in a small leaden basin, which can be closed with a lid of the same metal. A layer of fluorspar is put at the bottom of this vessel, mixed and covered with concentrated sulphuric acid. The platinum crucible rests on a leaden tripod. The leaden vessel after being covered and luted with moist linseed meal, is placed for a day or two in a warm place. The crucible is then taken out, and its contents cautiously evaporated by applying a gentle heat, as shown in Fig. 18, from the upper part of the crucible downward, till the whole of the ammonic fluoride has been driven off. The dry residue is dissolved in hydrochloric acid, and tested for bases. A small residue is usually left, which is filtered off and treated once more in the same manner.

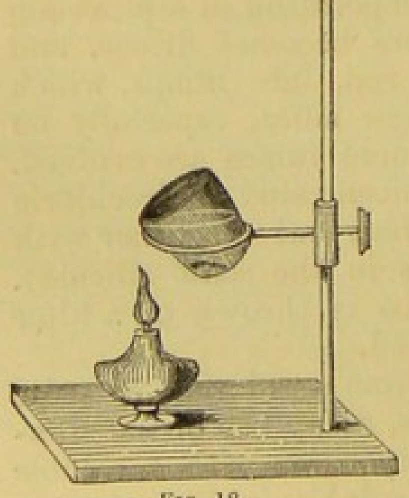

FIG. 18.

The same result may be obtained more expeditiously by treating the mineral in a platinum crucible with *liquid hydro-*

fluoric acid, and evaporating cautiously in a closet which stands in connection with the chimney, and which has a good in-draught of air. The residue is dissolved in hydrochloric acid. Any insoluble residue which may be left is separated by filtration and treated again with hydrofluoric acid. This treatment has generally to be repeated several times, before the whole of the bases are obtained in a soluble condition.

Treatment with $\mathbf{CaF_2}$ and concentrated $\mathbf{SO_2Ho_2}$ is objectionable, on account of the formation of insoluble $\mathbf{SOHo_2Cao''}$.

A less cumbersome yet equally satisfactory method for decomposing silicates containing alkalies is the following:—Mix ·5 grm. of finely powdered silicate intimately with ·5 grm. of pure AmCl, and then with 4 grms. of pure precipitated granular calcic carbonate,[*] and heat the mixture in a platinum crucible, placed in a slanting position, first gently and by means of a small Bunsen flame, from above gradually downwards, till the sal-ammoniac is completely converted into $\mathbf{CaCl_2}$. Then apply a stronger heat, and lastly heat for half an hour over a good Bunsen lamp. The sintered mass consists now of caustic lime, *disintegrated* silicate (rendered soluble in acids), and alkaline chlorides soluble in water, besides undecomposed $\mathbf{CaCl_2}$. It is next slaked and repeatedly extracted with small quantities of hot water at a time. The liquid after filtration is free from silica and contains the alkali metals as chlorides. The lime in solution is removed by precipitation with ammonia and ammonic oxalate, and the filtrate evaporated to dryness and gently ignited, when the fixed alkali salts are left behind. This method can only be worked with advantage with quantities of substance not exceeding ·5 grm.

All silicates insoluble in water and acids, no matter whether they contain alkali metals or not, *may be decomposed by fusion with alkaline carbonates* (fusion mixture). They are first ground up very finely in an agate mortar, then intimately mixed with three to four times their weight of fusion mixture and heated in a platinum crucible as long as any $\mathbf{CO_2}$ is given off. This may be done over a good Bunsen gas lamp or by means of a Herapath gas blowpipe. (A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established by a preliminary examination of the silicious substance in the dry way.) The silica is thus obtained in combination with the alkalies and dissolves in hot water, and the bases ($\mathbf{CaO}$, $\mathbf{MgO}$, $\mathbf{Al_2O_3}$, $\mathbf{Fe_2O_3}$, etc., etc.) are left as insoluble oxides or carbonates, and may be separated by filtration; or the whole mass is at once treated with dilute hydrochloric acid and evaporated to dryness. Silicic anhydride is left, and the bases are removed as chlorides by filtration. It is obvious that we must examine for the alkali bases in a separate portion, by treatment with hydrofluoric acid.

Pure amorphous silica dissolves completely, when boiled in a platinum vessel with an aqueous solution of fixed caustic or carbonated alkalies.

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[*] Prepared by precipitating a dilute solution of $\mathbf{CaCl_2}$ at 70° C. with excess of $\mathbf{COAmo_2}$, and washing the precipitate *thoroughly* with hot water by decantation.

SiO_2 is separated from **TiO_2** (titanic anhydride) by fusion with **SO_2HoKo** in a platinum crucible, and subsequent treatment with water; the **SiO_2** remains undissolved. The **TiO_2** is precipitated from the acidulated aqueous solution by long-continued boiling.

QUESTIONS AND EXERCISES.

1. Give instances of crystalline and amorphous silica.
2. Describe the reactions for **SiO_2** in the dry way.
3. Classify silicates according to their solubility in water and acids.
4. Explain the action of HF, or of **CaF_2** and concentrated **SO_2Ho_2**, upon silicates.
5. Describe how amorphous silica is obtained from **$SiNao_4$**, from quartz, or from felspar.
6. How would you ascertain the presence of potassium or sodium in a silicate, soluble in HCl, and in a silicate, insoluble in HCl, *e.g.*, in Bohemian glass?
7. What is the action of caustic and carbonated alkalies upon amorphous silica?
8. How is **TiO_2** separated from **SiO_2**?
9. How is silicon detected in pig-iron?

BORIC ACID, **BHo_3** (Orthoboric acid).—Is found in nature both combined and in the free state.

REACTIONS IN THE DRY WAY.

Most borates swell up when heated by themselves, and fuse into a transparent glass which dissolves metallic oxides, producing various colours. The free acid forms scaly crystals, possessing a pearly lustre and feeling peculiarly greasy to the touch.

When heated to 100° C. the crystals lose water and become converted into metaboric acid, **BOHo**. This acid fuses to a colourless transparent, glassy-looking mass,—*boric anhydride*, **B_2O_3**, which can be kept in a liquid condition without loss from volatilization.

A mixture of **SO_2HoKo** and a borate, heated on a platinum wire in a blowpipe flame, imparts a green colour to the flame, owing to the liberation of boric acid.

To detect *traces* of boric acid before the blowpipe, the borate is powdered and mixed with **SO_2HoKo** and **CaF_2**.* (Comp. page 137). The mixture is made into a stiff paste with a few drops of water, and cautiously introduced, on the loop of a platinum wire, into the *inner* blowpipe flame, when the outer flame acquires momentarily a *yellowish-green tint*, owing to the volatilization of boric fluoride, **BF_3**. Phosphates as well as copper salts, when moistened with sulphuric acid and heated in the *outer* flame, give likewise a green tint to the flame.

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* Three to four parts of the flux (consisting of one part of powdered **CaF_2** and four and a half to five parts of **SO_2HoKo**).

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF BORAX, $\mathbf{B}_4O_5Nao_2$.

The alkaline borates are soluble in water, all others are difficultly soluble, but none are absolutely insoluble. All borates dissolve in acids and ammonic chloride.

The precipitates produced by double decomposition of a soluble alkaline borate with salts of the alkaline earths, or with plumbic, argentic, mercurous, or ferrous salts, etc., are *white* or *yellowish-white*, and are readily soluble in acids and ammonic chloride.

The *free* acid dissolves in water and alcohol, and its solutions impart to a Bunsen gas flame a *fine green* colour. An alcoholic solution placed in a porcelain dish burns, when ignited, with the same characteristic flame, and the colour becomes all the more perceptible when the burning alcohol is stirred with a glass rod. It does not show in the presence of alkaline hydrates or carbonates, or of any other base. The reaction is equally vitiated by the presence of sodic or calcic chloride, or even by the presence of small quantities of an alkaline tartrate, free tartaric or phosphoric acid; but the green becomes again perceptible on the *addition of a little concentrated sulphuric acid.*

A green flame (of a somewhat greenish-blue tint, however) is obtained also by heating many metallic chlorides with alcohol and concentrated sulphuric acid (owing to the formation of ethylic chloride, $\left\{\begin{matrix} CH_3 \\ CH_2Cl \end{matrix}\right.$), also by passing hydrochloric acid gas into the flame of burning alcohol.

Boric acid, when combined with bases, requires first to be liberated, by the addition of a little concentrated sulphuric acid, before its alcoholic solution can produce the green flame.

If a borate cannot be decomposed by sulphuric acid, it is fused with potassic hydrate, and the fused mass taken up with alcohol. On the addition of concentrated sulphuric acid, the burning alcohol shows the characteristic green flame.

An aqueous solution of boric acid cannot be evaporated without loss of acid from volatilization.

An alcoholic solution of boric acid *colours turmeric paper reddish-brown*, especially on drying the strips of paper in a warm place (a water-oven). This colour becomes more intense in the presence of hydrochloric or sulphuric acid (even in the presence of nitric or tartaric acid). The colour produced by heating turmeric paper with hydrochloric acid is blackish-brown, and must not be confounded with the colour produced by boric acid. The dried paper acquires a blackish tint when dipped into alkalies.

Hydrofluoric acid (or $\mathbf{S}O_2Ho_2$ and $\mathbf{Ca}F_2$) decomposes all borates, with formation of volatile boric fluoride, thus :—

$$\mathbf{B}_4O_5Nao_2 + 6\mathbf{Ca}F_2 + 7\mathbf{S}O_2Ho_2 = 6\mathbf{S}OHo_2Cao'' + \mathbf{S}O_2Nao_2 + 4\mathbf{B}F_3 + \mathbf{O}H_2.$$

and if the gaseous boric fluoride be passed into water, it forms a peculiar acid —*hydrofluoboric acid*—the constitution of which is not well understood, thus :—

$$4\mathbf{B}F_3 + 3\mathbf{O}H_2 = \underset{\text{Hydrofluoboric acid.}}{3(\mathbf{B}F_3,HF)} + \mathbf{B}Ho_3.$$

This acid combines with bases, forming *borofluorides* or *fluoborates*, thus :—

$$\mathbf{B}F_3,HF + KHo = \mathbf{B}F_3,KF + \mathbf{O}H_2.$$

QUESTIONS AND EXERCISES.

1. How is metaboric acid obtained ?
2. Explain the reactions in the dry way for boric acid or borates.
3. Classify borates according to their solubility in water.
4. Explain the colour test for boric acid.
5. How are borates, insoluble in water, examined ?
6. Explain the action of HF upon boric acid.
7. State how you would prepare argentic borate, plumbic borate, hydrofluoboric acid, and potassic fluoborate.
8. Explain the action of boric acid upon turmeric paper.

HYDROCYANIC ACID (Prussic acid), HCy.—This acid* consists of hydrogen and the compound radical cyanogen, Cy, molecule $\left\{\begin{matrix}'\mathbf{C}'''\mathrm{N}''' \\ '\mathbf{C}'''\mathrm{N}'''\end{matrix}\right.$. It forms with metallic oxides salts, called *cyanides*, analogous in their chemical constitution to chlorides, bromides, etc. Cyanogen cannot be obtained by the direct combination of carbon and nitrogen, but an alkaline cyanide results from the action of caustic or carbonated alkalies upon nitrogenous organic bodies, such as fibrin, albumen, and gelatin at a high temperature. The best known cyanide, viz., potassic cyanide, KCy, unless specially purified, contains more or less potassic cyanate, CyKo, and potassic carbonate.

REACTIONS IN THE DRY WAY.

KCy and NaCy are not decomposed upon ignition in close vessels, as may be inferred from their mode of manufacture ; but when heated with free access of air, they are converted into cyanates. The same change takes place, only more speedily, when potassic cyanide is heated with less energetic oxidizing agents, such as $\mathbf{Mn}O_2$, $\mathbf{Pb}O$, $\mathbf{Cu}O$, $\mathbf{Sn}O_2$, etc., when the metal, or a lower oxide is left. Heated in the presence of metallic sulphides, it is converted into potassic sulphocyanate, CyKs. Potassic cyanide is on this account a most valuable deoxidizing (desulphurizing) agent, and is employed in blowpipe reactions, whenever a metallic oxide (or sulphide) has to be reduced to the metallic state. Cyanides of the heavy metals undergo decomposition upon ignition ; some (*e.g.*, the cyanides of the noble metals) break up into metal and cyanogen gas ; others into a metallic carbide and nitrogen (*e.g.*, the cyanides of iron); others again (such as $AgCy$, $\mathbf{Hg}Cy_2$, $\mathbf{Cu}Cy_2$, $\mathbf{Zn}Cy_2$) yield cyanogen gas, metallic silver, mercury, etc., and paracyanogen, —a brownish-black substance, which is isomeric with cyanogen, and which is usually expressed by the symbol Cy_n.

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* The compounds which the radicals cyanogen, ferro- and ferricyanogen, etc., are capable of forming will be treated somewhat more fully, since a thorough understanding of the various reactions is necessary, in order to successfully analyse cyanogen compounds.

This deportment of solid cyanides furnishes us with ready means of preparing cyanogen gas, either by *igniting dry* $\mathbf{Hg}Cy_2$, or $AgCy$; or *by heating two parts of dry yellow prussiate of potash*, or commercial potassic ferrocyanide, K_4FeCy_6, *with three parts by weight of dry* $\mathbf{Hg}Cl_2$.

Cyanogen is a colourless gas, of peculiar odour, burning with a beautiful purple or peach-blossom coloured flame, and yielding $\mathbf{C}O_2$ and N. The gas is nearly twice as heavy as air (sp. gr. 1·8), and since water dissolves about four times its own volume it must be collected over mercury, or by downward displacement. An aqueous solution decomposes spontaneously into a variety of products. When the gas is passed through a solution of caustic potash it is absorbed with formation of potassic cyanide and cyanate. It is one of the few gases which condense to a liquid at a moderate pressure (3·6 atmospheres).

All cyanogen compounds when ignited in an ignition-tube with excess of soda-lime, give up the whole of their nitrogen as ammonia.

REACTIONS IN THE WET WAY.

The *cyanides of the alkali metals and alkaline earthy metals are soluble in water*, the former readily, the latter with difficulty. The *cyanides of the heavy metals are insoluble in water*, with the exception of $\mathbf{Hg}Cy_2$; but are for the most part soluble in a solution of potassic cyanide, forming soluble *double cyanides*, which are frequently crystalline, and which upon ignition are decomposed like single cyanides, *i.e.*, the cyanide of the heavy metal breaks up into metal and cyanogen, or metal, carbon (carbide ?) and nitrogen, whilst the alkaline cyanide is not decomposed, and can be dissolved out from the residue.

The following is a list of some of the more important single cyanides, *i.e.*, cyanides which contain only one metal:—

Potassic	cyanide,	soluble in water	KCy
Sodic	„	„ „	NaCy
Baric	„	difficultly soluble in water ..	$\mathbf{Ba}Cy_2$
Zincic	„	insoluble in water	$\mathbf{Zn}Cy_2$
Cadmic	„	„ „	$\mathbf{Cd}Cy_2$
Nickelous	„	„ „	$\mathbf{Ni}Cy_2$
Cobaltous	„	„ „	$\mathbf{Co}Cy_2$
Ferrous	„	„ „	$\mathbf{Fe}Cy_2$
Cuprous	„	„ „	$'\mathbf{Cu}'_2Cy_2$
Mercuric	„	soluble in water	$\mathbf{Hg}Cy_2$
Argentic	„	insoluble in water	AgCy.

Some of these single cyanides are readily decomposed by acids, with evolution of hydrocyanic acid; others, especially the cyanides of iron, cobalt, and the noble metals (Au,Pt), may be boiled with moderately strong acids, without decomposition.

The action of dilute acids upon double cyanides shows clearly the existence of two distinct classes of double cyanides, viz.:—

1st. *Double cyanides which are readily decomposable, giving off hydrocyanic acid, when heated with dilute mineral acids.* They possess an alkaline reaction. Their alkaline cyanide is decomposed by dilute mineral acids into HCy and a salt of the alkali metal, and into a cyanide of the heavy metal, which remains in combination with the liberated HCy; or the latter is evolved and the metallic cyanide is precipitated; or both cyanides are decomposed, and the whole of the HCy is liberated, *e.g.*:—

$$(1)\ KAgCy_2 + \mathbf{N}O_2Ho = \underset{\text{Precipitated.}}{AgCy} + HCy + \mathbf{N}O_2Ko.$$

$$(2)\ K_2Zn''Cy_4 + 4HCl = \mathbf{Zn}Cl_2 + 2KCl + 4HCy.$$

2nd. *Double cyanides which possess a neutral reaction and give off no hydrocyanic acid, when treated with dilute hydrochloric acid, the negative element of the acid forming a salt with the alkali metal,* whilst the hydrogen or positive element, by uniting with the remaining elements, forms a new acid of a more complex nature, thus:—

$$K_4FeCy_6 + 4HCl = \underset{\substack{\text{Hydroferrocyanic}\\ \text{acid.}}}{H_4FeCy_6} + 4KCl.$$

$$K_6Fe_2Cy_{12} + 6HCl = \underset{\substack{\text{Hydroferricyanic}\\ \text{acid.}}}{H_6Fe_2Cy_{12}} + 6KCl.$$

$$K_6Co_2Cy_{12} + 6HCl = \underset{\substack{\text{Hydrocobalticyanic}\\ \text{acid.}}}{H_6Co_2Cy_{12}} + 6KCl.$$

The single, as well as easily decomposable double cyanides, which yield hydrocyanic acid, when treated with dilute mineral acids, are moreover remarkable for their highly poisonous character, whilst these latter—the double cyanides containing a non-decomposable cyanogen radical (*e.g.*, *ferrocyanogen*, $FeCy_6$, *cobalticyanogen*, Co_2Cy_{12})—are not poisonous.

It is obvious that all these complex cyanogen compounds—both decomposable and non-decomposable—may likewise be viewed as double cyanides.

The following list* contains some of the more interesting double cyanides, *i.e.*, cyanides containing more than one metal; the *easily decomposable* class being indicated by a comma placed between the cyanogen and the metal:—

Dipotassic zincic tetracyanide	K_2Zn,Cy_4.
,, cadmic ,, ...	K_2Cd,Cy_4.
,, nickelous ,, ...	K_2Ni,Cy_4.

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[*] Kekulé, Lehrbuch der organischen Chemie, I, p. 314.

Potassic argentic dicyanide.	KAg,Cy_2.
„ aurous „	KAu',Cy_2.
„ auric tetracyanide	KAu''',Cy_4.
Dipotassic cuprous tetracyanide.	$K_2{}'Cu'_2,Cy_4$.
„ platinous „	K_2Pt'',Cy_4.
Tetrapotassic diplatinic decacyanide	$K_4,{}'Pt'''_2Cy_{10}$.
„ ferrous hexacyanide (potassic ferrocyanide, *yellow prussiate*)	$K_4,FeCy_6$.
Hexapotassic diferric dodecacyanide (potassic ferricyanide, *red prussiate*).	K_6,Fe_2Cy_{12}.
Hexapotassic dicobaltic dodecacyanide (potassic cobalticyanide)	K_6,Co_2Cy_{12}.
Hexapotassic dichromic dodecacyanide.	K_6,Cr_2Cy_{12}.
„ dimanganic „	K_6Mn_2,C_{12}.

If we take, however, into account the different deportment of these double cyanides with dilute acids and with ferroso-ferric salts, with which the easily decomposable double cyanides give, from an acid solution, a precipitate of Prussian blue, whilst the others—the difficultly decomposable double cyanides—yield no hydrocyanic acid, when treated with dilute acids, and produce (with the exception of the ferro- and ferricyanogen compounds), no precipitate of Prussian blue with ferroso-ferric salts and hydrochloric acid, it becomes evident *that the complex groups of elements*, *ferrocyanogen*, $FeCy_6$, *ferricyanogen*, Fe_2Cy_{12}, *cobalticyanogen*, Co_2Cy_{12}, etc., *which behave like cyanogen* (itself a complex group of two elements, of carbon and nitrogen, or a compound radical), *may likewise be viewed as compound radicals*,* if by this term we denote a group of common and constant constituents found in a whole series of compounds, and capable of replacing multiples of Cl, Br, etc., in constant atomic proportions.

We are able, for instance, to produce by double decomposition, precipitates with soluble salts of almost all the heavy metals in which the potassium—or positive radical—is either entirely or partially exchanged for an equivalent quantity of a heavy metal, whilst the negative group of elements remains unaltered, thus :—

$$K_4FeCy_6 + SO_2Cuo'' = K_2Cu''FeCy_6 + SO_2Ko_2, \text{ or}$$
$$K_4FeCy_6 + 2SO_2Cuo'' = Cu''_2FeCy_6 + 2SO_2Ko_2.$$

On the addition of an alkaline hydrate or carbonate, the whole of the heavy metal is removed as hydrate, with formation of potassic ferrocyanide.

Easily decomposable soluble double cyanides give likewise precipitates with solutions of heavy metals, *e.g.*,

$$2KAgCy_2 + SO_2Zno'' = \underset{\text{Precipitated.}}{Zn''Ag_2Cy_4} + SO_2Ko_2;$$

but there is no evidence to show whether these precipitates are real compounds or only mixtures of *two* insoluble cyanides; nor is there any proof that alkaline hydrates reproduce the original double cyanide. Dilute sulphuric acid decomposes $\mathbf{Zn}Cy_2$ in the above precipitate, $AgCy$ being left behind; just as if no connection had apparently existed between the two cyanides. Alkaline hydrates or carbonates are without action upon easily decomposable cyanides. A few are decomposed by sulphuretted hydrogen, *e.g.*, K_2CdCy_4, K_2HgCy_4, $KAgCy_2$, with precipitation of a metallic sulphide; in others, such as K_2MnCy_4, K_2NiCy_4, K_2ZnCy_4, and K_2CuCy_4, the metal is only partially precipitated as sulphide, whilst $K_4Fe''Cy_6$ and $K_2Co''Cy_4$ are not precipitated at all.

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* Compound bodies, containing the complex radicals ferro-, ferri-, etc., cyanogen are viewed here as molecular compounds, and no constitutional formulæ have been attempted, although it would not be difficult to assign such formulæ to them, if the functions which the carbon and nitrogen atoms play in these compounds were sufficiently established.

It is evident from these changes that easily decomposable and difficultly decomposable double cyanides (ferro-, ferri-, cobalti-, and chromi-cyanides) differ not so much in their chemical structure and habitus, as in the degree of stability which they exhibit, varying with the individual nature of the metal which they contain.

We employ A SOLUTION OF POTASSIC CYANIDE, KCy.

$\mathbf{N}O_2Ago$ gives a permanent *white curdy* precipitate[*] of **argentic cyanide**, $AgCy$, only, when more than $1\mathbf{N}O_2Ago$ has been added for every $2KCy$. The precipitate is insoluble in dilute nitric acid, soluble in ammonic hydrate, sodic hyposulphite, and potassic cyanide. $AgCy$ resembles $AgCl$ so very closely that special experiments are required to distinguish it from the latter, or to detect hydrocyanic acid in the presence of a chloride.

This may be done (1) by boiling with dilute HCl (or less readily with $\mathbf{S}O_2Ho_2$), when HCy is evolved; (2) by igniting a mixture of $AgCl$ and $AgCy$, which has been entirely freed from argentic nitrate by washing with hot water, when $AgCy$ is decomposed into cyanogen, metallic silver, and paracyanogen. $AgCl$, on the other hand, fuses like $AgCy$, but without decomposition. On dissolving the residue in nitric acid and filtering, a precipitate of $AgCl$ is obtained, on the addition of hydrochloric acid, or a soluble chloride, the silver of which must have been present originally as cyanide. (DISTINCTION BETWEEN HCl AND HCy.)

Dilute mineral acids decompose potassic cyanide readily with evolution of HCy. On decomposing, therefore, a small quantity of KCy by dilute sulphuric acid in a small porcelain dish, and inverting another small dish, containing a drop or two of *yellow* ammonic sulphide, over it, the gaseous hydrocyanic acid, acting upon the ammonic sulphide, forms ammonic sulphocyanate, $CyAms$, and $AmHs$, thus:—

$$\mathbf{S}_2Am_2 + HCy = CyAms + AmHs,$$

which gives, on acidulating with hydrochloric acid, a characteristic *blood-red coloration* with $\mathbf{Fe}_2Cl_6$.

This constitutes one of the most delicate reactions for free hydrocyanic acid, as well as for soluble or easily decomposable cyanides.

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[*] $\mathbf{Hg}Cy_2$ is not precipitated by argentic nitrate.

$\mathbf{S}O_2Cuo''$, to which a solution of $\mathbf{S}OHo_2$ has been added, gives with KCy a *white* precipitate of **cuprous cyanide**, $'\mathbf{Cu}'_2Cy_2$, soluble in potassic cyanide ($K_2'Cu'_2Cy_4$).

$\mathbf{N}_2O_4Hg_2o''$ gives a *grey* precipitate of metallic mercury, whilst $\mathbf{Hg}Cy_2$ remains in solution, thus :—

$$'\mathbf{Hg}'_2Cy_2 = Hg + \mathbf{Hg}Cy_2.$$

Iron salts are among the most delicate reagents for hydrocyanic acid, or for soluble cyanides, on account of their tendency, especially in the presence of potassic hydrate, to form difficultly decomposable double cyanides (containing the compound acid radicals ferro- and ferri-cyanogen), which are of a characteristic blue colour. (Hence the name cyanogen, from κύανος, blue, and γεννάω, I generate.) The solution containing hydrocyanic acid, or a soluble cyanide, is first treated with a little potassic hydrate, then with a mixture of a ferrous and ferric salt (obtained by exposing a solution of ferrous sulphate for some time to the air), and heated. On the addition of dilute hydrochloric acid, in order to dissolve the ferrous and ferric hydrates, precipitated by the potassic hydrate, a fine *blue* precipitate or, in the case of a trace of HCy only, a *green* suspension of Prussian blue is obtained. The changes may be expressed by the equations—

$$(1)\ KHo + HCy = KCy + \mathbf{O}H_2.$$
$$(2)\ \mathbf{S}O_2Feo'' + 2KCy = \mathbf{Fe}''Cy_2\text{[*]} + \mathbf{S}O_2Ko_2.$$

$\mathbf{Fe}Cy_2$, by combining with 4KCy, forms the soluble double cyanide K_4FeCy_6.

$$(3)\ 2\mathbf{S}_3O_6Fe_2o^{vi} + 3K_4FeCy_6 = 3Fe''Cy_2,2'Fe'''_2Cy_6 + 6\mathbf{S}O_2Ko_2.$$

Free hydrocyanic acid dissolves mercuric oxide, with formation of mercuric cyanide, which is not precipitated by alkalies. $\mathbf{Hg}Cy_2$ exhibits considerable stability, compared with other cyanogen compounds. Boiling *dilute* $\mathbf{S}O_2Ho_2$ does *not* decompose it. HCl breaks it up into $\mathbf{Hg}Cl_2$ and HCy. When $\mathbf{S}H_2$ is passed through its aqueous solution it is decomposed into $\mathbf{Hg}S$ and HCy.

The alkali salts of the compound cyanogen radicals, $FeCy_6$, Fe_2Cy_{12}, Co_2Cy_{12}, are decomposed by moderately concentrated sulphuric acid with evolution of hydrocyanic acid.

This furnishes us with a convenient method for preparing a solution of hydrocyanic acid. Ten parts by weight of K_4FeCy_6 (yellow prussiate of potash) are distilled in a flask or retort with 36 to 40 parts of dilute sulphuric acid (one of acid to six of water). The flask or retort is connected with a Liebig's condenser and double-necked receiver, from which any uncondensed gas can be carried under a Bunsen lamp, and burnt. Every joint should be made *perfectly tight*, and the condenser-tube should dip into the water placed in the receiver. The reaction takes place according to the equation :—

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[*] $\mathbf{Fe}Cy_2$ is difficultly obtained in an isolated condition, as it forms in the presence of KCy potassic ferrocyanide, K_4FeCy_6, containing the compound cyanogen radical $FeCy_6$, which in its turn reacts upon the ferric salt.

$$2K_4FeCy_6 + 3SO_2Ho_2 = 6HCy + K_2Fe''FeCy_6 + 3SO_2Ko_2.$$

White residue
turning blue by exposure
to the atmosphere.

A solution of HCy, when left to itself, undergoes spontaneous decomposition, giving rise to the formation of several complex organic bodies, among which we find chiefly ammonic formate. A few drops of a mineral acid (SO_2Ho_2 dilute) added to the aqueous solution retards this decomposition considerably.

Hydrocyanic acid is exceedingly poisonous. Small quantities of the gaseous acid, when inhaled, cause a peculiar sensation in the throat, and are followed by headache, giddiness, and other disagreeable symptoms. Great care must therefore be taken in operating with HCy, as for instance, on pouring it from one vessel to another, or with cyanogen compounds generally, and for the purposes of analysis small quantities only should be operated upon at a time.

HYDROFERROCYANIC ACID, H_4FeCy_6.—This acid is *tetrabasic*, *i.e.*, its four hydrogen atoms can be replaced by four atoms of a monad or two atoms of a dyad metal. The potassium salt is prepared on a manufacturing scale by introducing nitrogenous animal substances (horn-shavings, etc.) and iron into fused wood-ashes. The fused mass is lixiviated with water and the salt allowed to crystallize out. It may also be prepared by decomposing Prussian blue with KHo or $COKo_2$ and separating the ferric hydrate by filtration, thus:—

$$3Fe''Cy_2,2'Fe'''_2Cy_6 + 12KHo = 3K_4FeCy_6 + 2Fe_2Ho_6.$$

Potassic ferrocyanide, $K_4FeCy_6 + 3Aq$, crystallizes in large lemon-yellow crystals; hence its name *yellow prussiate of potash.* Its positive element (potassium) can, by double decomposition, be replaced by other metals, either entirely or partially, and the property of cyanogen to form double cyanides is well illustrated by the deportment of the more complex ferrocyanides. This will be seen from the following list of some of the more common ferrocyanides:—

$K_4FeCy_6 + 3Aq.$
$Na_4FeCy_6 + 6Aq.$
$Am_4FeCy_6 + 3Aq.$
$Ba''_2FeCy_6 + 6Aq.$
$K_2Ba''FeCy_6 + 3Aq.$
$Ca''_2FeCy_6 + 12Aq.$
$K_2Ca''FeCy_6 + 3Aq.$
$Cu_2FeCy_6 + 4Aq.$
$K_2Cu''FeCy_6 + 2Aq.$
$K_2Fe''FeCy_6.$
$NaK_3FeCy_6 + 3Aq.$
$AmK_3FeCy_6 + 3Aq.$

REACTIONS IN THE DRY WAY.

K_4FeCy_6 fuses, when strongly ignited, and breaks up into nitrogen, potassic cyanide, and carbide of iron, or a mixture of carbon and iron, thus:—

$$K_4FeCy_6 = 4KCy + C_2Fe + N_2.$$

Heated with free access of air, or in contact with metallic oxides, the KCy is further converted into potassic cyanate, CyKo.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC FERROCYANIDE.

The alkaline ferrocyanides are readily soluble in water, the alkaline earthy ferrocyanides are difficultly soluble; those of iron and most other metals are insoluble in water, and many of them also insoluble in acids. They are decomposed on boiling with potassic hydrate with formation of a solution of potassic ferrocyanide, and an insoluble metallic hydrate. Some ferrocyanides are remarkable for their characteristic colour, notably so those of iron and copper; others are white, *e.g.*, those of the alkaline earthy metals, of Zn, Pb, Ag, Hg; greenish-white, *e.g.*, Ni''_2FeCy_6, Co''_2FeCy_6; reddish-white, *e.g.*, Mn''_2FeCy_6. Potassic ferrocyanide is employed, on this account, as a useful reagent in the qualitative examination of metals, especially of iron and copper.

NO_2Ago produces a *white* precipitate of **argentic ferrocyanide**, Ag_4FeCy_6, insoluble in dilute nitric acid and ammonic hydrate, soluble in potassic cyanide.

SO_2Cuo'', added in excess, gives with a solution of K_4FeCy_6 a *red (chocolate-coloured)* precipitate of **dicupric ferrocyanide**, Cu''_2FeCy_6, whilst an insufficient amount of the cupric salt gives a *brown* precipitate of **dipotassic cupric ferrocyanide**, $K_2Cu''FeCy_6$.

SO_2Feo'' gives a *light blue* precipitate of **dipotassic ferrous ferrocyanide**, $K_2Fe''FeCy_6$, thus:—

$$K_4FeCy_6 + \mathbf{SO_2Feo''} = K_2Fe''FeCy_6 + \mathbf{SO_2}Ko_2,$$

which is slowly *oxidized* by exposure to the air, or rapidly, by oxidizing agents, such as nitric acid, or chlorine water: a part of the potassium being removed as oxide, or chloride, thus:—

$$\underset{\text{Light blue precipitate.}}{2Fe''K_2FeCy_6} + Cl_2 = \underset{\text{Diferrous dipotassic ferricyanide.}}{Fe''_2K_2Fe_2Cy_{12}} + 2KCl,$$

or potassic ferricyanide in which four atoms of potassium have been replaced by two atoms of dyad iron.

Potassic ferrocyanide is, in fact, readily converted into potassic ferricyanide, $K_6Fe_2Cy_{12}$ (analogous to the conversion of ferrous salts into ferric salts), by various oxidizing agents, such as chlorine, nitric acid, potassic chlorate and hydrochloric acid, etc.

Fe_2Cl_6 gives an *intensely blue* precipitate of $3Fe''Cy_2, 2'Fe'''_2Cy_6$, called **Prussian blue**, thus:—

$$3K_4FeCy_6 + \mathbf{Fe_2}Cl_6 = 3Fe''Cy_2, 2'Fe'''_2Cy_6 + 12KCl,$$

which constitutes at once a most characteristic and delicate reaction for ferric salts and for ferrocyanogen (as well as for cyanogen, as has been already shown). This precipitate is insoluble in dilute mineral acids, but dissolves in oxalic acid to a blue liquid (blue ink), and in ammonic tartrate to a violet liquid. It is decomposed by caustic alkalies, as well as by calcic and even more readily and completely by magnesic carbonate (*magnesite*). On boiling with mercuric oxide, Prussian blue is entirely decomposed into $\mathbf{Hg}Cy_2$ and ferrous and ferric oxides, thus:—

$$3Fe''Cy_2,2'Fe'''_2Cy_6 + 9\mathbf{Hg}O = 9\mathbf{Hg}Cy_2 + 3\mathbf{Fe}O + 2\mathbf{Fe}_2O_3.$$

By adding an insufficient amount of $\mathbf{Fe}_2Cl_6$ to a solution of K_4FeCy_6, a blue precipitate is likewise obtained, which is, however, soluble in water, and is therefore called *soluble Prussian blue* (used for inks). It is generally thought to be composed of one part of Prussian blue and one of potassic ferrocyanide.

Concentrated sulphuric acid (about 10 parts by weight) decomposes potassic ferrocyanide (1 part by weight of the dry salt), with evolution of carbonic oxide (METHOD FOR PREPARING CARBONIC OXIDE); the nitrogen of the cyanogen, being converted into ammonia, is left as ammonic sulphate, thus:—

$$K_4FeCy_6 + 6\mathbf{S}O_2Ho_2 + 6\mathbf{O}H_2 = 6\mathbf{C}O + 2\mathbf{S}O_2Ko_2 + \mathbf{S}O_2Feo'' + 3\mathbf{S}O_2Amo_2.$$

When concentrated hydrochloric acid is added to an alkaline ferrocyanide, hydroferrocyanic acid separates in the cold, as a white crystalline powder, which turns rapidly blue. If ether be added to the solution of potassic ferrocyanide, previous to its precipitation with concentrated hydrochloric acid, the acid is obtained quite colourless.

HYDROFERRICYANIC ACID, $H_6Fe_2Cy_{12}$.—This acid is *hexabasic*, since its six atoms of hydrogen may be replaced by six atoms of a monad metal, or by three atoms of a dyad metal. Potassic ferricyanide is derived from K_4FeCy_6 by a process of oxidation, as, for instance, by passing chlorine into an aqueous solution of it, till a solution of ferric chloride produces no longer a blue precipitate, but imparts merely a brown coloration to the liquid. The change is expressed by the equation:—

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

It is effected by the abstraction of two atoms of the metal potassium from two parts of K_4FeCy_6. Two atoms of cyanogen are transferred to two molecules of $\mathbf{Fe}Cy_2$, whereby the ferrous cyanide is converted into ferric cyanide.

It is also called *red prussiate of potash*, on account of the dark red coloured crystals, which can be separated from potassic chloride by crystallization.

Reducing agents convert it into potassic ferrocyanide, especially in alkaline solutions. The transformation is effected by the addition of two atoms of the metal potassium. The ferric cyanide in the double cyanide is reduced to ferrous cyanide, thus:—

$$6KCy,'Fe'''_2Cy_6 + K_2 = 8KCy,2Fe''Cy_2, \text{ or } 2(4KCy,FeCy_2)$$
$$= 2K_4FeCy_6.$$

The following are instances of indirect oxidation effected by potassic ferricyanide :—

$\mathbf{S}H_2$ converts the ferri- into a ferrocyanide, with separation of sulphur,
KI " " " with precipitation of iodine,
$\mathbf{Cr}_2O_3$, or its salts, in the presence of KHo, is converted into $\mathbf{Cr}O_3$,
$\mathbf{Pb}O$ " " " " $\mathbf{Pb}O_2$,
$\mathbf{Mn}O$ " " " " $\mathbf{Mn}O_2$,
$\mathbf{Sn}O$ " " " " $\mathbf{Sn}O_2$,
$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$ " " " $\mathbf{C}O_2$,
KCy " " " CyKo,
$\mathbf{P}_2O_3$ " " " $\mathbf{P}_2O_5$,
$\mathbf{S}O_2$ " " " $\mathbf{S}O_3$.

$\mathbf{N}H_3$ gives with $K_6Fe_2Cy_{12}$ potassic and ammonic ferrocyanides with evolution of nitrogen gas, thus :—

$$6K_6Fe_2Cy_{12} + 16\mathbf{N}H_3 = 9K_4FeCy_6 + 3Am_4FeCy_6 + N_4.$$

Many organic substances, *e.g.*, sugar, dextrine, starch, alcohol, and even paper, are oxidized, in the presence of an alkali, to $\mathbf{C}O_2$ and $\mathbf{O}H_2$. Indigo is bleached. Phosphorus, sulphur, and iodine are converted by the action of $K_6Fe_2Cy_{12}$, in the presence of alkalies, into $\mathbf{P}OHo_3$, $\mathbf{S}O_2Ho_2$, $\left\{\begin{matrix}OI\\ OHo\end{matrix}\right.$.

Analogous to potassic ferrocyanide, ferricyanogen forms *double ferricyanides*, by the partial or entire replacement of the six atoms of the positive element, potassium, by different metals. The following are some of the more important metallic ferricyanides :—

$K_6Fe_2Cy_{12}$
$Na_6Fe_2Cy_{12} + Aq.$
$Ca''_3Fe_2Cy_{12} + 6Aq.$
$Ba''_2K_2Fe_2Cy_{12} + 3Aq.$
$Fe''_3Fe_2Cy_{12}$ (Turnbull's blue).

REACTIONS IN THE DRY WAY.

Potassic ferricyanide is decomposed upon ignition, yielding cyanogen and nitrogen, and leaving a residue, consisting of potassic cyanide, potassic ferrocyanide, Prussian blue, paracyanogen, carbon and iron.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF POTASSIC FERRICYANIDE.

The alkaline ferricyanides are readily soluble in water. The others are mostly insoluble.

$\mathbf{N}O_2Ago$ produces an *orange coloured* precipitate of **argentic ferricyanide**, $Ag_6Fe_2Cy_{12}$, insoluble in dilute nitric acid, but readily soluble in ammonic hydrate, and potassic cyanide.

$\mathbf{S}O_2Feo''$ gives a *blue* precipitate (*Turnbull's blue*) of $Fe''_3Fe_2Cy_{12}$, **triferrous ferricyanide,** which is decomposed by potassic hydrate into potassic ferrocyanide and ferroso- ferric hydrate :—

$$Fe''_3Fe_2Cy_{12} + 8KHo = 2K_4FeCy_6 + \mathbf{Fe}_3O_4,4\mathbf{O}H_2.$$

Fe_2Cl_6 produces no precipitate, but gives a *brownish coloration. The deportment of potassic ferro- and ferricyanide with iron salts enables us to distinguish between ferrous and ferric salts.*

HYDROCOBALTICYANIC ACID, $H_6'Co'''_2Cy_{12}$.—Solutions of cobaltous salts are precipitated by KCy. The precipitate consists of flesh-coloured or cinnamon-brown cobaltous cyanide, $CoCy_2$. Excess of potassic cyanide dissolves the precipitate, forming a readily decomposable double cyanide, which, on boiling, or on the addition of HCl, is converted into a difficultly decomposable double cyanide, analogous to potassic ferricyanide, with evolution of hydrogen, thus :—

$$2(4KCy,CoCy_2) + 2OH_2 = K_6Co_2Cy_{12} + 2KHo + H_2.$$

Potassic cobalticyanide.

This double cyanide is of great interest, because *it enables us to separate cobalt from nickel, both qualitatively and quantitatively.*

CYANIC ACID, CyHo.—Obtained in the form of potassic cyanate by the oxidation of KCy or K_4FeCy_6. This salt is very stable when heated by itself, but deliquesces in the air, and is broken up by water into an acid carbonate and ammonia, thus :—

$$CyKo + 2OH_2 = COHoKo + NH_3.$$

Potassic cyanate is invaribly found in commercial potassic cyanide, sometimes to a considerable extent.

REACTIONS IN THE DRY WAY.

It acts as a flux in blowpipe reactions, and is a powerful *oxidizing* agent. When heated with charcoal, it is converted into KCy, CO, and CO_2. On heating, therefore, a metallic oxide on charcoal, with KCy containing CyKo, the oxide is reduced to the metallic state.

REACTIONS IN THE WET WAY.

The cyanates of the alkalies, alkaline earths, and a few metallic oxides are soluble in water, but decompose rapidly with evolution of ammonia. The cyanates of silver, lead, mercurosum, cupricum, are insoluble in water.

NO_2Ago produces with potassic cyanate a *white* precipitate of **argentic cyanate,** CyAgo, *soluble* in ammonic hydrate, and in dilute nitric acid; AgCy is *insoluble* in nitric acid.

Moderately concentrated sulphuric or hydrochloric acid decomposes CyKo with effervescence, owing to the liberation of CyHo, which affects the eyes most painfully, and is recognised by its pungent odour, resembling that of strong acetic acid; the greater portion of the liberated acid is, however, decomposed at once by water into CO_2, and an ammonic salt, thus :—

$$2CyKo + 2SO_2Ho_2 + 2OH_2 = 2CO_2 + SO_2Ko_2 + SO_2Amo_2,$$

and it is by testing for ammonia, by means of caustic lime, that its presence can be shown.

SULPHOCYANIC ACID, CyHs.—Obtained in combination with potassium by heating KCy with sulphur or a metallic sulphide. Hence the usefulness of potassic cyanide for *reducing* metallic sulphides in blowpipe reactions.

REACTIONS IN THE DRY WAY.

CyKs can be fused out of contact with the air, without undergoing decomposition. It turns first brown, then green, and lastly indigo blue, but becomes again colourless on cooling. In contact with the air, CyKs is converted into cyanate and sulphate, with disengagement of SO_2. The sulphocyanates of the heavy metals are decomposed upon ignition, CS_2 being given off at first, and on raising the temperature a mixture of nitrogen and cyanogen is evolved, whilst a metallic sulphide is left :—

$$4{}^{Cy}_{Cy}Cus'' = N_2 + 3\left\{\begin{matrix}CN\\CN\end{matrix}\right. + 2CS_2 + 4CuS.$$

REACTIONS IN THE WET WAY.

We employ a SOLUTION OF AMMONIC SULPHOCYANATE, CyAms.

NO_2Ago produces a *white curdy* precipitate of **argentic sulphocyanate,** CyAgs, insoluble in water and in dilute acids; it is soluble in ammonic hydrate, from which it crystallises out on evaporation. It is also soluble in CyAms or CyKs, forming a double sulphocyanate (CyAgs, CyKs), from which water or hydrochloric acid precipitates granular—ammonic hydrate, crystalline CyAgs.

SO_2Cuo'' gives a *black* crystalline precipitate of **cupric sulphocyanate,** ${}^{Cy}_{Cy}Cus''$, which, on standing in the liquid is converted into **cuprous sulphocyanate,** ${}^{Cy}_{Cy}Cu_2s''$. This characteristic cuprous salt is obtained instantly by adding $SOHo_2$, or a solution of a ferrous salt to the cupric salt.

Fe_2Cl_6 produces an *intensely red solution*, owing to the formation of a soluble **ferric sulphocyanate**, $Cy_6Fe_2s^{vi}$. Alkaline sulphocyanates furnish us, on this account, with a *most delicate reaction for ferric salts.* This reaction serves also for the detection of sulphocyanogen and hydrocyanic acid. The blood-red colour is destroyed by $HgCl_2$. On introducing some metallic zinc into the blood-red solution, SH_2 is evolved.

QUESTIONS AND EXERCISES.

1. Explain the derivation of the term cyanogen.
2. Why are $\left\{\begin{matrix}CN\\CN\end{matrix}\right.$, $FeCy_6$ and Fe_2Cy_{12} viewed as compound radicals?
3. How are KCy and K_4FeCy_6 prepared? Describe their properties, as far as the analytical data illustrate them.
4. Explain the action of heat upon KCy and K_4FeCy_6, 1st, out of contact with air; 2nd, with free access of air.
5. What constitutes the usefulness of KCy as a reagent for blowpipe experiments?
6. Explain the changes which cyanides of the heavy metals undergo upon ignition.
7. How would you prepare cyanogen gas? Describe its properties.
8. Classify cyanides according to their solubility in water. Enumerate some of the more important single cyanides.
9. What is understood by soluble double cyanides? How are they classified, and how can the easily decomposable double cyanides be distinguished from the difficultly decomposable double cyanides?
10. Enumerate, 1st, easily decomposable double cyanides; 2nd, difficultly decomposable double cyanides.
11. Give reasons for the existence of the compound radicals ferro-, ferri- and cobalticyanogen in the double cyanides K_4FeCy_6, $Pb''_3Fe_2Cy_{12}$, $Cu''_3Co_2Cy_{12}$.
12. Explain the action of dilute acids upon single cyanides and upon easily decomposable double cyanides.
13. Explain the difference between a precipitate, produced by a solution of a salt

of a heavy metal with a solution of an easily decomposable double cyanide, or with an alkaline ferro- or ferricyanide.

14. What is the action of hydrated and carbonated alkalies upon the two classes of double cyanides?
15. Explain the action of $\mathbf{S}H_2$ upon the following cyanides and double cyanides: $\mathbf{Hg}Cy_2$, K_2CdCy_4, $KAgCy_2$, K_2MnCy_4, K_2CuCy_4, K_2CoCy_4, K_2NiCy_4.
16. How is AgCy distinguished from AgCl?
17. Describe the action of HCy upon $\mathbf{S}_2Am_2$, and explain how traces of HCy can be detected, in the presence of ferro- or ferricyanogen compounds.
18. How would you demonstrate the greater stability of $\mathbf{Hg}Cl_2$ over that of $\mathbf{Hg}Cy_2$?
19. Explain the use of ferroso-ferric salts for the detection of HCy.
20. How is HCy prepared? Describe its properties.
21. Describe shortly how yellow prussiate of potash can be prepared.
22. Enumerate some of the more common ferrocyanides.
23. How would you examine a ferrocyanide insoluble in acids, *e.g.*, *Prussian blue?*
24. Explain the action of KHo upon *Prussian blue* and upon *Turnbull's blue.*
25. Explain what reactions ferrous and ferric salts give with ferro- and ferricyanides.
26. Explain the formation of soluble Prussian blue.
27. What is the action of dilute or of concentrated sulphuric acid upon potassic ferrocyanide?
28. State how H_4FeCy_6 is prepared.
29. Explain the conversion of potassic ferro- into ferricyanide.
30. Give instances of the oxidizing action of potassic ferricyanide in alkaline solutions.
31. Enumerate some of the more important metallic ferricyanides.
32. How can argentic ferro- and ferricyanides be separated from each other?
33. What decomposition takes place when ferro- and ferricyanides are fused with a mixture of ammonic sulphate and nitrate?
34. How is CyHo recognized in the presence of a cyanide?
35. What is the action of concentrated $\mathbf{S}O_2Ho_2$ upon a cyanate?
36. What reactions take place when potassic cyanate is heated with charcoal, with $\mathbf{Mn}O_2$, or with $\mathbf{O}H_2$?
37. Explain the formation of potassic sulphocyanate, and state what change it undergoes when heated in contact with air.
38. Explain the action of nascent hydrogen upon ferric sulphocyanate.
39. Why does potassic sulphocyanate enable us to distinguish between ferrous and ferric salts?
40. Calculate the percentage composition of cuprous sulphocyanate, $\begin{matrix}Cy\\Cy\end{matrix}Cu_2s''$.

Chapter VIII.

REACTIONS OF THE ACIDS.

B. Organic Acids.

Most organic acids cannot be distinguished qualitatively as readily as inorganic acids. A few of the more generally occurring acids which can be readily detected, claim a short notice.

The greater number of organic acids consist of carbon, hydrogen, and oxygen; some also contain nitrogen. There is no organic acid known containing only two single atoms of an element, and only one containing three, viz., hydrocyanic acid, HCN ; whilst the number of atoms in a molecule of most organic acids, as for instance in stearic acid, $C_{18}H_{36}O_2$, is far greater than in any inorganic compound.

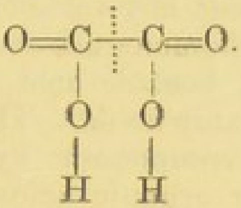
The element with which oxygen, hydrogen, and nitrogen are grouped in organic acids is *carbon*, which in most cases, probably in all, acts as a *tetrad* element.*

Groups of elements performing similar functions in organic acids, and built up invariably in the same number, are called *compound organic radicals.*

Nearly every organic acid contains one acidifying principle of two negative compound radicals, *e.g.* :—

Cyanogen (molecule) $\left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right.$ $N\equiv C \vdots C\equiv N$, or

Oxatyl (the molecule of which is dry oxalic acid) $\left\{\begin{matrix} COHo \\ COHo \end{matrix}\right.$



$$\begin{matrix} O{=}C & \vdots & C{=}O. \\ | & & | \\ O & & O \\ | & & | \\ H & & H \end{matrix}$$

The semi-molecule of each of these compound radicals contains one atom of carbon with one bond left free to combine with another element or group of elements, the other three bonds being satisfied, in cyanogen, by combining with triad nitrogen, or in oxatyl, with one atom of oxygen and one of hydroxyl. In the molecules the two free bonds of the carbon satisfy each other.

These radicals are closely related to each other. An aqueous solution of cyanogen (one volume of water dissolves about four volumes of the gas) is speedily transformed mainly into ammonic oxalate, thus :—

$$\left\{\begin{matrix} CN \\ CN \end{matrix}\right. + 4OH_2 = \left\{\begin{matrix} COAmo \\ COAmo \end{matrix}\right..$$

In the presence of a boiling solution of potassic hydrate, cyanogen evolves ammonia and produces potassic oxalate, thus :—

$$\left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right. + 2KHo + 2OH_2 = \left\{\begin{matrix} COKo \\ COKo \end{matrix}\right. + 2NH_3.$$

from which salt oxalic acid can be obtained.

Oxalic acid, on the other hand, may be converted into cyanogen, by transforming it into ammonic oxalate and submitting this salt to the action of heat, thus :—

$$\left\{\begin{matrix} CO(NH_4O) \\ CO(NH_4O) \end{matrix}\right. = \left\{\begin{matrix} CN''' \\ CN''' \end{matrix}\right. + 4OH_2.$$

Oxalic acid, or the molecule of the compound radical oxatyl, results from the oxidation of a large number of organic bodies, *e.g.*, sugar, woody fibre, etc., by the action of powerful oxidizing agents, such as concentrated nitric acid, and is resolved into products of the final oxidation of everything organic, viz., carbonic anhydride and water.

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* Frankland : Lecture Notes, vol. ii, page 2.

Heat, in fact, breaks up nearly all salts of organic acids. Those of alkaline and alkaline earthy bases, leave upon gentle ignition *carbonates*, with separation of *carbon*, and consequent blackening, oxalates excepted. The carbonaceous residue being soluble in water, indicates that the organic acid was combined with alkali metals, and if insoluble, with alkaline earthy bases. The decomposition is, moreover, accompanied in most instances by the evolution of volatile matter, of carbonic oxide and hydrocarbons, empyreumatic vapours and oils.

In the free state organic acids are either *volatile*, and can be distilled or sublimed, generally without undergoing decomposition and without leaving any carbonaceous residue, as for instance, formic acid, and its homologues acetic acid, etc. (or the acids of the fatty acid series); benzoic acid and others, belonging to the series of aromatic organic acids. These acids can be removed from any of their saline compounds by decomposition with dilute sulphuric acid. Other organic acids are *non-volatile*, and are decomposed when heated by themselves, leaving a carbonaceous residue; and the acids cannot be removed from their salts by distillation with sulphuric acid.

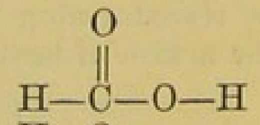
FORMIC ACID, $\left\{\begin{matrix}\mathrm{H}\\\mathrm{COHo}\end{matrix}\right.$.—Obtained in a great many chemical reactions, as a product of oxidation or decomposition. It is usually prepared by heating a mixture of equal weights of crystallized oxalic acid and glycerine to 75° C., and distilling with water—

$$\left\{\begin{matrix}\mathrm{COHo}\\\mathrm{COHo}\end{matrix}\right. = \left\{\begin{matrix}\mathrm{H}\\\mathrm{COHo}\end{matrix}\right. + \mathrm{CO_2}.$$

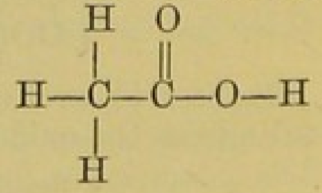
Formic acid distils at 100° C. It is of interest, as being the lowest possible acid in the series of fatty acids, a series which most comprehensively illustrates the structure of organic acids.

By a successive increment of CH_2, or by substituting for H—the positive element in formic acid—successively semi-molecules of the compound organic radicals methyl, CH_3, ethyl, C_2H_5, etc., the whole series of fatty acids can be obtained, thus :—

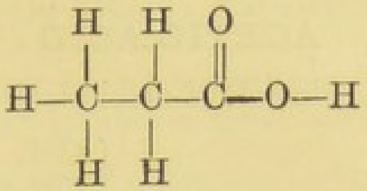
Formic acid $\left\{\begin{matrix}\mathrm{H}\\\mathrm{COHo}\end{matrix}\right.$



Acetic acid $\left\{\begin{matrix}\mathrm{H}\\\mathrm{CH_2}\\\mathrm{COHo}\end{matrix}\right.$ or $\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{COHo}\end{matrix}\right.$



Propionic acid $\left\{\begin{array}{l} H \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C_2H_5 \\ COHo \end{array}\right.$



$$\begin{array}{ccccccccc} & & H & & H & & O & & \\ & & | & & | & & \| & & \\ H & - & C & - & C & - & C & - & O - H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Butyric acid $\left\{\begin{array}{l} H \\ CH_2 \\ CH_2 \\ CH_2 \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C_3H_7 \\ COHo \end{array}\right.$

Stearic acid $\left\{\begin{array}{l} H \\ (CH_2)_{17} \\ COHo \end{array}\right.$ or $\left\{\begin{array}{l} C_{17}H_{35} \\ COHo \end{array}\right.$

The lower members of the series of fatty acids dissolve freely in water, whilst the more complex fatty acids, with largely increased molecular weights—to mention only stearic acid—are quite insoluble in water. Those containing more than three atoms of carbon per molecule exhibit a number of isomeric modifications, as yet more or less imperfectly studied.

REACTIONS IN THE DRY WAY.

Formates of the fixed alkalies and alkaline earthy bases, when heated out of contact with air, are decomposed into carbonates, and a little carbon, with disengagement of combustible gases—mainly carbonic oxide and hydrogen. Formates of the heavy metals give off CO_2, CO, and OH_2, leaving the metal (generally mixed with a little carbon).

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF SODIC FORMATE, $\left\{\begin{array}{l} H \\ CONao \end{array}\right.$.

All formates are soluble in water; some also in alcohol.

Formic acid and formates are readily recognized by their property of reducing salts of the noble metals, *e.g.*, $AuCl_3$, NO_2Ago, $N_2O_4Hg_2o''$, or $HgCl_2$, to the metallic state, with evolution of carbonic anhydride.

Potassic permanganate is likewise deoxidized by formic acid.

Formic acid or a formate, when heated with a solution of potassic dichromate and oil of vitriol, is broken up, with evolution of CO_2.

This *reducing action distinguishes formic acid from acetic acid and most of its homologues.*

When heated with concentrated sulphuric acid, formic acid and formates are broken up into water and carbonic oxide, which latter burns with a fine blue flame. (METHOD OF PREPARING CARBONIC OXIDE GAS.) The mixture does not blacken. The decomposition is expressed thus:—

$$\left\{\begin{array}{l} H \\ COHo \end{array}\right. + SO_2Ho_2 = CO + SO_2Ho_2 + OH_2.$$

ACETIC ACID (Vinegar), $\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.$.—Obtained either by the oxidation of alcohol, thus :—

$$\left\{\begin{matrix}CH_3\\CH_2Ho\end{matrix}\right. + O_2 = \left\{\begin{matrix}CH_3\\COHo\end{matrix}\right. + OH_2,$$

or by the destructive distillation of vegetable substances, especially of wood. Pure acetic acid boils at 118° C., and is prepared by decomposing dry sodic acetate (5 parts by weight) with concentrated sulphuric acid (6 parts by weight). The crude acid is placed over $\mathbf{Mn}O_2$, in order to destroy any $\mathbf{S}O_2$, and rectified by distillation over a little sodic acetate.

REACTIONS IN THE DRY WAY.

Acetates are decomposed upon ignition, yielding a peculiar inflammable volatile liquid called *acetone*, $\left\{\begin{matrix}CH_3\\COCH_3\end{matrix}\right.$, thus :—

$$2\left\{\begin{matrix}CH_3\\CONao\end{matrix}\right. = CONao_2 + \left\{\begin{matrix}CH_3\\COCH_3.\end{matrix}\right.$$

The acetates of the alkalies and alkaline earthy bases, when strongly ignited, leave a carbonate; those of the heavy metals leave either a metallic oxide, or the metal itself, mixed with carbon.

Heated with caustic alkalies (soda-lime), dry sodic acetate gives off *marsh-gas*, or *light carburetted hydrogen*, $\mathbf{C}H_4$, thus :—

$$3\left\{\begin{matrix}CH_3\\CONao\end{matrix}\right. + NaHo,CaHo_2 = 2CONao_2, + COCao'' + 3CH_4.$$

The gas can be collected in the usual manner over water, and on applying a light it burns quietly with a yellowish flame, with formation of water and carbonic anhydride. It forms one of the constituents of the gas-bubbles which are seen to rise from the bottom of stagnant waters, where decaying organic matter has accumulated. Hence its name *marsh-gas*.

Its specific gravity is ·554 when compared with air. Its molecular weight is 16, one litre weighing 8 criths. A mixture of marsh-gas and air—one part by volume of the hydrocarbon with 10 of air—explodes powerfully when a light is applied. Light carburetted hydrogen forms a constituent of ordinary coal-gas, and is likewise found in coal mines, where it gives frequently rise to explosions when mixed with air and fired. It is called by the miner *fire-damp*. The atmosphere left in the workings of a coal-pit, after an explosion of fire-damp has taken place, is called *choke-damp*, or *after-damp*, consisting to a large extent of carbonic anhydride.

REACTIONS IN THE WET WAY.

A SOLUTION OF SODIC ACETATE, $\left\{\begin{matrix}CH_3\\CONao,\end{matrix}\right.$ may be employed.

All acetates are soluble in water. Argentic and mercurous acetates are the least soluble.

On heating a solid acetate (or a concentrated aqueous solution of it) with alcohol and concentrated sulphuric acid, **acetic ether** (ethylic acetate), $\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COEto}\end{matrix}\right.$ (Et = ethyl) is formed which possesses a peculiar fragrant odour. The change is expressed thus:—

$$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CONao}\end{matrix}\right. + \mathrm{EtHo} + \mathbf{S}\mathrm{O_2Ho_2} = \left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COEto}\end{matrix}\right. + \mathbf{S}\mathrm{O_2HoNao} + \mathbf{O}\mathrm{H_2}.$$

Too much alcohol should be avoided lest common (or sulphuric) ether, $\mathbf{O}\mathrm{Et_2}$, be formed, the odour of which would mask that of the acetic ether.

By distilling an acetate with moderately dilute sulphuric acid in a retort, free acetic acid is obtained, which is recognized by its characteristic pungent odour. It *cannot* be oxidized by aqueous chromic acid.

$\mathbf{Fe}_2\mathrm{Cl}_6$ added to a solution of an acetate, produces a deep red-coloured solution, owing to the formation of ferric acetate. On boiling, the whole of the iron is precipitated as **basic ferric acetate,** in the form of *brownish-yellow flakes.* AmHo precipitates the iron from a solution of ferric acetate as ferric hydrate.

Ammonic acetate, especially in the presence of ammonia, dissolves several insoluble sulphates, *e.g.*, $\mathbf{S}\mathrm{O_2Pbo''}$, $\mathbf{S}\mathrm{O_2Cao''}$.

APPROXIMATE SEPARATION OF ACETIC ACID FROM ITS NEXT HIGHER HOMOLOGUES.—Add enough caustic potash to convert the acetic acid into binacetate and distil. The acid containing the least number of carbon atoms, being the stronger, is first neutralized, and if sufficient potash has been added, the distillate is obtained free from acetic acid.

STEARIC ACID, $\left\{\begin{matrix}\mathbf{C}_{17}\mathrm{H}_{35}\\ \mathrm{COHo}\end{matrix}\right.$.—Found in fatty bodies, *e.g.*, pure mutton fat, in combination with glycerine, $\left\{\begin{matrix}\mathrm{CH_2Ho}\\ \mathrm{CHHo}\\ \mathrm{CH_2Ho}\end{matrix}\right.$. When heated with solutions of caustic alkalies, the fat saponifies and the fatty acid forms with the alkali metal a *soap*, freely soluble in warm water, and the glycerine separates. On decomposing the soap by the addition of an acid (dilute hydrochloric or sulphuric acid), the fat which separates is found completely changed in character. It has an acid reaction to test-paper when in a melted state, and is soluble with the greatest facility in alcohol, from which it crystallizes in milky-white needles. Its composition is $\mathbf{C}_{18}\mathrm{H}_{36}\mathrm{O}_2$, or $\left\{\begin{matrix}\mathbf{C}_{17}\mathrm{H}_{35}\\ \mathrm{COHo}\end{matrix}\right.$. It melts at 54° C. Pure hard soap is *sodic stearate*, $\left\{\begin{matrix}\mathbf{C}_{17}\mathrm{H}_{35}\\ \mathrm{CONao}\end{matrix}\right.$, and contains generally—

20—25 per cent. of water
7— 8 „ „ soda (ONa_2)
and 67—73 „ „ stearic acid.

The analysis of soap is effected by treating 10 grms., cut up into thin slices, in a porcelain dish, with dilute hydrochloric acid, and heating gently for some time, till the whole of the soap is decomposed. The fatty acid floats on the surface. The dish is set aside to cool, when the fatty acid is obtained as a solid cake, which can be readily removed and dried between filter paper. Sodic chloride is left in solution, and is obtained on evaporation in crystals.

QUESTIONS AND EXERCISES.

1. What elements enter into the composition of organic acids?
2. State which compound organic radicals are met with in organic acids, and show the relation which exists between them.
3. How are the several salts of organic acids influenced by heat, and what inference can be drawn from this action?
4. Explain the structure of the several members of the fatty acid series. Give illustrations.
5. How is formic acid obtained, and what changes do formates undergo, when heated out of contact with air?
6. How can a formate be detected in the wet way? Give equations.
7. State how you would prepare pure carbonic oxide from baric formate.
8. You have given to you plumbic formate, how would you prepare therefrom formic acid and sodic formate?
9. State how acetic acid is prepared.
10. What is the action of heat upon dry acetates?
11. How would you prepare marsh-gas?
12. Explain the terms *fire-damp*, and *choke-damp*, or *after-damp*.
13. How can the composition of marsh-gas be shown experimentally?
14. Explain the action of acetic acid upon argentic carbonate or plumbic oxide.
15. What residue is left on igniting sodic acetate, calcic acetate, plumbic acetate, or argentic acetate?
16. Explain how you would obtain acetic ether, describe its composition and properties.
17. Give graphic formulæ for marsh-gas, cyanogen, acetic ether, acetone.
18. Explain the composition of hard soap.
19. A solution containing an unknown quantity of formic acid, when heated with solution of $AuCl_3$, yielded 2·235 grms. of metallic gold. How much formic acid by weight did the solution contain?
20. A quantity of crystallized argentic acetate leaves upon ignition 1·236 grm. of metallic silver. How much acetic acid does this correspond to?
21. How much dry sodic acetate must there be decomposed in order to obtain 20 litres of marsh-gas?

BENZOIC ACID, $\left\{\begin{matrix}C_6H_5\\COHo\end{matrix}\right.$, or shortly $\overline{Bz}Ho$.—Is found in many gums and balsams, from which it is obtained by sublimation. Heated in a tube open at both ends, the acid sublimes in long needles, giving off a very irritating vapour. Heated on platinum foil, benzoic acid burns with a luminous smoky flame.

The crystalline acid is very slightly soluble in water or acids, and floats on water. *Benzoates of tetrad metals are mostly insoluble in water, all others are soluble.*

Fe_2 Cl_6 gives a *pale yellow* precipitate of **basic ferric benzoate,** $\overline{Bz}_6Fe_2o^{vi},Fe_2O_3 + 15\,Aq$; and ammonic benzoate is employed sometimes for the separation of Fe^{iv} from Mn'' (compare page 41).

On distilling benzoic acid with lime or baryta, benzol (*benzene*), $\mathbf{C}_6H_6$, is obtained—

$$\left\{\begin{matrix}\mathbf{C}_6H_5\\ \mathbf{C}OHo\end{matrix}\right. + \mathbf{Ca}O = \mathbf{C}_6H_6 + \mathbf{C}OCao''.$$

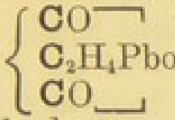
Dilute acids precipitate benzoic acid from aqueous solutions of benzoates; dilute nitric acid is without action upon it.

Heated with concentrated sulphuric acid, benzoic acid does not blacken, neither does it evolve $\mathbf{S}O_2$.

SUCCINIC ACID, $\left\{\begin{matrix}COHo\\ C_2H_4\\ COHo\end{matrix}\right.$, or briefly $\overline{Su}Ho_2$.—*Dibasic acid.*— Obtained by the distillation of amber, of fossil resin, and also by the long-continued action of nitric acid upon butyric, stearic, or margaric acids. The acid crystallizes in white plates, is readily soluble in water, alcohol, and ether, and is not acted upon by boiling nitric acid. Heated in a tube open at both ends, it sublimes in silky needles. Heated upon platinum foil, it burns with a blue flame and without smoke.

Succinates are decomposed upon ignition; the alkaline and alkaline earthy succinates leave a carbonate mixed with carbon.

Most succinates are soluble in water.

Plumbic acetate gives a *white* precipitate of **neutral plumbic succinate,**  $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}_2H_4Pbo''\\ \mathbf{C}O\end{matrix}\right.$, which is rendered basic by treatment with ammonic hydrate.

Fe_2 Cl_6 produces from a solution of neutral ammonic succinate, a *brownish-red, voluminous* precipitate of **basic ferric succinate,** $\overline{Su}_3Fe_2o^{vi},Fe_2O_3$, readily soluble in mineral acids. AmHo renders the precipitate darker by withdrawing a quantity of succinic acid as ammonic succinate, leaving a more basic succinate. (THIS REACTION SERVES FOR THE SEPARATION OF Mn'' FROM Fe^{iv}.)

On boiling the precipitate produced by ferric chloride from a solution of a succinate or benzoate, with ammonic hydrate, soluble ammonic salts of these acids are obtained which can be separated by filtration from the insoluble residue. On the addition of alcohol and **Ba**Cl_2 to the ammoniacal solution, a *white* precipitate of baric succinate is obtained, whilst benzoic acid gives no precipitate (DISTINCTION BETWEEN $\overline{Bz}Ho$ AND $\overline{Su}Ho_2$).

QUESTIONS AND EXERCISES.

1. How are benzoic and succinic acids prepared? Give graphic formulæ.

2. How would you distinguish $\overline{\mathrm{Bz}}\mathrm{Ho}$ from $\overline{\mathrm{Su}}\mathrm{Ho}_2$ in the dry way?
3. State how the precipitate produced by $\overline{\mathrm{Bz}}\mathrm{Ho}$ and $\overline{\mathrm{Su}}\mathrm{Ho}_2$ with $\mathbf{Fe_2Cl_6}$ assists us in distinguishing between these two acids.
4. How would you prepare benzol from benzoic acid?
5. You have given to you a mixture of plumbic benzoate and succinate. State how you would obtain the two acids in the free state.
6. 1·340 grm. of the argentic salt of an organic acid leaves upon ignition ·632 grm. of metallic Ag. What is the molecular weight of the acid?

OXALIC ACID, $\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.$—*Dibasic acid.*—Obtained by the oxidation of a large number of organic bodies, *e.g.*, sugar by nitric acid; or woody fibre, by the action of caustic alkalies. The free acid, $\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right. + 2\mathrm{Aq}$, is a violent poison. It crystallizes in rhombic prisms with two molecules of water of crystallization, which it loses when exposed to dry air, *i.e.*, it effloresces and crumbles to a powder. With bases it forms an important series of salts called *oxalates.* The acid being dibasic, two series of salts, *neutral* and *acid* oxalates, $\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COKo}\end{matrix}\right.$ and $\left\{\begin{matrix}\mathrm{COKo}\\ \mathrm{COHo}\end{matrix}\right.$, exist (besides some *super-acid* oxalates).

REACTIONS IN THE DRY WAY.

Oxalic acid when heated by itself, sublimes for the most part unchanged; a portion of it breaks up into CO, $\mathrm{CO_2}$ and some formic acid. Oxalates yield, upon ignition, different products of decomposition, according to the nature of the base contained therein.

Alkaline oxalates leave a *carbonate*, with slight blackening, and give off carbonic oxide.

Alkaline earthy oxalates leave a *carbonate*, together with *some caustic base*, if a strong heat be applied, and give off CO and $\mathrm{CO_2}$.

Oxalates containing *metallic bases* which do not form carbonates, or the carbonates of which are decomposed by heat, break up into metallic oxides, and give off equal volumes of CO and $\mathrm{CO_2}$, or into *metal*, as for instance argentic oxalate, giving off $\mathrm{CO_2}$.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF AMMONIC OXALATE, $\left\{\begin{matrix}\mathrm{COAmo}\\ \mathrm{COAmo}\end{matrix}\right.$.

Oxalates are either soluble in water, e.g., the alkaline oxalates and a few metallic oxalates; or *insoluble in water, but soluble in acids.*

$\mathrm{CaCl_2}$ ($\mathrm{SO_2Cao''}$ or $\mathrm{CaHo_2}$) precipitates even from very dilute solutions *white pulverulent* **calcic oxalate,** $\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\right.\mathrm{Cao''}$, readily soluble in hydrochloric or nitric acid; almost insoluble in oxalic or acetic acid, and in potassic or ammonic hydrate. Heat promotes the precipitation from very dilute solutions. This constitutes one of the most delicate reactions for oxalic acid.

$BaCl_2$ gives from solutions of neutral oxalates a *white* precipitate of **baric oxalate**, $\left\{\begin{matrix}CO\\CO\end{matrix}\right.Bao'' + Aq$, soluble in oxalic acid, readily soluble in hydrochloric or nitric acid.

NO_2Ago produces a *white* precipitate of **argentic oxalate**, $\left\{\begin{matrix}COAgo\\COAgo\end{matrix}\right.$, soluble in dilute nitric acid, and in ammonic hydrate.

Concentrated sulphuric acid decomposes oxalic acid or oxalates, on the application of a gentle heat, into CO and CO_2, without blackening, by withdrawing from the molecule of oxatyl a molecule of OH_2. The gaseous mixture is passed through a wash-bottle containing caustic soda or lime-water, and the carbonic oxide gas is collected over water. The gas burns with a *blue* flame. (USUAL METHOD FOR PREPARING CARBONIC OXIDE.)

Oxalic acid, or oxalates in the presence of free mineral acids, act *as reducing agents.*

Treat a little black oxide of manganese and oxalic acid, or an oxalate, with a few drops of concentrated sulphuric acid. Effervescence ensues. The gas which escapes is carbonic anhydride, thus :—

$$MnO_2 + \left\{\begin{matrix}COKo\\COKo\end{matrix}\right. + 2SO_2Ho_2 = 2CO_2 + SO_2Mno'' + SO_2Ko_2 + 2OH_2.$$

A solution of gold is reduced to metallic gold, thus :—

$$2AuCl_3 = 3\left\{\begin{matrix}COHo\\COHo\end{matrix}\right. = 6CO_2 + Au_2 + 6HCl.$$

Potassic permanganate is speedily reduced (decolorised).

QUESTIONS AND EXERCISES.

1. How is oxalic acid obtained ? Describe shortly its properties.
2. What changes does oxalic acid undergo, 1st, upon ignition ; 2nd, upon heating with SO_2Ho_2 ; 3rd, upon treatment with SO_2Ho_2 and MnO_2 or $Cr_2O_5Ko_2$; 4th, in contact with $AuCl_3$?
3. How would you distinguish calcic oxalate from calcic carbonate, fluoride, borate or phosphate ?
4. What takes place when potassic, argentic, calcic, or zincic oxalate is ignited by itself ?
5. How would you prepare pure carbonic oxide gas from sodic oxalate ?
6. Why is oxalic acid decomposed by concentrated sulphuric acid almost without any blackening ?
7. Calculate how much MnO_2 is contained in a sample of black manganic oxide, 2·2 grms. of which, when treated with $\left\{\begin{matrix}COKo\\COKo\end{matrix}\right.$ and SO_2Ho_2, yielded 1·662 grm. of CO_2.
8. The calcic salts in one litre of water are precipitated with ammonic oxalate. The precipitate yields upon ignition 1·695 grm. of $COCao''$. How much CaO does the water contain, 1st, per gallon, 2nd, per 100,000 parts ?

TARTARIC ACID, $\left\{\begin{matrix}COHo\\CHHo\\CHHo\\COHo\end{matrix}\right.$, shortly $\overline{T}Ho_2$—*Dibasic acid.*—

Found in grapes, tamarinds, pine-apples and several other fruits in the form of hydric potassic tartrate. The acid met with in commerce is prepared from the tartar or *argol*, an impure hydric potassic tartrate, deposited from the grape juice during fermentation. The acid forms colourless transparent crystals, very soluble in water, both hot and cold, and soluble also in alcohol. The aqueous solution undergoes gradual decomposition.

REACTIONS IN THE DRY WAY.

Tartaric acid is decomposed by heat, giving off a peculiar *odour*, resembling that of *burnt sugar* (caramel), and leaving a residue of carbon. Alkaline tartrates when heated in a test-tube, are decomposed with evolution of inflammable gases, leaving a mixture of finely-divided charcoal and carbonate (*black flux*), from which the carbonate may be extracted by water. The carbonaceous residue left upon igniting alkaline earthy tartrates contains an insoluble carbonate, and effervesces when treated with dilute hydrochloric acid. Tartrates of the heavy metals also undergo decomposition, accompanied by the characteristic odour of burnt sugar, and leave much carbon mixed with metallic oxide or metal.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF TARTARIC ACID, and for some reactions A SOLUTION OF A NORMAL SALT (*Rochelle salt*, or potassic sodic tartrate).

The alkaline tartrates are soluble in water, the acid salts less so than the neutral tartrates. *The normal tartrates of the alkaline earthy bases, of the earths and heavy metals, are difficultly soluble in water*, but dissolve readily in dilute tartaric acid. Alkalies fail to precipitate double tartrates, readily soluble in water, containing an alkaline and metallic base. Hence *the presence of tartaric acid serves to prevent the precipitation* of $\mathbf{Fe}_2\mathrm{O}_3$, $\mathbf{Cr}_2\mathrm{O}_3$, $\mathbf{Zn}\mathrm{O}$, $\mathbf{Ni}\mathrm{O}$, $\mathbf{Co}\mathrm{O}$, $\mathbf{Mn}\mathrm{O}$, $\mathbf{Cu}\mathrm{O}$, $\mathbf{Pb}\mathrm{O}$, $\mathbf{Bi}_2\mathrm{O}_3$, $\mathbf{Pt}\mathrm{O}_2$ or $\mathbf{Cd}\mathrm{O}$, whilst some other substance, *e.g.*, $\mathbf{P}\mathrm{OHo}_3$, if present, may be precipitated from an alkaline solution.

KCl (or some other potassium salt, especially the acetate) produces in a solution of free tartaric acid a *heavy white crystalline* precipitate of **hydric potassic tartrate,** $\overline{\mathrm{T}}\mathrm{HoKo}$, readily soluble in mineral acids and in alkalies and alkaline carbonates, insoluble in acetic acid. The precipitation is accelerated by agitation and by allowing to stand for some hours. Alkalies dissolve the precipitate, forming a normal tartrate, soluble in water, from which acetic acid reprecipitates the hydric potassic tartrate.

$\mathbf{Ca}\mathrm{Ho}_2$ added to excess, precipitates free tartaric acid as a *white* **calcic tartrate,** $\overline{\mathrm{T}}\mathrm{Cao}''$.

$\mathbf{Ca}\mathrm{Cl}_2$ (but not $\mathbf{S}\mathrm{O}_2\mathrm{Cao}''$, except on long standing,) precipitates from a solution of a normal tartrate, **white calcic tartrate** ($\overline{\mathrm{T}}\mathrm{Cao}''$, + 4 aq.), soluble in acids, even tartaric acid, in ammonic salts (AmCl), but not in ammonic hydrate. The precipitate, especially as long as it is amorphous *i.e.*, recently precipitated, is *soluble in cold potassic* or *sodic hydrate*, which is nearly free from carbonate, but is *reprecipitated on boiling* as a gelatinous mass, which *redissolves on cooling*.

NO_2Ago produces from a solution of a normal tartrate (*e.g.*, Rochelle salt) in the cold a *white curdy* precipitate of **argentic tartrate,** $\overline{T}Ago_2$. On filtering and dissolving some of the precipitate off the filter with a little dilute ammonic hydrate, and heating the solution in a *clean* test-tube or flask during ten to twenty minutes, in water, heated to about 66° C., the glass becomes coated with a fine silver mirror. (CHARACTERISTIC REACTION FOR TARTARIC ACID.)

$\overline{Ac}_2Pbo''$ gives a *white crystalline* precipitate of **plumbic tartrate,** $\overline{T}Pbo''$, from solutions of tartaric acid, or its soluble salts. The precipitate is soluble in nitric acid, and in ammonic hydrate; the latter giving rise to the formation of plumbic ammonic tartrate, which cannot be precipitated by AmHo.

Tartaric acid and ammonia dissolve SO_2Pbo''.

Concentrated SO_2Ho_2 decomposes tartaric acid, or a tartrate, on heating, with evolution of SO_2, CO_2, and CO, and separation of carbon.

QUESTIONS AND EXERCISES.

1. Describe some sources of tartaric acid.
2. Describe the decomposition which tartaric acid and tartrates undergo upon ignition.
3. What is the composition of *black flux?*
4. Explain the solvent action of tartaric acid upon certain tartrates in the presence of alkalies.
5. How can tartaric acid be detected in the wet way?
6. Give graphic formulæ for Rochelle salt, argentic and plumbic tartrates.

CITRIC ACID, $\left\{\begin{array}{ll} CHHo & (COHo)\\ CH & (COHo)\\ CH_2 & (COHo)\end{array}\right. + aq.$, or briefly $\overline{Ci}Ho_3$.—

Tribasic acid.—Obtained from orange or lemon-juice. Found also in many other fruits. It forms colourless prismatic crystals, which possess a pure and agreeable acid taste. They dissolve in cold and hot water, and in alcohol. The aqueous solution undergoes decomposition after a time. The *citrates* are very numerous, the acid forming, like phosphoric acid, three classes of salts by the replacement of one, two, or three atoms of hydroxyl by a corresponding amount of potassoxyl, etc.

REACTIONS IN THE DRY WAY.

On heating citric acid, it loses first its water of crystallization, then fuses, and is decomposed with disengagement of pungent and irritating acid fumes, leaving a less abundant carbonaceous residue than tartaric acid. Alkaline and alkaline earthy citrates leave a carbonate upon ignition.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF $\overline{\text{Ci}}\text{Ho}_3$ IN WATER, OR A SOLUTION OF A NORMAL ALKALINE CITRATE.

Potassic salts give no precipitate.

CaHo_2 gives no precipitate *in the cold* from a solution of citric acid, or of a neutral citrate; but *on heating*, a *white* precipitate of **calcic citrate**, $\overline{\text{Ci}}_2\text{Cao}''_3$, is obtained. (DISTINCTION BETWEEN TARTARIC AND CITRIC ACID.) When both citric and tartaric acid are present, the precipitate produced by **CaHo_2**, or **CaCl_2** in the cold is filtered off, and the clear filtrate boiled, when a further precipitate indicates citric acid.

CaCl_2 produces at first no precipitate *in the cold* from an aqueous solution of citric acid, or a soluble citrate; but on standing precipitation takes place and is all but completed, even in the cold, after 24 hours. On boiling a white precipitate of calcic citrate is obtained if the solution be neutral, or if it contain an excess of lime-water or ammonic hydrate. This precipitate is *insoluble in sodic or potassic hydrate*, but soluble both in ammonic salts and in acids.

Argentic citrate, dissolved in ammonic hydrate, does not form a mirror upon heating. Citric acid, like tartaric acid, prevents the precipitation of certain oxides, more especially of **Al_2O_3**, of Groups II and III, by caustic alkalies, on account of the formation of soluble double citrates, containing a metallic and alkali base.

Concentrated sulphuric acid decomposes citric acid or citrates slowly. On cautiously applying heat, **CO** and **CO_2** escape, at first without any blackening of the liquid, but on boiling for some time, **SO_2** is evolved, and carbon separates.

QUESTIONS AND EXERCISES.

1. Whence is citric acid derived?
2. Describe the tests which distinguish citric from tartaric acid.
3. Give graphic formulæ for citric acid.
4. How would you detect oxalic, tartaric, and citric acids contained in a liquid?
5. Why does the presence of citric or tartaric acid prevent the precipitation of **Al_2O_3** or **Fe_2O_3** by AmHo?
6. How would you separate phosphoric acid by precipitation with a magnesic salt from a solution containing phosphates of Al^{iv}, Fe^{iv}, and Mn''?

PRACTICAL EXERCISES.

In order to enable the analyst to acquire a thorough mastery over the reactions for bases and acids, some 25 to 30 simple substances should be analysed by the aid of the subjoined analytical tables, and the results recorded in the manner shown in the Appendix. The nature of these exercises will be sufficiently indicated by the following examples :—

1. Crystallized magnesic sulphate (Epsom salts).
2. Sodic sulphite.
3. Saltpetre.
4. Common sodic phosphate.
5. Potassic iodide.
6. Potassic oxalate.
7. Citric acid.
8. Calcic tartrate.
9. Sodic acetate.
10. Calcic phosphate.
11. Dried green vitriol.
12. Borax.

Preliminary to the analysis of more complex bodies, a number of double salts or mixtures of salts containing one or two bases, and one, two or more acids should be next examined, such as :—

Ammonic ferrous sulphate.
Common ammonium or potassium alum.
Microcosmic salt.
Potassic sodic tartrate (Rochelle salt).
Dipotassic calcic ferrocyanide.
Potassic chlorate and potassic nitrate.
Sodic chloride and potassic carbonate.
Potassic oxalate and potassic carbonate.
Ammonic chloride and sodic nitrate.
Ammonic magnesic phosphate.
Potassic bromide and iodide, and sodic chloride.

Complex bodies should be examined systematically, and the results carefully noted down in the analyst's laboratory book *immediately they are made*, and in the order indicated by the arrangement of the Analytical Tables. A careful preliminary examination in the dry way yields for the most part results which are decisive of the nature of the substance under examination. A few simple experiments are frequently sufficient to determine, in the case of simple salts, the nature of both base and acid, and in that of a compound substance, most bases and acids. Skill in blowpipe analysis is of paramount value in the analysis of well-defined minerals, as well as of complex mixtures. The student should, however, invariably control the results obtained by an examination of the solid substance in the dry way, by a most searching analysis in the wet way.

The exercises should be progressive, and should at first consist of artificial mixtures of clearly-defined composition: and lastly, of complex bodies, such as minerals, alloys, colours, slags, refuse-matter from various manufacturing processes, etc.

The following mixtures or compound bodies may be taken as types of the 20 or 30 substances that should be examined in order to enable the student to acquire proficiency in qualitative analysis:—

1. $\mathbf{N}_2O_4Pbo''$,
   $\mathbf{Hg}Cl_2$,
   AmCl,
   $\mathbf{C}OCao''$.

2. $\mathbf{Ca}Cl_2$,
   $\mathbf{Sr}Cl_2$,
   $\mathbf{Ba}Cl_2$.

3. $\mathbf{As}_2S_3$,
   AmCl,
   $\mathbf{N}O_2Ko$.

4. Ammonium alum,
   Chrome alum,
   Galena.

5. Chrome iron ore.

6. Type metal.

7. Stourbridge fire-clay.

8. $\mathbf{Cr}O_2Bao''$,
   $\mathbf{Fe}_2O_3$,
   $\mathbf{Ca}Cl_2$,
   Sulphur.

9. $\mathbf{Ba}Cl_2$,
   $\mathbf{P}OHoBao''$,
   $\left\{\begin{array}{l}\mathbf{C}OKo\\ \mathbf{C}OKo\end{array}\right.$

10. Ammonium alum,
    Chrome alum,
    $\mathbf{P}OHoNao_2$,
    $\mathbf{Fe}_2O_3$,
    $\mathbf{Si}O_2$.

11. $\mathbf{C}OBao''$,
    $\mathbf{P}_2O_2Bao''_3$,
    $\mathbf{S}O_2Bao''$,
    NaCl.

12. Ultramarine.

13. Guano.

14. Coprolite.

15. Material which has been used for purifying coal-gas.

16. Alkali waste.

TABLES

FOR THE

QUALITATIVE ANALYSIS

OF

SIMPLE AND COMPOUND SUBSTANCES, BOTH IN THE DRY AND WET WAY.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.

The physical properties of a substance under examination, such as its crystalline structure, its odour, colour, metallic lustre, hardness, density, are capable of throwing, in many cases, much light upon its composition, and should be carefully noted before subjecting the substance to a qualitative analysis.

Experiment.	Observation.	Inference.
I. HEAT A SMALL PORTION OF THE SUBSTANCE, IN THE STATE OF POWDER, IN A DRY TEST-TUBE, OR A PIECE OF COMBUSTION TUBE, CLOSED AT ONE END.	THE SUBSTANCE DOES NOT CHANGE.	Absence of organic substances, of volatile inorganic matter, of substances decomposed on ignition, of hygroscopic moisture, of water of crystallisation, and of water of hydration.
	THE SUBSTANCE CHANGES.	
	(A.) *Without decomposition.*	
	1. *The substance changes colour*, yellow whilst hot, white on cooling	**ZnO**.
	From yellow to reddish brown whilst hot, yellow when cold, fusible at a red heat	**PbO**.
	From white to yellowish brown when hot, dirty light yellow on cooling	**SnO_2**. [**TiO_2**.]
	From white to orange and reddish brown, dull yellow on cooling, fusible at an intense heat	**Bi_2O_3**.
	Dark red whilst hot, reddish brown on cooling	**Fe_2O_3**.
	2. *The substance fuses* and re-solidifies when the flame is removed	Mostly salts of the alkalies, and some salts of the alkaline earths (nitrates, chlorides, etc.)
	3. *The substance sublimes*	Several compounds of ammonium, mercury, and arsenic, also sulphur and iodine (plumbic chloride sublimes diffi-

		cultly). Volatile organic acids, *e.g.*, oxalic, benzoic, and succinic acids.
	The substance melts at a very gentle heat, heavy fumes appear in the tube, and the sublimate is white and crystalline	$\mathbf{Hg}Cl_2$.
	It sublimes without previous fusion, is yellow when hot, white when cold	$\mathbf{Hg}_2Cl_2$.
	The sublimate is black, and turns red on rubbing	$\mathbf{Hg}S$.
	The sublimate is yellow	$\mathbf{Hg}I_2$, $\mathbf{As}_2S_3$.
	It consists of reddish brown drops, yellow when cold	Free sulphur. Polysulphides.
	The sublimate consists of white octohedral crystals	$\mathbf{As}_2O_3$.
	The substance fuses into a yellow mass, and at a red heat sublimes entirely, forming crystalline needles	$\mathbf{Sb}_2O_3$.
	Violet vapour, feathery bluish-black crystals	Iodine.
	Odour of frankincense	Benzoic acid.
	Fumes which cause violent coughing ..	Succinic acid.
	Heavy white fumes, and white crystalline sublimate	Oxalic acid.
Confirm by heating a little of the dry substance with dry $\mathbf{C}ONao_2$, or black flux, in a bulb-tube.	Metallic mirror and globules of a metal ..	Mercury compounds.
	Black shining mirror, no metallic globules	Arsenical compounds.
	$\mathbf{N}H_3$ is given off	Ammonium compounds.
	$\mathbf{C}O_2$ is evolved	A free acid, *e.g.*, $\mathbf{As}_2O_3$, $\mathbf{As}_2O_5$, oxalic, benzoic, and succinic acids.
Test also specially for ammonium compounds by mixing a little of the substance in a mortar with soda-lime, and moistening with a few drops of water.	Odour of $\mathbf{N}H_3$	Ammonium compounds ($\mathbf{C}OAmo_2$, $\mathbf{P}OAmo_3$, $\mathbf{B}Amo_3$, are decomposed, and give off $\mathbf{N}H_3$ when heated by themselves). Alkaline chromates, borates, phosphates, etc., evolve likewise ammonia in the presence of ammonic salts.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

Experiment.	Observation.	Inference.
Confirm oxalic acid by heating in a test-tube with a little concentrated $\mathbf{S}O_2Ho_2$.	$\mathbf{C}O$ and $\mathbf{C}O_2$ are evolved	$\left\{\begin{array}{l}\mathbf{C}OHo\\ \mathbf{C}OHo\end{array}\right.$.
	(B.) *With partial or total decomposition.*	
	1. *The substance fuses, and gives off water of hydration* (sometimes without fusion), or water of *crystallisation*, becoming liquid at a low heat, *i.e.*, it fuses in its water of crystallisation; it then solidifies and fuses again when heated more strongly (igneous fusion), and swells up, or intumesces, considerably	Metallic hydrates. Salts containing water of crystallisation, *e.g.*, phosphates, borates, alums, etc.
Confirm by examining the condensed water with litmus-paper.	Alkaline reaction	Ammonium compounds.
	Acid reaction..	Free volatile acids, such as $\mathbf{N}O_2Ho$, HCl, $\mathbf{S}O_2Ho_2$, $\mathbf{S}OHo_2$, etc., or acid salts.
	2. *The substance gives off a gas or condensable vapour, with or without change of colour.*	
Confirm by introducing a glowing splinter of wood into the test-tube.	Oxygen is given off, causing a glimmering splinter of wood to burst into flame, and to burn brilliantly	Metallic peroxides, chlorates, perchlorates, nitrates, bromates, iodates.
	Oxygen mixed with other gases, *e.g.*, $\mathbf{S}O_2$, N, $\mathbf{N}_2O_4$, Cl, Br, I, is given off	From the decomposition of certain sulphates, of nitrates, nitrites, chlorates, hypochlorites, bromates, iodates.
Confirm by passing the gas through an acidulated solution of an alkaline chromate.	$\mathbf{S}O_2$ is given off, recognized by its suffocating odour, and its acid reaction with test-paper	Acid sulphites; also from the decomposition of sulphates, with or without evolution of oxygen, of earthy sulphites or hyposulphites; from the action of organic matter

Heat also a little of the powdered substance in a piece of combustion tubing, open at both ends.		upon sulphates, and from the oxidation of metallic sulphides and sulphocyanates.
Pass the gas through water and collect oxygen separately.	$\mathbf{N}_2\mathrm{O}_4$ and oxygen, or reddish-brown fumes come off; the oxygen gas supports combustion.	Nitrates of heavy metals, *e.g.*, of Pb, Bi.
Confirm by passing gas through lime- or baryta-water.	$\mathbf{C}\mathrm{O}_2$ is given off, which is a non-supporter of combustion. The gas precipitates lime- or baryta-water.	From the decomposition of carbonates (alkaline carbonates excepted); also from the decomposition of oxalates and cyanates.
Absorb the $\mathbf{C}\mathrm{O}_2$ by passing the gas through baryta-water, before collecting and igniting the $\mathbf{C}\mathrm{O}$ gas.	$\mathbf{C}\mathrm{O}$ is evolved, burning with a blue flame. .	From oxalates and formates.
The same applies to cyanogen gas, when mixed with $\mathbf{C}\mathrm{O}_2$.	CN is given off, having a peculiar odour, and burning with peach-blossom coloured flame	From cyanides of Ag, Hg, Cu, Zn, also from cyanates and sulphocyanates.
	Nitrogen, a non-supporter of combustion . .	$\mathbf{N}\mathrm{OAmo}$, or some fixed nitrite in the presence of ammonic salts (AmCl, etc.)
	$\mathbf{O}\mathrm{N}_2$, supporting combustion	$\mathbf{N}\mathrm{O}_2\mathrm{Amo}$, or some fixed nitrate in the presence of ammonic salts.
	$\mathbf{S}\mathrm{H}_2$ gas, recognized by its odour and action on lead paper	Hydrated sulphides, moist sulphites and hyposulphites.
	$\mathbf{N}\mathrm{H}_3$, possessing a characteristic pungent odour and alkaline reaction to test-paper	From ammonic salts, such as $\mathbf{C}\mathrm{OAmo}_2$, and others containing fixed acids (phosphates, borates); from cyanates in the presence of water, and from the decomposition of organic substances containing nitrogen, accompanied by carbonisation and evolution of offensive empyreumatic oils.
	$\mathbf{C}\mathrm{S}_2$ is sometimes given off	From the decomposition of sulphocyanates.
Confirm by passing the gas through a solution of potassic iodide, and starch paste.	Cl is given off, recognized by its pungent odour. The gas bleaches vegetable colours and liberates iodine from KI.	Several chlorides, such as the chlorides of the noble metals Pt, Au; also from certain chlorates and hypochlorites.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

Experiment.	Observation.	Inference.
	Br and I are given off, recognized by the odour of their vapour, or sublimate, and their action on starch paste.	Several bromides and iodides when heated by themselves with exclusion of air, or in the presence of atmospheric air; in the latter case with formation of oxides; also some bromates and iodates.
	Sulphur vapour, which condenses in the upper part of the tube in yellow drops, and burns with blue flame.	From the decomposition of metallic persulphides, *e.g.*, $\mathbf{Pt}S_2$, $\mathbf{Au}_2S_3$, $\mathbf{Sb}_2S_5$, $\mathbf{Sn}S_2$, $\mathbf{Fe}S_2$, which leave either a lower sulphide or the metal.
	3. The *substance becomes carbonised and evolves empyreumatic and other gaseous products of decomposition.*	From the decomposition of organic substances.
	Acetone is given off	From the decomposition of acetates.
Confirm by treating the residue with dilute hydrochloric acid.	The carbonate is soluble in water, and the solution has an alkaline reaction	Organic compounds of the fixed alkali metals.
	The carbonate is insoluble in water ..	Organic acids, combined with alkaline earthy metals.
	A carbonate is left which effervesces with dilute acids, whilst the original substance does not effervesce	Organic acids, combined with alkaline, or alkaline earthy bases.
II. HEAT A LITTLE OF THE SUBSTANCE UNDER EXAMINATION ON CHARCOAL BEFORE THE BLOWPIPE FLAME.	1. *The substance decrepitates*	NaCl, etc., etc.
	2. *The substance deflagrates*	Nitrates, chlorates, etc.
	3. *The substance fuses readily, and sinks into the charcoal, or forms a liquid bead*	Salts of alkalies and some salts of alkaline earths.
	4. *An infusible residue is left.*	

	(a.) *The residue is white* and highly luminous	$\mathbf{Ba}\mathrm{O}$, $\mathbf{Sr}\mathrm{O}$, $\mathbf{Ca}\mathrm{O}$, $\mathbf{Mg}\mathrm{O}$, $\mathbf{Al}_2\mathrm{O}_3$, $\mathbf{Zn}\mathrm{O}$, also $\mathbf{Si}\mathrm{O}_2$.
Confirm by treating the white infusible residue when cold with a few drops of $\mathbf{N}_2\mathrm{O}_4\mathrm{Coo}''$, and ignite again strongly.	Alkaline to test-paper	$\mathbf{Ba}\mathrm{O}$, $\mathbf{Sr}\mathrm{O}$, $\mathbf{Ca}\mathrm{O}$, $\mathbf{Mg}\mathrm{O}$.
	A fine blue mass is left	$\mathbf{Al}_2\mathrm{O}_3$, alkaline earthy phosphates, $\mathbf{Si}\mathrm{O}_2$, and many silicates.
	A flesh-coloured (or pink) mass is left ..	$\mathbf{Mg}\mathrm{O}$.
	,, green ,, ,, ...	$\mathbf{Zn}\mathrm{O}$.
	(b.) *The residue is coloured*..	$\mathbf{Cu}\mathrm{O}$, $\mathbf{Co}\mathrm{O}$, $\mathbf{Ni}\mathrm{O}$, $\mathbf{Mn}\mathrm{O}$, $\mathbf{Fe}_2\mathrm{O}_3$, $\mathbf{Cr}_2\mathrm{O}_3$.
Confirm by heating a small quantity of the residue in a clear borax bead on a platinum-wire, in the inner and outer blowpipe flame.	Oxidizing flame: green bead whilst hot, blue when cold. Reducing flame: red bead when cold	$\mathbf{Cu}\mathrm{O}$.
	Blue bead both in the oxidizing and reducing flame	$\mathbf{Co}\mathrm{O}$.
	Hyacinth-red to violet-brown bead when hot, yellowish to sherry-red when cold	$\mathbf{Ni}\mathrm{O}$.
Confirm the presence of Mn also by fusion with nitre and $\mathbf{C}\mathrm{ONao}_2$ on platinum-foil.	Amethyst-red bead in oxidizing flame. Colourless bead in reducing flame (usually not quite clear)	$\mathbf{Mn}\mathrm{O}$.
	Brownish-red bead when hot, light yellow or colourless when cold in the oxidizing flame; an olive-green to bottle-green bead in the reducing flame	$\mathbf{Fe}_2\mathrm{O}_3$ or $\mathbf{Fe}\mathrm{O}$.
Confirm the presence of Cr by fusion with nitre and fusion mixture on platinum-foil.	Green in oxidizing flame, ditto in reducing flame	$\mathbf{Cr}_2\mathrm{O}_3$.
III. HEAT IN THE INNER BLOWPIPE FLAME.	1. *The substance colours the outer flame.*	
Confirm by heating a little of the substances on a clean platinum-wire. (The chlorides of the different metals answer best. Borates should be decomposed with $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$.)	Golden-yellow	Na compounds.
	Violet	K ,,
	Yellowish-green	Ba ,,
	Crimson	Sr ,,
	Reddish	Ca ,,
	Green	Cu, $\mathbf{B}_2\mathrm{O}_3$.
	Blue	As, Sb, Pb, $\mathbf{Cu}\mathrm{Cl}_2$.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

Experiment.	Observation.	Inference.
	2. *The substance is reduced to the metallic state; the metal is volatile, and on passing through the outer flame yields an incrustation.*	
	A white incrustation and characteristic garlic odour	Compounds of arsenic.
	Incrustation yellow when hot, white when cold	Zn.
	Incrustation reddish-brown (readily volatilized)	Cd.
	3. *The substance is reduced to the metallic state*	Au, Ag, Cu, Pb, Sn, Sb, Bi (also Co, Ni, Fe).
Confirm by mixing a little of the substance with $\mathbf{C}\mathrm{ONao}_2$ and KCy, and heating on charcoal in the inner blowpipe flame.	(A.) *Without incrustation.*	
	Brilliant white metal	Ag.
	Yellow metal..	Au.
	Red scales or globules of a red metal ..	Cu.
	Metallic powders which cannot be fused into globules, but are magnetic	Fe, Co, Ni.
	(B.) *With incrustation*	Sn, Pb, Bi, Sb.
	Metal malleable; slight incrustation, which is yellow when hot, white when cold	Sn.
	Metal brittle; incrustation dark orange when hot, lemon-yellow when cold	Bi.
	Metal malleable; marks paper; incrustation lemon-yellow whilst hot, yellow when cold	Pb.

	Metal brittle; gives off white fumes when withdrawn from the flame, and becomes surrounded with a network of brilliant acicular crystals of $\mathbf{Sb}_2O_3$; incrustation white, and close to the substance.	Antimony compounds.
Heat a little of the substance mixed with dry $\mathbf{C}ONao_2$ (free from sulphate) in the reducing flame; place the fused mass on a bright silver coin and moisten it with water.	An alkaline sulphide is left; the silver is stained black, and the fused mass evolves $\mathbf{S}H_2$ when treated with dilute HCl.	Presence of sulphur, either in the form of a sulphide, or of a salt of an oxygen acid of sulphur.

Note 1.—Many of the changes observed on heating a substance by itself in a tube closed at one end occur again, when the substance is heated on charcoal, but may be neglected, as they are so much more readily studied by heating the substance in a tube.

Note 2.—A substance under examination may consist of several bodies, and the reactions which it gives may frequently obscure each other. Analytical tables, moreover, cannot possibly provide an explanation for every change that may be produced during the preliminary examination of a mixture of several substances. The analyst should, therefore, record faithfully every observation which he makes, though he may not be able at the time to draw an inference from it, and should endeavour to elicit by further experiments what substances are present in the mixture which he is called upon to examine in the dry way.

Absolute proof can, in many cases, only be obtained by an examination of a substance in the wet way.

Examination of a Substance in the Wet Way.

1st. *The substance under examination is a liquid.*—Examine it by means of well-prepared test-papers. The liquid is *neutral.* This excludes a large number of substances, since the greater proportion of normal salts of the metals possess an acid reaction. The liquid shows an *acid* reaction. This may arise from a free acid, or from the presence of a normal salt having an acid reaction, or, lastly, from an acid salt. Or the solution possesses an *alkaline* reaction, owing to the presence of a salt of alkaline reaction, of free alkalies or alkaline earths, and of cyanides or sulphides of the alkalies or alkaline earthy metals.

Evaporate a portion of the liquid to dryness on a watch-glass or platinum foil. It leaves no residue, and may consist of pure water only; or it leaves a residue; a larger portion of the liquid should then be evaporated to dryness in a porcelain dish and subjected to a preliminary examination in the dry way.

2nd. *The substance under examination consists of a solid body.*—If it occurs in large pieces, or in the form of a coarse powder, it should first be reduced by mechanical means to as fine a powder as possible.

Natural silicates and other compounds which are decomposed with difficulty by acids, are finely powdered in an agate mortar and then *levigated, i.e.,* stirred up repeatedly with water; the coarser particles of the powdered substance fall rapidly to the bottom, and the water holding the finer particles in suspension can be poured off. The coarser particles must then be ground again, and made to pass through a fresh process of levigation, till the *whole* of the substance is obtained in an equally fine state of division. By allowing the water to stand for some time, the whole of the suspended particles fall to the bottom of the vessel, and can be separated by decantation and filtration.

Ascertain whether the solid substance is *wholly* or *partly* soluble in water. This is done by boiling about a gramme of it in distilled water, allowing the undissolved portion to subside before decanting the supernatant liquid, and treating the undissolved portion again with boiling water as long as anything is dissolved. A drop of the solution, when evaporated on a watch-glass, or on platinum foil, should leave a visible spot.

The *aqueous extract* is set aside until the residue has in like manner been treated with acids. It should be tested with litmus-paper.

The *residue insoluble in water* is next treated with dilute hydrochloric acid, and heated for some time to boiling. The undissolved portion is allowed to subside and the clear fluid decanted. This operation should be repeated several times, both with dilute and concentrated hydrochloric acid. Boiling with HCl generally dissolves out whatever is soluble, and NO_2Ho has rarely to be resorted to. If an insoluble residue be left, treat with small quantities of aqua regia. Observe carefully what changes take place when the substance is treated with acids, especially whether any and what gases are disengaged.

The *residue insoluble in water and acids* should be carefully washed with distilled water, filtered, dried, and then mixed with three to four times its weight of dry $\mathbf{C}ONao_2$ and $\mathbf{C}OKo_2$ (fusion-mixture) and fused. The fusion is best performed in a platinum crucible, provided the insoluble residue does not contain any metals capable of forming alloys with platinum. This can be readily ascertained by an examination of the residue in the dry way.

It should be borne in mind that only BARIC, STRONTIC, CALCIC, AND PLUMBIC SULPHATES; PLUMBIC AND ARGENTIC CHLORIDES; $\mathbf{Si}O_2$, MANY SILICATES; NATIVE OR IGNITED $\mathbf{Al}_2O_3$ AND ALUMINATES; IGNITED $\mathbf{Cr}_2O_3$ and $\mathbf{Fe}_2O_3$; CHROME IRON ORE; $\mathbf{Sn}O_2$ (IGNITED OR AS TINSTONE); IGNITED $\mathbf{Sb}_2O_4$ (A FEW METAPHOSPHATES AND ARSENATES); $\mathbf{Ca}F_2$, AND A FEW OTHER NATIVE FLUORIDES; SULPHUR AND CARBON, are usually present in the residue.

Ag_4FeCy_6 and $Ag_6Fe_2Cy_{12}$, AgBr, AgI, and AgCy are decomposed into AgCl by boiling with aqua regia.

Solutions 1 and 2 may be examined separately, or they may be mixed and examined together. A separate analysis of the aqueous and acid extracts becomes necessary only when it is intended to show *how* the acids and bases are combined in a compound body.

The examination of a residue requiring fusion with alkaline carbonates is invariably conducted separately. The fused mass is boiled with water and filtered; the powder, insoluble in water, containing the base in the form of a carbonate (oxide or metal) is dissolved in HCl or $\mathbf{N}O_2Ho$. The aqueous extract is examined for acids, and the acid extract for bases.

Alloys are dissolved in dilute or concentrated HCl, sometimes with the aid of platinum foil, or with the addition of a few crystals of potassic chlorate, and their solutions examined as usual.

Cyanogen compounds are best destroyed by fusion in a porcelain crucible with 3 or 4 times their weight of a mixture of 3 parts of SO_2Amo_2 and 1 part of $\mathbf{N}O_2Amo$. The metals can then be detected in the residue in the usual manner.

Remark.—In order to economize time, the solution of a substance should be prepared at the same time as the examination in the dry way is conducted, and whilst the separation into groups is effected by means of the several group-reagents. The precipitates can then be well washed. Again, the time occupied in the evaporation of the filtrate from Group II, and in separating Fe^{iv}, Cr^{iv}, and Al^{iv} by means of $\mathbf{C}OBao''$ in Group III, may be employed in the examination of the precipitate produced by HCl or $\mathbf{S}H_2$, as well as in detecting the acids in the dry and wet way.

GENERAL TABLE FOR THE

To the greater portion of the original solution add HCl, as

The PRECIPITATE may contain—

$\mathbf{Pb}\mathrm{Cl}_2$,	white
AgCl,	,,
$\mathbf{Hg}_2\mathrm{Cl}_2$,	,,

(Note 2.)

Examine by Table I.

The FILTRATE (Note 3) is largely

The PRECIPITATE may contain—

$\mathbf{Hg}\mathrm{S}$,	black	Insoluble in sodic hydrate, or yellow ammonic sulphide.
$\mathbf{Pb}\mathrm{S}$,	,,	
$\mathbf{Bi}_2\mathrm{S}_3$,	,,	
$\mathbf{Cu}\mathrm{S}$,	,,	
$\mathbf{Cd}\mathrm{S}$,	yellow	

$\mathbf{Sn}\mathrm{S}$,	brown	Soluble in sodic hydrate, or yellow ammonic sulphide.
$\mathbf{Sn}\mathrm{S}_2$,	yellow	
$\mathbf{Sb}_2\mathrm{S}_3$,	orange	
$\mathbf{Sb}_2\mathrm{S}_5$,	,,	
$\mathbf{As}_2\mathrm{S}_3$,	yellow	
$\mathbf{Au}_2\mathrm{S}_3$,	black	
$\mathbf{Pt}\mathrm{S}_2$,	,,	

Examine by Table II.

EXAMINATION OF BASES.

long as a precipitate is produced, and heat gently. (Note 1.)

diluted with water (Note 4), saturated with gaseous $\mathbf{S}H_2$, and gently heated (Notes 5 and 6).

Evaporate the FILTRATE till free from $\mathbf{S}H_2$, then add a few drops of concentrated $\mathbf{N}O_2Ho$, and evaporate to complete dryness. If oxalates or organic matter (Note 7) be suspected (indicated by the blackening of the residue), heat to redness in a porcelain dish, but not otherwise. Treat the residue with a little concentrated HCl, add water and heat, when it dissolves either wholly or leaves a white residue of $\mathbf{Si}O_2$ (Note 8). Test a small portion of the HCl solution with ammonic molybdate, with the addition of concentrated nitric acid.

(A.) *No precipitate is obtained,* $\mathbf{P}OHo_3$ **is absent.**—Add AmCl, AmHo, and $\mathbf{S}Am_2$, to the remaining portion of the solution, heat to boiling, and filter quickly; wash well with hot water containing a few drops of ammonic sulphide.

(B.) *A precipitate is obtained,* $\mathbf{P}OHo_3$ **is present.**—Add AmCl and AmHo in slight excess to the remaining portion of the solution, heat gently and filter quickly; wash well with hot water. To the filtrate add $\mathbf{S}Am_2$ to slight excess, heat to boiling and filter. Wash with hot water containing a few drops of $\mathbf{S}Am_2$, and examine filtrates under Group IV. Transfer the two precipitates to a porcelain dish, and digest with a little $\mathbf{S}Am_2$ (Note 9). Filter off and wash well. Neglect filtrate (Note 10).

(A.) The PRECIPITATE may contain—	(B.) The PRECIPITATE may contain—	To the FILTRATE from III A. or III B. add AmHo and $\mathbf{C}OAmo_2$, heat gently (Note 12) and filter.	
		The PRECIPITATE may contain—	SOLUTION may contain—
$\mathbf{Al}_2Ho_6$, yellowish-white, gelatinous.	$\mathbf{Al}_2Ho_6$, yellowish-white, gelatinous.	$\mathbf{C}OBao''$, white.	$\mathbf{Mg}O$.
$\mathbf{Cr}_2Ho_6$, bluish-green.	$\mathbf{Cr}_2Ho_6$, bluish-green.	$\mathbf{C}OSro''$, „	$\mathbf{O}K_2$.
$\mathbf{Fe}S$, black.	$\mathbf{Fe}S$, black.	$\mathbf{C}OCao''$, „	$\mathbf{O}Na_2$.
$\mathbf{Zn}S$, white.	$\mathbf{Zn}S$, white.		
$\mathbf{Mn}S$, flesh-coloured.	$\mathbf{Mn}S$, flesh-coloured.		
$\mathbf{Ni}S$, black.	$\mathbf{Ni}S$, black.		
$\mathbf{Co}S$, „	$\mathbf{Co}S$, „ Together with the phosphates of (Cr) and Al, as well as of the alkaline earthy metals. (Note 11.)		
Examine by Table III A.	Examine by Table III B.	Examine by Table IV.	Examine by Table V.

NOTES TO GENERAL TABLE.

1. In case the original substance had to be dissolved in hydrochloric acid, $\mathbf{S}H_2$ may be passed at once.

2. In a saturated solution of a baric salt, HCl produces a white precipitate, soluble in hot water. From an alkaline solution HCl may precipitate $\mathbf{Si}Ho_4$ (gelatinous), $\mathbf{B}Ho_3$, $\overline{Bz}Ho$ [and uric acid] crystalline, also $\mathbf{Sb}_2O_5$ (amorphous). Metallic oxides, such as $\mathbf{Al}_2O_3$ and metallic sulphides, such as $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_3$, $\mathbf{Sb}_2S_5$, $\mathbf{Sn}S$, and $\mathbf{Sn}S_2$, which dissolve in NaHo or $\mathbf{S}_2Am_2$, may likewise be precipitated on the addition of HCl, and are best examined separately.

3. If arsenic has been detected in the preliminary examination, this filtrate, which may contain pentad arsenic, should be boiled with a solution of $\mathbf{S}OHo_2$, or $\mathbf{S}OHoAmo$, and the acid solution evaporated considerably to expel the $\mathbf{S}O_2$. Ba, Sr, and Pb, when present, may be precipitated either partly or wholly, as sulphates. The precipitate is best examined separately.

4. Certain oxychlorides, *e.g.*, of Bi, Sb, or Sn, may be precipitated on the first addition of dilute HCl, or water, but are readily redissolved on the addition of more acid, and on gently heating; or the precipitate may be disregarded, since $\mathbf{S}H_2$ readily converts the finely divided oxychlorides into the corresponding metallic sulphides.

5. $\mathbf{S}H_2$ often produces merely a precipitation of sulphur, owing to the presence of oxidizing agents, such as Cl, Br, I ($\mathbf{S}OHo_2$, $\mathbf{N}OHo$), $\mathbf{N}O_2Ho$, ClHo, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$, and $\mathbf{Cr}O_2Ho_2$, or of ferric salts. This precipitate is easily distinguished by its being white and remaining suspended in the solution. It may be neglected altogether. A brick red precipitate of $\mathbf{Pb}_2SCl_2$ often comes down from strongly acid (HCl) solutions, if the solution has not been sufficiently diluted with water. Cadmium is often left in solution, if too much acid be present.

6. $\mathbf{S}H_2$ should be passed once more through the filtrate, to make sure of the complete precipitation of all the metals of Group II.

7. Organic acids, *e.g.*, $\overline{T}Ho_2$, $\overline{Ci}Ho_3$, also sugar, etc., prevent the precipitation of $\mathbf{Al}_2Ho_6$, etc., in Group III. (Comp. p. 172.)

8. It is possible that this $\mathbf{Si}O_2$ may be mixed with other substances, *e.g.*, $\mathbf{Al}_2O_3$, $\mathbf{Cr}_2O_3$, $\mathbf{Fe}_2O_3$ (rendered insoluble by strong ignition), $\mathbf{S}O_2Bao''$, $\mathbf{S}O_2Sro''$, in which case it is necessary to examine it separately.

9. If the $\mathbf{S}Am_2$ were added simultaneously with the AmCl and AmHo, phosphates of Fe, Mn, Zn, Ni, and Co would be decomposed into sulphides, with formation of $\mathbf{P}OAmo_3$, which might produce a precipitate of a phosphate of the alkaline earthy bases, by acting upon salts of these bases other than phosphates, or act as a solvent for other phosphates in the presence of AmHo. (Comp. p. 54.)

10. This filtrate may contain $\mathbf{P}OHo_3$, a proof that a phosphate of the metals Fe, Zn, Mn, Ni, or Co was present in the original HCl solution, or, *vice versâ*, that all these metals (or one or several of them) may be present. (Comp. p. 54.)

11. Small quantities of borates and fluorides of the alkaline earthy metals may likewise be precipitated, together with the alkaline earthy phosphates, but need not be examined further, since their bases will be detected in Group IV, and their acids on examining in the usual way for acids.

12. The solution must not be boiled, since the AmCl, by double decomposition, dissolves the alkaline earthy carbonates forming chlorides and ammonic carbonate, which volatilizes with the aqueous vapour.

TABLE I.—SEPARATION OF THE METALS OF GROUP I.

<table>
<tr><td colspan="3">The precipitate may contain $\mathbf{Pb}Cl_2$, AgCl, $\mathbf{Hg}_2Cl_2$, also $\mathbf{B}Ho_3$, $\bar{B}zHo$ (uric acid) (Note 1). Wash the precipitate on the filter with hot water till it is quite free from $\mathbf{Pb}Cl_2$.</td></tr>
<tr><td rowspan="2">The SOLUTION may contain $\mathbf{Pb}Cl_2$
On cooling white acicular crystals fall out. Confirm by $\mathbf{Cr}O_2Ko_2$, or $\mathbf{S}O_2Ho_2$.
Presence of Pb.</td><td colspan="2">The white RESIDUE may consist of AgCl, $\mathbf{Hg}_2Cl_2$; heat gently with excess of dilute AmHo.</td></tr>
<tr><td>The SOLUTION may contain AgCl; acidulate with dilute $\mathbf{N}O_2Ho$.
A white curdy precipitate of AgCl is obtained.
Presence of Ag.</td><td>The RESIDUE is black, consisting of $\mathbf{N}H_2{}'Hg'_2Cl$.
Confirm by drying residue and heating with dry $\mathbf{C}ONao_2$ in a bulb-tube.
A metallic mirror and globules indicate—
Presence of Hg (as mercurosum).</td></tr>
</table>

Note 1.—Unless HCl be added in excess, and the solution gently heated, certain oxychlorides of Bi and Sb, as well as Sn (likewise $\mathbf{Si}Ho_4$, and a few other substances) may become precipitated in this group.

Table II.—SEPARATION OF

<table>
<tr><td colspan="5">The precipitate may contain $\mathbf{Hg}\mathrm{S}$, $\mathbf{Pb}\mathrm{S}$, $\mathbf{Bi}_2\mathrm{S}_3$, $\mathbf{Cu}\mathrm{S}$, $\mathbf{Cd}\mathrm{S}$, $\mathbf{Sn}\mathrm{S}$, $\mathbf{Sn}\mathrm{S}_2$, $\mathbf{Sb}_2\mathrm{S}_3$, $\mathbf{Sb}_2\mathrm{S}_5$, $\mathbf{As}_2\mathrm{S}_3$, (Comp. p. 95.) Wash the precipitate until free from</td></tr>
<tr><td colspan="5">Residue.—Wash well; boil in a little concentrated $\mathbf{N}\mathrm{O_2Ho}$, until all action ceases. Dilute with water; add dilute $\mathbf{S}\mathrm{O_2Ho_2}$, as long as a precipitate is produced; allow to cool and add an equal bulk of alcohol (methylated); filter.</td></tr>
<tr><td colspan="2">Residue.—May contain $\mathbf{Hg}\mathrm{S}$, $\mathbf{S}\mathrm{O_2Pbo''}$ and S. Boil in ammonic acetate: $\mathbf{S}\mathrm{O_2Pbo''}$ dissolves; allow to cool and filter.</td><td colspan="3">Solution.—Boil off the alcohol, add excess of AmHo; boil and filter.</td></tr>
<tr><td rowspan="2">Residue consists of $\mathbf{Hg}\mathrm{S}$ and S, or of S only.
Confirm by reducing the dried $\mathbf{Hg}\mathrm{S}$ in a bulb-tube with dry $\mathbf{C}\mathrm{ONao_2}$.
Metallic mirror and globules.
Presence of Hg. (as mercuricum.)</td><td rowspan="2">Solution.—Add $\mathbf{Cr}\mathrm{O_2Ko_2}$, yellow precipitate of $\mathbf{Cr}\mathrm{O_2Pbo''}$.
Presence of Pb.</td><td rowspan="2">The precipitate consists of $\mathbf{Bi}\mathrm{Ho_3}$. Dissolve in a few drops of dilute HCl; evaporate nearly to dryness and add water. Milkiness from $\mathbf{Bi}\mathrm{OCl}$.
Presence of Bi.</td><td colspan="2">Solution.—Acidulate slightly with HCl and pass $\mathbf{S}\mathrm{H_2}$; filter off and wash the precipitate with weak $\mathbf{S}\mathrm{H_2}$ water. Boil with dilute $\mathbf{S}\mathrm{O_2Ho_2}$ and filter.</td></tr>
<tr><td>Residue. — Dissolve in $\mathbf{N}\mathrm{O_2Ho}$; add slight excess of AmHo, then $\left\{\begin{array}{l}\mathbf{C}\mathrm{H_3}\\ \mathbf{C}\mathrm{OHo},\end{array}\right.$ and $\mathrm{K_4FeCy_6}$. Brown precipitate of $\mathrm{Cu_2FeCy_6}$.
Presence of Cu.</td><td>Solution. — Add AmHo and pass $\mathbf{S}\mathrm{H_2}$. Yellow precipitate of $\mathbf{Cd}\mathrm{S}$.
Presence of Cd.</td></tr>
</table>

Note 1.—$\mathbf{Cu}\mathrm{S}$ is somewhat soluble in $\mathbf{S}_2\mathrm{Am}_2$ and $\mathbf{Hg}\mathrm{S}$ in $\mathbf{S}\mathrm{Na}_2$. It is therefore advisable to If both $\mathbf{Cu}\mathrm{S}$ and $\mathbf{Hg}\mathrm{S}$ are present dissolve in

THE METALS OF GROUP II.

(Au and Pt must be tested for specially in a separate portion of the filtrate from Group I).
HCl; boil with NaHo, or $\mathbf{S}_2Am_2$, and filter (Note 1).

SOLUTION may contain As, Sb, Sn (Au and Pt) as sulpho-salts. Acidulate with dilute hydrochloric acid, $\mathbf{As}_2S_3$, $\mathbf{Sb}_2S_5$, and $\mathbf{Sn}S_2$ are reprecipitated. Filter and wash; digest with $\mathbf{C}OHoAmo$ and filter.

RESIDUE consists of $\mathbf{Sb}_2S_5$ and $\mathbf{Sn}S_2$. Dissolve in boiling HCl. Introduce into a Marsh's apparatus in which hydrogen is generated by means of pure Zn and HCl.

$\mathbf{Sb}H_3$ comes off. Collect as metallic Sb on porcelain or glass and identify the deposited metal by means of ClNao or dry HCl gas.

Presence of Sb.

The RESIDUE in the generating flask consists of Zn and Sn.
Detach the precipitated Sn from the strips of zinc; wash and dissolve in a little concentrated HCl by the aid of platinum-foil. Dilute with water, and add $\mathbf{Hg}Cl_2$. A white precipitate of $\mathbf{Hg}_2Cl_2$, or of grey metallic Hg, is obtained.

Presence of Sn.

SOLUTION contains $\mathbf{As}_2S_3$. Reprecipitate by adding HCl. Confirm the presence of As by reducing with KCy and $\mathbf{C}ONao_2$ in a bulb-tube.
Metallic mirror and garlic odour.

Presence of As.

---

issolve the precipitate in the absence of $\mathbf{Cu}S$ with $\mathbf{S}_2Am_2$, and in the absence of $\mathbf{Hg}S$ with $\mathbf{S}Na_2$.
S_2Am_2, when a little $\mathbf{Cu}S$ will be found in the solution.

TABLE III A.—SEPARATION OF THE

<table>
<tr><td colspan="4">A. $POHo_3$ is absent.—Dissolve the precipitate from Group IIIA. in a little dilute HCl, with the is perceptible. Filter off sulphur if necessary. Nearly neutralize solution with $CONao_2$; add possible. Pour off the clear liquid, which contains the chlorides of the metals Zn, Mn, Ni chlorides of Fe^{iv}, Al^{iv} and Cr^{iv}; throw the precipitate—which contains the hydrates (and basic hot water.</td></tr>
<tr><td colspan="4">SOLUTION.—Remove $BaCl_2$ by adding a few drops of dilute SO_2Ho_2; boil, allow to subside, and filter off SO_2Bao''. Nearly neutralize the filtrate with $CONao_2$, and add pure NaHo, till the solution becomes alkaline; boil and filter.</td></tr>
<tr><td rowspan="3">The SOLUTION may contain zinc as $ZnNao_2$. Add SH_2. White precipitate of ZnS.
Presence of Zn.</td><td colspan="3">The PRECIPITATE may contain $MnHo_2$, $CoHo_2$ and $NiHo_2$. Wash, dissolve in a little dilute HCl; nearly neutralize with AmHo; add excess of $\left\{\begin{matrix}CH_3\\COAmo\end{matrix}\right.$ and a little acetic acid; pass a rapid current of SH_2 for several minutes through the solution and filter.</td></tr>
<tr><td rowspan="2">The SOLUTION contains the manganese as acetate.
Add AmCl, AmHo and SAm_2.
Flesh-coloured precipitate of MnS.
Presence of Mn.</td><td colspan="2">RESIDUE.—Dissolve in HCl and $\left\{\begin{matrix}OCl\\OKo\end{matrix}\right.$; nearly neutralize with $CONao_2$; add a weak solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for some time, allow to cool (filter off any slight precipitate), and add a strong solution of ClNao; allow to stand for some time in a warm place, as long as a black precipitate forms, and filter.</td></tr>
<tr><td>PRECIP. — Ni_2Ho_6. Confirm by heating a small portion of it on a borax-bead before the blowpipe flame.
A yellowish to sherry-red bead.
Presence of Ni.</td><td>The SOLUTION contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate to dryness, and test a little of the residue before the blowpipe flame on a borax bead.
A blue bead in both flames.
Presence of Co.</td></tr>
</table>

Note 1.—If no pure NaHo can be procured, a comparative test should be made, by acidulating precipitating it with dilute HCl and AmHo. If the amount of precipitate thus obtaine whether Al be present or not in the mixture.

METALS OF GROUP IIIA.

ldition of a few small crystals of $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.$. Digest at a gentle heat, as long as any chlorous odour
COBao″ and shake well. Allow to subside in a flask kept corked, to exclude the air as much as
ad Co, as well as $\mathbf{Ba}Cl_2$, arising from the double decomposition of the $\mathbf{C}OBao''$, by the
lts) of Fe^{iv}, Al^{iv} and Cr^{iv}, as well as the excess of $\mathbf{C}OBao''$ employed—on a filter and wash with

Precipitate.—Dissolve in dilute HCl; remove the $\mathbf{Ba}Cl_2$ thus formed, by dilute $\mathbf{S}O_2Ho_2$ and filter. Nearly neutralize the filtrate with $\mathbf{C}ONao_2$, and add pure NaHo (free from alumina) (Note 1) in excess, and boil for some time. $\mathbf{Fe}_2Ho_6$ and $\mathbf{Cr}_2Ho_6$ are precipitated. $\mathbf{Al}_2Ho_6$ dissolves in excess of NaHo.

Precipitate.—Fuse with fusion-mixture and $\mathbf{N}O_2Ko$ on platinum foil. Dissolve the alkaline chromate which is thus formed in hot water, and filter.

Residue.—Dissolve in dilute HCl and add K_4FeCy_6.
A precipitate of Prussian blue.

Presence of Fe.

Dilute and test the original HCl solution specially for Fe'' and Fe^{iv} by means of a solution of $\mathbf{Mn}_2O_6Ko_2$, as well as by means of K_4FeCy_6, $K_6Fe_2Cy_{12}$, or CyAms.

Solution, yellow. Confirm by acidulating with $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ and adding $\left(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right.\right)_2Pbo''$.
Yellow precipitate of $\mathbf{Cr}O_2Pbo''$.

Presence of Cr.

Test the original substance specially for $\mathbf{Cr}_2O_3$ and $\mathbf{Cr}O_3$, by boiling a small portion with $\mathbf{C}ONao_2$. The filtrate contains the chromate, and the residue the $\mathbf{Cr}_2O_3$. The latter may be converted into a soluble alkaline chromate by fusion with $\mathbf{C}ONao_2$ and $\mathbf{N}O_2Ko$.

Solution.—Acidulate with dilute HCl and add AmHo in slight excess.
White gelatinous precipitate.

Presence of Al.

antity of sodic hydrate, about equal in bulk to that employed for redissolving the alumina, and
m the reagent alone, at all equals that of the $\mathbf{Al}_2Ho_6$ precipitate, it must remain doubtful

Table III B.—SEPARATION OF THE

<table>
<tr><td colspan="4">B. **$\mathbf{P}OHo_3$ is present.**—Dissolve the precipitate obtained according to the directions given in $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.$, if necessary. Digest at a gentle heat, as long as any chlorous odour is perceptible. metals Zn, Mn, Ni, Co, Al^{iv}, Cr^{iv}, Fe^{iv}, as well as phosphates of Cr^{iv}, Al^{iv}, Ba, Sr, Ca, and and $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ as long as a precipitate is produced. Heat gently, and filter hot.</td></tr>
<tr><td colspan="4">The SOLUTION may contain the chlorides of Al, Cr, Zn, Mn, Ni, Co (Ba, Sr, Ca, Mg), as well as the phosphates of the alkaline earthy metals. Add $\mathbf{Fe}_2Cl_6$ (Note 2), drop by drop, as long as a precipitate forms and till the colour of the supernatant fluid becomes red. The remaining phosphates of the alkaline earthy metals are thus decomposed. Digest for some time at a gentle heat; allow to subside and filter hot. Wash with hot water.</td></tr>
<tr><td colspan="3">The SOLUTION contains now only chlorides—possibly of all the metals of Group III, as well as of the metals of the alkaline earths—the whole of the phosphoric acid having been eliminated. Add AmCl, AmHo and $\mathbf{S}Am_2$. A black precipitate is obtained. Filter.</td><td rowspan="3">The PRECIPITATE consists of $\mathbf{P}_2O_2Fe_2o^{vi}$ and ferric acetate. Neglect.</td></tr>
<tr><td colspan="2">SOLUTION.—Add $\mathbf{C}OAmo_2$.</td><td rowspan="2">Examine PRECIPITATE according to Table IIIA for Co, Ni, Mn, Zn, Al and Cr.
Test a portion of the original substance, dissolved in water or HCl, for Fe'' and Fe^{iv}.</td></tr>
<tr><td>A white PRECIPITATE which may be—
$\mathbf{C}OBao''$,
$\mathbf{C}OSro''$,
$\mathbf{C}OCao''$.
Examine by Table IV (without, however, mixing it with the precipitate obtained in Group IV).</td><td>SOLUTION may contain Mg. Add $\mathbf{P}OHoNao_2$. White crystalline precipitate.
Presence of Mg. (as phosphate.)</td></tr>
</table>

Note 1.—Test a portion of this hydrochloric acid solution with ammonic molybdate fo Ca, Mg, were originally present, but only phosphates of Ni, Co, Mn, Zn and Fe, decomposable by

Note 2.—If $\mathbf{Fe}_2Cl_6$ produces no further precipitate with *a portion* of the acetic acid solution, dissolution of $\mathbf{Fe}S$ in HCl being frequently sufficient to decompose the whole of the phosphates Ca and Mg. In this case no ferric salt need be added to the *main portion* of the solution, and the

Note 3.—Instead of fusing with $\mathbf{Si}O_2$ and $\mathbf{C}ONao_2$, the presence of $\mathbf{P}_2O_2Al_2o^{vi}$ ($\mathbf{P}_2O_2Cr_2o^{vi}$ with NaHo, which dissolves $\mathbf{P}_2O_2Al_2o^{vi}$ and decomposes the ferric phosphate, with formation of reprecipitated.

METALS OF GROUP IIIb.

the General Table under Group III b., in dilute HCl, with the addition of a few crystals of
Filter off sulphur, if necessary (Note 1). The solution may now contain the chlorides of the
Mg. Nearly neutralize with a dilute solution of $\mathbf{C}ONao_2$; then add a solution of $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right.$

The PRECIPITATE may consist of $\mathbf{P}_2O_2Fe_2o^{vi}$, $\mathbf{P}_2O_2Al_2o^{vi}$ (Note 3), $\mathbf{P}_2O_2Cr_2o^{vi}$. Dry on the filter. Fuse in a platinum crucible with $\mathbf{Si}O_2$ and pure fusion mixture, together with a little $\mathbf{N}O_2Ko$. Dissolve in hot water, add $\mathbf{C}OAmo_2$; digest, allow to subside and filter.

<table>
<tr>
<td colspan="3">RESIDUE may consist of $\mathbf{Si}Ho_4$, $\mathbf{Si}_3O_3Fe_2o^{vi}$, $\mathbf{Si}_3O_3Al_2o^{vi}$ and $\mathbf{Fe}_2Ho_6$. Acidulate with HCl; evaporate to dryness and ignite gently. Extract with a few drops of concentrated HCl and hot water. Filter.</td>
<td rowspan="3">SOLUTION.—Add $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ and $(\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}O\end{matrix}\right.)_2Pbo''$.
Yellow precipitate. Presence of $\mathbf{Cr}O_3$, and therefore
Presence of Cr.
(*as phosphate*).
A white precipitate of $\mathbf{P}_2O_2Pbo''_3$ indicating the presence of $\mathbf{P}OHo_3$, may be neglected.</td>
</tr>
<tr>
<td colspan="2">SOLUTION.—Nearly neutralize with $\mathbf{C}ONao_2$, and add pure NaHo in excess. Heat and filter.</td>
<td rowspan="2">RESIDUE $\mathbf{Si}O_2$.
Neglect.</td>
</tr>
<tr>
<td>RESIDUE.—$\mathbf{Fe}_2Ho_6$. Confirm by dissolving in HCl and adding CyAms. A blood-red colour.
Presence of Fe
(*as phosphate*).</td>
<td>SOLUTION.—Acidulate with dilute HCl and add AmHo in slight excess.
A white gelatinous precipitate.
Presence of Al
(*as phosphate*).</td>
</tr>
</table>

phosphoric acid. The absence of a yellow precipitate proves that no phosphates of Al, Cr, Ba, Sr, $\mathbf{S}Am_2$. Proceed, therefore, to examine the solution at once by Table IIIA.

it is obvious that no phosphates of the alkaline earthy bases are left, the $\mathbf{Fe}_2Cl_6$ derived from the of the alkaline earthy metals in an acetic solution into ferric phosphate and chlorides of Ba, Sr, examination of the filtrate may at once be proceeded with according to Table IIIA.

is rarely met with) may also be ascertained by boiling the precipitated phosphates of Fe and Al $\mathbf{Fe}_2Ho_6$. Filter. Acidulate the filtrate with dilute HCl; add AmHo, when $\mathbf{P}_2O_2Al_2o^{vi}$ is

TABLE IV.—SEPARATION OF THE METALS OF GROUP IV.

<table>
<tr><td colspan="3">The precipitate may consist of $\mathbf{C}\mathrm{OBao}''$, $\mathbf{C}\mathrm{OSro}''$, $\mathbf{C}\mathrm{OCao}''$. Dissolve in a small quantity of dilute HCl. Evaporate to dryness on a water-bath. Pulverize the residuary chlorides (in the evaporating dish) with a pestle, and digest with absolute alcohol. Filter off through a small filter, and wash with absolute alcohol.</td></tr>
<tr><td rowspan="2">RESIDUE.—$\mathbf{Ba}\mathrm{Cl}_2$.
Confirm by dissolving in water and adding $2\mathrm{HF},\mathbf{Si}\mathrm{F}_4$, or $\mathbf{Cr}\mathrm{O}_2\mathrm{Ko}_2$.
Presence of Ba.</td><td colspan="2">SOLUTION.—Add dilute $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$ and filter. Digest the precipitated strontic and calcic sulphates at a gentle heat for some time, with a concentrated solution of $\mathbf{S}\mathrm{O}_2\mathrm{Amo}_2$ and a little AmHo, and filter.</td></tr>
<tr><td>RESIDUE.—$\mathbf{S}\mathrm{O}_2\mathrm{Sro}''$.
Confirm by treating with concentrated HCl and heating on the loop of a platinum-wire in a Bunsen gas flame.
Presence of Sr.</td><td>SOLUTION contains $\mathbf{S}\mathrm{O}_2\mathrm{Cao}''$.
Dilute with much water, and add $\left\{\begin{matrix}\mathbf{C}\mathrm{OAmo}\\ \mathbf{C}\mathrm{OAmo}\end{matrix}\right.$, a white precipitate.
Presence of Ca.</td></tr>
</table>

TABLE V.—SEPARATION OF THE METALS OF GROUP V.

<table>
<tr><td colspan="4">The SOLUTION may contain $\mathbf{Mg}\mathrm{O}$, $\mathbf{O}\mathrm{K}_2$, $\mathbf{O}\mathrm{Na}_2$ (Note 1). Evaporate to dryness, and ignite in a platinum crucible, until no more ammoniacal fumes come off.</td></tr>
<tr><td rowspan="3">Dissolve a small portion of the residue in water with the aid of a few drops of HCl, and filter, if necessary. To the clear filtrate add AmCl, AmHo, and $\mathbf{P}\mathrm{OHoNao}_2$; digest for some time at a gentle heat; stir well with a glass rod, and allow to stand for some time.
A white crystalline precipitate of $\mathbf{P}\mathrm{OAmoMgo}''$ (Note 2).
Presence of Mg.</td><td colspan="3">Dissolve the main portion of the residue in water, and a little dilute HCl; warm gently and add $\mathbf{Ba}\mathrm{Ho}_2$, drop by drop, as long as a precipitate of $\mathbf{Mg}\mathrm{Ho}_2$ is formed, and filter.</td></tr>
<tr><td rowspan="2">RESIDUE.—$\mathbf{Mg}\mathrm{Ho}_2$.
Neglect.</td><td colspan="2">SOLUTION.—Remove excess of $\mathbf{Ba}\mathrm{Ho}_2$ and $\mathbf{Ba}\mathrm{Cl}_2$ by the addition of a little $\mathbf{C}\mathrm{OAmo}_2$. Heat gently, and filter.</td></tr>
<tr><td>RESIDUE.—$\mathbf{C}\mathrm{OBao}''$.
Neglect.</td><td>SOLUTION.—Evaporate to dryness, and ignite. Test the residue on platinum wire, after moistening with water, in the inner blowpipe flame.
Yellow flame.
Presence of Na.
Reddish-violet flame when seen through indigo prism, or through blue glass.
Confirm by adding $\mathbf{Pt}\mathrm{Cl}_4$.
Presence of K.</td></tr>
</table>

Note 1.—Ammonic compounds are detected during the preliminary examination.

Note 2.—A slight *flocculent* precipitate is sometimes obtained, mostly due to aluminic phosphate, soluble in NaHo (from Al, dissolved in excess of AmHo in Group III), sometimes to the imperfect precipitation of the metals of the alkaline earths (Ba, Sr, Ca), especially in the presence of much magnesic and fixed alkaline chlorides. Before examining, therefore, for Mg, etc., add a few drops of ammonic oxalate, as well as sulphate, and filter off any slight precipitate which may be produced on digestion.

EXAMINATION FOR ACIDS.

Before proceeding to the examination for acids, the analyst will do well to consider carefully which acids can possibly be combined with the bases present. A perusal of the Table of Solubility of Salts, given in the Appendix, will materially aid him, and will probably save him much labour and time.

Some acids are detected on examining for bases, viz., As_2O_3, As_2O_5, SiO_2, and $POHo_3$ in combination with metals of Group III and IV, CrO_2Ho_2, CO_2, SH_2, $SOHo_2$, $SSOHo_2$, ClHo, NOHo, the six lastly mentioned acids on dissolving the substance in dilute HCl, or on adding HCl in Group I.

A careful preliminary examination for acids will probably lead to the detection of a further number of acids, *e.g.*, of HI, $\left\{\begin{matrix}OI\\OHo\end{matrix}\right.$, HBr, $\left\{\begin{matrix}OBr\\OHo\end{matrix}\right.$, and $\left\{\begin{matrix}OCl\\OHo\end{matrix}\right.$, NO_2Ho, (NOHo), HCl, (ClHo), HF, HCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$, CyHo and CyHs, $\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.$ and $\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.$. The presence of other organic acids is likewise indicated. When more than one of these acids is present, the detection is somewhat more difficult, and the results obtained by a preliminary examination for acids require to be carefully confirmed by the examination of the solution. Thus a chloride in the presence of a nitrate, when treated with concentrated SO_2Ho_2, evolves chlorine and red fumes of lower oxides of nitrogen; in the presence of a chromate, brownish-red fumes of CrO_2Cl_2. $HgCl_2$, Hg_2Cl_2, or $SnCl_4$ does not evolve HCl when treated with SO_2Ho_2. Polysulphides, when treated with HCl, evolve SH_2, with separation of sulphur. SO_2 and SH_2, when evolved simultaneously, destroy each other, etc.

When the preliminary examination gives no distinct indication of the presence of any of the acids just mentioned, SO_2Ho_2, BHo_3, $POHo_3$, SiO_2 will have to be looked for.

The analyst will have to bear in mind that acids cannot be detected in the same systematic order as bases, and that he ought, therefore, never to be satisfied till he has confirmed the presence of acids by the most characteristic *special* tests.

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
TREAT A LITTLE OF THE POWDERED SUBSTANCE IN A TEST-TUBE WITH DILUTE HCl, AND HEAT GENTLY.	Certain acids are given off— 1. WITHOUT DECOMPOSITION. A colourless and inodorous gas is evolved, which precipitates lime- or baryta-water	$\mathbf{C}O_2$, from carbonates, likewise from cyanides and cyanates containing carbonates.
Confirm by passing the $\mathbf{S}O_2$ through an acidulated solution of $\mathbf{Cr}O_2Ko_2$	A gas is evolved having the odour of burning sulphur	$\mathbf{S}O_2$, from sulphites.
Test the gas with lead-paper	A gas is given off, possessing a most fœtid odour—the odour of rotten eggs	$\mathbf{S}H_2$, from metallic sulphides (with the exception of $\mathbf{Cu}S$, $\mathbf{S}Ag_2$, $\mathbf{Bi}_2S_3$, $\mathbf{Hg}S$, $\mathbf{Pt}S_2$, $\mathbf{Au}_2S_3$, and $\mathbf{As}_2S_3$).
	Reddish-brown fumes	$\mathbf{N}_2O_3$, from nitrites.
	A colourless gas, possessing the odour of bitter almonds	HCy, from cyanides.
	2. WITH DECOMPOSITION. A yellowish-green gas, of suffocating odour, bleaching vegetable colours	Cl, from hypochlorites, also from decomposition of $\mathbf{Cr}O_2Ho_2$ by HCl.
	$\mathbf{S}O_2$ is evolved, and yellow sulphur is precipitated	From hyposulphites.
	$\mathbf{C}O_2$ is given off, accompanied by the pungent odour of $CyHo$. $AmCl$ being formed at the same time, and the residue gives off $\mathbf{N}H_3$ when heated with $\mathbf{Ca}Ho_2$	From decomposition of cyanates.
HEAT ANOTHER PORTION OF THE SOLID SUBSTANCE WITH MODERATELY CONCENTRATED $\mathbf{S}O_2Ho_2$	Certain acids are given off— 1. WITHOUT DECOMPOSITION.	$\mathbf{C}O_2$, $\mathbf{S}O_2$, $\mathbf{S}H_2$, $\mathbf{N}_2O_3$, HCy (already recognized on treating with dilute HCl).
	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$ is given off	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$, from acetates.
Confirm by distilling with $EtHo$ and concentrated $\mathbf{S}O_2Ho_2$	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OEto\end{matrix}\right.$ is given off	$\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.

PRELIMINARY EXAMINATION FOR ACIDS—*continued.*

Experiment.	Observation.	Inference.
	Pungent acid fumes	HCl, HF, HCy.
	2. WITH DECOMPOSITION	$\mathbf{S}SOHo_2$, ClHo, CyHo (already noticed).
	A gas is evolved, possessing the odour of bitter almonds	HCy (from ferro- and ferricyanides).
Confirm by causing the gas to act upon $\mathbf{S}_2Am_2$, and adding $\mathbf{Fe}_2Cl_6$.	Blood-red colouration	Cyanogen compounds.
TREAT A LITTLE OF THE SUBSTANCE WITH CONCENTRATED $\mathbf{S}O_2Ho_2$, AND WARM GENTLY (not sufficiently, however, to volatilize the $\mathbf{S}O_2Ho_2$).	Certain acids are given off— 1. WITHOUT DECOMPOSITION	$\mathbf{N}O_2Ho$, HCl, HCy, HF, $\overline{Bz}Ho$, $\overline{Su}Ho_2$.
Confirm HCl by heating with $\mathbf{Mn}O_2$ and $\mathbf{S}O_2Ho_2$.	Cl gas is evolved, recognized by its odour, its action upon vegetable colours, and upon KI and starch paste	HCl.
Confirm HF by etching on glass.	Heavy suffocating fumes, which corrode glass	HF.
Confirm $\mathbf{N}O_2Ho$ by adding concentrated $\mathbf{S}O_2Ho_2$ to a solution of the salt, and $\mathbf{S}O_2Feo''$. (If a chlorate as well as a nitrate be present, ignite previous to treating with $\mathbf{S}O_2Ho_2$ and $\mathbf{S}O_2Feo''$.)	A brown ring is formed	$\mathbf{N}O_2Ho$.
	2. WITH DECOMPOSITION	ClHo and CyHo (already noticed), $\mathbf{S}H_2$, HI, HBr, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$, $\mathbf{Cr}O_2Ho_2$, formic, tartaric and citric acids, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, CyHs, H_4FeCy_6, $H_6Fe_2Cy_{12}$.
	$\mathbf{S}H_2$, as well as $\mathbf{S}O_2$, are evolved, owing to the action of the liberated sulphur upon $\mathbf{S}O_2Ho_2$.	Metallic sulphides.

	Oxygen is given off, and the yellow chromate is changed into green chromic sulphate	$\mathbf{Cr}O_2Ho_2$.
	Chloric peroxide, a greenish-yellow, highly explosive gas is given off	$\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$.
	Detonation in the test-tube on the application of heat	
Confirm HBr and HI by distilling with $\mathbf{Mn}O_2$ and concentrated $\mathbf{S}O_2Ho_2$.	Bromine is evolved (together with HBr and $\mathbf{S}O_2$), which condenses to a reddish-brown liquid; the gas colours starch paste yellow	HBr and $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ho\end{matrix}\right.$.
	Iodine is given off; violet fumes and sublimate colouring starch paste blue	HI.
	Chlorine is evolved	HCl, in the presence of $\mathbf{Cr}O_2Ho_2$.
	Chlorine and nitrous fumes are given off ..	HCl, together with $\mathbf{N}O_2Ho$ or $\mathbf{N}OHo$.
	$\mathbf{C}O$ is given off, without blackening ..	Formic acid.
	The substance blackens, owing to separation of carbon, with evolution of $\mathbf{C}O$, $\mathbf{C}O_2$, and $\mathbf{S}O_2$, and gives off the characteristic odour of burnt sugar	$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}HHo\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{matrix}\right.$ and $\left\{\begin{matrix}\mathbf{C}HHo(\mathbf{C}OHo)\\ \mathbf{C}H(\mathbf{C}OHo)\\ \mathbf{C}H_2(\mathbf{C}OHo)\end{matrix}\right.$
Pass gases through a solution of NaHo. The $\mathbf{C}O$ burns with a blue flame.	$\mathbf{C}O$ and $\mathbf{C}O_2$ are evolved without blackening	Oxalic acid.
	The acid is decomposed into $\mathbf{C}O$ and $\mathbf{N}H_3$, the latter remaining combined with the acid	Cyanides, ferro- and ferricyanides.
	$\mathbf{C}O_2$ is given off, and ammonic sulphate is left	Cyanates.
	$\mathbf{C}O_2$ and $\mathbf{S}H_2$ are evolved with separation of sulphur, which reacts upon the $\mathbf{S}O_2Ho_2$ and forms $\mathbf{S}O_2$, ammonic sulphate being left	Sulphocyanates.
	No gas or vapour is evolved	$\mathbf{Si}O_2$, $\mathbf{B}Ho_3$, $\mathbf{P}OHo_3$, $\mathbf{S}O_2Ho_2$, $\mathbf{As}OHo_3$, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$.
	A gelatinous mass or a flaky powder is left..	$\mathbf{Si}Ho_4$ from soluble silicates, or from silicates, decomposable by acids.
	Scaly crystals separate, possessing a pearly lustre	$\mathbf{B}Ho_3$.

PREPARATION OF SOLUTIONS FOR ACIDS.

Great care ought to be bestowed upon the preparation of the solutions required for the examination of acids. On boiling a portion of the substance under examination with $CONao_2$ nearly all the metals other than alkalies are precipitated in the form of carbonates, basic carbonates, or oxides.

(It is necessary to decompose the salts first in order to prevent the precipitation by the several reagents employed for the detection of acids in the wet way, *e.g.*, of Ba, Sr, Ca, or Pb, on the addition of $\mathbf{S}O_2Cao''$ or $\mathbf{S}O_2Mgo''$; of Ag, $'Hg'_2$ or Pb, by $\mathbf{Ba}Cl_2$ or $\mathbf{Ca}Cl_2$; of Fe and others by AmHo, etc., etc.)

The precipitate produced by $CONao_2$ (which reagent ought to be added in the least possible excess) is filtered off, and the filtrate tested with a few more drops of $CONao_2$. If no further precipitation takes place, the solution is heated to boiling, and

1. Dilute HCl added to a portion of it, as long as CO_2 is evolved, and till the solution is rendered distinctly acid.

(Small quantities of $\mathbf{S}O_2Nao_2$ and NaCl are almost invariably contained in the commercial $\mathbf{C}ONao_2$; it is therefore necessary to test a portion of the aqueous, or HCl solution of the substance, prepared without the intervention of $\mathbf{C}ONao_2$, for $\mathbf{S}O_2Ho_2$ by means of $\mathbf{Ba}Cl_2$. A nitric acid solution of the original substance is in like manner tested for HCl by adding $\mathbf{N}O_2Ago$.)

2. Another portion of the alkaline filtrate is rendered acid by means of dilute $\mathbf{N}O_2Ho$ and boiling.

3. A third portion is rendered acid by means of dilute $\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.$; and lastly—

4. A fourth portion of the alkaline solution is *carefully neutralized* by first adding dilute $\mathbf{N}O_2Ho$, drop by drop, and boiling, as long as CO_2 is evolved, and till the solution is distinctly acid to test-paper: then by adding a few drops of very dilute AmHo, till the solution gives a neutral reaction with blue and red litmus-papers. *The strictest attention should be paid to these directions*, and the least possible excess of either acid or alkali should be employed, since the precipitation of several acids is prevented by the formation of an ammonic salt in anything like large quantities, on account of the formation of a soluble double salt, *e.g.*, ammonic calcic tartrate, ammonic calcic citrate, etc.

If the preliminary examination for bases has shown the presence of ammonic salts, it is necessary to decompose them by boiling with caustic NaHo, before preparing Solution IV.

Ebullition or fusion with $\mathbf{C}ONao_2$ decomposes the phosphates of the alkaline earths but very imperfectly, and the phosphoric acid so combined is invariably detected by means of $\mathbf{Mo}O_2Amo_2$. (Comp. Table III B.)

If organic acids are present in combination with heavy metals (viz., those of Groups I and II), SH_2 should be passed through the slightly acid (HCl) solution and the precipitate filtered off. The solution is freed from SH_2 by boiling, then rendered slightly alkaline by means of a few drops of NaHo and tested by means of $CaCl_2$ (ammonic salts should be carefully avoided).

No further notice need be taken of the following acids: CO_2, SH_2, SO_2, NOHo, ClHo, $\left\{\begin{matrix}CH_3\\ COHo\end{matrix}\right.$, since they can be detected with certainty by a preliminary examination, and as they would, for the most part, be lost on acidulating the solutions.

Portion Acidulated with HCl.

SO_2Ho_2.—On the addition of $BaCl_2$ a white precipitate, insoluble on boiling.

$SiHo_4$.—On the addition of AmCl or $COAmo_2$ a gelatinous precipitate, requiring no further confirmation, since SiO_2 is left on evaporating the filtrate from Group II with NO_2Ho.

H_4FeCy_6.—On the addition of Fe_2Cl_6 a deep blue precipitate.
" " SO_2Feo'' light " "
$H_6Fe_2Cy_{12}$.— " " " dark deep " "
" " Fe_2Cl_6 a brown coloration only.—If both acids are present, filter off, after adding Fe_2Cl_6, and observe the colour of the filtrate. On the addition of $SnCl_2$, or $SOHo_2$, to the filtrate, a blue precipitate is immediately obtained, confirmatory of the presence of $H_6Fe_2Cy_{12}$.

CyHs.—Fe_2Cl_6 produces a blood-red coloration, which is destroyed by $HgCl_2$ and not by HCl (the red colour which acetic acid imparts to a solution of Fe_2Cl_6 is destroyed by HCl).

$2HF,SiF_4$.—On the addition of $BaCl_2$ a gelatinous translucent precipitate of BaF_2,SiF_4 is obtained, which is decomposed by strong acids. Confirm by heating the precipitate, when volatile SiF_4 is given off. AmHo precipitates gelatinous $SiHo_4$ with formation of AmF, BaF_2 and OH_2.

Portion Acidulated with NO_2Ho.

HCl.—On the addition of NO_2Ago a white curdy precipitate, soluble in AmHo. For the distinction between *hydrochloric and chloric acids* comp. p. 126.

HBr.—On the addition of NO_2Ago a yellowish-white precipitate, difficultly soluble in AmHo. Confirm by adding chlorine water to the original solution, and shake up with ether. Bromine dissolves to a yellowish-red liquid.

$\left\{\begin{matrix}OBr\\ OHo\end{matrix}\right.$.—On the addition of NO_2Ago a white amorphous precipitate, little soluble in water and dilute NO_2Ho, easily soluble in AmHo.—AgBr and $\left\{\begin{matrix}OBr\\ OAgo\end{matrix}\right.$ may be separated by washing with water. Argentic bromate being soluble may be detected in the solution by the addition of $SOHo_2$, when a precipitate of AgBr is obtained.

For *the distinction between HBr and HCl*, comp. page 122.

HI.—On the addition of NO_2Ago a yellowish white precipitate, scarcely soluble in AmHo. Confirm by the blue colour imparted to starch paste by the iodine liberated by $\mathbf{N}_2\mathrm{O}_3$ gas.

$\left\{\begin{matrix}\mathbf{O}\mathrm{I}\\ \mathbf{O}\mathrm{Ho}\end{matrix}\right.$.—On the addition of $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$ a white precipitate of $\left\{\begin{matrix}\mathbf{O}\mathrm{I}\\ \mathbf{O}\mathrm{Ago}\end{matrix}\right.$, sparingly soluble in dilute $\mathbf{N}\mathrm{O}_2\mathrm{Ho}$, soluble in AmHo (AgI is insoluble), whence AgI is precipitated on the addition of $\mathbf{S}\mathrm{OHo}_2$. On adding acetic acid to a mixture of an iodide and iodate the former is instantly decomposed, iodine being set free,—most readily recognised by the delicate iodide of starch reaction.

Distinction between HCl and HI.—HCl in the presence of HI cannot be distinguished in the same ready manner as HCl in the presence of HBr. The two acids are precipitated by $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$. The precipitate is digested with AmHo and filtered, AgI being insoluble in AmHo. Dilute $\mathbf{N}\mathrm{O}_2\mathrm{Ho}$ reprecipitates white AgCl from the filtrate.

Distinction between HCl, HBr, and HI.—Precipitate the HI as $\mathbf{Cu}_2\mathrm{I}_2$ by means of $\mathbf{S}\mathrm{O}_2\mathrm{Cuo}''$ and $\mathbf{S}\mathrm{O}_2\mathrm{Feo}''$ or $\mathbf{S}\mathrm{OHo}_2$, and filter. Remove the cupric and ferric salts by a little pure NaHo, evaporate the filtrate to dryness, and examine for HCl and HBr by testing one portion for HCl with $\mathbf{Cr}_2\mathrm{O}_5\mathrm{Ko}_2$ and $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$, and another for HBr by chlorine-water and ether.

HCy.—On the addition of $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$ a white curdy precipitate, soluble in AmHo and alkaline cyanides.

In order *to distinguish* HCy *in the presence of* HCl, filter off precipitate, wash well, and ignite in a porcelain crucible to red heat. Dissolve the metallic Ag left by the decomposition of AgCy with a little hot $\mathbf{N}\mathrm{O}_2\mathrm{Ho}$, and test the clear solution with HCl. A curdy white precipitate indicates HCy. Confirm also by the reaction with ferroso-ferric salts, KHo and HCl in a fresh portion of the solution.

Distinction between HCl, HBr, HI, and HCy.—Test specially for HCy, before proceeding to the examination of the other acids as described, by treating a small quantity of the mixed salts in a porcelain dish with very dilute $\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2$, and causing the evolved HCy to act upon a drop of $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$, or a little $\mathbf{S}_2\mathrm{Am}_2$, contained in a second porcelain dish, inverted over the one containing the mixed salts. A white precipitate of AgCy is obtained; or the CyAms which is formed gives a blood-red colour with ferric salts, affording equally conclusive evidence of the presence of HCy.

$\left.\begin{matrix}\mathrm{CyHs}\\ \mathrm{H}_4\mathrm{FeCy}_6\\ \mathrm{H}_6\mathrm{Fe}_2\mathrm{Cy}_{12}\end{matrix}\right\}$ are likewise precipitated on the addition of $\mathbf{N}\mathrm{O}_2\mathrm{Ago}$, and are insoluble in dilute $\mathbf{N}\mathrm{O}_2\mathrm{Ho}$. The first and second form salts which are insoluble in AmHo, whilst $\mathrm{Ag}_6\mathrm{Fe}_2\mathrm{Cy}_{12}$ is readily soluble. These acids are, however, best detected in the portion acidulated with HCl.

No other cyanogen compound but a cyanide gives off HCy when treated with very dilute $\mathbf{S}O_2Ho_2$, and it is therefore possible also to distinguish HCy in the presence of $CyHs$, $CyHo$, H_4FeCy_6, $H_6Fe_2Cy_{12}$.

PORTION ACIDULATED WITH $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$.

HF.—On the addition of $\mathbf{Ca}Cl_2$ a white gelatinous precipitate. $\mathbf{S}O_2Ho_2$ is likewise precipitated by $\mathbf{Ca}Cl_2$ in an acetic acid solution; it is therefore necessary invariably to test specially for HF, by etching on glass.

$\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$.—On the addition of $\mathbf{S}O_2Cao''$ a white precipitate of $\left\{\begin{matrix}\mathbf{C}O\\ \mathbf{C}O\end{matrix}\right.Cao''$ is obtained, which on ignition leaves $\mathbf{C}OCao''$, soluble with effervescence in $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$. (Calcic fluoride is not affected.)

$\mathbf{Cr}O_2Ho_2$.—On the addition of plumbic acetate a yellow precipitate.

$\mathbf{P}OHo_3$.—On the addition of $\mathbf{Fe}_2Cl_6$ a yellowish-white gelatinous precipitate from a solution of a soluble phosphate, or a phosphate decomposable by boiling with $\mathbf{C}ONao_2$. Arsenic acid, if present, should be first removed by means of $\mathbf{S}H_2$.

PORTION RENDERED NEUTRAL.

$\overline{T}Ho_2$.—On the addition of $\mathbf{Ca}Cl_2$ a white precipitate, soluble in $AmCl$ or cold KHo.—$\mathbf{S}O_2Ho_2$, $\left\{\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}\right.$, HF, $\mathbf{P}OHo_3$, $\mathbf{As}OHo_3$, $\mathbf{B}Ho_3$, $\mathbf{Si}Ho_4$, $\mathbf{C}O_2$, $\mathbf{S}OHo_2$, are likewise precipitated by $\mathbf{Ca}Cl_2$ from a neutral solution, and $\overline{T}Ho_2$ can obviously be detected only by further special tests in the presence of any of these acids. The most characteristic reaction consists in warming some $\overline{T}Ago_2$, dissolved in very little dilute $AmHo$, in a water-bath, until a bright mirror of metallic silver is obtained on the sides of the test-tube.

$\overline{Ci}Ho_3$.—On the addition of $\mathbf{Ca}Cl_2$ no precipitate is obtained till excess of $AmHo$, or $\mathbf{Ca}Ho_2$, has been added and the solution boiled.

The detection of tartaric and citric acids—indicated during the preliminary examination by a strong odour of burnt sugar—requires great care and strict attention to the few points of distinction which exist between them. The precipitate produced by $\mathbf{Ca}Cl_2$ in the cold should be filtered off, and the filtrate tested for $\overline{Ci}Ho_3$, by adding a drop of $AmHo$ and boiling, when a fresh precipitate of calcic citrate is obtained. $\overline{Ci}Ago_3$ dissolved in dilute $AmHo$, forms a less lustrous mirror, and only after boiling for a long time.

BHo_3.—**$CaCl_2$** produces from a concentrated solution of a borate a whitish precipitate soluble in AmCl. Boric acid is also indicated in the preliminary examination by the swelling up of some of its saline compounds, and the precipitation of a concentrated solution of a borate with concentrated **SO_2Ho_2** or HCl.

More delicate, however, is the reaction which boric acid gives with turmeric paper, and the colour which boric fluoride imparts to the flame. (Comp. page 137 and 148.)

$\overline{Bz}Ho$.—On the addition of **Fe_2Cl_6** a pale yellow precipitate. Confirm by the reactions which a benzoate gives in the preliminary examination, since a precipitate of **Fe_2Ho_6** is frequently mistaken for ferric benzoate, owing to imperfect neutralization.

$\overline{Su}Ho_2$.—On the addition of **Fe_2Cl_6** a reddish brown precipitate.

For *the distinction between benzoic and succinic acids*, compare page 169.

APPENDIX I.

REACTIONS OF THE RARE METALS.

METALS are termed rare when they occur in nature to a limited extent, and, for the most part only, in certain minerals, and in certain localities. Some of the heavy metals, possessing very little affinity for oxygen, such as PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM, and IRIDIUM, are found *native*, and associated with the native metals PLATINUM and GOLD. Others are found in combination with *oxygen*, such as TITANIUM, URANIUM, TANTALUM, and NIOBIUM ; with *sulphur* or *arsenic*, such as TUNGSTEN or WOLFRAM, MOLYBDENUM, VANADIUM, THALLIUM, and INDIUM.

Others, especially the rare metals usually classified among the so-called light metals, having a specific gravity for the most part of less than 5, and yielding insoluble oxides which are mostly specifically heavier than their metals, such as GLUCINUM, ZIRCONIUM, THORIUM, CERIUM, LANTHANUM, DIDYMIUM, YTTRIUM, ERBIUM, are chiefly met with in nature as *oxides*, in combination with silica (sometimes combined with titanic, niobic, and tantalic acids) ; and lastly, the rare metals of the so-called alkali group, whose oxides possess the most pronounced basic character and are soluble in water, such as LITHIUM, RUBIDIUM, and CAESIUM, are chiefly met with as *salts*,—carbonates, phosphates, or silicates—and in a soluble condition, in sea-water, or in certain mineral springs.

The rare metals cannot be studied with advantage, without taking into account their mineralogical associations ; and, as many of them have as yet been imperfectly investigated, they present difficulties, to be overcome only by careful attention, not merely to the distinctive analytical features, but to their general chemical history.

The following is the analytical position assigned to these metals by the various group-reagents :—

Group I. *Precipitated by HCl :*—Tungsten, as tungstic acid ; niobium, as niobic acid ; thallium, as chloride. (Tantalum, as tantalic acid, and molybdenum, as molybdic acid, are soluble in excess of HCl.)

Group II. *Precipitated by* SH_2, *from a HCl solution, as sulphides :—*

(A.) *Insoluble in yellow ammonic sulphide :—* Palladium, rhodium, osmium, and ruthenium.

(B.) *Soluble in yellow ammonic sulphide:*—Gold, platinum, iridium, molybdenum, tellurium, and selenium.

Group III. *Precipitated by AmCl, AmHo, and* SAm_2*:*—Uranium, indium (thallium), as *sulphides;* glucinum or beryllium, thorium, zirconium, cerium, lanthanum, didymium, yttrium, erbium, titanium, tantalum, and niobium, as *hydrates.* Vanadium, precipitated as *sulphide*, on adding HCl to the filtrate.

Group IV. None.

Group V. Lithium, caesium, and rubidium.

METALS OF THE ALKALIES.

The alkali metals, CAESIUM, RUBIDIUM (potassium, sodium), and LITHIUM are remarkable for their highly electropositive character, the powerful alkaline nature of their oxides and hydrates, and the very general solubility of their salts. Caesium appears to be the most highly electropositive member, whilst lithium shows the least electropositive character. They exhibit analogous gradations in their respective combining weights, fusion-points, specific gravity, action upon water, and the solubility of their carbonates, thus:—

	Caesium.	Rubidium.	Potassium.	Sodium.	Lithium.
Atomic weights	133	85·5	39·1	23	7
Fusion-points..	Below 38·5	38·5° C.	62·5° C.	96° C.	180° C.
Specific gravity at 15° C. ..	(?)	1·516	·865	·97	·59
Action of the metals upon water......	Decomposes water in the cold, the hydrogen becoming inflamed.	Do.	Do.	Do., but does not generally inflame the hydrogen.	Do., but with less violence.
Solubility of the respective carbonates ..	$COCso_2$ Highly deliquescent, absorbing water speedily from the air.	$CORbo_2$	$COKo_2$	$CONao_2$ Not deliquescent.	$COLio_2$ Difficultly soluble in water.

Lithium, in fact, appears to form the connecting link between the alkali metals and the metals of the alkaline earths. This is shown more especially by the comparatively insoluble nature of its phosphate and carbonate.

REACTIONS OF THE RARE METALS OF THE ALKALI-GROUP.

1. **CAESIUM**, Cs. Atomic weight, 133.—Occurs in very small quantities in many mineral waters, as CHLORIDE, and in a few minerals (*Lepidolites*); in large quantities in the rare felspathic mineral *Pollux*, found in Elba, said to contain 34 per cent. of Caesia.

Both caesium and rubidium were discovered by Bunsen and Kirchhoff in 1860, whilst examining spectroscopically the saline residue left on evaporating large quantities of the *Dürkheim* mineral water. The metal caesium has not yet been isolated, but has been obtained in the form of an amalgam. The hydrate, $CsHo$, is very soluble, both in water and alcohol, and very strongly alkaline. The carbonate, $COCso_2$, resembles potassic and rubidic carbonate, but is soluble in 5 parts of boiling alcohol. (DISTINCTION FROM $COKo_2$, $CONao_2$, AND $CORbo_2$, WHICH ARE PRACTICALLY INSOLUBLE IN ALCOHOL.)

REACTIONS IN THE DRY WAY.

When heated on platinum wire, in the inner flame of the blowpipe, volatile caesium salts impart an intense **sky-blue** colour to the outer flame. (Hence the name of the metal, from *caesius*, sky-blue.) When examined with the aid of a spectroscope, principally two intensely **sky-blue** lines, Csα and Csβ, close upon the strontium line, Srδ, are seen (together with various other less distinctly visible lines in the orange, yellow, and green).

REACTIONS IN THE WET WAY.

USE A SOLUTION OF CAESIC CHLORIDE, CsCl.

$PtCl_4$ (**Platinic chloride**) produces a *light yellow crystalline* (octahedral) precipitate of the **double chloride of caesium and platinum,** $2CsCl,PtCl_4$, very difficultly soluble in boiling water—·377 parts in 100 of water. The corresponding potassic platinic chloride is dissolved by repeated treatment with boiling water.

$\overline{T}Ho_2$ (**tartaric acid**) produces a *colourless transparent crystalline* precipitate of **hydric caesic tartrate,** $\overline{T}HoCso$; about 8 times more soluble in water than the corresponding rubidium salt.

Method of Separation of Cs from Rb.—$SnCl_4$, added to a solution of the chlorides of Na, K, Li, Rb, and Cs, containing free HCl, forms a heavy white precipitate, consisting of nearly pure caesic stannic chloride, $2CsCl,SnCl_4$. By recrystallization from a hot hydrochloric acid solution, the crystals are obtained pure. This reaction affords an easy method of detecting caesium in a mixture of the alkaline chlorides. A hydrochloric solution of $SbCl_3$ acts similarly, by precipitating a crystalline double chloride of $CsCl, SbCl_3$. The precipitate is decomposed by water, but can be washed without decomposition with concentrated HCl. The other alkaline chlorides (K, Na, and Rb) are *not* precipitated.

2. **RUBIDIUM,** Rb. Atomic weight, 85·5.—Occurs widely diffused in nature. It is met with, although only in very small quantities, in a large number of minerals, in *Lepidolites* and in mineral waters, likewise in the ashes of many plants, such as tobacco, coffee, beetroot, &c. The metal is obtained, like potassium, by heating the carbonate with carbon. It is white, more easily fusible and convertible into vapour than potassium, and takes fire spontaneously in air. Its oxide, rubidia, ORb_2, is a powerful base, and its salts, like the corresponding caesium salts, are isomorphous with those of the metal potassium. The hydrate, RbHo, is strongly alkaline, and very soluble in water and alcohol. The carbonate, $CORbo_2$, is a deliquescent salt, insoluble in alcohol.

REACTIONS IN THE DRY WAY.

Volatile rubidium salts, when heated on a platinum wire in the inner blowpipe flame, colour the outer flame **dark red** (hence the name rubidium, from *rubidus*, dark red). When examined spectroscopically, two **dark red** lines, Rbδ, and Rbγ, on the extreme left of the solar spectrum and close to the potassium line, together with two distinctly **violet** lines, and several weaker lines in the yellow, readily distinguish rubidium compounds.

REACTIONS IN THE WET WAY.

A SOLUTION OF RUBIDIC CHLORIDE, RbCl is employed.

$PtCl_4$ (**platinic chloride**) produces a *light yellow crystalline* (octahedral) precipitate of **rubidic platinic chloride,** $2RbCl,PtCl_4$, very difficultly soluble in boiling water. The solubility of the double chlorides of platinum and potassium, rubidium, or caesium is respectively as 5·18, ·634, and ·377 in 100 parts of boiling water. (*Method of Separation of K from Rb and Cs.*)

$\overline{T}Ho_2$ **(tartaric acid)** yields a *white* precipitate of **hydric rubidic tartrate,** $\overline{T}HoRbo$, which is soluble in 10·3 parts of water of 25° C.

Rubidium and caesium resemble potassium, also, in forming *alums*, which differ considerably in their solubility in water. 100 parts of water of 17° C. dissolve 13·5 parts of potassium-alum, 2·27 of rubidium—and only 0·62 parts of caesium-alum.

Separation of Caesium from Rubidium.—The several platinum salts are first prepared; and after having been gently heated in a current of hydrogen, the CsCl and RbCl can be separated from the metallic platinum by hot water. The two chlorides are next converted into carbonates, by digestion with $COAgo_2$. The solution can then be evaporated to dryness, and the $COCso_2$ extracted with boiling alcohol, $CORbo_2$ being insoluble. Or the carbonates may be converted into acid tartrates, by adding to the solution twice as much tartaric acid as is necessary to neutralise it. The two tartrates are separated by fractional crystallisation, hydric rubidic tartrate crystallising out first, being about 8 times more insoluble in water than the hydric caesic tartrate. On ignition, the pure tartrate yields again the carbonate, from which the various salts may then be prepared.

3. **LITHIUM,** Li. Atomic weight, 7.—Appears to be widely diffused in nature, although it is found, in anything like quantities, only in a few SILICATES, especially in *lithia mica* or *lepidolite* (2 to 5 per cent. of Li), in *petalite* and *spodumene*, and in a few PHOSPHATES, such as *triphylline*, or ferrous [manganous] lithic phosphate, $3P_2O_2Feo''_3$, $POLio_3$ (with 3 to 4 per cent. of Li), and *amblygonite* (6 to 9 per cent. of Li). It has also been found in many mineral springs—most abundantly as yet in a mineral spring in Cornwall—in sea-water, in the ashes of various kinds of tobacco, and other plants, and in some meteorites.

The metal lithium is much less oxidisable than potassium and sodium. It makes a lead-grey streak on paper. When freshly cut, it has the colour of silver: but it tarnishes quickly, on exposure to the air, becoming slightly yellow. It is harder than potassium and sodium, but softer than lead. It floats on rock oil, and is the lightest of all known solids, its specific gravity being only ·59. It decomposes water at the ordinary temperature, with evolution of hydrogen, forming lithic hydrate, $LiHo$, but does not melt, and it ignites in air only far above its melting point (180° C.). The oxide, OLi_2, is not deliquescent. The metal is prepared by passing a powerful galvanic current into fused lithic chloride.

REACTIONS IN THE DRY WAY.

Lithium salts are more fusible than potassium or sodium salts, and impart a very distinct **carmine-red** colour to the blowpipe flame, when heated on platinum wire. An excess of potassium salt does not materially interfere with the production of this colour; but the presence of a small quantity of soda gives rise to a yellow flame. Lithic phosphate requires to be moistened first with hydrochloric acid. Silicates containing lithia must first be decomposed by means of oil of vitriol, or by fusion with calcic sulphate, or also by treatment with hydrofluoric acid. By means of the spectroscope the occurrence of very minute traces of lithium may be readily detected by a brilliant **crimson** band, $Li\alpha$, between the lines B and C, and sometimes a faint yellow line, if the flame of a good Bunsen burner be employed.

REACTIONS IN THE WET WAY.

WE EMPLOY A SOLUTION OF LITHIC CHLORIDE, LiCl.

$PtCl_4$ produces no precipitate.

$POHoNao_2$ (**hydric disodic phosphate**)—but not the corresponding potassium salt—produces on boiling a *white* precipitate of **lithic phosphate,** $2POLio_3 + Aq$, very little soluble in cold water (2500 parts), soluble in HCl, and reprecipitated only, on boiling, after neutralisation with $AmHo$.

Lithic Carbonate, especially after having been fused, is difficultly soluble in cold water, hence alkaline carbonates yield from concentrated solutions of lithium salts a crystalline precipitate of lithic carbonate, $COLio_2$ (1 part of the carbonate requires 100 parts of cold water for its solution, but less of boiling water). It is insoluble in alcohol.

Hydric lithic tartrate is soluble.

Lithic silicofluoride is almost insoluble.

Separation of Lithium.—From potassium, as well as caesium and rubidium, it may be separated by means of $PtCl_4$. From sodium, by converting the two alkalies into the chlorides, evaporating to dryness, and treating the dried chlorides in a stoppered bottle with a mixture of ether and absolute alcohol. In the course of a few days the $LiCl$ will be found dissolved out, $NaCl$ (like KCl) being insoluble in absolute alcohol and ether.

Remark.—The student will now have no difficulty in constructing a table for the separation of these five metals.

EXTRACTION OF LITHIUM FROM TRIPHYLLINE.—Dissolve the powdered ore in HCl, with a little NO_2Ho (in order to convert Fe'' into Fe^{iv}), neutralize with $AmHo$, when $P_2O_2Fe_2o^{vi}$, and $P_2O_2Mno''_3$ are precipitated. The solution, on filtering, may contain some more phosphoric acid, which may be removed by adding SBa, and filtering off the precipitated $POHoBao$. On removing the excess of SBa, with a few drops of SO_2Ho_2, and evaporating the filtrate, and driving off the ammonium salts by gentle ignition, lithic chloride is left. The hydrate may be prepared from this by evaporation with sulphuric acid (so as to obtain SO_2Lio_2), and addition of $BaHo_2$, and filtering. The excess of $BaHo_2$ is next cautiously removed from the filtrate by means of SO_2Ho_2. On evaporation, white crystalline, strongly alkaline, lithic hydrate, $LiHo$, is left.

REACTIONS OF THE RARE METALS OF GROUP III.

Group III comprises the Rare Metals URANIUM, INDIUM (THALLIUM), GLUCINUM, THORIUM, ZIRCONIUM, CERIUM, LANTHANUM, DIDYMIUM, TITANIUM, TANTALUM, NIOBIUM, YTTRIUM, ERBIUM, and VANADIUM.

In considering the reactions by which these rare bodies may be recognized, we cannot do better than avail ourselves of the classification which nature itself has traced out in the groups of rare minerals in which they occur. As it is extremely difficult to commercially obtain any of their salts in a pure state, and as the price charged for them puts them out of the reach of most students, it will be preferable to sketch out briefly, also, how the minerals themselves can be made to furnish the several salts, when once the mineralogical character and locality of the minerals have marked them out as likely to contain any rare metals.

(A.) *Rare metals precipitated by the group-reagents* $AmCl$, $AmHo$, and SAm_2, *in the form of oxides* (*hydrates*).

Besides the metals aluminium and chromium, already treated of in the main portion of the book, there are :—

1. **GLUCINUM** (Beryllium) Gl'' (or Be''). Atomic weight, 9·4.—This metal occurs only in a few minerals, and is found very locally, as a SILICATE, in *phenacite*, $SiGlo_2$ (45 per cent. of GlO), combined with aluminic silicate; in

beryl, $\mathrm{Si_6O_6Al_2o^{vi}Glo''_3}$ (13·8 per cent. of GlO), and in *smaragdite*, in *euclase*, and some other rare minerals, such as *leucophane*.

The metal is prepared, like the metal aluminium, from the chloride. It is white, and has a specific gravity of 2·1. It resembles aluminium in dissolving in HCl, as well as KHo, with evolution of hydrogen. Its oxide forms a white powder, insoluble in water. It may be prepared by fusing finely-powdered native silicate with 4 parts of its weight of fusion-mixture, decomposing the mass with HCl, and evaporating to dryness to separate the $\mathrm{SiO_2}$. From the HCl filtrate both the $\mathrm{Al_2O_3}$ and GlO are precipitated by means of AmHo. On boiling the precipitate, however, for some time with AmCl, $\mathrm{NH_3}$ is evolved, and glucinum is dissolved out as chloride, $\mathrm{Gl''Cl_2}$. The insoluble $\mathrm{Al_2Ho_6}$ remains behind. Pure glucina can then be precipitated from the filtrate by means of AmHo, as gelatinous hydrate, $\mathrm{GlHo_2}$, which on ignition yields the white anhydrous glucina, GlO, of specific gravity 3·08.

From the oxide we can obtain the salts by dissolving in the respective acids, or by double decomposition, from one of its soluble salts. Glucina resembles alumina, inasmuch as it combines also both with acids and bases. Its salts are colourless, and of a sweet, slightly astringent taste; they show an acid reaction.

REACTIONS IN THE DRY WAY.

Glucinum compounds give no characteristic reactions in the dry way. $\mathrm{N_2O_4Coo''}$ yields a grey mass.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF GLUCINIC SULPHATE, $\mathrm{SO_2Glo''}$.

The **group-reagents** AmHo and $\mathrm{SAm_2}$, as well as the fixed caustic alkalies and alkaline earthy bases, precipitate **glucinic hydrate**, $\mathrm{GlHo_2}$ (flocculent), soluble, like $\mathrm{Al_2Ho_6}$, in excess of the fixed alkalies, but not in ammonia. On boiling, $\mathrm{GlHo_2}$ is almost completely reprecipitated from a dilute NaHo or KHo solution. (DISTINCTION FROM $\mathrm{Al_2O_3}$.) Like $\mathrm{Al_2O_3}$, it is reprecipitated also on the addition of AmCl.

$\mathrm{COAmo_2}$ gives a *white* precipitate of **glucinic carbonate**, $\mathrm{COGlo''}$, freely soluble in excess, reprecipitated as basic carbonate on boiling. (DISTINCTION FROM $\mathrm{Al_2O_3}$.)

$\mathrm{CONao_2}$, or $\mathrm{COKo_2}$, precipitates likewise white carbonate, soluble only in large excess of the precipitants.

$\mathrm{COBao''}$ precipitates glucinum completely, even in the cold.

Besides these characteristic reactions, we may mention the difficultly soluble **double sulphate** $\mathrm{\begin{matrix}SO_2Ko\\SO_2Ko\end{matrix}Glo''} + 3\mathrm{Aq}$, which the readily soluble glucinic sulphate forms, when brought together with potassic sulphate.

SEPARATION OF $\mathrm{Al_2O_3}$ FROM GlO.—Dissolve in HCl; pour slowly, and with continued stirring, into a warm concentrated solution of $\mathrm{COAmo_2}$. A precipitate forms, consisting of $\mathrm{Al_2Ho_6}$, the solution containing the glucinum as double carbonate. Neutralize with HCl; boil and add AmHo. $\mathrm{GlHo_2}$ is precipitated.

2. **ZIRCONIUM**, $\mathrm{Zr^{iv}}$. Atomic weight, 89·6.—Found as SILICATE, chiefly in the rare mineral *zircon*, $\mathrm{SiZro^{iv}}$. The silicate is not attacked by acids, and the finely elutriated substance must be decomposed by fusion at a high temperature with fusion-mixture. The mass is extracted with water, evaporated to dryness with HCl, in order to remove $\mathrm{SiO_2}$, and to decompose the insoluble, sandy-looking **disodic zirconate**, $\mathrm{ZrONao_2}$, and is then precipitated with ammonia. The metal itself has been obtained in white metallic looking scales, of specific gravity 4·1, by the decomposition of the double fluoride of potassium and zirconium, $\mathrm{2KF,ZrF_4}$, by means of metallic aluminium. The hydrate is a voluminous white body, resembling $\mathrm{Al_2Ho_6}$. It dries up to yellowish, transparent lumps, $\mathrm{ZrHo_4}$, which dissolve readily in acids. On ignition, this hydrate

loses its water, and undergoes a molecular change, when the dioxide, or zirconic anhydride, ZrO_2, is no longer soluble in dilute acids.

Zirconium salts, obtained by dissolving the hydrate in dilute acids, are colourless, and of an astringent taste.

REACTIONS IN THE DRY WAY.

Of all the earthy oxides, ZrO_2 is the only one which remains entirely unaltered when submitted to the action of the oxyhydrogen blowpipe, and gives out the most intense and the most fixed light. Moistened with N_2O_4Coo'', and intensely heated, the mass becomes of a **dirty violet** colour. With borax, ZrO_2 yields a *colourless* glass which becomes slightly *opaque* when cold.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF ZIRCONIC SULPHATE, $S_2O_4Zro^{iv}$.

The **group-reagents**, SAm_2 or $AmHo$, produce a *white flocculent* precipitate of **zirconic hydrate**, $ZrHo_4$, insoluble in excess; insoluble also in $NaHo$ or KHo (DISTINCTION FROM Al AND Gl).

KHo, or $NaHo$, same precipitate, insoluble in excess, not dissolved by a boiling solution of $AmCl$ (DISTINCTION FROM Gl).

$COAmo_2$ produces a *white flocculent* precipitate of a **basic carbonate**, readily soluble in excess, reprecipitated on boiling (DISTINCTION FROM Al).

$COKo_2$ and $CONao_2$, same precipitate, redissolves in a large excess of $COKo_2$, especially of $COHoKo$ (DISTINCTION FROM Al).

$COBao''$ gives no precipitate in the cold, and precipitates glucinum salts imperfectly, even on boiling.

Oxalic acid gives a *bulky* precipitate of **zirconic oxalate** (DISTINCTION FROM Al AND Gl), insoluble in excess, difficultly soluble in HCl, soluble in excess of ammonic oxalate (DISTINCTION FROM Th).

HF produces no precipitate (DISTINCTION FROM Th AND Y).

$SSONao_2$ precipitates **zirconic hyposulphite** $(SSO)_2Zro^{iv}$ (DISTINCTION FROM Y, Er, AND Di). The separation takes place on boiling, even in the presence of 100 parts of water to one of ZrO_2 (DISTINCTION FROM Ce AND La).

Zirconic sulphate, $S_2O_4Zro^{iv}$, forms with potassic sulphate an insoluble **double sulphate** of Zr and K, insoluble in excess of SO_2Ko_2 (DISTINCTION FROM Al AND Gl). When precipitated cold, it dissolves readily in a large proportion of HCl, but is almost insoluble in water, and HCl, when the SO_2Ko_2 is added to a hot solution (DISTINCTION FROM Th AND Ce).

Turmeric paper, when dipped into a hydrochloric acid solution of a zirconium salt, acquires a *brownish-red* colour after drying in the water-bath (DISTINCTION FROM Th). But titanic acid—the only other metal which affects turmeric paper under the same circumstances—colours the paper *brown*, and its presence may therefore prevent the zirconium from being recognized. If the TiO_2 be, however, first reduced, by means of zinc and HCl, to the state of sesquichloride—the reduction being marked in the solution by a change of colour to pale violet or blue—it no longer colours turmeric paper, and any change in the colour of the latter is then due to zirconium alone. The reaction requires great care, however, as, on exposure of the paper to air, the Ti'''_2O_3, passing again to the state of $Ti^{iv}O_2$, would in its turn colour the turmeric paper, and thus render the observation doubtful.

Certain chemical discrepancies in the behaviour of the zirconium compounds, but more especially the fact that the specific gravity of zircons from various localities differs greatly, have led chemists to suspect that ZrO_2 really consists of a mixture of two or more closely allied oxides, like the metals of the yttrium and cerium group. No method has, however, as yet been devised for isolating any other oxide.

3. **THORIUM,** Th^{iv}. Atomic weight 234.—Found in a few rare minerals only, viz., in *thorite* (*orangite*), consisting principally of a hydrated silicate $(3SiTho^{iv}.4OH_2)$, in *monacite* and *pyrochlor*.

Thorite is decomposed by moderately concentrated SO_2Ho_2, and also by concentrated HCl. The oxide or anhydride, ThO_2, is white when cold, yellow when hot. The moist hydrate dissolves readily in acids; the dried hydrate only with difficulty. Thorium salts containing colourless acids are white.

REACTIONS IN THE DRY WAY.

ThO_2, when heated before the blowpipe, remains infusible; it imparts no tinge to the flame, and gives a *colourless* borax bead. It yields no characteristic reaction with N_2O_4Coo''.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF THORIC SULPHATE, $S_2O_4Tho^{iv}$.

SAm_2, or AmHo (**group-reagents**), precipitates the *white gelatinous* **hydrate,** $ThOHo_2$, insoluble in excess.

KHo, or NaHo, same precipitate, insoluble in excess (DISTINCTION FROM Al AND Gl).

$COAmo_2$, $COKo_2$, or $CONao_2$, precipitates *white* **basic thoric carbonate,** readily soluble in an excess of the precipitants, difficultly soluble in dilute solutions (DISTINCTION FROM Al). From a solution in $COAmo_2$ thoric carbonate is reprecipitated, even at 50° C.

COBao″ precipitates thorium salts completely in the cold.

Oxalic acid produces a *white* precipitate (DISTINCTION FROM Al AND Gl), not soluble in excess nor in dilute mineral acids; soluble in ammonic acetate, containing free acetic acid (DISTINCTION FROM Y AND Ce).

HF precipitates *gelatinous* **thoric tetrafluoride,** ThF_4, which becomes *pulverulent* after some time; the precipitate is insoluble in water, and in HF (DISTINCTION FROM Al, Gl, Zr, AND TiO_2).

$SSONao_2$ precipitates **thoric hyposulphite,** $(SSO)_2Tho^{iv}$, mixed with sulphur, from neutral or acid solutions. The precipitation is not complete (DISTINCTION FROM Y, Er, AND Di).

A boiling concentrated solution of SO_2Ko_2 precipitates slowly, but completely, the whole of the thorium sulphate as *white crystalline* insoluble **potassio-thoric sulphate** $(SO_2)_4Ko_4Tho^{iv} + 2OH_2$ (DISTINCTION FROM Al AND Gl), soluble with difficulty in cold, and also in hot water, readily on the addition of some HCl.

4. **YTTRIUM,** Y″. Atomic weight, 61·7; and 5, **ERBIUM,** Er″. Atomic weight, 112·6.—These very rare elements are only found in a few minerals, in *ytterbyte*, or *gadolinite*, *orthite*, *yttrotantalite*, etc. The metals have never been obtained pure. Yttrium and erbium always occur together in nature, and closely resemble the metals of the cerite group. They differ from most other earths in being completely soluble in acids, even after ignition, and from the cerite oxides, by not forming an insoluble double sulphate with potassic sulphate. In other respects the two exhibit almost the same behaviour with reagents, and can only be approximately separated from each other. The colour of the yttrium salts is white. Erbium salts have a more or less bright rose tint, crystallise readily, and possess a sweet astringent taste. Anhydrous YCl_2, is not volatile (DISTINCTION FROM Al, Gl, AND Zr.)

REACTIONS IN THE DRY WAY.

No peculiar reaction with borax, no colour to the flame, and a **greyish-blue** coloured mass with N_2O_4Coo''.

REACTIONS IN THE WET WAY.

USE SOLUTIONS OF THE NITRATES, N_2O_4Yo'' and N_2O_4Ero'', and test them side by side.

SAm_2, or $AmHo$ (**group-reagents**) precipitates the **hydrates**, insoluble in excess. Large excess of SAm_2 somewhat prevents the precipitation of yttric hydrate.

KHo, or $NaHo$, precipitates *white* **hydrates**, YHo_2, or $ErHo_2$, insoluble in excess (DISTINCTION FROM Al AND Gl). The precipitation of yttrium by alkaline hydrates is not prevented by the presence of $\overline{T}Ho_2$ (DISTINCTION FROM Al, Gl, Th, AND Zr), yttrium being slowly but completely precipitated as **tartrate**, $\overline{T}Yo''$.

$COKo_2$, and $CONao_2$ precipitate *white* **carbonates**, difficultly soluble in excess, more readily soluble in $COHoKo$, and in $COAmo_2$ (but not so readily as $COGlo''$). On boiling the whole of the yttria is deposited (DISTINCTION OF Y FROM Al, Gl, Th, Ce, AND Di). $AmCl$ decomposes $COYo''$, with evolution of NH_3 and CO_2, and formation of YCl_2. Saturated solutions of $COYo''$, in $COAmo_2$, have a tendency to deposit the double carbonate, $\begin{matrix}COAmo\\COAmo\end{matrix}Yo''$.

$COBao''$ produces with erbium salts no precipitate, either in the cold, or on heating; and yttrium salts are but imperfectly precipitated on heating. (DISTINCTION OF Er AND Y FROM Al, Gl, Th, Ce, La, Di).

Oxalic Acid produces a precipitate of *white* **yttric oxalate**, $\left\{\begin{matrix}CO\\CO\end{matrix}\right.Yo'',OH_2$. (DISTINCTION OF Y FROM Al AND Gl), insoluble in excess, difficultly soluble in dilute HCl, and partially dissolved by boiling with ammonic oxalate. Erbium salts are likewise precipitated as oxalate, $\left\{\begin{matrix}CO\\CO\end{matrix}\right.Ero'',OH_2$, in the form of a light *rose-coloured*, heavy sandy powder.

HF precipitates *white amorphous* **hydrated yttric fluoride**, insoluble in water and HF; soluble, before ignition, in mineral acids; decomposed only by strong SO_2Ho_2. (DISTINCTION OF Y FROM Al, Gl, Zr, AND Ti.)

A cold saturated solution of SO_2Yo'' becomes turbid between 30°—40° C., and on boiling, is precipitated almost entirely.

SO_2Ero'' forms with SO_2Ko_2, **potassio-erbic sulphate,** $S_2O_4Ko_2Ero''$, difficultly soluble in cold water, when hydrated, but readily soluble in the anhydrous condition, and on warming.

Potassic yttric sulphate, $S_2O_4Ko_2Yo''$, dissolves readily in water, and in a solution of SO_2Ko_2 (DISTINCTION OF Y AND Er FROM Th, Zr, and THE METALS OF THE CERITE GROUP).

When erbium nitrate is heated on a platinum wire in a gas flame, it imparts an intense *greenish* colour to the flame, which, when seen through the spectroscope shows bright lines in the yellow and green, also in the orange and in the blue in an otherwise continuous spectrum. These bright lines coincide with certain black, so-called absorption-bands, which erbium gives when white light is passed through a concentrated solution of its salts. These absorption-bands are characteristic for erbium, as yttrium solutions show none under like circumstances.

SEPARATION OF Y FROM Er.—The* different solubility of the nitrates of erbium and yttrium in water has been made available for the separation of these two closely allied metals. On heating a mixture of their nitrates to incipient decomposition, and dissolving the residue in boiling water, the solution deposits on cooling rose-red crystals of basic erbic nitrate, $N_2O_3(ErO_2)''Ero''$, whilst the mother-liquor contains chiefly yttric nitrate. By repeating this same process of separation several times over, the earths may be obtained pure by finally igniting the nitrates.

6. **CERIUM,** Ce'' and ^{iv}. Atomic weight, 92. 7. **LANTHANUM,** La''. Atomic weight, 92·8. 8. **DIDYMIUM,** Di''. Atomic weight, 96. These three

rare metals constitute, like yttrium and erbium, a group which may conveniently be studied together. The most abundant of the few cerium minerals is *cerite*, a hydrated SILICATE of the three metals, Ce, La, and Di, as well as of iron and calcium, $\mathbf{Si}[Ceo''Lao''Dio''Feo''Cao'']_2$. The finely-powdered mineral is readily and completely decomposed by boiling with concentrated HCl, or aqua regia ; or by fusion with fusion-mixture ; or lastly, by boiling with concentrated $\mathbf{S}O_2Ho_2$.

CERIUM —This metal exists both in the dyad, pseudo-triad, and tetrad condition. Thus it forms the several oxides :—

$Ce''O$	$'Ce'''_2O_3$	$Ce^{iv}O_2$ and	$Ce_3O_4 = CeO,Ce_2O_3$.
Cerous oxide.	Ceric oxide (sesquioxide.)	Ceric dioxide.	Ceroso-ceric oxide, or triceric tetroxide.

Cerous and ceric oxide are both capable of combining with acids to form two series of salts, of which the cerous are the more stable and most important. They are colourless, or slightly amethyst-red and acid to litmus. Cerous chloride is not volatile (DISTINCTION FROM Al, Gl, AND Zr). Cerous sulphate is not entirely soluble in boiling water.

REACTIONS IN THE DRY WAY.

All cerium compounds give with borax, or microcosmic salt, in the outer flame, a clear bead which is *dark red* while hot (DISTINCTION FROM THE PRECEDING EARTHS), fainter or nearly *colourless* on cooling. In the inner flame, a *colourless* bead, or if ceric oxide is present, a *yellow opaque* bead is obtained. Lanthanum compounds give colourless beads, and didymium compounds give with borax colourless, or, if in large quantity, pale *rose-coloured* beads, in both flames, and with microcosmic salt, in the reducing flame, an *amethyst-red* bead, inclining to *violet*.

REACTIONS IN THE WET WAY.

A. **CEROUS COMPOUNDS.**—We employ A SOLUTION of CEROUS CHLORIDE, $Ce''Cl_2$.

$\mathbf{S}Am_2$ (**group-reagent**) throws down the *white* **cerous hydrate,** $CeHo_2$, insoluble in excess.

AmHo precipitates a **basic salt,** insoluble in excess ; the presence of $\overline{T}Ho_2$ prevents the precipitation by AmHo (DISTINCTION FROM Y), but not by KHo.

KHo, or NaHo, precipitates *white* **cerous hydrate,** insoluble in excess, which turns yellow on exposure to the air, or when acted upon by oxidising agents, such as chlorine water, sodic hypochlorite, etc., being converted into the *yellow* hydrated **ceroso-ceric oxide,** $Ce_3O_4,3OH_2$ (DISTINCTION FROM Al AND Gl).

$\mathbf{C}OKo_2$, $\mathbf{C}ONao_2$, or $\mathbf{C}OAmo_2$, produces a *white* precipitate of **cerous carbonate,** $\mathbf{C}OCeo''$, sparingly soluble in excess of the fixed carbonates, somewhat more soluble in $\mathbf{C}OAmo_2$; insoluble in water and $\mathbf{C}O_2$; decomposed by dilute acids.

$\mathbf{C}OBao''$ precipitates cerium salts slowly, but completely on standing.

Oxalic Acid, or **Ammonic oxalate,** precipitates cerium compounds completely, even from moderately acid solutions, as a *curdy white* precipitate (turning slowly crystalline) of **cerous oxalate,** $\left\{\begin{matrix}\mathbf{C}O\\\mathbf{C}O\end{matrix}\right.Ceo''$, insoluble in excess of the precipitants (DISTINCTION FROM Zr), but soluble in a large excess of HCl. On ignition cerous oxalate leaves yellowish-white ceroso-ceric oxide, Ce_3O_4 (DISTINCTION FROM Al AND Gl, which form soluble oxalates).

A saturated solution of potassic sulphate produces a *white crystalline* precipitate of **potassio-cerous-sulphate,** $\mathbf{S}_2O_4Ko_2Ceo''$, even from somewhat acid solutions (DISTINCTION FROM Al AND Gl); difficultly soluble in cold water, readily soluble on heating; quite insoluble in a saturated solution of SO_2Ko_2 (DISTINCTION FROM Y AND Er); soluble in much dilute HCl. With dilute solutions the precipitate takes some time to form.

This characteristic precipitate, as well as the easily distinguishable oxalate, and the yellow precipitate of ceroso-ceric oxide—free from La and Di, precipitable in the filtrate as oxalates—which oxidizing agents produce, serve to distinguish cerium from all other metals.

SEPARATION OF Ce FROM La AND Di.—A convenient method of oxidizing and separating cerous salts consists, according to *Gibbs*, in treating with PbO_2 and dilute NO_2Ho (analogous to the oxidation of manganous to a higher oxide), when the solution turns yellow, even if only small quantities of cerium be present. By evaporating the yellowish solution to dryness and heating sufficiently to drive off part of the NO_2Ho, so as to form a basic ceric nitrate, insoluble in water or dilute NO_2Ho, lanthanum and didymium can be dissolved out as nitrates. After removing the plumbic nitrate from the solution by SH_2, the La and Di are precipitated as oxalates. The residuary basic ceric nitrate is dissolved in fuming NO_2Ho, any lead removed by SH_2, and the cerium precipitated as oxalate.

B. **CERIC COMPOUNDS**,—Salts of $'Ce'''_2O_3$, such as the sulphate, oxalate, etc., are yellow, and are either difficultly soluble, or insoluble, in water. Dyad cerium appears, in fact, to give rise to more stable compounds: thus Ce_2O_3, when heated with HCl does not form Ce_2Cl_6, but yields $2CeCl_2 + Cl_2$.

Oxidizing agents, such as Cl, passed into a solution of KHo, containing $CeHo_2$ in suspension, sodic hypochlorite, PbO_2 and NO_2Ho, HgO and potassic permanganate, convert cerous into ceric compounds, and furnish methods for the separation of Ce from La and Di. Reducing agents produce the reverse chemical action. Cerium resembles in this respect iron rather than aluminium.

LANTHANUM.—This metal forms only proto-salts, which are colourless, when free from didymium salts, and possess a sweet astringent taste. Lanthanic oxide is white, and is not altered, even by strong ignition (DISTINCTION FROM Ce), being still readily soluble in acids. Both the oxide and the hydrate turn red litmus paper blue. It decomposes ammonium salts, in solution, on boiling, with evolution of NH_3. Lanthanum resembles in this respect magnesium. A solution, saturated in the cold, of lanthanic sulphate deposits a portion of the salt already at 30° C. (DISTINCTION FROM Ce″). In its reactions lanthanum closely resembles cerium.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF LANTHANIC CHLORIDE, $La''Cl_2$.

SAm_2, or AmHo, precipitates basic salts which pass milky through the filter, on washing.

KHo, or NaHo, precipitates **lanthanic hydrate**, $LaHo_2$, insoluble in excess, unalterable in the air, or in the presence of oxidizing agents (DISTINCTION FROM Ce).

$COAmo_2$ gives a precipitate which is insoluble in an excess of the precipitant (DISTINCTION FROM Ce).

$COKo_2$, or $CONao_2$, $COBao''$, **oxalic acid**, or **potassic sulphate**, give the same precipitates as with cerium salts.

When the slimy precipitate which a cold dilute solution of lanthanic acetate yields, on supersaturation with AmHo, is washed repeatedly with cold water, and a few small crystals of iodine added to it, a *blue* coloration is produced which gradually pervades the entire mixture (*characteristic for La compounds only*).

DIDYMIUM.—This metal forms likewise only proto-salts, coloured a pure pink, like the sulphate, or rose-red; sometimes a faint violet, like the nitrate. The oxide is pure white and remains soluble in acids when strongly ignited. (The existence of a peroxide $Di^{iv}O_2$ is doubtful.) In contact with water it is slowly converted into the hydrate, without acquiring an alkaline reaction. It rapidly attracts CO_2, and is readily dissolved by the weakest acids. It expels ammonia from ammonium salts when boiled with them. The chloride, $DiCl_2$, is not volatile. The nitrate, on heating, is converted into a basic salt, $N_2O(DiO_2)''_3Dio'' + 5Aq$. (DISTINCTION FROM La), which is grey when hot and also when cold (DISTINCTION FROM Er). A saturated solution of didymic sulphate begins to deposit red crystals of the salt at 53° C. until at 100° C., one part of the salt only is held in solution by 50 parts of water (METHOD OF SEPARATION OF La FROM Di). Didymium salts resemble in their chemical deportment lanthanum and cerium salts.

REACTIONS IN THE WET WAY.

We may employ A SOLUTION OF THE CHLORIDE, $Di''Cl_2$, or Sulphate, SO_2Dio''.

SAm_2, or AmHo (**group-reagents**), precipitates **basic salt**, insoluble in AmHo, but slightly soluble in AmCl, with displacement of NH_3.

KHo, or NaHo, precipitates *gelatinous* **didymic hydrate**, $DiHo_2$, resembling Al_2Ho_6, but of a pale-rose colour. It is insoluble in excess, and does not alter in the air.

$COKo_2$, $CONao_2$, or $COAmo_2$, produces a copious precipitate of **didymic carbonate**, $CODio''$, insoluble in excess of the precipitants (DISTINCTION FROM Ce), but slightly soluble in a concentrated solution of AmCl.

$COBao''$ precipitates didymium compounds slowly (more slowly than Ce or La), and never completely.

Oxalic acid precipitates didymium salts, $\left(\left\{\begin{array}{l}CO\\CO\end{array}\right.Dio'' + 4Aq\right)$, almost completely, **ammonic oxalate** completely. The precipitate is difficultly soluble in cold HCl, but dissolves on heating.

A concentrated solution of SO_2Ko_2, or better still, SO_2Nao_2, precipitates didymium solutions more slowly and less completely than cerous solutions, as a *rose-white* **potassio-didymic sulphate**, $S_2O_4Ko_2Dio'' + Aq$, slightly soluble in water, less soluble in an excess of the reagent, difficultly soluble in hot HCl.

When a ray of white light is sent through a didymium solution, and examined by the spectroscope, dark bands are seen in the continuous spectrum. Dilute solutions show these absorption bands in the yellow and green, concentrated solutions exhibit, in addition, several other well defined narrower bands in various other parts of the spectrum.

Remark.—In order to master still more completely the reactions for the 8 earthy metals already treated of, the student should tabulate them according to the scheme given on page 52, when the slight differences which exist between many of their reactions, and which often furnish the only means for their separation, are brought out still more prominently.

9. **TITANIUM,** Ti'' and ^{iv}. Atomic weight 50.—This, as well as the two next following metals (usually treated of in Group III, because they are precipitated by the group reagents, AmCl, AmHo, and SAm_2), differ entirely from the previously treated metals. Their anhydrides, $Ti^{iv}O_2$, $Ta^{v}_2O_5$, and $Nb^{v}_2O_5$, are essentially acids, analogous to SiO_2, SnO_2, Sb_2O_5, etc., and are found in nature either in the uncombined state (TiO_2), or combined with various metallic bases, as TITANATES, TANTALATES, and NIOBATES.

Titanium is found as ANHYDRIDE (almost pure) in the minerals *Rutile*, *Anatase*, and *Brookite;* combined with bases, chiefly lime, in *Titanite*, $TiOCao''$, in titaniferous iron, $n(Fe_2O_3)$, $m(TiORo'')$, and is found in small quantities in many iron ores, in fire-clays, and generally in *Silicates*. (Hence its occurrence in blast-furnace slags, as *Nitride*, **$TiCy_2,3Ti_3N_2$**, in bright copper-coloured cubes.)

Titanium forms several oxides, of which two are known with certainty, and one whose existence is probable, viz. :—

$Ti''O$	$'Ti'''_2O_3$	$Ti^{iv}O_2$.
Titanous oxide (probable).	Titanic oxide (sesquioxide).	Titanic anhydride.

The last oxide, acting as a weak base, and forming mostly very unstable salts, and likewise as an acid, is the only one which is of sufficient importance to be studied analytically.

In order to prepare some pure titanic anhydride, finely-powdered *rutile* is fused with 3 parts of **$COKo_2$**, the fused mass powdered and treated with cold water, which removes **SiO_2** and alkaline silicates, and leaves insoluble **potassic titanate**, **$TiOKo_2$**, together with ferric oxide. This is washed by decantation or on a filter, with cold water, and dissolved in cold dilute HCl. On diluting *considerably* with water and heating to boiling, *for some time*, the whole of the titanium is precipitated as **meta-titanic hydrate** **Ti^{iv}**OHo_2 (Fe being held in solution by the acid), which differs from (ortho) titanic acid in being quite insoluble in all acids, except strong sulphuric acid, whilst titanic hydrate (obtained by precipitation with alkalies), of exactly the same composition, is readily soluble even in dilute **SO_2Ho_2**, or HCl. The precipitated meta-titanic acid is usually tinged yellow, owing to some ferric oxide which is carried down with it. It is best, therefore, to filter off, to wash with a solution of AmCl, and redissolve the precipitate in strong **SO_2Ho_2**. After dilution with water, it is reprecipitated once more by *long-continued boiling*, and is then all but free from iron. (METHOD OF SEPARATION FROM Al, Gl, Y, AND Th.) A more expeditious method for separating the iron oxide consists in precipitating the two metals from the dilute acid solution by means of ammonic sulphide, as **FeS** and **$TiOHo_2$**, and to treat the precipitate with aqueous sulphurous acid, which dissolves the **FeS**, and leaves pure ortho-titanic acid.

Another method consists in fusing the titanium compound with 6 times its weight of **SO_2HoKo**, till it yields a clear mass, soluble in a large quantity of cold water, acidulated with dilute **SO_2Ho_2**, from which meta-titanic acid is precipitated as above. **SiO_2**, if present, is not attacked by **SO_2HoKo**, and remains in the insoluble residue.

Pure **TiO_2** may also be obtained by fusion with acid potassic fluoride, and dissolving the fused mass in dilute HCl. **Potassic titanic fluoride**, $2KF,$**TiF_4**, which is difficultly soluble in water (1 part requires 96 parts at 14° C.), is collected on a filter and washed with cold water, and purified by recrystallisation from boiling water. Its aqueous solution, when precipitated with AmHo, yields **titanic hydrate**, which on ignition is converted with incandescence into pure **titanic anhydride**—*white*, when only feebly ignited, *yellowish* or *brownish*, when intensely ignited.

> **SiO_2**, or silicates, containing traces of **TiO_2**, may be decomposed with HF. **SO_2Ho_2** must likewise be added in order to prevent a portion of the titanium from being volatilized with the **SiF_4**.

REACTIONS IN THE DRY WAY.

Titanium compounds, when heated on charcoal, before the blowpipe, are not reduced to the metallic state (DISTINCTION FROM In). Heated in a borax bead (on charcoal), or better still, in a bead of microcosmic salt, pure **TiO_2**, or a titanate, containing bases which do not themselves colour the borax bead, yields in the outer flame, a *colourless* glass, but in the inner flame, a glass which is **yellow** while hot, but assumes a **violet** colour on cooling. The reduction is promoted by the addition of a little zinc or tin. If some **SO_2**Feo'' be added, the bead obtained in the inner flame becomes **blood-red**.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF TITANIC ACID, in HCl.

SAm_2, AmHo, KHo, or NaHo, alkaline carbonates, as well as $COBao''$, produce a *bulky white* precipitate of **(ortho-) titanic hydrate**, $Ti^{iv}OHo_2$, which is insoluble in an excess of the precipitants. When thrown down in the cold, and washed with cold water, it is readily soluble in dilute HCl, or in dilute SO_2Ho_2. Washing with hot water converts it into *insoluble* **meta-titanic hydrate**. The presence of $\overline{T}Ho_2$ prevents the precipitation. (Iron, as well as Ni, Co, Zn, and U, which are precipitated by SAm_2 in the presence of $\overline{T}Ho_2$ and AmHo (the metal Mn is *not*), may thus be separated from TiO_2.)

K_4FeCy_6 produces a *dark-brown* precipitate.

Infusion of galls, *brownish* precipitate, which speedily turns *orange-red*.

$POHoNao_2$ throws down the titanic acid almost completely from an acid solution as a *white gelatinous phosphate*, which when washed and dried leaves a **basic salt**, $2TiO_2,P_2O_5$, or $P_2O(TiO_4)^{iv}Tio^{iv}$.

Metallic tin, or zinc, immersed in a HCl solution of TiO_2, evolves hydrogen and reduces the $Ti^{iv}O_2$ to $'Ti'''_2O_3$, which gives rise to a *pale violet* or *blue* coloration and finally throws down a *dark violet* precipitate, which is rapidly reoxidised to white TiO_2, with decomposition of the water, or when exposed to the air. This reaction frequently reveals the presence of TiO_2, in the analysis of iron ores, during the process of reduction with zinc, previous to the estimation of iron by potassic permanganate.

10. **TANTALUM**, Ta^{v}. Atomic weight, 182. 11. **NIOBIUM**, Nb^{v}. Atomic weight, 94.—This group of metals occurs only in a few minerals, found, as yet, in a few localities, and, then only, in small quantities. The difficulty of detecting mere traces of them may account for their having been overlooked in others in which they have since been found, viz., in *tinstone* and *wolfram*.

In some of the minerals, either tantalum or niobium prevails, such as in *tantalite* and in *niobite* (*columbite*). They are META- compounds and may be expressed by the general formula:—$m(TaO_2)_2Feo'' + n(NbO_2)_2Feo''$. In *yttrotantalite*—the ORTHO-compound—of the formula:—$Ta_2O_2(Nb_2O_2)Ro''_3$, R'' stands for $Y''[Er'', Ce'', U'', Fe'', Ca'']$ and in *euxonite*, *woehlerite*, and *pyrochlor*, the metal niobium occurs as a PYRO-niobate, combined with fluorides, viz.,

$$(3Nb_2O_3Ro''_2), 5(NaK)F.$$

Tantalum and niobium exist chiefly in the pentad condition, as is evidenced by the composition of their oxides (anhydrides), chlorides, fluorides, etc., etc., viz.:—

Tantalic anhydride,	$Ta^{v}_2O_5$.	Chloride, $Ta^{v}Cl_5$.	Fluoride, $Ta^{v}F_5$.
Niobic „	$Nb^{v}_2O_5$.	„ $Nb^{v}Cl_5$.	„ $Nb^{v}F_5$.

A lower oxide, $'Ta^{iv}_2O_4$, and sulphide, $'Ta^{iv}_2S_4$, are said to exist. In tantalates, and niobates, the acids closely resemble arsenic, or phosphoric acid; they can exist as meta- $Ta^{v}(Nb^{v})O_2Ho$, pyro- $Ta^{v}_2(Nb^{v}_2)O_3Ho_4$, or ortho- $Ta^{v}(Nb^{v})OHo_3$ tantalic (niobic) acid.

TANTALIC and **NIOBIC ANHYDRIDES** are prepared from tantalites, or niobites, by fusing the finely powdered mineral with 3 parts of SO_2HoKo. The fused mass is extracted with water, whereby the bases are principally removed as sulphates. The residuary Ta_2O_5, and Nb_2O_5, are washed and fused once more with hydric potassic sulphate, etc. The residue after having been well washed is dissolved in HF, and a boiling solution of HF,KF gradually added to it. The liquid, on cooling, or on concentration, yields difficultly soluble **potassic fluo-tantalate,** $2KF,TaF_5$ (soluble in about 150—200 parts of water only), whilst the mother-liquors contain **potassic fluo-oxyniobate,** $2KF, NbOF_3, OH_2$ which is soluble in 12·4 to 13 parts of water (*Distinction also from titanium, which forms* KF, TiF_4, *soluble in* 96 *parts of water*). These two salts may be purified by recrystallisation; and on decomposing them, by heating with SO_2Ho_2, tantalic and niobic sulphates, and potassic sulphate, are left; this latter can be boiled out with water. When SO_2Ho_2 is expelled from the insoluble tantalic, or niobic sulphate, by strong ignition, or by heating in an atmosphere of ammonic carbonate, Ta_2O_5, or Nb_2O_5, is left.

TANTALUM.—The anhydride is a white powder. When strongly ignited it turns a pale yellow, without emitting any light, and becomes insoluble in HCl, or strong SO_2Ho_2. (DISTINCTION FROM TiO_2.)

Fused with KHo, it is rendered soluble in water; fused with NaHo, it forms chiefly **sodic meta-tantalate,** TaO_2Nao, insoluble in excess of NaHo, but soluble in water. When a solution of soda is added to this solution, sodic tantalate is precipitated. Hydrated tantalic acid dissolves in HF, from a concentrated solution of which KF precipitates the fine, *needle shaped*, **potassic fluo-tantalate**. By prolonged boiling with water, this soluble salt changes to an insoluble compound, $Ta_2O_5,2KF,TaF_5$, the formation of which affords the means of detecting the smallest quantity of fluo-tantalate in mother-liquors, containing potassic fluo-oxyniobate.

REACTIONS IN THE DRY WAY.

Microcosmic salt dissolves Ta_2O_5 to a colourless bead in both flames, and does not acquire a blood-red tint by the addition of ferrous sulphate (DISTINCTION FROM TiO_2).

REACTIONS IN THE WET WAY.

USE A SOLUTION OF TaO_2Ko in water.

The tantalates of the alkali metals are soluble in water, all others (formed by double decomposition) are insoluble in water and decomposed by acids.

HCl precipitates Ta_2O_5, at first, then redissolves it in excess.

CO_2 passed through a solution of an alkaline tantalate, precipitates acid, or **anhydro-tantalate**.

AmHo, or SAm_2, precipitates from a HCl solution **tantalic hydrate,** or an acid ammonic tantalate; $\overline{T}Ho_2$ prevents the precipitation.

AmCl, or SO_2Amo_2, precipitates **tantalic hydrate,** TaO_2Ho.

K_4FeCy_6 gives from acidified solutions, a *yellowish-white* precipitate which turns *brown* by the addition of a few drops of AmHo, and is soluble in larger quantities.

$K_6Fe_2Cy_{12}$, a *yellow* precipitate.

Infusion of galls, added to an acidified (SO_2Ho_2 or HCl) solution of an alkaline tantalate, forms a *light-yellow* precipitate, soluble in alkalies.

Metallic zinc and HCl do not reduce Ta_2O_5, and no blue coloration (or only a very faint one) is observed (DISTINCTION FROM Nb_2O_5).

NIOBIUM.—Niobic anhydride, Nb_2O_5, is white, but turns transiently yellow when ignited. By strong ignition in hydrogen, it is converted into $Nb^{iv}_2O_4$. Like tantalic anhydride, it combines both with bases and acids. Concentrated sulphuric acid dissolves niobic anhydride, unless it has been too strongly ignited, and the solution remains clear, on the addition of much water (DISTINCTION FROM Ta_2O_5).

On fusing with caustic potash, a clear mass consisting chiefly of potassic metaniobate, NbO_2Ko, is obtained, which is readily soluble in water, but is precipitated as sodic salt, on the addition of NaHo. Sodic meta-niobate, obtained by fusion with caustic soda, behaves like the corresponding meta-tantalate.

REACTIONS IN THE DRY WAY.

Microcosmic salt dissolves $\mathbf{Nb}_2O_5$ readily; in the outer flame, a bead, colourless whilst hot, is obtained; in the inner flame the bead acquires a **violet, blue,** or **brown** colour, according to the quantity of the acid present, and a **red** colour, when a little ferrous sulphate is dissolved in it.

REACTIONS IN THE WET WAY.

USE AN AQUEOUS SOLUTION OF POTASSIC NIOBATE.

The niobates of the alkalies are soluble in water, all others are insoluble, and are decomposed by acids.

Mineral acids, especially **sulphuric acid,** even at the ordinary temperature, precipitate **niobic hydrate,** nearly insoluble in the acid. (*The precipitation of tantalic hydrate requires the aid of heat.*)

Oxalic acid does not affect alkaline niobates.

SAm_2, or AmHo, precipitates from acidified solutions of $\mathbf{Nb}_2O_5$ the **hydrate,** containing ammonia, soluble in hydrofluoric acid.

AmCl precipitates the acid, but only slowly and incompletely, more especially if in the presence of alkaline carbonates.

K_4FeCy_6 gives, with a solution of an alkaline niobate which has been acidulated with sulphuric or hydrochloric acid, a *red* precipitate.

$K_6Fe_2Cy_{12}$, a *bright yellow* precipitate.

Infusion of Galls, an *orange-red* precipitate.

A piece of zinc immersed in an acidulated solution, forms a *beautiful blue* precipitate, which after a time changes to *brown*. (*Tantalates yield none or only a faint blue colour*).

(B.) *Rare Metals, precipitated by the Group-reagents, AmCl, AmHo and* $\mathbf{S}Am_2$, *in the form of Sulphides.*

1. **URANIUM,** U'' and pseudo-triad. Atomic weight, 120 [240 (?)].—Uranium is not a very abundant metal; it is found principally in *pitch-blende,* which contains from 40 to 90 per cent. of uranoso-uranic OXIDE, $\mathbf{U}_3O_4$; in *uranium-ochre,* or SULPHATE; and in *uranite* or *uranium mica,* which is a calcic (cupric) uranic PHOSPHATE. In small quantities it exists in several rare minerals, such as euxenite, yttrotantalite, &c.

Uranium salts are almost always obtained from *pitch-blende.* The $\mathbf{U}_3O_4$ therein, is associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely powdered, freed by elutriation from the lighter earthy impurities, roasted for a short time to remove part of the sulphur and arsenic, then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water, and the solution filtered from a brick-red residue of ferric oxide, ferric arsenate and plumbic sulphate. On evaporation, the aqueous solution yields crystals of the nitrate, which by dissolving in ether and setting aside for spontaneous evaporation, are obtained pure. When recrystallised once more from boiling water, they consist of pure **uranylic nitrate,** $\mathbf{N}_2O_4(U_2O_2)o'',6\mathbf{O}H_2$; in which $('\mathbf{U}''_2O_2)''$ or **uranyl** acts as a compound dyad radical, analogous to the monad compound radicals antimonyl, $(\mathbf{Sb}'''O)'$, bismuthyl $(\mathbf{Bi}'''O)'$, &c.

Uranium exists as a dyad and pseudo-triad metal. It forms with oxygen two salifiable oxides, together with two intermediate oxides, thus—

Uranous oxide.	Uranic oxide or uranylic oxide.	Intermediate oxides	
$\mathbf{U}''O$	$'\mathbf{U}'''_2O_3$, or $(\mathbf{U}_2O_2)''O$	$\mathbf{U}_3O_4$, or $'\mathbf{U}'''_2O_3,\mathbf{U}''O$ (dark green.)	$\mathbf{U}_4O_5$, or $'\mathbf{U}'''_2O_3,2\mathbf{U}''O$ (black.)

Uranous chloride.	Uranylic chloride.	Pentachloride.
$\mathbf{U}Cl_2$	$(\mathbf{U}_2O_2)''Cl_2$	$\mathbf{U}_2Cl_5$

Uranous sulphate.	Uranylic sulphate.
$\mathbf{S}O_2O_2U$, or $\mathbf{S}O_2Uo''$	$\mathbf{S}O_2O_2(U_2O_2)''$, or $\mathbf{S}O_2(U_2O_2)o''$

Uranic oxide and its hydrate combine both with acids to form uranylic salts, and with the oxides of the more electro-positive metals to form acid uranates, of the general formula, $\left\{\begin{array}{l}(\mathbf{U}_2O_2)''Ro\\ O\\ (\mathbf{U}_2O_2)''Ro\end{array}\right. + x\mathbf{O}H_2$, analogous to dichromates, disulphates, etc. These are yellow, insoluble in water, but are decomposed by acids. Disodic diuranate (*uranium yellow*) is much used as a pigment in glass and porcelain manufactures.

REACTIONS IN THE DRY WAY.

Borax and microcosmic salt give with uranium compounds, in the inner flame of the blowpipe **green** beads, in the outer flame **yellow** beads, which acquire a **yellowish-green** tint on cooling. The oxides of uranium are not reduced by fusion with $\mathbf{C}ONao_2$ on charcoal.

REACTIONS IN THE WET WAY.

A. **URANOUS COMPOUNDS**.—USE A SOLUTION OF URANOUS SULPHATE, $\mathbf{S}O_2Uo''$. (Prepared by dissolving uranoso-uranic oxide in hot oil of vitriol, diluting with water and evaporating *in vacuo*.)

Uranous salts constitute powerful *reducing* agents. They are green, or greenish-white, and yield green aqueous solutions.

$\mathbf{S}Am_2$ forms a *black* precipitate of **uranous sulphide,** $\mathbf{U}''S$.

AmHo, KHo, or NaHo, throws down *red-brown gelatinous* **uranous hydrate,** $\mathbf{U}''Ho_2$.

$\mathbf{C}OKo_2$, $\mathbf{C}ONao_2$, or $\mathbf{C}OAmo_2$, precipitates *green* **uranous hydrate**, soluble in excess, especially in excess of $\mathbf{C}OAmo_2$.

Uranous salts become oxidized to uranic salts by exposure to air, or by treatment with nitric acid, etc. Gold and silver salts are speedily reduced by them, and ferric salts are reduced to ferrous salts.

B. **URANIC COMPOUNDS**.—USE A SOLUTION OF URANIC NITRATE, $\mathbf{N}_2O_4(U_2O_2)o''$.

Uranic salts are yellow, they are mostly soluble in water, and are reduced to uranous salts by $\mathbf{S}H_2$ and by alcohol, or ether, in sunlight.

$\mathbf{S}Am_2$ produces in the cold a *chocolate-brown* precipitate of **uranylic sulphide,** containing also ammonic sulphide and water. It is insoluble in yellow ammonic sulphide. On warming or boiling the liquid which contains the uranylic sulphide, $(\mathbf{U}_2O_2)S$, suspended in it, the precipitate splits up into sulphur and black uranous oxide, $\mathbf{U}''O$, which is insoluble in excess of $\mathbf{S}Am_2$. Uranylic sulphide dissolves readily in neutral ammonic carbonate. [METHOD OF SEPARATION OF U FROM Zn, Mn, AND Fe.]

AmHo, KHo, or NaHo, produces a *yellow* precipitate, consisting of **acid uranate** of the alkali metal; insoluble in excess of the precipitant; not precipitated in the presence of tartaric acid.

The ammonia precipitate is soluble in a solution of ammonic carbonate, and $\mathbf{S}Am_2$ does *not* precipitate the uranium from this solution.

$\mathbf{C}OKo_2$, $\mathbf{C}ONao_2$, or $\mathbf{C}OAmo_2$, gives a *light yellow* precipitate, consisting (in the case of potassic carbonate), of **potassio-uranic carbonate ;** *readily soluble in an excess of the precipitant.* By treating the liquid with dilute sulphuric acid, as long as effervescence takes place, an acid uranate is precipitated. [METHOD OF SEPARATION OF U FROM Al AND Fe^{iv}.]

$\mathbf{C}OBao''$ completely precipitates a solution of a uranic salt, even in the cold. [*Separation of 'U''' from Ni'', Co'', Mn'', Fe'', and Zn.*]

K_4FeCy_6 produces a *reddish-brown* precipitate. (*Most delicate special reaction.*)

$K_6Fe_2Cy_{12}$ produces no change.

Metallic zinc does not precipitate metallic uranium from its solutions.

2. **THALLIUM**, Tl' and $'''$. Atomic weight, 204.—This metal was discovered by Crookes in 1861. It occurs in many kinds of copper and iron pyrites, but invariably in very minute quantities; also in many kinds of crude sulphur, in some of the deposits from the flues leading from the pyrites furnaces to the lead chambers of sulphuric acid works, and in the deposits in the chambers themselves. It has, moreover, been found in lepidolite, in preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of some plants, and in some saline waters.

The metal is most economically extracted from thalliferous flue-dust. The dust is stirred up with boiling water, the insoluble portion allowed to settle, and the clear supernatant liquid syphoned off. On the addition of concentrated hydrochloric acid, impure thallious chloride, $TlCl$, is precipitated. This impure chloride is dissolved in concentrated sulphuric acid, evaporated till the hydrochloric acid, as well as the greater portion of the sulphuric acid, has been driven off, then dissolved in boiling water, and a rapid current of sulphuretted hydrogen passed through the solution, whereby all the metals of the SH_2 group are precipitated. On now introducing plates of zinc into the dilute acid filtrate, spongy metallic thallium is precipitated, which can be readily removed from the zinc, and obtained in lumps or bars by pressure. It must be preserved under water.

The salts may be prepared by dissolving the metal in the respective acids, or by the double decomposition of soluble thallium salts.

Thallium forms two series of compounds:—thallious and thallic. In the thallious the metal exists as a monad, and in the thallic as a triad. Thus we have:—

Thallious oxide	OTl_2	Thallic oxide	$Tl_2'''O_3$
Thallious chloride ..	$TlCl$	Thallic chloride ..	$Tl'''Cl_3$, etc.,

together with several intermediate compounds.

In some of its chemical relations thallium differs from all other metals. In many respects it resembles the alkali metals, as, for instance, in forming the readily soluble and highly alkaline thallious oxide and carbonate, an insoluble double platinum salt, an alum, analogous to ordinary potash alum, and a series of thallious phosphates, analogous to the alkaline phosphates. In most other respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity.

REACTIONS IN THE DRY WAY.

Thallium compounds impart an intense **green** colour to the blowpipe flame. The spectrum of thallium shows only one **emerald-green** line, Tl*a*, and hence its name from θαλλός, green.

REACTIONS IN THE WET WAY.

A. **THALLIOUS COMPOUNDS**.—We employ A SOLUTION OF THALLIOUS SULPHATE, SO_2Tlo_2.

Thallious salts are for the most part colourless and soluble in water, such as the nitrate, sulphate, phosphate, tartrate, and acetate. Some are difficultly soluble, *e.g.*, the carbonate and chloride, and a few are almost insoluble, *e.g.*, the iodide. They react neutral to test-paper, and possess a slight metallic taste. Thallious oxide, OTl_2, is colourless and fusible; it dissolves in water, the solution is colourless, alkaline, caustic, and absorbs carbonic anhydride from the air. It also dissolves in alcohol.

Thallious salts are difficultly converted into thallic salts; powerful oxidising agents, such as nitric acid, are without effect on them. They require boiling and evaporating with aqua regia to convert them into the higher salts.

SH_2 does not precipitate strongly acidified thallious solutions unless As_2O_3 be present, when a part of the thallium is carried down with the arsenious sulphide, as a brownish-red precipitate. Neutral or very slightly acidified solutions are incompletely precipitated by SH_2. From acetic acid solutions the whole of the thallium is thrown down as *black* **thallious sulphide,** STl_2.

SAm_2 (**group-reagent**) precipitates the whole of the thallium as **thallious sulphide,** insoluble in ammonia, alkaline sulphides, or potassic cyanide. Readily soluble in dilute hydrochloric, sulphuric, or nitric acids, but difficultly soluble in acetic acid. When exposed to air, thallious sulphide is rapidly converted into thallious sulphate. On heating it fuses and volatilises.

KHo, NaHo, or AmHo, does not precipitate aqueous solutions of thallious salts.

Carbonated alkalies produce a precipitate only from concentrated solutions, $COTlo_2$ being soluble in 20 parts of water.

HCl, or a soluble chloride (bromide), throws down *white* **thallious chloride,** TlCl; the precipitate subsides readily, and is unalterable in the air. It is very slightly soluble in boiling water, and still less so in hydrochloric acid.

KI precipitates, even from the most dilute thallious solutions, *light yellow* **thallious iodide,** TlI, which is almost entirely insoluble in water, but somewhat more soluble in a solution of potassic iodide. *This constitutes the most delicate reaction for thallious salts.*

CrO_2Ko_2 precipitates *yellow* **thallious chromate,** CrO_2Tlo_2, insoluble in cold nitric or sulphuric acid.

$PtCl_4$ precipitates difficultly soluble, *pale orange coloured* **thallious platinic chloride,** $2TlCl,PtCl_4$.

Zinc precipitates metallic thallium.

B. **THALLIC COMPOUNDS.**—We employ A SOLUTION OF THALLIC CHLORIDE, $Tl'''Cl_3$.

Thallic salts are easily distinguished from thallious salts by their behaviour with caustic and carbonated alkalies, which precipitate *brown gelatinous* **thallic hydrate,** $Tl'''OHo$, insoluble in excess.

Thallic oxide is scarcely acted on by concentrated sulphuric acid in the cold; on heating, thallic sulphate, $(SO_2)_3Tlo'''_2,7OH_2$ is obtained. When a solution of thallic sulphate is boiled, oxygen is given off and a thallious salt left. When treated with HCl, thallic oxide yields the chloride $Tl'''Cl_3$, as a white crystalline mass, which on heating splits up into TlCl and Cl_2.

HCl, or a **soluble chloride (bromide),** produces no precipitate.

SH_2 reduces thallic to thallious salts, with precipitation of sulphur.

$\left\{\begin{matrix}COHo\\COHo\end{matrix}\right.$ produces a *white* pulverulent precipitate.

$POHoNao_2$ gives a *white gelatinous* precipitate.

$AsOHo_3$, or a soluble arsenate, gives a *yellow gelatinous* precipitate.

CrO_2Ko_2 does not precipitate thallic salts.

KI gives a precipitate of TlI and I_2.

3. **INDIUM,** In^{iv}, and pseudo-triad. Atomic weight, 113·4.—Has hitherto only been found as a rare and insignificant constituent of some zinc ores (*zinc-blende* from Freiberg), in the metallic zinc prepared from these ores, and in tungsten.

Indium is a white, highly lustrous metal, resembling platinum, soft and ductile, of specific gravity 7·42. It fuses easily at 176° C. It is not oxidized in the air or in water. Dilute HCl or SO_2Ho_2 dissolve it readily, hydrogen being given off. Concentrated sulphuric acid dissolves it with evolution of SO_2. This is readily soluble also in cold dilute nitric acid. The oxide, $'\mathbf{In}'''_2O_3$, is brown when hot, straw-coloured when cold, and is readily reduced when heated on charcoal, or in a current of hydrogen gas. A black dioxide, $\mathbf{In}^{iv}O_2$, exists likewise.

The principal salts of indium, viz., the sulphate, $(\mathbf{SO}_2)_3\ In_2o^{vi}$, $9\mathbf{O}H_2$. the nitrate, $\mathbf{N}_3O_6Ino'''$, and the chloride, $\mathbf{In}'''Cl_3$, are freely soluble in water. The chloride is volatile and hygroscopic.

REACTIONS IN THE DRY WAY.

Indium and its compounds impart to the flame a peculiar *bluish* tinge. When examined with the aid of a spectroscope two characteristic **blue** lines can be seen, a bright one in the blue, and a feebler one in the violet. They are however very transient. The sulphide gives more persistent lines than the chloride.

REACTIONS IN THE WET WAY.

We may employ A SOLUTION OF ANY OF THE ABOVE SALTS.

$\mathbf{S}H_2$ produces no precipitate in the presence of a strong acid. Indium is, however, precipitated like the metal zinc, from slightly acid solutions, or in the presence of acetic acid. The slimy precipitate of **indic sulphide**, $'\mathbf{In}_2'''S_3$, is of a fine *yellow* colour.

$\mathbf{S}Am_2$ produces at first a *white* precipitate from a solution, containing ammonic tartrate, said to consist of $'\mathbf{In}'''_2S_3$ and hydrogen. It turns *yellow* on the addition of acetic acid. The sulphide is insoluble in cold, but soluble in hot $\mathbf{S}Am_2$, and on cooling it separates again of a *white* colour.

KHo, NaHo, or AmHo, produces a *white bulky* precipitate of **indic hydrate**, $\mathbf{In}'''Ho_3$, resembling aluminic HYDRATE, quite insoluble in KHo or AmHo. The presence of $\overline{T}Ho_2$ prevents the precipitation.

Alkaline carbonates precipitate *white gelatinous* **carbonate.** When recently precipitated it is soluble in ammonic carbonate, but not in the fixed alkaline carbonates. On boiling, indic carbonate separates again.

$\mathbf{CO}Bao''$ precipitates indic salts in the cold, as basic salts. (DISTINCTION FROM ZN, MN, CO, NI, and FE.)

$\mathbf{PO}HoNao_2$ throws down a *bulky white* precipitate.

Alkaline oxalates produce a *crystalline* precipitate.

Zinc precipitates the metal in the form of white shining laminæ.

4. **VANADIUM,** V''' and ^{v}. Atomic weight, 51·3.—Occurs only in a few very rare minerals, principally in *vanadite*, or *plumbic vanadate and oxychloride*, $\mathbf{V}_3O_3Pbo''_4\left(\begin{smallmatrix}O\\Cl\end{smallmatrix}Pb\right)'$, analogous in composition to *pyromorphite* (comp. p. 102); also to a very small extent in many iron ores (clay and pea iron ores), and, as Roscoe recently discovered, in the copper-bearing beds at Alderley Edge, and Mottram St. Andrews, in Cheshire.

Vanadite may be made the starting point for preparing the several vanadium compounds. The mineral is dissolved in nitric acid, and the lead and arsenic precipitated by $\mathbf{S}H_2$, which at the same time reduces the vanadic pentoxide, $\mathbf{V}^{v}{}_2O_5$, to tetroxide, $\mathbf{V}^{iv}{}_2O_4$. The blue filtered solution is then evaporated to dryness and the residue digested in ammonia, when the vanadic tetroxide becomes reoxidised into pentoxide. The ammonic vanadate can be precipitated as a white powder from this solution by introducing a lump of sal-ammoniac, being scarcely soluble in a saturated solution of AmCl. By exposure to a temperature below redness, in an open crucible, ammonia is expelled and $\mathbf{V}^{v}{}_2O_5$ is left.

Vanadium forms several oxides, oxychlorides, chlorides, sulphides, which show that the metal is closely allied to the phosphorus and arsenic group. Thus we have :—

Oxides.	Oxychlorides.	Chlorides.	Sulphides.
${}'V''_2O_2$	—	VCl_2	—
V'''_2O_3 (black)	—	VCl_3	—
${}'V^{iv}_2O_4$ (blue)	—	VCl_4	${}'V^{iv}_2S_4$
$V^{v}_2O_5$	$V^{v}OCl_3$	—	$V^{v}_2S_5$

The most important of these compounds is the pentoxide, or vanadic anhydride, identical in composition with phosphoric, arsenic, antimonic, tantalic and niobic anhydrides. It combines in different proportions with bases, forming like the other anhydrides referred to, three series of salts, viz., *ortho-*, *pyro-*, and *meta-vanadates*. Fused with $CONao_2$, it yields sodic ortho-vanadate, $VONao_3$; but when boiled with a solution of an alkali, it forms the meta-vanadate, the latter class of vanadates being more stable than the ortho-salts. Alkaline vanadates are soluble in water, inversely to the quantity of free alkali, or alkaline salt present. Hence they are precipitated from their solutions by excess of alkali, or by salts (AmCl). (*Most characteristic reaction.*)

Vanadic anhydride has a reddish-yellow colour, and is difficultly soluble in water (1,000 parts), forming a light yellow solution, which reddens litmus paper. It dissolves also in the stronger acids to red or yellow solutions, which become frequently decolorized by mere boiling. It unites, however, with bases more readily than with acids.

A sulphuric acid solution of the acid when considerably diluted with water, and treated with zinc or sodium amalgam and warmed gently, turns first blue, then green, and finally from lavender to *violet*. The V_2O_5 becomes reduced to ${}'V''_2O_2$; and on the addition of AmHo, a brown precipitate of the hydrate of the dioxide (hypovanadious acid) forms, *which absorbs oxygen more rapidly than any other known reducing agent*, and bleaches organic colouring matter (indigo solution, etc.) as quickly as chlorine.

Many organic substances, such as oxalic or tartaric acid, sugar, alcohol, reduce vanadic acid, especially in the presence of strong mineral acids, to the blue ${}'V^{iv}_2O_4$. The same takes place when SO_2, or SH_2, are added to its solutions in acid.

REACTIONS IN THE DRY WAY.

Borax dissolves V_2O_5 to a clear bead, *colourless*, or, with large quantities of the anhydride, *yellow*, in the outer flame, beautiful *green* in the inner flame. With larger quantities of vanadic acid it looks brownish whilst hot, and only turns *green* on cooling.

REACTIONS IN THE WET WAY.

USE A SOLUTION OF SODIC METAVANADATE, VO_2Nao.

Orthovanadates are generally yellow or reddish-yellow, both in the liquid and solid state. By boiling in water, the orthovanadates of the alkalies are converted into colourless metavanadates. On the addition of an acid to a solution of a neutral or orthovanadate, the solution becomes yellowish-red, owing to the formation of anhydro-salts.

Ammonic, baric, and plumbic metavanadates are but sparingly soluble in water. The alkaline vanadates are more soluble in pure water, than in water containing free alkali, or a salt: hence they are precipitated in the presence of the latter. All are soluble in nitric acid, but insoluble in alcohol.

SAm_2 (**group-reagent**) produces a brown coloration in the liquid, and on acidulating with HCl, or better with SO_2Ho_2, the soluble ammonic sulpho-vanadate is decomposed, and *brown* **pentasulphide,** V_2S_5, mixed with sulphur, is precipitated; the liquid at the same time generally acquires a blue colour. It dissolves with red-brown colour in aqueous solutions of alkaline carbonates, hydrates, and sulphhydrates.

If an acidified solution of an alkaline vanadate be shaken up with ether containing peroxide of hydrogen, the aqueous fluid acquires a **red-brown** colour, like that of ferric acetate, whilst the ether remains colourless. *This reaction is extremely delicate.*

Vanadic and chromic acids are the only acids whose salts give rise to red-coloured solutions. They are, however, differently affected by reducing agents.

REACTIONS OF THE RARE METALS OF GROUP II.

Group II comprises the Rare Metals, precipitated as Sulphides by SH_2, *from a Hydrochloric Acid Solution*, viz :—

(A.) *As Sulphides, insoluble in yellow Ammonic Sulphide* :—PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM.

1. **PALLADIUM**, Pd$''$ and ^{iv}. Atomic weight, 106·5.—Occurs *native* in platinum ores, principally, however, *alloyed* with gold and silver, in a gold ore found in Brazil. The gold dust is fused together with silver, and the granular alloy heated with nitric acid, in which silver and palladium only dissolve. On the addition of sodic chloride, silver is removed as chloride, and the palladium may then be precipitated as palladious cyanide, by means of mercuric cyanide, and decomposed by ignition.

The metal greatly resembles platinum, but is somewhat darker in colour. Its specific gravity is 11·8. Of all the so-called platinum metals it fuses most readily, difficultly in an ordinary fire, but easily in the oxy-hydrogen flame. Palladium is sparingly soluble in pure nitric acid, but dissolves more readily in the red acid. It dissolves slightly in boiling concentrated sulphuric acid, but is readily attacked by fusing with hydric potassic sulphate. The true solvent for it, as for most other platinum metals, is aqua regia. Palladium forms several oxides and chlorides, in which the metal exists either as a dyad or tetrad, thus :—

Palladious oxide......	$Pd''O$	Chloride......	$Pd''Cl_2$
Palladic „	$Pd^{iv}O_2$	„	$Pd^{iv}Cl_4$.

The lower oxide is obtained on gently igniting palladious nitrate. It is black, and its hydrate dark brown. Both part with their oxygen upon intense ignition, leaving spongy palladium. The nitrate may be prepared from the metal by dissolving in nitric acid and concentration over a water-bath. It forms then a brownish-red non-crystallisable mass.

Palladious salts are mostly soluble in water; they are brown or reddish-brown; their dilute solutions are yellow.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF PALLADIOUS NITRATE, N_2O_4Pdo''.

OH_2 precipitates a *brown* **basic salt,** from solutions containing slight excess of acid only.

SH_2, or **SAm_2**, throws down from acid or neutral solutions *black* **palladious sulphide, PdS**, insoluble in **SAm_2**, but soluble in boiling hydrochloric acid, and readily soluble in aqua regia.

KHo, or NaHo, precipitates a *yellowish-brown* **basic salt,** soluble in excess.

$COKo_2$, or **$CONao_2$**, precipitates *brown* **palladious hydrate, $PdHo_2$**, soluble in excess, reprecipitated on boiling.

AmHo, or **$COAmo_2$**, produces no precipitate from the nitrate, but decolorises the dark brown solution.

HI, or **soluble iodides** give, even in very dilute solutions, a *black* precipitate of **palladious iodide, PdI_2**, somewhat soluble in excess of KI. (*Most characteristic reaction for* **Pd**. It serves for the detection of iodine in the presence of chlorine and bromine.)

$HgCy_2$ gives a *yellowish-white gelatinous* precipitate of **$PdCy_2$**, readily soluble in KCy, and in AmHo. Slightly soluble in HCl. It leaves on ignition spongy metallic palladium.

CyAms gives no precipitate, even after the addition of SO_2. (DISTINCTION FROM CU.)

$SnCl_2$ produces a *brownish-black* precipitate, soluble in HCl, to an intense green solution.

Palladious salts are reduced to the metallic state by phosphorus, **$SOHo_2$**, **N**OKo, $\left\{\begin{array}{l}H\\COHo\end{array}\right.$, metallic zinc or iron, alcohol, etc.

Palladious chloride, obtained by dissolving **PdS** in boiling HCl, is precipitated by ammonia as *flesh-coloured* **ammonio - palladious chloride,** $N_2H_6Pd''Cl_2$, soluble in AmHo to a colourless fluid, from which HCl reprecipitates it as a yellow crystalline chloride, identical in composition.

AmCl does not precipitate palladium salts.

KCl precipitates a *brownish-red octahedral* **double chloride**, 2KCl, **$PdCl_2$**, insoluble in absolute alcohol; soluble in water to a dark-red fluid.

All palladium salts are decomposed by ignition, leaving metallic palladium.

2. **RHODIUM**, Rh$''$, ^{iv}, and ^{vi}, also a pseudo-triad. Atomic weight, 104·4.—Found in small quantity in platinum ores, and frequently to a considerable extent in platinum residues.

It is a whitish-grey metal, less ductile than platinum, and scarcely softened, even in the flame of the oxy-hydrogen blowpipe. The specific gravity of unfused rhodium is 10·64, that of the pure metal, after fusion, 12·1. Rhodium is unalterable in the air at ordinary temperatures, but oxidises at a red heat. It also combines with chlorine at a red heat. *When pure it resists the action of the strongest acids, even of aqua regia;* but when alloyed with other metals, as with Pb, Bi, Cu, and Pt, it is soluble in aqua regia; when, however, alloyed with Au, or Ag, it does not dissolve. It is oxidized by fusion with solid caustic potash and nitre. Fusion with hydric potassic sulphate converts it into soluble **potassic rhodic sulphate, $S_2O_6(Rh'''K_3O_6)^{vi}$.** Mixed with sodic chloride, and ignited in a current of chlorine, a **double chloride of sodium** and **rhodium**, $3NaCl,Rh'''Cl_3,12OH_2$, is formed, which is likewise easily soluble in water.

Rhodium forms several oxides, chlorides, sulphides, etc., in which the metal exists as a dyad, tetrad (pseudo-triad), or hexad element, thus:—

	Oxides.
Rhodious oxide	$Rh''O$.
Rhodic ,, ...	$'Rh'''_2O_3$.
,, dioxide	$Rh^{iv}O_2$.
Rhodic trioxide (anhydride, acting as a weak acid)	$Rh^{vi}O_3$.

	Chlorides.		Sulphides.
Rhodious chloride......	$Rh''Cl_2$.	Rhodious sulphide....	$Rh''S$.
Rhodic chloride........	$Rh'''Cl_3$. or $'Rh'''_2Cl_6$.	Rhodic ,, ...	$'Rh_2'''S_3$.

The most important compounds are the **Rh_2Cl_6** and **Rh_2O_3**. Rhodium salts are obtained with difficulty, owing to the insolubility of the metal and its oxide in acids. Their solutions are generally rose-coloured.

REACTIONS IN THE WET WAY.

We may employ A SOLUTION OF POTASSIO-RHODIC SULPHATE, or of THE DOUBLE CHLORIDE OF SODIUM AND RHODIUM.

SH_2, or **SAm_2**, precipitates from a hot solution, *brown* **rhodic sulphide,** **Rh_2S_3**, insoluble in **SAm_2**, but soluble in boiling nitric acid.

KHo, or $NaHo$, gives with the chloride a *yellowish-brown* precipitate of **rhodic hydrate**, $\mathbf{Rh_2Ho_6}$, soluble in excess ; in other rhodic salts this precipitate appears only on boiling.

From a solution of rhodic chloride, KHo, producing at first no precipitate, gives, on the addition of alcohol, a *brown* precipitate of **rhodic hydrate.**

$AmHo$ gives also a *yellow* precipitate, only formed, however, after some time, soluble in HCl.

KI produces a slight *yellow* precipitate.

Metallic zinc precipitates black metallic rhodium.

$\mathbf{NOKo}$ (**potassic nitrite**) gives with the chloride an *orange-yellow* precipitate, which is slightly soluble in water, but readily soluble in HCl.

Rhodium is distinguished from the other platinum metals by its insolubility in aqua regia, its solubility in fusing $\mathbf{SO_2HoKo}$, and the behaviour of its chloride with potash and alcohol.

3. **OSMIUM,** Os'', ^{iv}, ^{vi}, and ^{viii}, also a pseudo-triad. Atomic weight, 199·2.—Found chiefly as a natural alloy of *osmium iridium* in platinum ores, which remains behind undissolved, when the ores are treated with aqua regia, in the form of white, metallic-looking, hard grains. This alloy is attacked by mixing it with common salt, or potassic chloride, and exposing it in a glass or porcelain tube to a current of moist chlorine gas. Osmic acid is formed, which volatilises, and can be condensed and fixed by passing the fumes into a solution of caustic potash. Iridium remains behind in the tube as a double chloride, $2KCl,IrCl_4$. This salt is obtained in *reddish-black* regular octahedra, by recrystallisation from water. The alkaline solution is evaporated with excess of sal-ammoniac, and leaves on ignition of the dry residue, and extraction with water, metallic osmium, as a black powder, or grey, and with metallic lustre. The densest metal has a specific gravity of 21·4. Intense white heat volatilises the metal, but does not melt it. In contact with air, it burns the more readily the finer the metal is divided, and is converted into **osmic anhydride,** $\mathbf{Os^{viii}O_4}$. Red fuming nitric acid, or aqua regia, dissolves osmium likewise, and oxidizes it to $\mathbf{OsO_4}$. Very intensely ignited, osmium is rendered insoluble in acids, and has to be fused with nitre, and then distilled with nitric acid, when $\mathbf{OsO_4}$ distils over.

Osmium combines with oxygen, or chlorine, etc., in several proportions, thus :—

Osmious oxide	$\mathbf{Os''O}$	Osmious chloride....	$\mathbf{Os''Cl_2}$
Osmic ,, ...	$\mathbf{'Os'''_2O_3}$	Osmic ,, (not isolated)	$\mathbf{'Os'''_2Cl_6,6KCl}$
Osmic dioxide	$\mathbf{Os^{iv}O_2}$	Osmic tetrachloride..	$\mathbf{Os^{iv}Cl_4}$
Osmious anhydride ..	$\mathbf{Os^{vi}O_3}$	——	—
Osmic anhydride	$\mathbf{Os^{viii}O_4}$	——	—

The two highest oxides combine with bases, and form **osmites** and unstable **osmates.** $\mathbf{OsO_4}$ is remarkable for its peculiar, exceedingly irritating, and offensive odour, resembling that of Cl and I. It attacks the mucous membrane and the lungs, and is excessively poisonous. It is absorbed by water, and is precipitated from its solutions by all metals, even by mercury and silver, as a black metallic powder. On heating a mixture of finely-divided osmium, or of the sulphide, with potassic chloride in a stream of chlorine gas, a double chloride, $\mathbf{Os_2}Cl_6 6KCl, 3OH_2$, is obtained, which crystallises from water in dark red-brown, regular octahedra. The salt is insoluble in alcohol.

The solution of this double chloride is more stable than that of the osmium chlorides, and may conveniently be employed for studying the reactions.

REACTIONS IN THE WET WAY.

$\mathbf{SH_2}$, or $\mathbf{SAm_2}$, gives a *brownish-black* **sulphide**, $\mathbf{Os''S}$, which only separates when a strong acid is present. The precipitate is insoluble in $\mathbf{SAm_2}$.

KHo, or $NaHo$, $AmHo$, or $COKo_2$, produces a *brownish-red* precipitate of **hydrated osmic dioxide**, $Os^{iv}Ho_4$.

On fusing the double chloride with $CONao_2$, dark grey OsO_2 is obtained.

Heated with tannic acid, or alcohol, with addition of HCl, the double chloride is reduced to the *blue* osmious chloride, $Os''Cl_2$.

A solution which contains osmic acid (an osmate) is remarkable for its great **oxidising** power. It decolorises indigo solution, separates iodine from KI, converts alcohol into aldehyde and acetic acid. **Sodic sulphite** yields a deep violet coloration, and *dark blue* **osmious sulphite**, $SOOso''$, gradually separates. Ferrous sulphate produces a *black* precipitate of OsO_2. Stannous chloride produces a *brown* precipitate, soluble in HCl, to a brown fluid. All compounds of osmium yield the metal when ignited in a current of hydrogen.

4. **RUTHENIUM**, Ru'', ^{iv}, ^{vi}, and ^{viii}, also a pseudo-triad. Atomic weight, 104·4.—Found in small quantity only, in that portion of the platinum ores which remains behind, after treating with aqua regia. It is a greyish-white metal, closely resembling iridium, and very difficultly fusible. When heated in the air it becomes covered with *bluish-black* **ruthenic oxide**, Ru_2O_3, insoluble in acids. When pure, it is insoluble in acids, being barely acted upon by aqua regia; fusion with hydric potassic sulphate even remains without action upon it.

It is attacked, either by fusion with caustic potash and nitre, or potassic chlorate, and is converted thereby into **potassic ruthenate**, $Ru^{vi}O_2Ko_2$, a dark green mass, soluble in water to an orange coloured fluid, which tinges the skin black, from separation of black ruthenic oxide. Acids (NO_2Ho) throw down the black hydrate.

Or it may be rendered soluble by ignition with potassic chloride in a current of chlorine gas, being thus converted into **potassic ruthenic chloride**, $2KCl,Ru^{iv}Cl_4$.

Ruthenium forms several oxides, chlorides, etc., thus :—

Ruthenious oxide	$Ru''O$.	Ruthenious chloride	$Ru''Cl_2$
Ruthenic „	$'Ru'''_2O_3$	Ruthenic chloride	$'Ru'''_2Cl_6$
Ruthenic dioxide	$Ru^{iv}O_2$	Ruthenic tetrachloride ..	$Ru^{iv}Cl_4$
Ruthenic trioxide .... (anhydride).	$Ru^{vi}O_3$	(known only in combination).	
Ruthenic tetroxide .... (perruthenic anhydride).	$Ru^{viii}O_4$		

REACTIONS IN THE WET WAY.

We may employ a SOLUTION of RUTHENIC CHLORIDE, $'Ru'''_2Cl_6$, prepared by dissolving in HCl the ruthenic hydrate, precipitated by nitric acid, from a solution of potassic ruthenate. It forms an orange-yellow coloured solution, which on heating is resolved into HCl and Ru_2O_3.

SH_2 produces at first no precipitate, but after some time the fluid acquires an *azu-reblue* tint, and deposits *brown* **ruthenic sulphide**, Ru_2S_3. *This reaction is very delicate and characteristic.*

SAm_2 produces a *brownish-black* precipitate, difficultly soluble in excess.

KHo precipitates *black* **ruthenic hydrate**, Ru_2Ho_6, insoluble in alkalies, but soluble in acids.

$CyKs$ produces, in the absence of other platinum metals, after some time a *red* coloration, which gradually changes to *purple-red*, and, upon heating, to a *fine violet tint* (*very characteristic*).

KCl, or $AmCl$, produces in concentrated solutions *crystalline glossy violet* precipitates of the **double chlorides**, difficultly soluble in water, insoluble in alcohol. They are decomposed on boiling with water, with separation of black ruthenious oxychloride.

$NOKo$ forms a double salt, $3NOKo, N_3O_3Ruo'''$, readily soluble in an excess of the alkaline nitrite. On the addition of a few drops of colourless SAm_2, the solution assumes a splendid *dark red* colour, changing to *brown*, without precipitation of sulphide.

Metallic zinc produces at first a fine *azure-blue* coloration (owing to the reduction of $'Ru'''_2Cl_6$ to $Ru''Cl_2$), which subsequently disappears, ruthenium being deposited in the metallic state.

(B.) As *Sulphides, soluble in yellow ammonic sulphide* :—IRIDIUM, MOLYBDENUM, TELLURIUM, and SELENIUM.

1. **IRIDIUM**, Ir'', ^{iv}, and ^{vi}, also as a pseudo-triad. Atomic weight, 198.—Found in platinum ores alloyed with platinum, chiefly, however, in combination with osmium, left behind as a native alloy in the form of very hard metallic-looking brittle grains, when the ore is treated with aqua regia. In this condition, or when reduced at a red heat by hydrogen, from any of its compounds, *it is insoluble in every acid.* Fusion with acid potassic sulphate oxidises, but does not dissolve it (DISTINCTION FROM Rh). When fused with caustic soda in a silver crucible with access of air or with sodic nitrate, it is likewise oxidised, but the compound of Ir_2O_3 and soda is only partially soluble in water. By the action of aqua regia the latter is dissolved to a *deep black* liquid, containing the **double chloride of iridium and sodium**, $2NaCl,IrCl_4$. This same compound is also obtained when a mixture of the iridium powder and dry sodic chloride is heated in a glass or porcelain tube in a current of chlorine gas, and the residue dissolved out with water.

Iridium forms numerous compounds with oxygen, chlorine, iodine, sulphur, etc., in which the metal exists as a dyad, pseudo-triad, tetrad, or hexad, as will be seen from the following list :—

	Oxides.
Iridious oxide	$Ir''O$.
Iridic ,,	$'Ir'''_2O_3$.
Iridic dioxide (most stable)	$Ir^{iv}O_2$.
,, hydrate (bulky, indigo coloured)	$Ir^{iv}Ho_4$.
Iridic anhydride (not known in the free state)	$Ir^{vi}O^3$.

Chlorides.	Iodides.	Sulphides.
$Ir''Cl_2$.	$Ir''I_2$.	$Ir''S$ greyish-black.
$'Ir'''_2Cl_6$.	$'Ir'''_2I_6$.	$'Ir'''_2S_3$ brownish-black.
$Ir^{iv}Cl_4$.	$Ir^{iv}I_4$.	

All iridium chlorides are capable of forming crystalline double chlorides with the chlorides of the alkali metals.

REACTIONS IN THE WET WAY.

A SOLUTION OF THE DOUBLE CHLORIDE OF SODIUM AND IRIDIUM, $2NaCl,IrCl_4$, may conveniently be employed.

SH_2 first decolorises the iridium solution, with separation of sulphur and reduction of the $Ir^{iv}Cl_4$ to $'Ir'''_2Cl_6$, and finally precipitates *brown* **iridic sulphide**, $'Ir'''_2S_3$.

SAm_2 produces the same precipitate, readily soluble in excess.

KHo or NaHo, added in excess, colours the solution *greenish*, and precipitates a little *brownish-black* **potassic double chloride**. On heating the liquid with exposure to the air, it acquires at first a reddish tint, which changes afterwards to *azure-blue* (DISTINCTION FROM Pt), and when evaporated to dryness and taken up with water, a colourless solution is obtained, and a *blue* deposit of **iridic dioxide** is left undissolved.

KCl precipitates *dark brown* **potassic iridic chloride**, $2KCl,IrCl_4$, insoluble in a concentrated solution of potassic chloride.

AmCl throws down from concentrated solutions a *dark red* powder, consisting of small octahedral crystals of the **ammonic double chloride**, $2AmCl,\mathbf{Ir}Cl_4$, insoluble in a concentrated solution of the precipitant.

Reducing agents, such as potassic nitrite, oxalic acid, ferrous sulphate, stannous chloride, mercurous nitrate, reduce this double salt (as well as the potassic double chloride) especially when in hot solutions, to the sesquisalt, *e.g.* :—

$$2(2KCl,\mathbf{Ir}^{iv}Cl_4) + 4\mathbf{N}OKo = 6KCl,'\mathbf{Ir}'''_2Cl_6 + 2\mathbf{N}O_2Ko + \mathbf{N}_2O_2.$$

The double chloride crystallises out on cooling.

When $\mathbf{Ir}^{iv}Ho_4$ is suspended in a solution of potassic nitrite, and the solution saturated with sulphurous acid and boiled, with renewal of the water, as long as $\mathbf{S}O_2$ is given off, the whole of the iridium is converted into insoluble *brownish-green* **iridic sulphite**, $\mathbf{S}O(IrO)''o'',4\mathbf{O}H_2$ (SEPARATION FROM Pt).

Metallic zinc precipitates black metallic iridium.

NOTE.—For the separation of the so-called platinum metals we must refer the student to some larger work on Chemistry, such as "Watts' Dictionary."

2. **MOLYBDENUM**, Mo'', ^{iv}, ^{vi}, and ^{viii}, also as a pseudo-triad. Atomic weight 96.—Occurs only in a few minerals, more especially in molybdic disulphide (*Molybdenite*, $\mathbf{Mo}^{iv}S_2$, resembling graphite, and as plumbic molybdate (*wulfenite, or yellow lead ore*), $\mathbf{Mo}O_2Pbo''$.

Molybdic anhydride, $\mathbf{Mo}O_3$, serves for the preparation of ammonic molybdate, a reagent largely used now in determining phosphoric acid, and best obtained from *molybdenite*, by first roasting the ore, at a red heat, in an open vessel, and dissolving the impure anhydride in strong ammonia. An acid ammonic molybdate, $\left\{\begin{array}{l}\mathbf{Mo}O_2Amo\\ O\\ \mathbf{Mo}O_2Amo\end{array}\right. + \mathbf{O}H_2$, crystallises out, on cooling, in large transparent crystals. The metal is prepared by intensely heating the oxide in a charcoal-lined crucible. It is a silver-white, brittle and exceedingly infusible metal, of specific gravity 8·6. It is not affected by exposure to the air, but when heated it becomes first brown, then blue, and finally white, passing through various stages of oxidation till it is converted into molybdic anhydride, $\mathbf{Mo}O_3$. Molybdenum is insoluble in HCl, but is acted upon by $\mathbf{N}O_2Ho$, or aqua regia, being converted into the anhydride, if sufficient nitric acid be present.

It forms with oxygen, chlorine, sulphur, etc., compounds in which the metal exists as a dyad, pseudo-triad, tetrad, hexad, and octad ; thus :—

	Oxides.	Chlorides.	Sulphides.
Molybdous oxide,	$\mathbf{Mo}''O$.	$\mathbf{Mo}''Cl_2$.	
Molybdic ,,	$'\mathbf{Mo}'''_2O_3$.	$'\mathbf{Mo}'''_2Cl_6$.	
=	$\mathbf{Mo}O,\mathbf{Mo}O_2$.	—	
Molybdic dioxide,	$\mathbf{Mo}^{iv}O_2$.	$\mathbf{Mo}^{iv}Cl_4$.	$\mathbf{Mo}^{iv}S_2$ (the native *molybdenite*).
Molybdic trioxide or anhydride,	$\mathbf{Mo}O_3$.	—	$\mathbf{Mo}^{vi}S_3$ (sulphomolybdic anhydride).
		—	$\mathbf{Mo}^{viii}S_4$ (per-sulphomolybdic anhydride).

The higher oxide (anhydride) and sulphides form oxy- and sulpho-salts,—*molybdates* and *sulpho-molybdates*. Black molybdous hydrate, $\mathbf{Mo}''Ho_2$, forms with acids *molybdous salts*, which absorb oxygen readily from the air, and are powerful reducing agents. The principal salts are, however, the *molybdates*.

REACTIONS IN THE DRY WAY.

Molybdic anhydride, when heated on charcoal, in the outer flame, first melts, and is then partly volatilised and forms a yellow crystalline sublimate on the charcoal which turns white, on cooling ; in the inner flame it is reduced to the metallic state (even without $\mathbf{CO}Nao_2$) ; the metal can be obtained as a grey powder, on levigating the charcoal. With borax, all oxides of molybdenum give in the outer flame a bead which is *yellow*, when hot, and *colourless*, on cooling; in the inner flame, a *dark-brown* bead, which is opaque, when excess of molybdenum has been used.

REACTIONS IN THE WET WAY.

We employ A SOLUTION OF AMMONIC MOLYBDATE.

The alkaline molybdates are soluble in water. Most others are insoluble.

Nitric, or hydrochloric acid, precipitates *white* **molybdic acid**, MoO_2Ho_2, from a concentrated solution of a molybdate, soluble, however, in a large excess of the acid.

SH_2 gradually precipitates from acidulated solutions *brownish-black* **molybdic tersulphide**, MoS_3, soluble in alkaline sulphides to sulpho-salts, which are decomposed again by acids with precipitation of MoS_3, especially on the application of heat. On the addition of a *little* SH_2 only, the molybdate solution acquires at first a *blue* tint; added in larger quantities, it produces a precipitate, and the supernatant fluid appears *green*, till on the addition of excess of SH_2 the whole of the metal separates, though slowly, as a tersulphide.

SAm_2 gives a similar precipitate, soluble in excess.

Reducing agents, such as $SnCl_2$, $N_2O_4Hg_2o''$, Zn and HCl, etc., produce changes, marked chiefly by alterations in colour.

The principal and most characteristic reaction for molybdic anhydride consists, however, in precipitating it in a *nitric acid solution*, as *yellow* **phospho-molybdate**, or **arsenio-molybdate**, by the addition of a mere trace of a soluble phosphate, or arsenate. (Comp. p. 142.)

3. **TELLURIUM**, Te$''$, ^{iv} and ^{vi}. Atomic weight 128.—Occurs in a few places, and in small quantities only, as *native* metal (*graphic and foliated tellurium*); more often in combination with Au, Ag, Bi, Pb, as a (*sulpho*)-*telluride*, analogous to arsenides, etc.; or as TELLUROUS ACID, in combination with metallic bases.

Tellurium exhibits all the physical properties of a metal, and resembles antimony in its general appearance. It is a white, brittle, but readily fusible metal, which may be *sublimed* in a glass tube. When heated in the air it burns with a *greenish-blue* flame, emitting thick white fumes of **tellurous anhydride**, TeO_2, The metal is insoluble in HCl, but dissolves readily in NO_2Ho, forming TeO_2, a white substance which fuses to a yellow fluid, at a gentle heat, and volatilises on stronger ignition in the air. Tellurous anhydride dissolves barely in water, and the solution does not redden litmus; readily in HCl, less so in NO_2Ho. It also dissolves freely in potash, or soda, slowly in ammonia, forming alkaline **tellurites**. On dilution with water, white tellurous hydrate, $TeOHo_2$, is precipitated from an acid solution. A nitric acid solution slowly deposits crystalline tellurous anhydride, even without the addition of water.

Tellurium forms several oxides, chlorides, sulphides, etc., in which the metal is a dyad, tetrad, or hexad; thus:—

	Oxides.
Tellurous oxide (anhydride)	$Te^{iv}O_2$.
,, acid	$TeOHo_2$.
Telluric oxide (anhydride)	$Te^{vi}O_3$.
,, acid	TeO_2Ho_2.

	Chlorides.	Sulphides.
Tellurous, or dichloride	$TeCl_2$.	—
Telluric, or tetrachloride	$TeCl_4$.	TeS_2.
	—	TeS_3.

It also forms with hydrogen a gaseous compound, *tellurietted hydrogen* or) *hydrotelluric acid*), $Te''H_2$.

Both the di- and ter-oxides are capable of forming with metallic bases salts called *tellurites* and *tellurates*. The alkaline and alkaline earthy tellurites—formed by fusing tellurous acid with the carbonates of these metals—are all more or less soluble in water; all others obtained by double decomposition are insoluble. The tellurates of the alkali metals, prepared in like manner, are also soluble in water; the others are insoluble. They can be prepared by double decomposition.

The sulphides of this metal act as sulpho-acids, forming with the alkaline sulphides, *sulpho-tellurites* and *tellurates*.

REACTIONS IN THE DRY WAY.

When tellurites, or tellurates, are heated with charcoal and $\mathbf{CO}Ko_2$, they are reduced to **potassic telluride,** $\mathbf{Te}''K_2$, which produces a black stain on a moist silver plate, and is soluble in water, forming a dark-red solution. When HCl is added to this solution **hydrotelluric acid gas,** $\mathbf{Te}''H_2$, is evolved, resembling $\mathbf{S}H_2$ in smell, and soluble in water, to a *pale-red* solution, which is decomposed in contact with air, with deposition of metallic tellurium.

All compounds of tellurium are readily reduced on charcoal in the inner flame. The reduced metal is volatilised and forms a white scarcely visible deposit of tellurous anhydride on the charcoal. Stannous chloride colours it black, owing to the separation of metallic tellurium.

With borax or microcosmic salt a clear colourless bead is obtained, which when heated on charcoal, is rendered grey and opaque, owing to reduced metal.

REACTIONS IN THE WET WAY.

A. **TELLURIC COMPOUNDS.**—USE A SOLUTION OF POTASSIC TELLURATE, $\mathbf{Te}O_2Ko_2$ (obtained by fusing potassic tellurite with nitre).

HCl does not decompose tellurates in the cold, but on boiling the solution chlorine is evolved, and on dilution with water tellurous acid, $\mathbf{Te}OHo_2$, is precipitated, soluble only in a considerable excess of HCl. (DISTINCTION OF $\mathbf{Te}O_3$ FROM $\mathbf{Te}O_2$.)

B. **TELLUROUS COMPOUNDS.**—USE A SOLUTION OF POTASSIC TELLURITE, $TeOKo_2$.

HCl decomposes this solution and precipitates *white* **tellurous acid.** Tellurium resembles in this respect Sb and Bi compounds.

$\mathbf{S}H_2$ precipitates from acid solutions *brown* **tellurous sulphide,** $\mathbf{Te}S_2$, resembling in colour $\mathbf{Sn}S$, and very freely soluble in ammonic sulphide.

Reducing agents, *e.g.*, $SONao_2$, $\mathbf{Sn}Cl_2$, metallic zinc and HCl, a solution of sulphurous acid, etc., reduce tellurium compounds and precipitate black metallic tellurium, which is *insoluble* in an aqueous solution of potassic cyanide.

4. **SELENIUM,** Se'', ^{iv}, and ^{vi}. Atomic weight, 79.—Found *native*, also as SELENIDE of Cu, Pb, Hg, Ag, Fe, etc. It is occasionally found in the flue-dust of roasting furnaces, and as a *seleniferous deposit* in the lead chambers of sulphuric acid works, where the acid is manufactured from seleniferous pyrites.

It resembles the non-metallic element, sulphur, in many respects, *e.g.*, in exhibiting alike allotropic changes; in others the metal tellurium. It is a brittle dark-brown substance, fuses at 200° C., and vaporises at about 700° C., and may be sublimed. Heated in air it burns with a bluish flame and forms **selenious anhydride,** $\mathbf{Se}O_2$, whilst at the same time a disagreeable odour of decaying horse-raddish is given off. The same oxide is formed when selenium is dissolved in nitric acid, or aqua regia. Selenates containing **selenic anhydride,** $\mathbf{Se}O_3$, are formed by heating selenium, or its compounds, with carbonates and nitrates of the alkalies. These oxides form two series of salts, viz., *selenites* and *selenates*. The selenites are the more stable of the two.

REACTIONS IN THE DRY WAY.

Selenium compounds are reduced, when heated with $CONao_2$, on charcoal, in the inner blowpipe flame, and may be readily recognised by the characteristic smell of horse-raddish which they give off. If the saline residue, which contains sodic selenide, $SeNa_2$, be placed on a bright silver coin and moistened with a drop of water, a black stain is produced on the silver. Treated with dilute HCl, it evolves gaseous **hydroselenic acid** (seleniętted hydrogen), SeH_2, analogous in composition and properties to sulphuretted hydrogen. It is an inflammable, fœtid, poisonous gas, very soluble in water. The aqueous solution of SeH_2 gradually deposits selenium on exposure to air; it precipitates **selenides** from solutions of many metallic salts.

REACTIONS IN THE WET WAY.

A. **SELENIC COMPOUNDS**.—USE A SOLUTION OF POTASSIC SELENATE, SeO_2Ko_2.

Selenates are stable salts, closely resembling the sulphates. They are soluble in water with the exception of the barium, strontium, calcium and lead salts, which are insoluble in water and in dilute acids.

HCl decomposes selenates, on boiling; *chlorine* is evolved, and the salt is reduced to a selenite. (DISTINCTION FROM SeO_2.)

SH_2 does not produce a precipitate, till the selenate has been reduced to selenite, by boiling with HCl.

$BaCl_2$ produces a *white* precipitate of **baric selenate**, SeO_2Bao'', insoluble in water and in dilute acids; decomposed by boiling HCl.

B. **SELENIOUS COMPOUNDS**.—USE A SOLUTION OF AN ALKALINE SELENITE.

The normal alkaline selenites are soluble in water, most others are insoluble; all acid selenites are soluble. HCl dissolves but does not decompose selenites.

SH_2 produces from an acid solution of a selenite, a *lemon-yellow* precipitate of **selenious sulphide**, SeS_2 (?), which almost immediately breaks up into its component elements $Se + S_2$, but is readily soluble in ammonic sulphide.

$BaCl_2$ gives a *white* precipitate of *baric selenite*, $SeOBao''$, soluble in dilute HCl, or NO_2Ho.

Reducing agents, such as SO_2, alkaline sulphites, $SnCl_2$, metallic Zn, and Fe, precipitate from acidulated (HCl) solutions metallic selenium, as a *red* powder, which turns *grey* at a high temperature and is *soluble* in KCy solution. (SO_2Feo'' is without action.) Metallic copper is immediately coated black when placed in a warm solution containing hydrochloric acid, and on standing, the solution turns light red, from separation of metallic selenium.

Group I comprises the Rare Metals precipitable by HCl, viz., the metal TUNGSTEN, or WOLFRAM, which is precipitated as tungstic acid, WO_2Ho_2, and THALLIUM precipitated as thallious chloride, TlCl. Several other metals already treated of in Group III besides THALLIUM, viz., NIOBIUM, TANTALUM, MOLYBDENUM, are likewise precipitated, but the precipitated acids (NbO_2Ho, TaO_2Ho and MoO_2Ho_2) dissolve again in an excess of hydrochloric acid.

1. **TUNGSTEN**, or **WOLFRAM**, W^{iv} and ^{vi}. Atomic weight 184.—This metal occurs in nature as teroxide in the form of tungstates, in combination with the bases CaO, FeO, MnO, in the minerals *wolfram*, $WO_2\,[Feo''\ Mno'']$ and *tungsten*, WO_2Cao''.

The metal can be obtained by intensely heating the oxide in a current of hydrogen. It forms an iron-grey powder, very difficultly fusible, and becomes again oxidised to tungstic anhydride, WO_3, when heated in air. Dry chlorine gas converts it into *dark violet*, WCl_6, which sublimes, and a more volatile red compound, WCl_4. Both chlorides are decomposed by water into the corresponding hydrates, with formation of HCl. The metal is insoluble, or scarcely soluble, in acids, even in aqua regia.

The following are some of the more important compounds which tungsten forms with oxygen, chlorine, and sulphur.

	Oxides.	Chlorides.	Sulphides.
Tungstic anhydride (lemon-yellow)	$W^{vi}O_3$.	$W^{vi}Cl_6$.	$W^{vi}S_3$.
Tungstic dioxide (brownish-black)	$W^{vi}O_2$.	$W^{iv}Cl_4$.	
Intermediate (blue-coloured) oxide	W_2O_5.	WCl_5.	
=	$W^{iv}O_2,W^{vi}O_3$ =	WCl_4,WCl_6.	

Tungstic anhydride can be prepared from *wolfram* or *tungsten*, by digesting the finely divided mineral in aqua regia, till it is completely decomposed, and evaporating to dryness on a water-bath. The metallic chlorides are dissolved out with acidulated water, and the residue, which contains a little silica and sometimes niobic acid, washed with alcohol and treated with ammonia. Tungstic acid is dissolved, and silicic and niobic acids are left behind. From the ammonia salt, pure anhydride is obtained by the evaporation of the filtrate and ignition.

REACTIONS IN THE DRY WAY.

When heated on charcoal in the reducing flame, together with $CONao_2$ and KCy, tungstic anhydride is reduced to a black powder, containing metallic tungsten. Heated with microcosmic salt, tungsten compounds give a *colourless* bead in the outer flame; in the inner flame a *blue* bead, which on the addition of a little SO_2Feo'' changes to **blood-red**. The addition of tin changes the red bead to blue or green.

REACTIONS IN THE WET WAY.

WE MAY EMPLOY A SOLUTION OF SODIC TUNGSTATE, WO_2Nao_2.

The alkaline tungstates are soluble in water, all others are insoluble, and can be obtained by double decomposition.

Mineral acids (HCl, NO_2Ho, or SO_2Ho_2) precipitate *white* **tungstic acid,** WO_2Ho_2. It turns *yellow* on boiling, and is quite insoluble in excess of the acids. (DISTINCTION FROM MoO_3.) Non-volatile acids (*e.g.*, phosphoric, tartaric) precipitate it likewise, but the precipitate is *soluble* in excess. It is also readily soluble in AmHo.

SH_2 produces no precipitate from an acid solution, but reduces the tungstic acid to the blue oxide, W_2O_5.

SAm_2 produces no precipitate from alkaline tungstates, but on acidulating with HCl, *light brown* **tungstic tersulphide,** WS_3, is precipitated, slightly soluble in pure water, but insoluble in the presence of salts. The solution is coloured blue. The precipitated sulphide dissolves readily in ammonic sulphide.

$SnCl_2$ gives at first a *yellow* precipitate; on acidulating with HCl and applying heat, the precipitate acquires a beautiful *blue* colour. *This reaction is very delicate and highly characteristic.*

APPENDIX II.

REAGENTS.

SOLVENTS.

Distilled Water.*—Obtained by condensing steam by means of a tin worm. The first portions of the condensed water usually contain carbonic anhydride and ammonic carbonate, and should be rejected.

Impurities.—When evaporated in a platinum vessel, distilled water should not leave a solid residue, either organic or mineral. Ammonic sulphide ought not to give a precipitate (Cu, Pb, Fe), neither ought basic plumbic acetate to cause a turbidity (CO_2, $COAmo_2$). No turbidity or precipitate should be produced, moreover, on the addition of ammonic oxalate (lime), baric chloride (sulphates), or argentic nitrate (chlorides). Pure distilled water is colourless, inodorous, and tasteless.

Water used for Nessler's test should be specially distilled in a glass retort with a few pieces of caustic potash, and the distillate rejected as long as the Nessler solution indicates any traces of ammonia.

Alcohol (Methylated Spirit), C_2H_5Ho or EtHo.—Ordinary methylated spirit (*i.e.*, ethylic alcohol, 90 p. c., mixed with 10 p. c. of wood spirit or methylic alcohol) may be employed for most purposes. It can be rendered absolute by shaking with well dried potassic carbonate and distilling the clear spirit in a flask or retort from a water-bath.

Impurities.—Commercial methylated spirit frequently leaves a residue on evaporation, if so, it should be rectified by distillation. It should be without action upon litmus papers.

Ether, OEt_2.—The ordinary ether (methylated, *i.e.*, prepared from methylated alcohol) of commerce, is pure enough.

ACIDS.

Sulphuric Acid,* SO_2Ho_2.—Common oil of vitriol may be used in all operations with which its usual impurities (lead, arsenic, iron, lime, nitric acid) do not interfere. Sulphuric acid, free from arsenic, should be employed for generating arseniettted or antimoniettted hydrogen, and an acid free from lead, whenever this metal has to be precipitated as sulphate. Sulphuric acid, free from nitric acid and nitric peroxide, ought to be employed in testing for nitric acid by means of ferrous sulphate.

Impurities.—Pure sulphuric acid is colourless, and leaves no residue on evaporation in a porcelain dish. When a solution of ferrous sulphate is poured upon it in a narrow test-tube, it should not form a brown ring where the two liquids come in contact (nitric acid and nitric peroxide), nor strike a blue colour when a highly diluted solution of the acid is added to a solution of pure potassic iodide and starch paste (nitric peroxide). The presence of arsenic is best ascertained by passing a current of sulphuretted hydrogen through the dilute acid, or by generating hydrogen from zinc free from arsenic, and passing the gas through an ignited combustion tube (Marsh's test, Fig. 14). Plumbic sulphate is frequently found in sulphuric acid, and is precipitated on diluting with water, being less soluble in dilute than in concentrated acid. Hydrochloric acid should cause no turbidity (lead) where the two liquids meet.

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* The asterisk marks the more important reagents.

The pure acid can readily be bought now, and the student should not attempt to purify the crude acid.

Dilute Sulphuric Acid.*—Prepared by pouring slowly one part by measure of the concentrated acid (sp. gr. 1·8) into five parts by measure of distilled water, with continuous stirring. Thin glass vessels (beakers) or a porcelain dish should be employed, as much heat is evolved. Allow the plumbic sulphate to subside, and decant or syphon off the clear liquid.

Nitric Acid,* *Aqua fortis*, $\mathbf{N}O_2Ho$.—Should be colourless, and leave no residue on evaporation in a glass dish.

Impurities.—Sulphuric and hydrochloric acids. Dilute considerably, and test portions with baric nitrate and argentic nitrate.

Dilute Nitric Acid.*—Prepared by diluting one part of pure commercial acid (sp. gr. 1·38 to 1·45) with three parts of distilled water.

Crude Nitric Acid.*—May be employed for all experiments in which the above impurities do not interfere, *e.g.*, in the preparation of $\mathbf{N}_2O_2$ or $\mathbf{N}_2O_3$ by the action of nitric acid upon copper or arsenious anhydride.

Concentrated Hydrochloric Acid,* Muriatic Acid, HCl.—Should be colourless, and leave no residue on evaporation.

Impurities.—Ferric chloride, sulphurous and sulphuric acids, arsenic. The acid should not impart a blue colour to a solution of KI and starch paste (Cl or $\mathbf{Fe}_2Cl_6$). On adding a few drops of a solution containing iodide of starch, the blue colour should not be destroyed ($\mathbf{S}O_2$). The dilute acid should remain clear on the addition of a solution of baric chloride ($\mathbf{S}O_2Ho_2$). Sulphuretted hydrogen, when passed through the dilute acid, should not produce a precipitate (arsenic), nor should ammonic sulphocyanate redden the diluted acid (iron).

Dilute Hydrochloric Acid.*—Pure commercial acid, sp. gr. 1·16, is diluted with three times its bulk of distilled water.

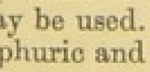
Crude Hydrochloric Acid.*—Should be employed whenever the impurities which it contains do not interfere with the object in view, as for instance in the preparation of chlorine from manganic dioxide.

Aqua Regia or Nitrohydrochloric Acid.—Prepared, when required only, by mixing one part of concentrated nitric acid with three to four parts of hydrochloric acid.

Sulphurous Acid, $\mathbf{S}OHo_2$.—Prepared by acting with concentrated sulphuric acid upon copper, and passing the gas into water. The solution should be kept in a well-stoppered bottle.

Carbonic Acid Water.—A solution is prepared by acting with hydrochloric acid upon marble, and passing the evolved carbonic anhydride into water.

Chlorine Water.—A solution of chlorine in water is readily prepared. It should be kept in a well-stoppered bottle, and in a dark place, since on exposure to light, it is speedily converted into HCl with evolution of oxygen.

Acetic Acid,*  $\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.$. Pure commercial acid of sp. gr. 1·04, diluted with one part of water may be used. It should leave no residue on evaporation.

Impurities.—Sulphuric and hydrochloric acids, lead, copper, iron, lime.

Tartaric Acid, $\bar{T}Ho_2$.—A solution is prepared when required only, as the acid undergoes decomposition in an aqueous solution. One part by weight of commercial tartaric acid of sufficient purity is dissolved in three parts of water (*i.e.*, 1 grm. in 3 c.c. of water).

Impurities.—Tartaric acid contains sometimes gypsum and calcic tartrate, which are best tested for by igniting a few crystals on platinum, extracting the residue, if any, with a few drops of dilute HCl, and adding to one portion $BaCl_2$, to another AmHo, and $\left\{\begin{matrix}\mathrm{COAmo}\\ \mathrm{COAmo}\end{matrix}\right.$.

Oxalic Acid, $\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.$. The commercial acid is sufficiently pure. It should not leave more than a trace of a residue on ignition.

Impurities.—Iron, potassic and sodic oxalates, lime. Dissolve one part by weight of the crystallized acid, $\left\{\begin{matrix}\mathrm{COHo}\\ \mathrm{COHo}\end{matrix}\right.$, + 2 aq., in ten parts by measure of water.

Hydrofluoric Acid, HF.—A solution stored up in a gutta-percha bottle is best bought, as its preparation involves expensive apparatus. It should leave no fixed residue on evaporation to dryness.

Hydrofluosilicic Acid, $2HF,SiF_4$.—A solution of this acid in water is prepared as described, p. 138. It should be made sufficiently strong to precipitate a soluble baric salt readily.

Impurities.—Owing to the mode of preparation the acid is often contaminated with sulphuric acid. It should not produce a precipitate in a solution of a strontic salt (SO_2Ho_2).

Hydrosulphuric Acid, SH_2.—Prepared when required. In well appointed laboratories sulphuretted hydrogen is now usually stored in a gasholder over oil, and supplied like coal gas from small taps, in closets, connected with the chimney. The gas, whether obtained from a constant generating apparatus, or from a gasholder, should invariably be passed through a wash-bottle containing water. A saturated solution of sulphuretted hydrogen in water answers most purposes of the analyst. It should be kept in a well-stoppered bottle, since sulphuretted hydrogen decomposes rapidly when in contact with air with formation of sulphur acids and precipitation of white sulphur.

If the gas be required entirely free from AsH_3, it should be generated by acting with pure HCl (concentrated) upon native *grey antimony* Sb_2S_3.

BASES AND METALS.

Potassic Hydrate,* KHo, **or Sodic Hydrate**, NaHo.—Usually obtained in commerce in the form of sticks or lumps, which may be dissolved in twenty parts of water.

Impurities.—Silica, alumina, phosphoric, sulphuric, and hydrochloric acids (sulphates and chlorides, often in not inconsiderable quantities), and carbonic acid. On dissolving in water, and allowing the suspended matter to subside, the clear solution may be syphoned off.

Pure sodic hydrate is indispensable for the separation of alumina from the oxides of iron and chromium.

Ammonic Hydrate,* AmHo.—The *liquor ammoniæ* of commerce, sp. gr. ·88, is diluted with distilled water till the liquid has a sp. gr. of ·96 = 10 per cent. of NH_3.

Impurities.—A solution of ammonia should be colourless; on neutralizing with pure HCl it should remain inodorous. When evaporated in a glass or platinum dish, it should not leave any residue. Ammonia contains frequently traces of sulphuric and hydrochloric acids, and sometimes not inconsiderable quantities of ammonic carbonate, when it produces a white precipitate on the addition of lime water.

Baric Hydrate,* $BaHo_2$.—Obtained by dissolving in a stoppered bottle one part of crystallized baric hydrate, $BaHo_2 + 8aq.$ in twenty parts of water. Allow to subside and syphon off into another well-stoppered bottle.

Impurities.—The solution commonly called *baryta-water* should, on precipitating with pure SO_2Ho_2, give a filtrate which leaves no fixed residue on evaporating to dryness in a platinum vessel.

Calcic Hydrate,* $CaHo_2$.—Freshly slaked lime in powder is used in qualitative analysis, as well as a solution of lime, so-called *lime-water*. This is prepared by dissolving in *cold* distilled water some freshly slaked lime, allowing to subside in a stoppered bottle, and syphoning off the clear liquid into another bottle. Lime-water contains about one part of lime dissolved in 600 of water.

Ammonic Sulphide,* SAm_2.—Prepared by saturating three parts of ammonic hydrate with sulphuretted hydrogen gas, whereby $SHAm$ is formed. On diluting this solution of hydric ammonic sulphide with two parts of ammonic hydrate, a sulphide is obtained which contains a little free ammonia. The concentrated solution may be diluted with ten times its bulk of water. It should be kept in well-stoppered bottles. Calcic or magnesic salts should not be precipitated ; nor should the solution leave a residue on evaporation and ignition. The oxygen of the air decomposes it gradually into NH_3, OH_2 and yellow $SSAm_2$.

Yellow Ammonic Sulphide, $SSAm_2$.—Used for the solution and conversion of SnS into SnS_2. It may be prepared by digesting the neutral SAm_2 with flowers of sulphur and filtering the liquid.

Sodic Sulphide, SNa_2.—Prepared by saturating one portion of a solution of sodic hydrate with sulphuretted hydrogen, and adding to it the second portion. A little ferrous sulphide, which is generally precipitated, is filtered off. The solution must be kept in a well-stoppered bottle.

SALTS.

Potassic Sulphate, SO_2Ko_2.—Dissolve one part of the commercial salt in twelve parts of water.

Potassic Iodide, KI.—The commercial salt is generally sufficiently pure. Dissolve in sixty parts of water. Pure KI should be free from iodate and carbonate. It should not colour starch paste blue on the addition of dilute SO_2Ho_2.

Potassic Nitrite, $NOKo$.—Dissolve one part of the commercial salt in two parts of water, when required for use.

Potassic Chromate, CrO_2Ko_2.—Dissolve the salt of commerce in ten parts of water.

Impurities.—Sulphuric acid. The solution ought not to become turbid on the addition of dilute HCl and $BaCl_2$.

Dipotassic Dichromate, $Cr_2O_5Ko_2$.—Purify the commercial salt by recrystallisation till it is free from SO_2Ko_2, and dissolve one part in ten of water.

Potassic Metantimonate, $SbO_2Ko + 5$ aq.—Prepared by deflagrating in a Hessian crucible one part of finely powdered antimony with four parts of saltpetre. Pour the fused mass on a stone slab. Powder it, and boil with twelve parts of water for two or three hours, and filter, when a clear and neutral solution is obtained. KCl and $AmCl$ should not precipitate it.

Potassic Ferrocyanide,* K_4FeCy_6, and **Ferricyanide**, $K_6Fe_2Cy_{12}$.—These salts can be purchased in a state of sufficient purity. They are dissolved, in small quantities at a time, in twelve parts of water.

Potassic Sulphocyanate, $CyKs$, or **Ammonic Sulphocyanate** $CyAms$.—Dissolve in ten parts of water.

Impurities, such as $\mathbf{SO_2Ho_2}$, do not interfere with the reactions.

Sodic Carbonate,* $CONao_2$.—Procure the *pure* salt, which should be free from sulphate and chloride. The solution should not give a precipitate after conversion into a nitrate, when treated with concentrated $\mathbf{NO_2Ho}$ and $\mathbf{MoO_2Amo_2}$, and should not leave a residue, insoluble in water, on acidulating with pure HCl and evaporating to dryness ($\mathbf{SiO_2}$).
Dissolve the dry salt in five parts of water.

Hydric Disodic Phosphate,* $POHoNao_2 + 12\,aq$.—Recrystallize the commercial salt and dissolve one part of pure salt in ten parts of water.

Impurities.—Sulphate and chloride.—Ammonic hydrate should not cause any turbidity on warming (alkaline earthy phosphates).

Sodic Acetate, $\left\{\begin{array}{l}CH_3\\CONao\end{array}\right. + 6\,aq$.—The commercial salt generally contains sodic sulphate. If a pure salt cannot be procured, sodic acetate may be prepared by neutralising pure sodic carbonate with pure acetic acid. Dissolve the salt in ten parts of water.

Sodic Acetate and Acetic Acid.—Dissolve 20 grms. of pure crystallized $\left\{\begin{array}{l}CH_3\\CONao\end{array}\right.$ in 160 c.c. of water, and add 40 c.c. of concentrated $\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.$. This solution is used for the precipitation of ferric, aluminic, and chromic phosphates.

Hydric Sodic Sulphite, $SOHoNao$.—Dissolve one part of the salt in five parts of water. Hydric ammonic sulphite may frequently be used with greater advantage.

Sodic Hyposulphite, $SSONao_2 + 5\,aq$.—Readily procurable in a pure state. Dissolve one part of the salt in forty parts of water.

Sodic Hypochlorite, $ClNao$.—Prepared by shaking up one part of bleaching powder with ten parts of water, and adding a saturated solution of commercial sodic carbonate as long as a precipitate is produced. Allow to subside, and syphon off.

Ammonic Oxalate,* $\left\{\begin{array}{l}COAmo\\COAmo\end{array}\right. + aq$.—Purify the commercial salt by recrystallization and dissolve one part in twenty-four parts of water.

Impurities.—The salt should leave no fixed residue on ignition. Sulphuretted hydrogen or ammonic sulphide ought not to produce a turbidity or a precipitate.

Ammonic Carbonate,* $COAmo_2$.—Prepared by dissolving one part of the commercial sesquicarbonate, after scraping off from the lumps any foreign matter, in four parts of water and adding one part of strong ammonia solution. If a precipitate of ferric hydrate be thrown down, it is allowed to subside, and the clear solution is syphoned off.

Impurities.—Iron, lead, sulphuric and hydrochloric acids. The salt should volatilize completely and give no precipitate with baric chloride, or argentic nitrate (after acidulating with hydrochloric or nitric acid respectively), also no precipitate with sulphuretted hydrogen or ammonic sulphide.

Hydric Ammonic Carbonate. $COHoAmo$.—Obtained in colourless rhombic prisms, on passing carbonic anhydride to supersaturation into a concentrated solution of ammonia. The salt is employed for the separation of $\mathbf{As_2S_3}$ from $\mathbf{Sb_2S_3}$ and $\mathbf{SnS_2}$. A saturated solution is prepared when required.

Ammonic Chloride,* $AmCl$.—The commercial salt (sal-ammoniac) usually contains iron. Purify by adding to the solution a little ammonic hydrate. Allow the ferric hydrate to subside and neutralize the alkaline filtrate exactly with pure HCl. The salt should leave no fixed residue on ignition. Dissolve in five parts of water.

Ammonic Molybdate, MoO_2Amo_2.—This salt may be purchased. It is dissolved in strong ammonia and allowed to stand for some time. A slight yellow precipitate containing ferric hydrate, usually subsides. The clear fluid is poured into concentrated nitric acid as long as the molybdic acid which at first precipitates is entirely redissolved. The nitric acid solution should remain colourless on boiling. A yellow precipitate indicates contamination with phosphoric acid, and the reagent should not be used, till it remains clear on digestion.

Ammonic Sulphate, SO_2Amo_2.—Recrystallize the commercial salt from an ammoniacal solution in order to separate iron. Keep a saturated solution for use.

Ammonic Nitrate, NO_2Amo.—The commercial salt is dissolved, when required, to a saturated solution. It should leave no residue when ignited on platinum.

Baric Chloride,* $BaCl_2 + 2$ aq. The commercial salt is rarely pure enough, and not unfrequently contains lead. It should not give a precipitate with sulphuretted hydrogen or ammonic sulphide, nor should a residue be left after precipitating the whole of the barium by pure sulphuric acid and evaporating the filtrate in a platinum dish. Purify, if necessary, by passing a current of sulphuretted hydrogen, filtering and recrystallizing. Dissolve in ten parts of water.

Baric Nitrate, N_2O_4Bao''.—Should not be precipitated by argentic nitrate, as it is sometimes employed, instead of baric chloride, in order to avoid introducing any chlorine into a solution. Pure baric acetate answers the same purpose. For other impurities, test as for baric chloride. Dissolve one part in 15 parts of water.

Baric Carbonate,* $COBao''$.—Prepared by precipitation of pure baric chloride with Ammonic carbonate and $AmHo$. Wash well till free from $AmCl$; stir up the precipitated baric carbonate with water to a thick creamy consistency, and keep it for use in a stoppered bottle. Shake up before using this reagent.

Calcic Chloride,* $CaCl_2 + 6$ aq.—The commercial salt is dissolved in five parts of water. The solution should be neutral to test-papers, and should not be precipitated by ammonic sulphide (iron).

Calcic Sulphate, SO_2Cao''.—A saturated solution is prepared by repeatedly shaking up gypsum ($SOHo_2Cao'' +$ aq.) with water, allowing to subside, and syphoning off the clear liquid.

Magnesic Sulphate.—Dissolve the commercial salt ($SOHo_2Mgo'' + 6$ aq.) (recrystallized, if necessary) in ten parts of water.

Magnesia Mixture.—Dissolve 55 gms. of crystallized $MgCl_2$ in distilled water, add 70 grms. of $AmCl$ and 350 c.c. of concentrated solution of ammonic hydrate, and make up to 1 litre.

Ferrous Sulphate.—The commercial salt ($SOHo_2Feo'' + 6$ aq.) is pure enough. Dissolve as required for use in ten parts of water.

Ferric Chloride,* Fe_2Cl_6.—Prepared by dissolving freshly precipitated and well washed Fe_2Ho_6 in pure HCl, keeping the ferric hydrate in excess. Allow to cool, dilute with an equal bulk of water and filter.

Plumbic Acetate,* $\left(\left\{\begin{matrix}CH_3\\CO\end{matrix}\right.\right)_2Pbo''$. Dissolve the commercial salt in ten parts of water.

Argentic Nitrate,* NO_2Ago.—Prepared either from silver (pure), or from a silver alloy (a silver coin), by dissolving in pure nitric acid, and precipitation as $AgCl$. Filter off the cupric salt, and wash thoroughly with hot water; transfer to a porcelain dish, and introduce clean strips of zinc. Collect the finely divided silver on a filter, wash thoroughly with hot water, acidulated with a little sulphuric acid, and dissolve in dilute nitric acid. Evaporate the solution to dryness, and fuse the residue gently. Dissolve in twenty parts of water.

Mercurous Nitrate.—Dissolve the crystals of the commercial salt $\begin{matrix}NO_2\\NO_2\end{matrix}Hg_2o''$ + 2 aq., in 20 parts of cold water, acidulated with 1·2 parts of nitric acid. Keep some metallic mercury in the filtered solution.

Mercuric Chloride, $HgCl_2$.—Dissolve the commercial corrosive sublimate in twenty parts of water.

Nessler's Solution.—Dissolve 3·5 grms. of KI in 10 c.c. of water; next dissolve 1·6 grm. of $HgCl_2$ in 30 c.c. of water: add the mercury solution gradually, and with continuous agitation to the solution of potassic iodide, until the precipitate ceases to be re-dissolved; then add 60 c.c. of potassic hydrate and filter. Keep in a small bottle, out of contact with ammonia fumes.

This reagent is of great value for the detection of mere traces of ammonia.

Cupric Sulphate.—The commercial salt ($SOHo_2Cuo''$ + 4 aq.) is purified by repeated crystallisation. Dissolve the crystals in ten parts of water.

Impurities.—Iron, zinc.

Cupric Chloride, $CuCl_2$.—Prepared by dissolving cupric oxide in HCl.

Cuprous Chloride, $'Cu'_2Cl_2$.—Obtained by digesting $CuCl_2$ with metallic copper and HCl.

Stannous Chloride, $SnCl_2$.—Prepared by boiling pure granulated tin in concentrated HCl, with the aid of a piece of platinum foil. Dilute with four volumes of water, acidulated with HCl. Keep the filtered solution over granulated tin in a small stoppered bottle.

Auric Chloride, $AuCl_3$.—Prepared by dissolving pure gold in aqua regia, evaporating to dryness on a water-bath and dissolving in water.

Platinic Chloride, $PtCl_4$.—Dissolve some platinum scraps in aqua regia. Precipitate with AmCl. Collect precipitate on a Swedish filter-paper; wash with strong alcohol; dry and ignite in a porcelain crucible, gently at first, and lastly to intense redness. Redissolve the spongy platinum in aqua regia. Evaporate repeatedly to dryness on a water-bath, with addition of HCl. Dissolve in ten parts of water. Pure platinic chloride should dissolve completely in pure alcohol.

METALS AND OXIDES.

Zinc, free from arsenic, granulated, and in the form of strips or sticks.

Iron (*steel*), *copper, tin, lead, platinum* (used in the form of wire, bars, sheet, turnings) and *mercury* can be obtained of sufficient purity for the purposes of qualitative analysis.

Metallic Lead free from Silver.—Prepared by precipitation of plumbic acetate by metallic zinc.

Plumbic Dioxide, PbO_2.—Readily prepared by digesting red lead in boiling dilute nitric acid. The brown powder is well washed by decantation, and lastly on the filter.

Manganic Dioxide, MnO_2.—Use the powdered commercial black oxide.

Hydric Peroxide, O_2H_2, or Ho_2.—A solution may be prepared by passing a current of carbonic anhydride through water in which baric peroxide is suspended. The precipitated baric carbonate is filtered off. The commercial article usually contains a little free mineral acid, such as HCl or SO_2Ho_2, added in order to prevent its spontaneous decomposition. Hydrofluosilicic acid is also sometimes met with, used probably (in excess) to remove any soluble barium salt.

Reagents used for Fusions and for Blowpipe Reactions.

Sodic Carbonate,* $CONao_2$.—Should be free from sulphate and chloride.

Fusion Mixture* or White Flux.—Consisting of dry $CONao_2$ and $COKo_2$, mixed in the proportion of their combining weights, *i.e.*, 106 + 138, or in the proportion of 10 to 13.

Pure carbonates free from silica, chlorides, and sulphates, should be procured, as their purification cannot be effected without using silver and platinum vessels.

Black Flux.—Prepared by igniting crystals of *Rochelle salt* (potassic sodic tartrate) in a platinum crucible. The residue consists of carbon and alkaline carbonates.

Hydric Ammonic Sodic Phosphate,* $POHoAmoNao + 8$ aq. (**Microcosmic Salt**).—The salt should be dried and used in the form of a powder. On being heated in a loop of platinum wire it is converted into PO_2Nao.

Potassic Cyanide,* KCy.—Exceedingly useful for reducing metallic oxides and sulphides, either in the crucible or on charcoal. For blowpipe reactions a mixture of equal parts of KCy and $CONao_2$ (or fusion mixture), is preferable, because it sinks readily into the charcoal and yields metallic globules of great purity. For the separation of Ni and Co the salt is dissolved, when required, in twenty parts of cold water, as its aqueous solution is rapidly decomposed.

Potassic Nitrate,* NO_2Ko.—Used as an oxidizing agent. The commercial salt should be purified by dissolving the crystals in hot water to a saturated solution, and allowing to cool in a porcelain dish with continuous stirring. The nitrate falls out first as a fine white powder, and the impurities, *e.g.*, phosphate, sulphate, or chloride, are left in the mother-liquor.

Potassic Chlorate,* $\left\{\begin{matrix}OCl\\OKo\end{matrix}\right.$.—This salt can readily be obtained pure, *i.e.*, free from chloride. Either by itself, or in conjunction with hydrochloric acid, it serves as a powerful oxidizing agent.

Borax,* $B_4O_5Nao_2 + 10$ aq.—The crystals should be gently heated in a platinum crucible till the water of crystallization has been driven off, and the mass kept powdered and ready for use in blowpipe reactions.

Hydric Potassic Sulphate, SO_2HoKo.—Prepared by heating in a platinum dish 87 parts of normal potassic sulphate with 49 parts of pure sulphuric acid, till the clear mass fuses steadily. Pour out on a porcelain slab, and keep the lumps in a bottle.

Cobaltous Nitrate, N_2O_4Coo''.—Used in solution only. Should be free from other metals. Dissolve the commercial salt in ten parts of water.

Vegetable Colouring Matters.—Test-papers.

Litmus Solution.—Its preparation has been described in my *Introduction to Inorganic Chemistry*, p. 9.

Turmeric Paper.—Prepared by digesting at a gentle heat one part of turmeric root with six parts of alcohol. Filter and soak strips of porous paper with the yellow extract. The dried papers should exhibit a fine yellow tint. Like litmus-papers, they serve for the detection of free alkalies. All test-papers should be kept in well-stoppered bottles or wooden boxes.

Indigo Solution.—Prepared by gradually stirring four to six parts of *fuming* sulphuric acid into one part of *finely* divided indigo, and allowing the mixture to stand for 48 hours, before pouring it into 20 parts of water. Filter, and keep for use in a dark place. The solution of indigo is used for detecting nitric acid, chloric acid, and free chlorine, owing to the formation of products of oxidation of a yellow colour.

APPENDIX III.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER, AND ACIDS.

Names of Salts.	Soluble in Water.	Soluble in, or decomposed by Acids.	Insoluble in Water and Acids.
Carbonates	Alkaline carbonates, and acid carbonates of Ba, Sr, Ca, Mg, Fe″, Mn, and [Pb.]	All other carbonates are decomposed by dilute acids, with evolution of $\mathbf{C}O_2$. (Spathose iron ore, and dolomite are decomposed with difficulty.)	None.
Sulphates	Most sulphates, with the exception of those mentioned in Column III and IV. ($\mathbf{S}O_2Ago_2$ is difficultly soluble.)	A few basic sulphates, such as of Hg″, ′Hg′$_2$, Fe^{iv}, Bi‴, Sn″.	The sulphates of Ba, [Pb,] Sr, Ca (Comp. p. 110), and the *red* chromic sulphate.
Sulphites	Alkaline sulphites, and the acid sulphites of the alkaline earthy metals.	All other sulphites are decomposed by acids ($\mathbf{C}O_2$ and $\mathbf{B}Ho_3$ excepted), with evolution of $\mathbf{S}O_2$.	None.
Hyposulphites	Most hyposulphites are soluble in water. ($\mathbf{SS}OBao''$, $\mathbf{SS}OAgo_2$, and $\mathbf{SS}OPbo''$ are but little soluble.)	All other hyposulphites are decomposed by acids, with evolution of $\mathbf{S}O_2$ and separation of sulphur.	None.
Sulphides	Alkaline and alkaline earthy sulphides. ($\mathbf{Ca}\mathbf{S}$ and $\mathbf{MgS}$ are only sparingly soluble.)	All other sulphides are decomposed by HCl, with evolution of $\mathbf{S}H_2$, or by $\mathbf{N}O_2Ho$, or aqua regia, with separation of sulphur. (Comp. p. 116.)	None.

Nitrates	Most nitrates with the exception of a few basic nitrates (Bi, Hg).	A few basic nitrates, which are readily soluble in dilute $\mathbf{NO}_2\mathrm{Ho}$.	None.
Nitrites	All nitrites. ($\mathbf{NO}\mathrm{Ago}$ is somewhat difficultly soluble.)	—	—
Chlorides	Most chlorides, with the exception of those mentioned in Column IV.	[A few oxychlorides.]	The chlorides of Ag, $'\mathrm{Hg}'_2$, [Pb] ($\mathbf{Cu}_2\mathrm{Cl}_2$, $\mathbf{Au}'\mathrm{Cl}$, $\mathbf{Pt}''\mathrm{Cl}_2$). (Comp. p. 122.)
Chlorates	All chlorates.	—	—
Hypochlorites	All hypochlorites.	—	—
Bromides	Most bromides, with the exception of those mentioned in Column IV.	—	The bromides of Ag, $'\mathrm{Hg}'_2$, Pb (less soluble in water than the $\mathbf{Pb}\mathrm{Cl}_2$) and of $'\mathbf{Cu}'_2$ (soluble in HCl).
Bromates	All bromates.	—	—
Iodides	Most iodides, with the exception of those mentioned in Column IV.	$\mathbf{Pb}\mathrm{I}_2$, $\mathbf{Hg}\mathrm{I}_2$, $\mathbf{Hg}_2\mathrm{I}_2$ (decomposed into $\mathbf{Hg}\mathrm{I}_2$ and Hg); $\mathbf{Cu}_2\mathrm{I}_2$ decomposed by $\mathbf{NO}_2\mathrm{Ho}$ with evolution of I.	The iodides of Ag, [$'\mathrm{Hg}'_2$, Pb, Hg'', and $'\mathrm{Cu}'_2$]. (Comp. p. 132.)
Iodates	The alkaline iodates only dissolve readily in water.	Baric, plumbic, argentic, and other iodates dissolve more or less readily in acids ($\mathbf{NO}_2\mathrm{Ho}$).	None.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER, AND ACIDS—*continued.*

Names of Salts.	Soluble in Water.	Soluble in, or decomposed by Acids.	Insoluble in Water and Acids.
Fluorides	The alkaline fluorides and a few others, especially AgF, $\mathbf{HgF}_2$. (Comp. p. 136.)	The fluorides of the alkaline earthy metals, of lead, and a few other metals.	Fluorspar, decomposed by concentrated $\mathbf{SO}_2\mathrm{Ho}_2$ only.
Silicofluorides	Most silicofluorides are more or less readily soluble in water. The least soluble are those of the alkalies and alkaline earthy metals.	$\mathbf{BaF}_2,\mathbf{SiF}_4$ is sparingly soluble in HCl.	None.
Phosphates (ortho-) ..	The alkaline phosphates only.	All other phosphates are soluble in acids.	None.
Pyrophosphates	Alkaline pyrophosphates.	All others.	None.
Metaphosphates	The alkaline and a few metallic metaphosphates.	Most others.	—
Silicates	Potassic and sodic silicates are mostly soluble.	Others are decomposed by acids, with separation of $\mathbf{Si}\mathrm{Ho}_4$. All silicates are decomposed by HF.	Many natural silicates. (Comp. p. 145.)
Borates	The alkaline borates. All others are difficultly soluble in water, but none are absolutely insoluble.	All borates dissolve in acids.	—
Cyanides	The cyanides of the alkali and alkaline earthy metals, as well as $\mathbf{Hg}\mathrm{Cy}_2$.	Most other (single) insoluble cyanides are readily decomposed by acids. (Comp. p. 151.)	AgCy is insoluble in dilute $\mathbf{N}\mathrm{O}_2\mathrm{Ho}$, but is decomposed by aqua regia.

Ferrocyanides	The alkaline ferrocyanides are readily soluble in water; the alkaline earthy ferrocyanides are difficultly soluble.	Most others are soluble in dilute acids (HCl). Comp. p. 157.) Prussian blue dissolves in oxalic acid.	Ag_4FeCy_6, insoluble in dilute $\mathbf{N}O_2Ho$, is decomposed by boiling with aqua regia.
Ferricyanides	The alkaline ferricyanides are readily soluble in water. The others are mostly difficultly soluble or insoluble.	Most others are insoluble in dilute HCl.	The ferricyanides, insoluble in acids, are decomposed by aqua regia. Both ferro- and ferricyanides are decomposed by boiling with KHo. (Comp. p. 156.)
Cobalticyanides	Cobalticyanides of K, Na, Ba, Sr, Ca, and Mg are soluble, also the salts of Fe^{iv}, Hg and Pb.	Most others are insoluble in acids (HCl).	Some (Cu and Ag) are insoluble in acids, but are decomposed by KHo.
Cyanates	The cyanates of the alkalies and alkaline earthy metals, also a few metallic cyanates, are soluble in water.	The few other cyanates which exist are decomposed by dilute $\mathbf{N}O_2Ho$.	—
Sulphocyanates	The sulphocyanates of the alkaline and alkaline earthy metals, also of Cu, Hg, Fe^{iv}, are soluble in water.	The few other characteristic sulphocyanates, *e.g.*, of $'Cu'_2$, Ag, $'Hg'_2$, and Pb, are more or less readily decomposed by acids ($\mathbf{N}O_2Ho$).	—
Formates	All formates are soluble in water.	—	—
Acetates	All acetates are soluble in water. (Argentic and mercurous acetates are difficultly soluble.)	—	—
Benzoates	Benzoates of K, Na, Ba, Sr, Ca, Mg, and of Mn, Zn, Fe'', are soluble in water.	Ferric, cupric, argentic, plumbic, mercurous and mercuric benzoates are soluble in acids.	—

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER, AND ACIDS—*continued.*

Names of Salts.	Soluble in Water.	Soluble in, or decomposed by Acids.	Insoluble in Water and Acids.
Succinates	Most succinates are soluble in water.	Succinates of Fe^{iv}, Cu, Ag, Hg, and Pb dissolve readily in acids.	—
Oxalates	The alkaline oxalates, as well as of Cr^{iv}; most others are difficultly soluble or insoluble in water.	All other oxalates are soluble in acids.	—
Tartrates	The normal alkaline tartrates are soluble in water, the acid less so than the normal salts.	The normal tartrates of the alkaline earths, earths and heavy metals are mostly difficultly soluble in water, but dissolve readily in mineral acids (HCl) and in tartaric acid.	—
Citrates	The alkaline citrates are soluble in water; most others are insoluble, or difficultly soluble.	Citrates insoluble in water dissolve readily in acids.	—
Arsenates and Arsenites ..	The alkaline arsenates and arsenites are soluble in water; most others are insoluble.	Arsenates and arsenites insoluble in water, dissolve in acids, and frequently also in ammonic salts.	None.
Chromates	The chromates of the alkalies, as well as of Sr, Ca, Mg, Zn, Mn, Fe^{iv}, Cu are soluble in water. Most others are insoluble.	All chromates insoluble in water dissolve in acids (in concentrated HCl, with evolution of chlorine, and in concentrated SO_2Ho_2, with liberation of oxygen).	Ignited plumbic chromate.

APPENDIX IV.

(A.) EXAMINATION OF A SIMPLE SALT.

Preliminary Examination for Base.

Substance given: white crystalline, readily soluble in water, reaction of solution alkaline.

Experiment.	Observation.	Inference.
Heated some of the powdered substance in a dry test-tube.	Gave off water; fused; was slightly blackened; gave off CO, burning with a blue flame.	Oxalate, formate.
Treated residue with water, and filtered. Tested with litmus paper.	The residue dissolved; the solution reacted strongly alkaline.	
Added dilute HCl. . . .	Effervescence, whilst before ignition the substance did not effervesce.	Alkaline oxalate.
Tested HCl extract on platinum wire in a Bunsen's gas flame.	Violet flame	Potassium.

Examination of Solution for Base.

Added HCl.				
No pp. Absence of Group I.	Added a solution of SH_2 to the same solution.			
	No pp. Absence of Group II.	To a *fresh* portion of the solution added AmCl, AmHo, and SAm_2.		
		No pp. Absence of Group III.	To the same solution added $COAmo_2$.	
			No pp. Absence of Group IV.	The solution may contain — MgO, OK_2, ONa_2. Tested a fresh portion of solution specially for K by adding HCl and $PtCl_4$, *yellow crystalline* precipitate. **Presence of K.**

PRELIMINARY EXAMINATION FOR ACID.

Experiment.	Observation.	Inference.
Treated a portion of the powdered substance with concentrated SO_2Ho_2.	CO and CO_2 given off, with slight blackening of substance.	
Passed gases into lime-water and applied a light to the unabsorbed gas.	White precipitate in lime-water; gas burnt with blue flame.	From decomposition of oxalate.

EXAMINATION OF SOLUTION FOR ACID.

Acidulated with HCl.	Acidulated with NO_2Ho.	Acidulated with $\left\{\begin{matrix}CH_3\\COHo\end{matrix}\right.$.
No precipitates.	No precipitates.	$CaCl_2$ a white pp. SO_2Cao'' ,, Presence of $\left\{\begin{matrix}COHo.\\COHo\end{matrix}\right.$

Found **Potassic Oxalate.**

(B.) EXAMINATION OF A COMPOUND SUBSTANCE.

PRELIMINARY EXAMINATION FOR BASES.

Compound given: a dirty white powder.

Experiment.	Observation.	Inference.
Heated some of the powdered substance in a dry test-tube.	Substance fused. Gave heavy white fumes, which condensed in the upper part of the tube.	Compounds of Am, Hg, As, etc.
	Gave off reddish-brown fumes and a gas which supported combustion. The residue was yellowish, whilst hot, dirty white, on cooling.	From decomposition of nitrates of Pb, Bi, etc.
Heated a portion of the substance, mixed with $CONao_2$, in a bulb-tube.	NH_3 given off. Mirror and metallic globules.	Am and Hg compounds.
Heated some of the powdered substance on charcoal before the blowpipe flame.	Substance gave off heavy fumes, and was partly reduced to the metallic state. The metal was malleable; the incrustation yellow.	Pb.
	A portion of the ignited mass appeared strongly luminous.	Alkaline earthy bases.

EXAMINATION OF SOLUTION FOR BASES.

Substance dissolved partly in water, partly in HCl with evolution of CO_2. On mixing the two solutions, acicular crystals of $PbCl_2$ fell out. Filtered off. Confirmed presence of lead by means of CrO_2Ko_2 or SO_2Ho_2.

<table>
<tr><td colspan="4">Passed a current of SH_2.</td></tr>
<tr><td rowspan="3">A black pp.</td><td colspan="3">Evaporated filtrate to dryness, with a few drops of NO_2Ho. Took up with dilute HCl. Added AmCl, AmHo, and SAm_2.</td></tr>
<tr><td rowspan="2">No pp.
Absence of Group III.</td><td colspan="2">To the same solution added $COAmo_2$.</td></tr>
<tr><td>A white pp.</td><td>On evaporating filtrate to dryness, and igniting, no fixed residue was left. Absence of Mg, K, Na.</td></tr>
</table>

EXAMINATION OF PRECIPITATE PRODUCED IN GROUP II.

<table>
<tr><td colspan="4">Washed precipitate till free from HCl, and boiled with SAm_2.</td></tr>
<tr><td colspan="3">Residue.—Boiled with NO_2Ho. Diluted with OH_2, and added dilute SO_2Ho_2, and methylated spirit. Filtered.</td><td rowspan="3">Solution.—Acidulated with dilute HCl. No yellow precipitate. Absence of As, Sb, and Sn.</td></tr>
<tr><td colspan="2">Residue.—Boiled in ammonic acetate, and filtered.</td><td rowspan="2">Solution.—SH_2 added to a portion of solution gave no precipitate. Absence of Bi, Cu, Cd.</td></tr>
<tr><td>Residue.—Dried and ignited in a bulb-tube, with dry $CONao_2$. Metallic mirror and globules. Presence of Hg.</td><td>Solution.—Added CrO_2Ko_2, yellow precipitate. Presence of Pb.</td></tr>
</table>

EXAMINATION OF PRECIPITATE PRODUCED IN GROUP IV.

Dissolved precipitate in a little dilute HCl. Tested a portion of the solution with SO_2Cao''—no precipitate, even after some time. **Absence of Ba and Sr.** Confirmed presence of Ca by adding to another portion of the solution AmHo and $\left\{\begin{array}{l}COAmo\\COAmo\end{array}\right.$. A white precipitate. **Presence of Ca.**

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
Treated with dilute HCl.	Effervescence. The gas precipitated lime-water.	CO_2.
Treated with concentrated SO_2Ho_2.	Cl and nitrous fumes.	HCl and NO_2Ho.
Confirmed HCl by heating substance with MnO_2, and SO_2Ho_2.	Chlorine evolved.	HCl.
Ditto NO_2Ho by means of SO_2Ho_2 and SO_2Feo''.	A brown ring was formed.	NO_2Ho.

EXAMINATION OF SOLUTION FOR ACIDS.

Prepared solution by boiling some of the powder with a solution of $CONao_2$; filtered and acidulated with—

HCl.	NO_2Ho.	$\left\{\begin{array}{l}CH_3\\COHo\end{array}\right.$	Neutral solution.
No precipitates.	NO_2Ago, white curdy pp., soluble in AmHo. **Presence of HCl.**	No precipitates.	No precipitates.

Found—Bases: HgO, PbO, CaO, OAm_2.
Acids: CO_2, NO_2Ho, HCl.

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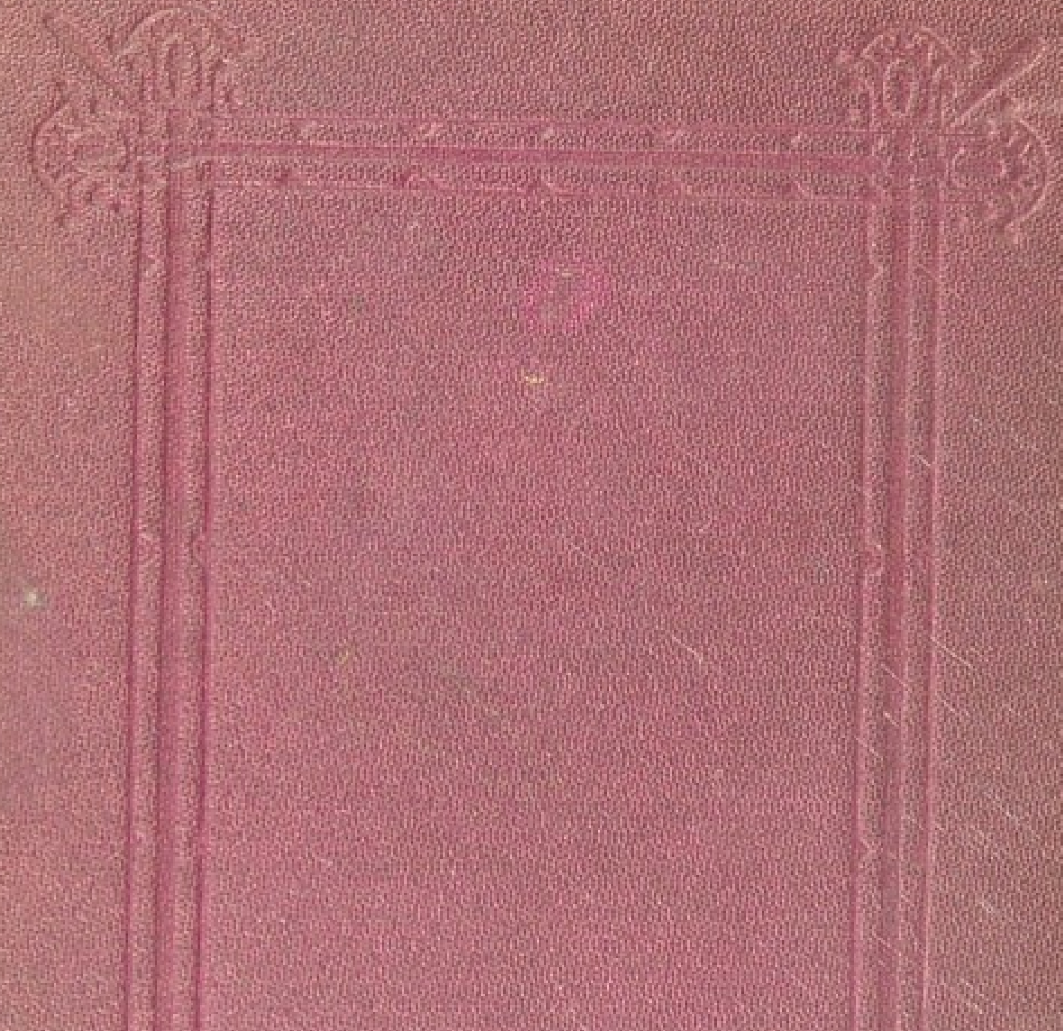[illegible] & Co., Printers, Great Windmill Street, Haymarket.