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JOHN VAN VOORST, 1 PATERNOSTER-ROW.

A MANUAL

OF

QUALITATIVE

CHEMICAL ANALYSIS.

A MANUAL

OF

QUALITATIVE CHEMICAL ANALYSIS.

BY

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PREFACE.

It has been the intention of the Authors, in writing the present work, to prepare a complete Manual of Qualitative Chemical Analysis for the use of Laboratory Students, while it is hoped that more advanced experimenters also will find in it ample information concerning the rarer subjects of research. In attempting to accomplish this double purpose, care has been taken to avoid perplexing the beginner with the descriptions of the less common substances; with this intention, such descriptions are printed in small type. The present volume is not an account of general chemistry, nor does it contain descriptions of the apparatus employed, or of technical processes; for information on these points, reference must be made to special treatises*: but it aims to be a complete and systematic Guide to Qualitative Analysis, and to represent the present condition of this department of chemical science.

To the following features of the present work the Authors would request the attention of Chemists, and of all those engaged in instructing pupils in Chemical Analysis:—

1. In the First Part of the volume, at the end of each group

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* Mr. C. Greville Williams's admirable work will afford the student every information concerning apparatus and manipulation, while Dr. Odling's forthcoming Manual will convey, on all points connected with theoretical and descriptive chemistry, the most exact and trustworthy information, and also an able explanation of the grounds upon which the system of notation and equivalents adopted in the present work is based.

of elements or salts, concise Tables are given, which show at a glance the most striking properties of the more common substances, as well as their most characteristic reactions.

2. The student is gradually accustomed to the use of chemical language, symbols, and formulæ, while, on the first mention of any new reaction, the equation representing it is clearly expressed, and the rationale of the process given.

3. In describing the salts and reactions of the various acid and basic radicals, *the same order is invariably preserved.* The monobasic salts come first, then the bibasic, and lastly the tribasic,—the basic elements commencing with those most decidedly positive.

4. If, in treating of any basic or acid-radical, a salt of characteristic properties is described, *the corresponding salt of all basic or acid-radicals subsequently spoken of is invariably noticed.*

5. The most characteristic compounds of each radical are printed in a conspicuous type.

6. Facilities are afforded for the progress of the student, in the simple analytical schemes appended to each group.

7. In the Second Part of the work, "The Method of Analysis" is described, ample directions and Tables being given,—while something is still left to the judgment of the pupil, who may frame tables for his own use from a study of the reactions, &c. detailed in Part I.

8. While the best methods of procedure in separations and testings are given, endeavour is made to impress on the student the necessity of an exact acquaintance with the nature of the processes concerned.

By such means as those which they have just indicated, the Authors trust that they have attained to some degree of unity and simplicity, as well as of completeness, in the present treatise.

The atomic weights employed in the present volume are those of Gerhardt,—the atomic weights of Oxygen, Sulphur, Selenium, Tellurium, and Carbon being doubled, and the atomic weights of all the other elements remaining the same as those usually adopted. These alterations have long been made by Continental chemists; in England they have been strongly advocated by Professors Brodie and Williamson and Dr. Odling; and they have quite recently received the sanction of a large portion of the eminent British chemists. May the Authors hope that their work will be found to supply, in some degree, that want of a suitable handbook of analysis which must be caused by these changes?

ERRATA.

Page 24, line 13 from bottom, *for* "anhydrous chloric acid, or chloric anhydride," *read* "the chloric radical."

,, 52, ,, 23, *for* "$H_2C_4H_4O_5$," *read* "$H_2C_4H_4O_6$."

,, 61, ,, 12, *for* "to dissolved," *read* "to be dissolved.

,, 65, ,, 20, *for* "$H_2C_4H_4O_5$," *read* "$H_2C_4H_4O_6$."

,, 66, ,, 3, *halve the equation.*

,, 96, ,, 15, *for* "soda," *read* "sodium."

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Notation and nomenclature adopted in the present work.		Ordinary notation.
ClCl	CHLORINE	Cl
HCl	hydrochloric acid	HCl
KCl	chloride of potassium	KCl
$MnCl_2$	bichloride of manganese	$MnCl_2$
HNO_3	nitric acid	$HO. NO_5$
$AgNO_3$	nitrate of silver	$AgO. NO_5$
CNCN *or* CyCy	cyanogen	C_2N
KCN *or* KCy	cyanide of potassium	KC_2N
KCNO *or* KCyO	cyanate of potassium	KO, C_2NO
KCNS *or* KCyS	sulphocyanide of potassium	KC_2NS_2
HH	hydrogen	H
HHO *or* H_2O	WATER	HO
HHO_2 *or* H_2O_2	binoxide of hydrogen	HO_2
KHO	hydrate of potassium	KO. HO
KKO *or* K_2O	oxide of potassium	KO
KKO_2 *or* K_2O_2	binoxide of potassium	KO_2
ClClO *or* Cl_2O	hypochlorous anhydride	ClO
HClO	,, acid	HO. ClO
KClO	hypochlorite of potassium	KO. ClO
HHS *or* H_2S	hydrosulphuric acid	HS
KHS	sulphydrate of potassium	KS. HS
KKS *or* K_2S	sulphide of potassium	KS
$HHSO_4$ *or* H_2SO_4	sulphuric acid	$HO. SO_3$
$KHSO_4$	sulphate of potassium and hydrogen	$KO. SO_3, HO. SO_3$
$KKSO_4$ *or* K_2SO_4	sulphate of potassium	$KO. SO_3$
HHHN *or* H_3N	AMMONIA	NH_3
HHHP *or* H_3P	phosphuretted hydrogen	PH_3
$HHHPO_4$ *or* H_3PO_4	phosphoric acid	$3HO. PO_5$
$NaHHPO_4$ *or* NaH_2PO_4	phosphate of 1-sodium	$NaO. 2HO. PO_5$
$NaNaHPO_4$ *or* Na_2HPO_4	phosphate of 2-sodium	$2NaO. HO. PO_5$
$NaNaNaPO_4$ *or* $Na_3 PO_4$	phosphate of 3-sodium	$3NaO. PO_5$

A MANUAL OF CHEMICAL ANALYSIS (QUALITATIVE).

PART I.—CHEMICAL REACTIONS.

CHAPTER I.

INTRODUCTION.

TERRESTRIAL matter has been found by the researches of chemists to be capable of resolution into about sixty-two elements or simple bodies; of these nearly half are of frequent occurrence, while the remainder are comparatively rare. Thus every substance met with in nature is either an element or a combination containing two or more elementary bodies, either mechanically or chemically blended. When it is desired to ascertain what simple bodies exist in any given form of matter, chemical analysis is resorted to.

The student who seeks to become fitted for this method of inquiry, should investigate carefully the chemical properties of the simple substances, since it is only by observations founded upon them that he will be able to distinguish the various constituents of the bodies that may be presented to him for examination.

Investigation into the chemical properties of the elements has shown that many of them are diametrically opposed to one another, and thus two great classes may be formed, characterized by the possession of most antagonistic properties: to one of the classes the term "basic elements" has been applied, and to the other that of "acid elements." These classes have also been named "metals" and "metalloids" respectively, as well as "electro-negative" and "electro-positive" elements. Attempts, however, at absolute classification fail, since it is found that some of the simple bodies occupy an intermediate position, and, strictly belonging to neither division, serve to connect the extremes together. To place them therefore somewhat in the form of an *arc*, is preferable to arranging them in two columns under distinct heads. Potassium (K) thus commences the list of basic elements, and chlorine (Cl) begins that of the acid elements; while the elements connecting the lower ends of the scales partake, to some extent, and in certain circumstances, both of the basic and acid character.

BASIC ELEMENTS.

Symb.	Name.	Equiv.
✓ K	Potassium	39·
✓ Na	Sodium	23·
✓ Li	Lithium	7·
Ba	Barium	68·5
Sr	Strontium	44·
Ca	Calcium	20·
Mg	Magnesium	12·
Y	Yttrium	?
E	Erbium	?
Tb	Terbium	?
✓ Ce	Cerium	47· ?
La	Lanthanum	47· ?
Di	Didymium	50· ?
Th	Thorinum	59·6
Zr	Zirconium	33·6
Be or Gl	Glucinum	6·9
✓ U	Uranium	60·
Al	Aluminium	13·7
Cr	Chromium	26·
✓ Fe	Iron	28·
Mn	Manganese	27·5
Co	Cobalt	30·
Ni	Nickel	29·
✓ Zn	Zinc	32·6
Cd	Cadmium	56·
✓ Cu	Copper	32·
✓ Ag	Silver	108·
✓ Hg	Mercury	100·
✓ Pb	Lead	103·5
✓ Bi	Bismuth	208·
Pd	Palladium	53·3
✓ Sn	Tin	58·
✓ Sb	Antimony	120·3
Pt	Platinum	98·7
R	Rhodium	52·2
Ru	Ruthenium	52·2
Ir	Iridium	99·
Os	Osmium	99·6
Au	Gold	197·
H	Hydrogen	1·
W	Tungsten	92·
Mo	Molybdenum	48·
V	Vanadium	68·6

ACID ELEMENTS.

Equiv.	Name.	Symb.
35·5	Chlorine	Cl.
✓ 80·	Bromine	Br
✓ 126·	Iodine	I
19·	Fluorine	F
16·	Oxygen	O
✓ 32·	Sulphur	S
79·	Selenium	Sc
128·4	Tellurium	Te
✓ 12·	Carbon	C
✓ 11·	Boron	Bo
✓ 22·	Silicon	Si
14·	Nitrogen	N
31·	Phosphorus	P
✓ 75·	Arsenic	As
184·	Tantalum	Ta
?	Pelopium	Pe
?	Niobium	Nb
25·	Titanium	Ti

Notwithstanding its want of strict correctness, a more arbitrary and absolute division into basic and acid elements is a very convenient one for analytical purposes; and in accordance with this classification, we will now proceed to consider the chemical properties of matter.

CHAPTER II.

THE BASIC ELEMENTS.

The bodies which constitute this class are those elements known by the name of metals, together with the gas hydrogen. The metals are for the most part solid bodies, although one, mercury, is liquid, and thus forms a link between the solid basic elements and the gaseous one, hydrogen. From its close resemblance to the other basic elements, this gas also is expected, if ever sufficiently condensed, to appear in the metallic form. The metals are characterized by peculiar physical properties, the chief of which are "metallic" lustre, and power of conducting heat and electricity; but the first of these properties, although frequently quoted as an unmistakeable proof of the metallic character of a body, is so dependent upon the state of aggregation of its particles, being entirely lost if the metal is reduced to a fine powder, as to be of little value; while the power of conducting electricity and heat is to be considered but doubtful evidence of metallic character. Chemical characteristics are the best criteria of the basic nature of a body; that is to say, it must possess properties powerfully opposed to those of the acid elements.

The great class of basic elements may be thus subdivided:—

1. Metals which are lighter than water (H_2O), and decompose it at common temperatures:—

Potassium = K. Sodium = Na. Lithium = Li.

2. Metals which are heavier than water (H_2O), and decompose it at common temperatures:—

Barium = Ba. Strontium = Sr. Calcium = Ca. Magnesium = Mg.

3. Metals, the majority of which expel hydrogen (H) from hydrochloric acid (HCl) at common or boiling temperatures:—

Yttrium = Y. Erbium = E. Terbium = Tb. Cerium = Ce. Lanthanium = La. Didymium = Di. Thorinum = Th. Zirconium = Zr. Glucinum = Gl. Uranium = U. Aluminium = Al. Chromium = Cr. Iron = Fe. Manganese = Mn. Nickel = Ni. Cobalt = Co. Zinc = Zn.

4. Metals, the majority of which do not expel hydrogen (H) from hydrochloric acid (HCl), even at the boiling temperature:—

Cadmium = Cd. Copper = Cu. Silver = Ag. Mercury = Hg. Lead = Pb. Bismuth = Bi. Palladium = Pd. Tin = Sn. Antimony = Sb. Arsenic = As. Platinum = Pt. Rhodium = R. Iridium = Ir. Ruthenium = Ru. Osmium = Os. Gold = Au. Tungsten = W. Molybdenum = Mo. Vanadium = V.

5. The gas Hydrogen = H.

SUBDIVISION I.

POTASSIUM, SODIUM, AND LITHIUM.

These metals possess a silvery lustre; they are of less specific gravity than water. They are very difficult of preparation, on account of their great affinity for oxygen, with which they are often found combined in nature. A bright surface of any one of these metals becomes immediately tarnished if exposed for a moment to the air, a combination with the atmospheric oxygen being effected. Under the influence of the same affinity they decompose water, which is a chemical compound of oxygen and hydrogen, combining with its oxygen and setting free its hydrogen.

I. **Potassium** = K. Potassium may be readily recognized by placing a small portion of it on the surface of water; the water is decomposed by the potassium, which becomes red-hot (a circumstance of frequent occurrence in chemical actions); the evolved hydrogen is then set on fire by the heated potassium, and burns with a violet flame, the colour being due to the presence of a small quantity of vaporized metal. Owing to its great tendency to combine with oxygen, potassium is always preserved under some liquid which contains none of that element: the liquid generally employed is Persian naphtha.

Potassium is a brilliant metal of bright silvery lustre; at the temperature of the air it may be cut with a knife, but at the freezing-point it is brittle; at 57°·7 C. it melts, and at a low red heat distils. Its density is only 0·865, the density of water being considered as 1·000.

II. SODIUM=Na. The metal sodium bears a remarkable resemblance to potassium. If placed upon water it acts upon it with the utmost energy, fuses, and rolls, as a red-hot globule, rapidly from side to side of the containing vessel; the heat, however, does not rise sufficiently to inflame the hydrogen evolved unless the movement of the metal be impeded or confined, as by placing it upon a moistened piece of paper, to a smaller area; the hydrogen is then kindled and burns with an orange-yellow flame, owing to particles of sodium being vaporized with it. Like potassium, sodium cannot be exposed to the air, and must be protected from it in a similar manner.

The lustre of sodium is as brilliantly white as that of silver; the metal is as soft as potassium at the ordinary temperature of the air, melts at 90° C., and distils at a lower temperature than potassium. Its specific gravity is 0·972.

III. LITHIUM=Li. This metal is far rarer than either of the two preceding; like them it decomposes water, but not with their extreme energy. If exposed to the air it combines with the oxygen, and is therefore kept out of contact with that element.

Lithium has the colour and brightness of polished silver; at common temperatures it is harder than potassium or sodium, but softer than lead; it is also capable of welding, *i. e.* of junction by pressure. It melts at 180° C., and cannot be distilled. It is the lightest of all solid bodies, its specific gravity being only 0·5936.

Metals which are lighter than Water, and decompose it at common temperatures.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.	Melting-point.
Potassium. .	K	39	bluish white	·865	57°·7 C.
Sodium . . .	Na	23	yellowish white	·972	90°
Lithium . . .	Li	7	white	·5936	180°

SUBDIVISION II.

BARIUM, STRONTIUM, CALCIUM, AND MAGNESIUM.

These metals are for the most part of a colour closely resembling that of gold: they are of greater specific gravity than water. To a powerful affinity for oxygen is superadded an incapability of volatilization by heat, which renders them still more difficult of preparation than the members of the preceding class. They tarnish in the air from formation of oxide, and decompose water, although not with the extreme energy of potassium, sodium, and lithium.

I. Barium=Ba. The metal barium decomposes water at the common temperature. It has a yellow colour.

II. Strontium=Sr. The metal strontium decomposes water at the ordinary temperature. It has a golden colour, and a specific gravity of 2·5418.

III. Calcium=Ca. The metal calcium decomposes water at the ordinary temperature. It is of a pale yellow colour, and its specific gravity is 1·5778. Its hardness approaches that of gold.

IV. Magnesium=Mg. The metal magnesium does not decompose water at the common temperature, but is oxidized by hot water. It is white, and has the specific gravity of 1·87.

Metals which are heavier than Water, and decompose it at common temperatures.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.	Melting-point.
Barium . . .	Ba	68·5	yellow	4·5?	red heat
Strontium . .	Sr	44·	yellow	2·5418	?
Calcium . . .	Ca	20·	pale yellow	1·5778	bright red heat
Magnesium .	Mg	12·	white	1·87	low red heat

SUBDIVISION III.

YTTRIUM, ERBIUM, TERBIUM, CERIUM, LANTHANIUM, DIDYMIUM, THORINUM, ZIRCONIUM, GLUCINUM, URANIUM, ALUMINIUM, CHROMIUM, MANGANESE, IRON, COBALT, NICKEL, ZINC.

These metals are either dull white, greyish white, or bluish white. Their specific gravity varies from 2·56 to 8·8. The majority of them are produced with as much difficulty as those of the second class; this additional disadvantage also attaches to some of them, that the substances of which they form part are themselves found in very small quantity. Iron and zinc are the most easily obtained, then nickel, cobalt and aluminium, next chromium and manganese, whilst the remainder are of extremely rare occurrence. Many among them are tarnished by exposure to the air, moist air exerting a far more powerful effect than air when dry. Some of these metals decompose water slowly at ordinary temperatures, expelling its hydrogen; but most of them evolve hydrogen from hydrochloric acid, combining with its chlorine. A new characteristic is to be remarked in this class of metals, viz. the power which some of them possess of being attracted by the magnet.

I. The first ten metals are almost unknown, and are not likely to fall into the hands of the student.

II. Aluminium=Al. The metal aluminium does not decompose water even in the slightest degree at the boiling temperature, nor does it tarnish in dry or moist air; if, however, it is heated in the air, it burns and becomes wholly converted into its oxide (Al_4O_3). This metal does not decompose water to which nitric or sulphuric acid has been added, but it acts readily upon hydrochloric acid, expelling the hydrogen and combining with the chlorine.

Aluminium is a white metal, but has a slightly bluish tinge; it is somewhat less brilliant than silver; it is malleable; it melts at a red heat. Its density is 2·56. It is not magnetic.

III. Chromium=Cr. The metal chromium behaves with water as aluminium; it does not oxidize in the air at ordinary temperatures, but at a red heat it absorbs oxygen readily from the air, and is converted into its oxide (Cr_4O_3). The accounts of its action on hydrochloric acid vary.

Chromium is a greyish-white metal, very brittle, and requiring the heat of the most powerful furnace for fusion. Its density is 8·9. It appears to become magnetic below the freezing-point.

IV. MANGANESE=Mn. The metal manganese decomposes water at the ordinary temperature, therein differing from the other members of the subdivision. It may naturally be inferred that it readily absorbs oxygen from the air also, and must for this reason be preserved under coal-tar naphtha. It of course expels the hydrogen from hydrochloric acid.

This metal is of a grey colour, but with little metallic lustre; it is brittle, and requires the heat of the wind-furnace to effect its fusion. Its density is 8·01.

V. IRON=Fe. The metal iron exerts a very slight action on water at a temperature of 50° or 60° C., but when exposed to the joint action of air and moisture it absorbs oxygen with great avidity, forming the oxide well known as rust (Fe_4O_3). On account of its tendency to combine with oxygen when moisture is present, it is always necessary to cover this metal when exposed to the weather with paint or some such substance, which may form a protective coat between it and the atmosphere. It decomposes hydrochloric acid with great readiness.

Iron has a peculiar grey colour and lustre, and a fibrous structure which confers great toughness. It has the property of welding at a white heat. It melts at 1550° C., and at a higher temperature volatilizes slightly. Its density is 7·87. This metal is powerfully magnetic.

VI. COBALT=Co. The metal cobalt decomposes water above the ordinary temperature, but not when cold, nor does it absorb oxygen from the air except when heated. It decomposes hydrochloric acid slowly.

It has a reddish-grey lustre, and, like iron, a somewhat fibrous structure. It melts at about the same temperature as iron. Its density is about 8·6. It is generally stated to be magnetic, although some doubts are entertained upon this point.

VII. NICKEL=Ni. The metal nickel bears a strong resemblance to cobalt. It does not oxidize in water or moist air at ordinary temperatures. It decomposes hydrochloric acid slowly.

It has a greyish-white lustre, and in structure resembles iron and cobalt. It melts at a temperature rather higher than the melting-point of iron. The density is 8·82. It is magnetic, but less powerfully so than iron.

VIII. ZINC=Zn. The metal zinc is a peculiar one, having but little in common with the four preceding, which all present a strong family likeness. It does not decompose water at the ordinary temperature, or remove oxygen from dry air. In moist air it becomes covered with a thin film of oxide, which protects the metal beneath. If heated in the air it burns with a greenish light, forming the oxide Zn_2O. It decomposes hydrochloric acid readily.

Its lustre is bluish white. It melts at 412° C., and volatilizes at a red heat. Its density is 6·9 after fusion, and 7·19 after compression by rolling. It is not magnetic.

Metals, the majority of which expel Hydrogen from Hydrochloric Acid at the common or boiling temperature.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity after fusion.	Melting-point.
Aluminium	Al	13·7	white	2·56	red heat
Chromium .	Cr	26·	greyish white	8·9	wind-furnace
Manganese .	Mn	27·5	grey	8·01	wind-furnace
Iron	Fe	28·	grey	7·87	1550° C.
Cobalt . . .	Co	30·	reddish grey	8·6	1550° ?
Nickel . . .	Ni	29·	grey	8·82	1600° ?
Zinc	Zn	32·6	bluish white	6·9	412°

SUBDIVISION IV.

CADMIUM, COPPER, SILVER, MERCURY, LEAD, BISMUTH, PALLADIUM, TIN, ANTIMONY, ARSENIC, PLATINUM, RHODIUM, RUTHENIUM, IRIDIUM, OSMIUM, GOLD, TUNGSTEN, MOLYBDENUM, VANADIUM.

The prevailing colour of these metals is white, one, however, copper (Cu) is red, and one, gold (Au), is yellow. Their specific gravity varies from 5·75 to 21·47. The greater number of them are very easily obtained from the compounds (ores) in which they exist in nature, and as these ores are tolerably abundant, they exert an important influence upon civilization. Those found in the largest quantity and obtained with the greatest ease are lead, copper, tin, silver, mercury, gold, bismuth, antimony, and arsenic; platinum and palladium are of rarer occurrence, and the remainder are very seldom met with. As a rule they do not, when exposed to the air, combine with its oxygen, or at the most become covered with but a slight film of oxide or tarnish; so comparatively slight indeed is their affinity for oxygen, that the oxides of many of them are decomposed by heat alone into metal and oxygen. As a class also they exert no action upon water or hydrochloric acid. These metals are not magnetic.

I. Cadmium = Cd. The metal cadmium does not decompose water at the ordinary temperature, and only slightly tarnishes upon exposure to air; it is nevertheless a very oxidizable metal at a higher temperature, and when heated in the air burns with the formation of an oxide (Cd_2O) of a brown or brownish-yellow colour. Hydrochloric acid acts upon it but slowly.

The colour of cadmium is white with a tinge of blue; it is soft and flexible, crackling like tin when bent; it is very fusible, melting below a red heat; it volatilizes somewhat below the boiling-point of mercury (360° C.), and its vapour has no odour. The density of the metal is 8·604 after fusion, and 8·694 after hammering.

II. Copper = Cu. The metal copper does not decompose water at the ordinary temperature, and but very slowly when raised to a high degree of heat. On exposure to moist air it tarnishes, and when heated in the air it absorbs oxygen and yields two oxides

(Cu_4O and Cu_2O); these, however, do not yield up their oxygen when further heated. Hydrochloric acid acts upon this metal with great difficulty.

Copper has a well known red colour; it is malleable; at about 788° C. it melts, and volatilizes sensibly at a very elevated temperature. Its density after fusion is 8·85, and after hammering 8·95.

III. SILVER=Ag. The metal silver does not decompose water, or withdraw oxygen from dry or moist air; if, however, it is heated in contact with air, at an elevated temperature it absorbs, or more properly, dissolves oxygen, but yields it up again on a further increase of heat. It is acted upon by hydrochloric acid with the greatest difficulty.

The peculiar lustre of silver is perhaps more beautiful than that of any other metal. It is very malleable. At about 1000° C. it melts, and volatilizes slowly at a very high degree of temperature. Its density is 10·47 after fusion, and 10·51 after hammering.

IV. MERCURY=Hg. The metal mercury does not decompose water at any temperature, nor does it combine with oxygen when exposed to dry or moist air; if heated in the air it combines with oxygen, forming the oxide (Hg_2O), which is again resolved into its constituents at a higher degree of heat. Hydrochloric acid is not decomposed by this metal.

The great peculiarity of mercury is its liquidity at common temperatures; at —40° C., however, it becomes solid, and at 360° C. it boils, and is converted into a colourless vapour. In lustre and colour it resembles silver, yet has a tinge of the blue-grey hue of lead. Its density is 13·59 at 4° C.

V. LEAD=Pb. The metal lead does not decompose perfectly pure water; it tarnishes slightly in moist air; if heated in the air it rapidly absorbs oxygen, and the oxide thus formed (Pb_2O) is not decomposed by heat alone into metal and oxygen. Hydrochloric acid acts upon this metal with great difficulty.

Lead is a metal of a bluish-white lustre, very malleable, melting at 334° C., and volatilizing to a considerable extent at high temperatures. Its density is 11·445, and increases slightly by hammering.

VI. BISMUTH=Bi. The metal bismuth appears not to decompose water if the latter is quite free from air; it tarnishes slightly in damp air; and if heated in the air is converted into its oxide (Bi_2O_3), which is not decomposed by heat. Hydrochloric acid acts upon it very slowly.

Bismuth is of a reddish-white colour, rather brittle; it melts at 247° C., and can be distilled at a very high temperature. Its density is 9·82, and is slightly diminished by compression.

VII. PALLADIUM = Pd. The metal palladium does not decompose water; it does not tarnish in the air unless heated, when a blue film of oxide appears on the surface which vanishes upon further heating: cold hydrochloric acid does not attack it.

Palladium is a metal of a greyish-white colour; it does not melt at the temperature of the blast-furnace. Its density is 11·3 after fusion, and 11·8 after hammering.

VIII. TIN = Sn. The metal tin does not decompose water, nor does it absorb oxygen from the air; heated in the air it forms an oxide which an accession of temperature does not decompose; it is but slowly attacked by hydrochloric acid in the cold.

Its brilliant white colour is well known; it is malleable, and melts at a temperature of 228° C. Its density is 7·291 after fusion, and 7·299 after rolling.

IX. ANTIMONY = Sb. The metal antimony does not decompose water or attract oxygen from the air at ordinary temperatures; heated in the air it oxidizes, and the oxide produced is not decomposed at an increased heat: cold hydrochloric acid acts upon it with extreme slowness.

It has a bluish-white colour, is very brittle, melts at 430° C., and has a density of 6·71.

X. ARSENIC = As. The so-called metal arsenic does not decompose water freed from air, nor does it absorb oxygen from dry air. It becomes oxidized by exposure to air and water, or to moist air only. When heated in the air it burns into an oxide not easily decomposable by heat. Hydrochloric acid is readily decomposed by this body.

The metal has a steel-grey colour, is very brittle, and volatilizes without melting at 300° C. Its density is 5·75.

XI. Platinum = Pt. The metal platinum does not decompose water except at a most elevated temperature; it does not absorb oxygen from the air at any temperature, nor does hydrochloric acid exert any action upon it.

Its colour is white with a tinge of grey. It is malleable, and possesses the property of welding at a white heat. It melts only at the temperature of the oxyhydrogen blowpipe. Its density is 21·16 after fusion, and 21·45 after hammering.

XII. The metals rhodium, iridium, ruthenium, and osmium are very rare, and are not likely to come in the way of the student.

XIII. Gold = Au. The metal gold does not decompose water, nor does it tarnish in the air or absorb oxygen from it at any temperature: it is wholly unattacked by hydrochloric acid.

Its rich yellow colour is well known. It melts at about 1200° C.; its ductility is very considerable. Its density is 19·2 after fusion, and 19·3 or 19·4 after hammering.

XIV. The metals tungsten, molybdenum, and vanadium are not likely to pass through the hands of the student.

Metals, the majority of which do not expel Hydrogen from Hydrochloric Acid, even at the boiling temperature.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity (after fusion).	Melting point.
Cadmium . .	Cd	56·	bluish white	8·604	below a red heat
Copper . . .	Cu	32·	red	8·85	788°
Silver	Ag	108·	brilliant white	10·47	1000°
Mercury . .	Hg	100·	bluish white	13·59	−40°
Lead.	Pb	103·5	bluish white	11·44	334°
Bismuth . .	Bi	208·	red	9·82	247°
Palladium. .	Pd	53·3	greyish white	11·3	oxyhyd. blowpipe
Tin	Sn	58·	brilliant white	7·291	228°
Antimony . .	Sb	120·3	bluish white	6·7	430°
Arsenic . . .	As	75·	steel grey	5·75	?
Platinum . .	Pt	98·7	greyish white	21·16	oxyhyd. blowpipe
Gold	Au	197·	deep yellow	19·2	1200°

SUBDIVISION V.

HYDROGEN.

The only member of this subdivision is the gas hydrogen, which, from the numerous chemical analogies which it bears to the metals, is expected, if ever condensed, to appear in the metallic form; its gaseous state at ordinary temperatures is no argument against this view, since it must be remembered that many of the metals, as mercury, zinc and sodium, are known as transparent gases at an elevated temperature; it has not yet, however, been condensed, and so the features which its liquid or solid forms may present are merely a matter of conjecture.

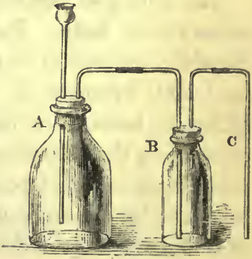
Hydrogen is an exceedingly abundant element, occurring in combination with oxygen as water; its affinity for this body and for chlorine is very great, as exemplified by the facts stated above, which show that only a few of the metals have, by reason of their superior affinity, the power of directly expelling hydrogen from these combinations.

Since hydrogen is a substance frequently employed in chemical operations, and as it differs in many material points from the elements of the same class which have been described, it is important that the student should prepare it and examine its properties.

It occurs in nature, as many of the metals do, combined with oxygen, and in this form of combination (H_2O) it constitutes a large part of terrestrial matter; it also occurs in commerce combined with various other elementary and compound bodies, forming a large class of substances to which the name of acids has been assigned, such as hydrochloric (HCl), sulphuric (H_2SO_4), and nitric acid (HNO_4); from any one of these compounds hydrogen may be set free by employing a suitable process, or in other words, by presenting to the hydrogen compound some substance which has a greater tendency to combine with that body with which the hydrogen is united than the hydrogen itself possesses. Thus, if potassium be added to water, hydrogen (H) and the substance called potash, or hydrate of potassium (KHO), are obtained; for, as the result of all the forces brought into play, the potassium acts just as if it had a greater tendency to unite with the oxygen than the hydrogen has, with which the oxygen is previously combined. And if, again, zinc is added to hydrochloric or to sulphuric acid, hydrogen is likewise, and for the same reasons, liberated, with the simultaneous production of chloride or sulphate of zinc, as the case may be. By one of these latter methods the student invariably isolates this element, using the apparatus shown in the accompanying diagram.

The hydrochloric acid and zinc are placed in the generator (A), and some water in the wash-bottle (B) for the purification of the gas; the delivery-tube (C) dips beneath the surface of some water in a basin, while the bubbles of hydrogen are caught as they issue in test-tubes previously filled with water, and inverted, with their mouths just below the level of the water in the basin.

Fig. 1.



The following observations and experiments should be made with this substance:—

Hydrogen is a transparent colourless gas, scarcely soluble in water, 1 volume of water dissolving only ·015 of a volume of hydrogen. When pure it is inodorous, but, as commonly prepared, it has a peculiar odour which is easily recognized. It does not combine with oxygen at common temperatures, but if a small portion only of the gas be highly heated by the application of a burning body, that part then combines with the atmospheric oxygen present, and the heat evolved by this chemical union is sufficient to raise another portion of the gas to the temperature at which this combination takes place; this is repeated until the whole of the hydrogen is converted into its oxide water (H_2O). Thus if a light be applied to the gas in a tube or other vessel having its mouth open to the air, a blue flame is seen to move slowly down till it reaches the bottom, marking, in fact, in its passage the surface of the unconsumed hydrogen.

The foregoing experiment may be so modified as to burn all the hydrogen at once; for this purpose it is only necessary to mix the gas thoroughly with half its bulk of oxygen and apply intense heat to any portion of the mixture, as by the application of a burning body; oxygen is then ready at every point to combine with the hydrogen; and so great is the heat evolved that the vapour of the water formed is expanded suddenly and immensely, and the result is an explosion. A less violent result is obtained by mixing air instead of oxygen with the gas; and by lighting either mixture in an open test-tube all unpleasant effects are obviated.

The density of this element, hydrogen, is less than that of any other known body. The density of gaseous bodies is, however, generally referred to that of air as a standard, and air being taken as 1·000, hydrogen is ·0692. This low density is well exemplified by taking two tubes which have been filled with the gas, uncovering their mouths, and holding one in its ordinary, and the other in an inverted position; from the former the gas may be shown to have escaped almost immediately, for on the application of a lighted taper a few seconds only after the uncovering, no ignition will take place; the second vessel will, however, retain its contents for a considerable length of time, for it will be found that the gas in it will take fire after the lapse of some minutes, on the approach of the lighted taper.

A peculiarity with regard to this gas is, that if burnt at a jet (formed conveniently of an upright tube with a fine point and small aperture, inserted in the cork of the washing-bottle figured above, instead of the ordinary delivery-tube), and a tube of about $\frac{3}{4}$-inch internal diameter be placed cautiously over the flame so as not to extinguish it, a variety of peculiar notes are produced, some of which are remarkably clear and musical.

All chemical reactions, or changes which take place when bodies act chemically upon each other, are rendered most distinctly intelligible by being placed in the form of an equation, and the student should familiarize himself with the method of so expressing them. Thus in the changes above alluded to as taking place in the production of hydrogen, the decomposition of water by potassium is clearly shown in the following manner:—

$$H_2O+K=\underbrace{KHO}_{\text{Hydrate of potassium.}}+H \qquad 2\left.\begin{matrix}H\\H\end{matrix}\right\}O+\left.\begin{matrix}K\\K\end{matrix}\right\}=2\left.\begin{matrix}K\\H\end{matrix}\right\}O+$$

In the same way the decomposition of hydrochloric or sulphuric acid by zinc may be exhibited:—

$$HCl+Zn=\underbrace{ZnCl}_{\text{Chloride of zinc.}}+H \qquad 2\left.\begin{matrix}H\\Cl\end{matrix}\right\}+\left.\begin{matrix}\overset{''}{Zn}\\\cancel{Zn}\end{matrix}\right\}=\cancel{2}\left.\begin{matrix}\overset{''}{Zn}\\Cl_2\end{matrix}\right\}+$$

$$H_2SO_4+2Zn=\underbrace{Zn_2SO_4}_{\text{Sulphate of zinc.}}+2H \qquad \left.\begin{matrix}\cancel{SO}^2\\H^2\end{matrix}\right\}O^2+\left.\begin{matrix}\overset{''}{Zn}\\\cancel{Hg}\end{matrix}\right\}=\left.\begin{matrix}\cancel{SO}^2\\Zn^1\end{matrix}\right\}O$$

CHAPTER III.

THE ACID ELEMENTS.

Under this title are comprehended the remainder of the elementary bodies. The acid elements are also sometimes termed "non-metallic elements" and "salt radicals." Although for the most part possessed of properties powerfully antagonistic to those of the basic elements, they do not all bear to each other the strong resemblance exhibited in the case of the latter class of bodies; they may, however, be arranged in subdivisions, each containing a few members which present among themselves many points of accordance. The state of physical aggregation in which these substances exist, is as varied as that which the basic elements present; the majority of them occur in the solid form, one, bromine, in the liquid, and several in the gaseous condition.

The class of acid elements may for convenience sake be thus subdivided:—

1. Bodies which, in combining with hydrogen, lose nothing of their acid character:—

Chlorine=Cl.} Bromine=Br. Iodine=I.} Fluorine=F.}
Cl I F

2. Bodies, the acid character of which is masked by combination with hydrogen:—

Oxygen = ~~O.~~ Sulphur = ~~S.~~ Selenium = ~~Se.~~ Tellurium = ~~Te.~~

3. Bodies which lose their acid character completely by combining with hydrogen:—

Carbon = C. Boron = Bo. Silicon = Si. Tantalum = Ta. Niobium = Nb. Pelopium = Pe. Titanium = Ti.

4. Bodies which acquire a basic character by combining with hydrogen:—

Nitrogen = N. Phosphorus = P. Arsenic = As.

SUBDIVISION I.

CHLORINE, BROMINE, IODINE, FLUORINE.

The three former of these substances are known, the fourth has never yet been isolated; they are possessed of the most energetic tendency to combine with the basic elements, and it is this obstacle which has always hitherto prevented the isolation of the last member of the group, fluorine. The intensity of their chemical attraction for the bodies most opposed in chemical character is well exhibited by the fact that many metals, upon simply being brought into contact with these substances, ignite, burning in the act of combination; and as may be readily supposed, the compounds thus formed are as difficult of decomposition as they are easy of production. The first member, chlorine, is a gas; the second, bromine, a liquid; and the third, iodine, a solid: fluorine is believed to be a gas. As will be seen hereafter, the three first members of this group exhibit a most singular family resemblance both in their chemical and physical properties, and it is generally thought that some far more intimate connexion subsists between them than any of which we are at present aware.

I. Chlorine = Cl. The non-metallic element, or salt-radical chlorine, is a gas at all ordinary temperatures and pressures, but under a considerably increased pressure it liquefies; no combination of cold and pressure has, however, yet proved capable of effecting its solidification.

Chlorine occurs in nature in combination with many of the metals, but its most abundant source is common salt, NaCl, which exists so largely in the sea and in extensive deposits in different parts of the earth.

From common salt, chlorine is frequently prepared by a method which consists essentially of two processes joined into one:—the mode of proceeding is to add sulphuric acid (H_2SO_4) to a mixture of black oxide of manganese (Mn_2O_2) and common salt (NaCl), and to apply heat, when chlorine is given off, and may be collected either over *hot* water or by displacement. For the better understanding of this process, the action may be supposed to be divided into two parts; the first consisting of the addition of sulphuric acid (H_2SO_4) to chloride of sodium (NaCl): here a simple interchange between the basic and acid elements occurs, the result being the production of sulphate of soda (Na_2SO_4) and hydrochloric acid (HCl), thus—

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl;$$

and the second action being that of the black oxide of manganese, Mn_2O_2, upon the hydrochloric acid, the final result being represented thus—

$$Mn_2O_2 + 4HCl = 2MnCl + 2H_2O + 2Cl.$$

A very usual way of preparing chlorine is by performing the latter only of the processes given above, that is, to commence with Mn_2O_2 and HCl, hydrochloric acid being a cheap article of commerce. The student will do well to prepare chlorine by both methods, and to observe the following properties of the gas, collecting it both by displacement and over warm water:—

(α) It has a peculiar yellowish-green colour, whence its name; it has also a peculiar unmistakeable odour: both of these characters it imparts to water when dissolved in that liquid.

(β) It has the property of bleaching almost all animal and vegetable colours; the presence, however, of a trace at least of water is necessary before submitting the coloured substances under examination to the action of the gas.

(γ) It exerts a very singular action on some bodies containing carbon and hydrogen, by reason of its tendency to combine with their hydrogen, forming hydrochloric acid, their carbon being consequently set free as soot: this is well shown by the introduction of paper dipped in turpentine, or of a lighted taper, into a jar of chlorine.

(δ) It imparts no colour to starch-paste.

The specific gravity of chlorine gas is 2·44; being thus much heavier than atmospheric air, it may be collected in vessels filled with that fluid, by allowing it to issue from a delivery-tube at the bottom of the jar to be filled; in virtue of its superior density it immediately occupies the floor of the jar or bottle, and, gradually rising, buoys up the air upon its surface, until it finally expels it wholly.

Chlorine gas is soluble in cold water; its maximum solubility is in water at 8° C., 1 volume of water at that temperature dissolving 3·04 volumes of the gas; at 50° C., 1 volume dissolves only 1·09 volume; and at 100° C., the temperature of boiling water, it dissolves nothing. In collecting chlorine over water, then, the temperature of the latter is an important point.

As a chemical agent, chlorine is among the most powerful with which we are acquainted, its affinity for the basic elements being so great, that many metals when introduced into the gas in the form of leaf or fine powder, burst into flame from the great energy of their chemical combination: the basic element hydrogen also, when mixed with this gas and exposed to the bright light of the sun or of the voltaic arc, explodes from the same cause. By reason of these powerful affinities it is a very dangerous gas to breathe, since the fine structure of the lungs is very liable to injury from exposure to energetic chemical agents.

II. **Bromine** = Br. The non-metallic element, or salt-radical bromine, is a reddish-brown liquid, boiling at 63° C., and becoming solid at —22° C.

Bromine is an element of somewhat rare occurrence in nature; it is chiefly found in combination with sodium (Na), magnesium (Mg), and calcium (Ca), in sea-water and some mineral springs, and more rarely as the mineral, bromide of silver (AgBr). The method for its isolation is the same as that adopted in the case of chlorine; hydrobromic acid being at first set free, is immediately decomposed by black oxide of manganese, Mn_2O_2, which oxidizes its hydrogen, liberating the bromine, which condenses in the liquid form: by this process the student should prepare a small quantity of bromine and observe—

(α) Its physical characters, such as its colour, odour, great volatility, and its solubility in water.

(β) Its bleaching power, somewhat inferior to that of chlorine.

(γ) Its far less powerful action on hydrocarbons.

(δ) That, when brought into contact with starch-paste (made by boiling starch in water), it produces a beautiful series of colours, varying from pale yellow to the richest orange, according to the amount of bromine present.

In the liquid state bromine has a density of 2·966, in the gaseous, of 5·39.

One part of water at 15° C. dissolves ·03003 of liquid bromine. The bromine escapes from its aqueous solution on heating, just as chlorine does.

Bromine is a substance which, in its chemical relations, bears a striking resemblance to chlorine, forming compounds with the various metals possessed of chemical and physical properties almost identical with those of the chlorides. What we, for convenience sake, call the power of chemical attraction, is, however, less between the bromine and the basic element than that manifested by chlorine, which latter element consequently, in many circumstances, removes bromine from its combinations, taking its place. Bromine vapour, although not so injurious to the human organism as chlorine, nevertheless, if breathed in any quantity, acts very detrimentally; and the liquid bromine, if left in contact with the skin, produces a wound very difficult to heal.

III. Iodine=I. The non-metallic element, or salt-radical iodine, is a solid at ordinary temperatures, of a metallic grey colour, and somewhat resembling in appearance the substance known as plumbago or black-lead. Iodine crystallizes in rhomboidal plates, and also in rhombic octahedra, which belong to the same system.

Iodine occurs in nature associated with bromine and chlorine, in the waters of the sea and of various mineral springs, being chemically combined with sodium (Na), calcium (Ca), and magnesium (Mg): it is also sometimes met with combined with silver (Ag). Its great source, however, is the ash obtained by burning sea-weeds: these plants extract the very minute quantity of iodine contained in sea-water, and by continually storing it up in their organisms, succeed in accumulating, comparatively speaking, so large a quantity of iodine as to repay the cost of extraction. It is prepared in precisely the same manner as the two former elements, hydriodic acid being in the first place produced and immediately submitted to the action of black oxide of manganese ($Mn_2 O_2$). The student should prepare a small quantity of iodine by acting with sulphuric acid ($H_2 SO_4$) and $Mn_2 O_2$ upon some iodide of potassium, and observe—

(*a*) Its physical characters both in the solid and gaseous condition, its colour and odour, the crystallization of the solid iodine from the vapour on cooling, and its solubility in water.

(β) Its bleaching power, far feebler than that of chlorine or bromine.

(γ) Its comparatively feeble action on hydrocarbons.

(δ) The very fine and characteristic blue colour which is produced when iodine and starch-paste are mixed.

Iodine melts at the temperature of 107° C., and boils at 180° C., but it passes into the gaseous state long before it reaches its boiling-point, appearing as a violet vapour of exquisite colour. Its density in the solid state at 17° C. is 4·948, and in the gaseous condition 8·716.

Iodine is less soluble in water than bromine, one part of water dissolving ·007 of its weight of iodine.

This element bears a strong general likeness to the two preceding elements in its chemical characters; it also resembles them in odour, &c. Its chemical affinities are, however, weaker than those of bromine, and it is displaced from its combinations by that element, just as bromine itself is expelled by chlorine.

IV. Fluorine=F. The non-metallic element, or salt-radical fluorine, has not yet been isolated.

Bodies which in combining with Hydrogen lose nothing of their acid character.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.	Melting-point.	Boiling-point.
Chlorine . .	Cl	35·5	V.* greenish yellow L. yellow	V. 2·44 L. 1·33	... ...	... ...
Bromine . .	Br	80·	V. red L. red-brown	V. 5·39 L. 2·966	−22° C.	63°
Iodine. . . .	I	126·	V. violet S. blue-black	V. 8·716 S. 4·948	107°	180°

SUBDIVISION II.

OXYGEN, SULPHUR, SELENIUM, TELLURIUM.

All these substances are known, and can be easily isolated; the two former in fact occur in great abundance, and nearly pure in nature. They are very slightly inferior to the former group in their power of uniting with the basic elements, and when thus combined, they form compounds which are difficult of decomposition. The first member of this subdivision, oxygen, is a gas; the other three are solids, at common temperatures. As a family, they bear almost as strong a resemblance to each other as do the members of the first subdivision. One remarkable feature, however, must be noticed with regard to oxygen and sulphur, the two most abundant elements of this group,—bodies whose properties have been very thoroughly investigated. These elements enjoy the power of combining, not only with basic elements, but also with nearly all bodies of their own class: oxygen, *e.g.*, forms chemical compounds with every known simple substance except fluorine, and when it combines with an acid element, the resulting compound, as might naturally be expected, possesses in a marked degree the characteristic acid properties of its two constituents.

I. Oxygen = O. The non-metallic element, or salt-radical oxygen, is a gas at all known temperatures and pressures.

---

* V.=vapour; L.=liquid; S.=solid.

The great reservoir of this gas is the atmosphere, of the total volume of which it constitutes one-fifth; and by reason of its power of combining with every other known element, fluorine only excepted, it is also an abundant constituent of the earth's crust. It is the presence of this substance which fits the air for the support of animal life: the pure gas inhaled into the lungs does not prove poisonous.

The simplest method of isolating this element is by heating some compound in which it exists not very closely combined, for the action of heat is often one of decomposition; and thus if we select a combination of mercury (Hg) with oxygen (O), oxide of mercury (Hg_2O) in fact; or of silver (Ag) with oxygen (O), oxide of silver (Ag_2O); we shall find that these bodies will split into metal on the one hand, and into oxygen gas on the other, by the simple elevation of temperature. If we employ a still higher degree of heat, other oxides, such as that of manganese (Mn_2O_2), will be found to part with a portion of their oxygen. But the most usual method is to heat the substance known as chlorate of potassium ($KClO_3$), which is a compound containing the basic element potassium (K), united to an acid body called a compound salt-radical, and composed of two acid elements, namely, chlorine (Cl) and oxygen (O), in the proportion of three equivalents of oxygen to one equivalent of chlorine. This compound is called anhydrous chloric acid, or chloric anhydride. When chlorate of potassium ($KClO_3$) is heated, the 3O are expelled, and the compound called chloride of potassium (KCl) remains, according to the following equation—

$$KClO_3 = KCl + 3O.$$

This is the method which the student should employ in the preparation of this element. The following properties of oxygen gas are to be noticed:—

(α) It is without colour and odour, and does not perceptibly dissolve in water.

(β) It does not exert a bleaching power like chlorine.

(γ) A taper or match just blown out, but with the wick still glowing, is immediately rekindled when plunged into this gas, and burns with much increased brilliancy and rapidity; this is the most common test for the presence of oxygen.

(δ) A piece of sulphur (S), ignited in the air, burns with much increased brilliancy when placed in this gas. The same effect is observed, though in a still more marked degree, in the case of phosphorus (P). Carbon (C), too, burns with great energy, and so also does the metal iron (Fe), when plunged while red-hot into a jar of oxygen.

The specific gravity of oxygen gas is 1·1057. It is slightly soluble in water, 1 volume dissolving ·035 of a volume of the gas; this very trifling solubility does not interfere with its being collected over water, which is by far the most convenient method of storing gases. In the free state it is not so energetic a chemical agent as chlorine and its congeners, at least at common temperatures, a few rare cases excepted; but when its temperature is raised, it combines with both basic and acid elements with perhaps greater energy than chlorine itself, and forms compounds of similar or nearly equal stability. These compounds are readily produced by heating the substance whose combination with oxygen we are desirous of obtaining, before their introduction into that gas; a union immediately begins, the temperature of the heated body is very much augmented, and a brilliant light is frequently kept up until the supply either of the oxygen or of the substance introduced is exhausted. Very striking effects are obtained by the combustion of heated iron, sulphur, carbon and phosphorus in this manner.

II. Sulphur=S. The non-metallic element, or salt-radical sulphur, is a solid at ordinary temperatures.

This element is met with, uncombined, in extensive deposits which abound in volcanic districts; its great European source is Sicily. It is also largely diffused through the earth's crust in combination with various metals, and occurs in almost all waters in the form of sulphates, and in some springs as sulphuretted hydrogen (H_2S). The great abundance of sulphur in the uncombined state renders it almost wholly unnecessary to extract it from any of its compounds; it is, however, sometimes obtained as a kind of bye-product in the manufacture of other substances.

Native sulphur is purified by simple distillation, and then sent into commerce. The student should observe with this substance:

(α) Its physical properties, colour, fusibility, and volatility.

(β) Its power of combining, when heated, with the atmospheric oxygen.

(γ) Its power of combining with metals (such as copper [Cu]) when they are plunged into its vapour.

The specific gravity of sulphur in its ordinary solid form is 2·087; it melts at 120° C., and boils at 440°, becoming at that temperature a transparent gas of an orange colour, with a specific gravity of 6·654. Between, however, the temperatures of melting and ebullition, sulphur undergoes very peculiar changes of consistence, becoming up to the temperature of 260° C. more viscous, instead of more fluid, with each augmentation of heat. If sulphur thus heated be suddenly cooled, it presents none of the original features of the substance before fusion, as seen in the following comparison. Ordinary sulphur is yellow, this is brown: ordinary sulphur crystallizes well either in acute rhombic octahedra or in long rhombic prisms, while this presents no trace of crystalline structure: ordinary sulphur is extremely brittle, this is as elastic as india-rubber. The present instance is the first which has been hitherto brought under the student's notice of an element existing in two forms or distinct states, but some of the elements shortly to be considered exhibit this peculiarity even more distinctly. To this phenomenon the term *allotropy* has been assigned. There are several other *allotropic* modifications of sulphur in addition to those just described. As a chemical agent sulphur is less energetic than oxygen, but it must not be forgotten that the solid form in which it usually exists is an obstacle to powerful chemical action; this is shown by the fact that sulphur in the gaseous condition combines energetically with many metals, which become red-hot in the act of combination; it can be considered therefore only slightly inferior to oxygen in chemical energy.

III. Selenium = Se. The non-metallic element, or salt-radical selenium, is of comparatively rare occurrence; in most of its physical and chemical properties it strongly resembles sulphur. Its ordinary form is that of a reddish-brown solid, with a somewhat metallic lustre. It fuses at 100° C., and if heated beyond this point and suddenly cooled, yields a viscous allotropic modification similar to that of sulphur. Selenium boils at a low red heat, and is converted into a yellow vapour. In its chemical properties it resembles sulphur still more closely, if possible, than in its physical characteristics.

IV. Tellurium = Te. The non-metallic element, or salt-radical tellurium, is even rarer than selenium; it occurs in nature combined with certain metals. In its physical properties it assimilates closely to the basic elements, but in its chemical tendencies it is allied to sulphur and selenium. It is white with a metallic lustre, crystalline, brittle, and has a density of 6·2. It is rather more fusible than antimony, and volatilizes at a red heat.

Bodies, the acid character of which is masked by combination with Hydrogen.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.	Melting-point.	Boiling-point.
Oxygen ...	O	16·	(colourless)	V. 1·1057	...	...
Sulphur ...	S	32·	V. L. S. yellow	V. 6·654 S. 2·087	120° C.	440°
Selenium ..	Se	79·	V. yellow S. red-brown	S. 4·3	100°	low red heat
Tellurium.	Te	128·4	dull white	6·26	low red heat	red heat

SUBDIVISION III.

CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, TITANIUM.

The first three bodies are all known in the isolated state; they are comparatively destitute of affinity for the basic elements;

carbon, however, is an exception, as it has a very powerful tendency to unite with hydrogen, a union which takes place in many proportions; it also combines with the metals. They all combine with oxygen, like the members of the two preceding classes, to form compound salt-radicals or acid bodies. In many of their characters these three elements bear a strong family resemblance to one another. They are all solids. The remaining four elements of this group are of very rare occurrence.

I. CARBON=C. The non-metallic element, or salt-radical carbon, is a solid at ordinary temperatures.

There is no element which enters into so large a number of compound bodies as carbon. It forms a great part of the organic world, the animal and vegetable kingdoms; and organic chemistry includes the history not only of all the compounds of carbon occurring in nature, but also of a countless host of such compounds produced from time to time by artificial aid. Carbonic acid (CO_2), a combination of carbon and oxygen, is the great reservoir of this element; and just as marine plants withdraw iodine (I), as we have seen, from sea-water, so does terrestrial vegetation remove carbonic acid (CO_2) from its reservoir the atmosphere (in which, however, it exists in small proportion), decomposes it, and accumulates the carbon in various forms of combination with hydrogen, nitrogen, and oxygen. Since many animals live on plants, and carnivorous animals prey on the herbivorous, the whole organized world is thus supplied with the necessary carbon. The carbon is restored to the atmosphere by various processes of civilized life, but especially by the respiratory process going on in the animal organism. The great deposits of coal which occur in many parts of the earth's crust are chiefly combinations of carbon with hydrogen, but they also contain some nitrogen, oxygen, and small quantities of other bodies; they result from the gradual decomposition of vegetable matters out of contact with air.

Carbon, as it usually occurs, is infusible, inodorous, and cannot be distilled. It exhibits allotropy in a more marked degree even than sulphur or selenium, occurring in three very distinct modifications. The first form, known as diamond, is transparent—the hardest of all bodies—and magnificently crystalline, the crystals, which are octahedra, having a density of 3·35: in the second condition carbon presents itself in the form of hexagonal plates, of bluish-black metallic lustre, soft and unctuous to the touch, with a specific gravity of 1·9 to 2·3; this second form is known as plumbago, black-lead, and graphite; while the third variety is densely black, without lustre or any trace of crystalline structure; it occurs in numerous varieties of anthracite, charcoal, jet, and gas-coke, and in soot, lamp-black, &c. In this third form carbon has a specific gravity varying greatly in different cases. The first variety, or diamond, is termed α-carbon; the second, β-carbon; and the third, γ-carbon.

The peculiar characteristics of the different kinds of carbon mentioned above are well known: the great brilliancy of the diamond,—the unctuous feel of graphite,—the rich black and considerable hardness of jet, anthracite, or cannel coal,—the dense, heavy and compact structure of the coke from gas-retorts,—the very light spongy texture of wood-charcoal, and the pulverulent lamp-black, are familiar to every one. There is, however, one property which the student should observe with regard to wood-charcoal especially, viz. its power of absorbing and retaining gases; one volume of this substance absorbing of ammonia, for instance, 90 volumes; of carbonic acid, 35; and of oxygen, 9 volumes.

As a chemical agent carbon has little power, possessing as it does, but a slight tendency to combine with other elementary bodies, oxygen and sulphur excepted. The chemist has therefore little influence in effecting artificial combinations between carbon and other bodies directly. Nevertheless there is no element which plays a more active or universal part in the chemistry of nature than carbon.

II. Boron = Bo. Of the non-metallic element, or salt-radical boron, but little was known until recently. It resembles carbon in being tasteless and odourless, and in being, if at all volatile, but doubtfully so. Boron differs from carbon by being soluble to a slight extent in water, and by not forming compounds with hydrogen, hydrogen and oxygen, or hydrogen, oxygen, and nitrogen (N), in the same way as carbon. It occurs in nature combined with oxygen. Boron, like carbon, may be obtained in three distinct forms. The first variety, or *diamond* of boron (α-Bo), is a brilliant and extremely hard substance, crystallizing in acute octahedra; the second resembles graphite or plumbago most closely in its appearance, and is termed *graphitoidal* boron, or (β-Bo), while the third variety has no trace of crystalline structure, but is a soft brown powder (γ-Bo).

III. SILICON = Si. The non-metallic element, or salt-radical silicon, has been recently investigated. In most of its properties it resembles boron, and like that element, occurs in three allotropic forms, the *octahedral*, the *graphitoidal*, and the *amorphous*.

IV. The other four bodies which are placed in this group, on account of a certain resemblance which they bear to silicon in some physical and chemical characters, are of very rare occurrence; titanium is met with more frequently than the others. They stand, together with vanadium, molybdenum, tungsten and arsenic, on the neutral ground between the basic and acid elements.

Bodies which lose their acid character completely by combination with Hydrogen.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.
Carbon	C	12	D.* (colourless) G. metallic blue-black A. black	D. 3·3 to 3·5 G. 1·9 to 2·3 A. ?
Boron.........................	Bo	11	D. (colourless) G. metallic blue-black A. black	D. ? G. ? A. ?
Silicon	Si	22	D. (colourless) G. metallic blue-black A. brown	D. ? G. 2·49 A. ?

* D. refers to the *diamond* form of the element; G. to the *graphitoidal*; A. to the *amorphous*.

SUBDIVISION IV.

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY.

These four bodies form a very peculiar group, the members of which are linked together by close chemical similarities, although differing greatly in their physical character: nitrogen, for instance, is a gas which has never been condensed; phosphorus is a solid occurring in two allotropic forms; and arsenic is a substance frequently classed among the metals. For the true metallic elements these substances have little affinity, although they do combine with some of them, especially with the more energetically basic; but for hydrogen they have a greater chemical attraction, uniting with three equivalents of that substance to form gases which partake in a greater or less degree of the basic character of the hydrogen. Perhaps the most striking compounds they yield are those with oxygen, with which element these radicals unite in several proportions; the combinations which contain three or four equivalents of oxygen being most energetic compound acid-radicals.

I. Nitrogen = N. The non-metallic element, or salt-radical nitrogen, is a gas at all known temperatures and pressures.

It forms four-fifths of our atmosphere, in which it is commonly said only to subserve the end of diluting the oxygen, and preventing it thus from exerting too violent an action on the animal respiratory organs, and the processes of combustion which are continually taking place upon the earth's surface; but it is probable that it plays another very important part in nature's economy, and that the vegetable world has the power of withdrawing it in some manner from the atmosphere, and consolidating it in the various organisms in which it occurs combined with carbon, hydrogen, and oxygen.

This element is prepared directly from the air, in which it exists merely mechanically mixed, not chemically combined, with oxygen, by removing the latter; this is done by the introduction of a substance capable of combining with the oxygen, leaving meanwhile the nitrogen unabsorbed; there is no difficulty in finding such an agent. If the metal copper (Cu), *e.g.*, be heated in a tube and atmospheric air passed over it, the copper withdraws the oxygen, so that the gas collected at the delivery-tube is pure nitrogen. Or, again, if a portion of air be confined in a jar over water and a piece of sulphur (S) or phosphorus (P), contained in a cup floating on the liquid, be ignited by a red-hot wire, the sulphur or phosphorus in burning combines with the oxygen, leaving the nitrogen free: the oxygen compound of sulphur (or phosphorus) formed is absorbed and dissolved by the water. By this second method the student had better prepare some nitrogen, and notice—

Fig. 2.

That any substance which burns in the atmosphere is immediately extinguished upon being plunged into this gas, simply because it is no longer in contact with an element with which it can combine.

The gas nitrogen has a specific gravity of ·972; it is less soluble in water even than oxygen, water dissolving only ·016 of its volume. Its chemical actions in the free state are so feeble, that nitrogen is commonly chosen as the type of chemical indifference; the elements for which it seems to have considerable affinity are potassium (K), sodium (Na), &c., hydrogen (H), carbon (C), and oxygen (O); but unlike most of the other elements which have passed under review, nitrogen is not known to combine with any other element *directly*; the only exceptions to this behaviour are in the cases of titanium (Ti), and perhaps of boron (Bo). Titanium combines with nitrogen with the utmost avidity, precisely in the same way as the metals with oxygen or chlorine, &c.

II. Phosphorus = P. The non-metallic element, or salt-radical phosphorus, is a solid at the ordinary temperature.

Phosphorus, oxidized as phosphoric acid, is very widely distributed throughout nature, although it occurs in small quantities. It is found in most rocks and soils; from thence it passes into the various vegetable organisms, these in their turn supplying it to animals, to whom it is strictly essential for the formation of their skeleton.

The bones of animals, which contain, after calcination and removal of the organic constituents, 77 per cent. of *phosphate* of calcium, constitute the great source whence phosphorus is obtained. They are digested with sulphuric acid (H_2SO_4), which removes the greater part of their calcium as sulphate of calcium (Ca_2SO_4), leaving an acid phosphate of calcium (CaH_2PO_4). This, when thoroughly dried and then ignited, is intimately mixed with one-fourth its weight of wood-charcoal, the mixture being afterwards placed in an earthen retort and strongly heated. Part of the oxygen of the phosphate of calcium is removed by the carbon, and phosphorus distils over. The annexed equation expresses this decomposition symbolically:—

$$4(CaPO_3)+5C=5CO+Ca_4P_2O_7+2P.$$

Air is of course carefully excluded in this experiment.

The student should examine the following properties of phosphorus:—

(α) Its "phosphorescence," the lambent greenish-blue light which it exhibits when exposed to the air in a dark place.

(β) Its ready fusibility: for this purpose a small piece should be placed in a flask, then be covered with water, and afterwards heated gently.

(γ) Its ready inflammability when heated in the air.

(δ) Its inflammability even under water, if melted and supplied with sufficient oxygen. For this experiment a few small pieces of phosphorus are to be placed at the bottom of a beaker in contact with some crystals of chlorate of potassium ($KClO_3$) (a salt which was mentioned when treating of oxygen). The fragments are then to be covered an inch or two deep with water, and afterwards sulphuric acid (H_2SO_4) poured upon them by means of a funnel-tube, so as to reach the chlorate before dilution with the water. The chloric acid thus set free ($HClO_3$)

being a body which parts readily with its oxygen, is at once decomposed by the phosphorus, which burns vividly with formation of phosphoric acid.

Phosphorus, as it usually occurs, is a solid having the density of 1·83; it melts at 44° C., and boils at 290°, forming a vapour the density of which has been found to be 4·355. Phosphorus is insoluble in water, but excessively soluble in bisulphide of carbon (CS_2). Its affinity for oxygen is so very great, that if exposed to this gas it gradually combines with it, becoming converted into oxide; and if the temperature be but slightly raised, this affinity increases so greatly that the phosphorus enters into combustion. This element presents the peculiarity which has been stated to belong to sulphur, carbon, boron, and silicon, namely, that of *allotropy*, and which oxygen also probably presents, since *ozone* seems to be only a modification of that element. If the ordinary phosphorus is exposed to a heat of 215°—250° C. out of contact with the air, it becomes converted into the second variety (β-P), which, by further heating to the temperature of 260° C., may be reconverted into the original form. The differences between these two forms of the element are these:—ordinary phosphorus (α-P) is a wax-like solid, translucent and nearly colourless; its specific gravity is 1·83, and it combines with oxygen at 75° C. with inflammation, and is phosphorescent at ordinary temperatures; while the second variety (β-P) is a red uncrystallizable solid with an almost metallic lustre on the fractured surface, with a specific gravity of 2·089, and admitting of exposure to atmospheric air without combining with its oxygen, unless heated to 260°, the point at which the ordinary modification is regenerated; it is not in the least degree phosphorescent. A third variety of phosphorus (γ-P) has been obtained by heating ordinary phosphorus considerably higher than its melting-point, and then suddenly cooling it. In this state it is black, but will recover its former translucence, &c. when fused and slowly cooled.

III. Arsenic = As. The non-metallic element, or salt-radical arsenic (for so we may venture to call it, although since it has some claims to be considered a basic element we have already, in Chap.

II., mentioned it among those bodies), is a solid at the ordinary temperature.

Arsenic is sometimes found in a pure state in nature, but more frequently associated with metals, such as iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), &c.; it is obtained in the form of an oxide by heating these compounds in a current of air, and from this the arsenic is separated by the action of carbon.

The student should observe—

(α) The volatility of this substance, and its peculiar physical characteristics, and particularly its garlic odour.

(β) Its ready conversion into a white crystalline sublimate (As_2O_3), when heated in a current of air.

Arsenic has a metallic appearance, with a steel-grey lustre. It crystallizes in tetrahedra, and is very brittle. Its density is 5·75 in the solid form, 10·39 in the gaseous. It volatilizes at 300° C. It is tasteless, insoluble in water, but soluble in hydrochloric acid (HCl). When powdered arsenic is thrown into a jar of chlorine gas, it combines with that gas, forming chloride of arsenic ($AsCl_3$). Arsenic combines very readily with hydrogen to form arseniuretted hydrogen (AsH_3), but does not seem capable, like nitrogen, of forming a stable compound containing another equivalent of hydrogen, together with one equivalent of some such acid radical as chlorine, in which compound the group *YH_4 plays the part of a powerful basic radical. Some arsenic compounds have indeed been obtained formed on this type, but they are in general very unstable.

IV. ANTIMONY=Sb. This substance, which has already been noticed among the basic elements, may also be regarded as a body possessed of acid characters. In its combinations it closely resembles arsenic, and forms with hydrogen an analogous compound, antimoniuretted hydrogen (SbH_3). Antimony is the link between this class of salt radicals and the basic elements, of which latter the metal bismuth is generally considered to present the greatest resemblance to antimony.

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* Y represents nitrogen, phosphorus, &c.

Bodies which acquire a basic character by combining with Hydrogen.

Name.	Symbol.	Equivalent.	Colour.	Specific gravity.	Melting-point.	Boiling-point.
Nitrogen	N	14·	(colourless)	·972	...	...
Phosphorus ..	P	31·	α. white β. red γ. black	V. S. α. 1·83 β. 2·089	α. 44·2 β. 250·	290°
Arsenic	As	75·	steel-grey	V. 10·39 S. 5·75	...	300°
Antimony ...	Sb	120·3	white	6·71	4·30	white heat

CHAPTER IV.

THE LAWS OF CHEMICAL COMBINATION.

The two great classes of elements with which the student has now become acquainted have the most powerful attraction for each other; they combine together, and in so doing are said to exercise mutual chemical affinity. When hydrogen (or any other basic element) unites with oxygen (or any other acid element), the properties which these elements possessed previous to their combination are nullified, and in the compound produced we no longer recognize the characters of its components. The extent of this neutralization varies with the nature of the combining bodies, and is more or less perfect as the elements concerned occupy more or less completely corresponding positions in their respective scales. Thus when potassium combines with chlorine, or sodium with bromine, or barium with iodine, or calcium with fluorine, or iron with sulphur, or hydrogen with oxygen, substances are produced which are said to be perfectly neutral, since in them no indication of the specific properties of the basic or acid constituent can be observed; but if a body at the summit of the basic scale be united with one low in the opposite list, or *vice versâ*, then the properties of the more energetic element are found to predominate over those of the weaker, and the resulting compound exhibits either basic or acid properties: the two classes of such compounds, which are particularly abundant, are by an unfortunate nomenclature termed *bases* and *acids*, on account of their exhibiting, for the reason above given, either basic or acid properties; they are the combinations which oxygen produces with the metals, and hydrogen with the salt-radicals.

The doctrine of DEFINITE PROPORTIONS lies at the very foundation of the science of chemistry, and when any two elements are said to combine, it must be understood that they unite in well-defined ratios of weight and volume, which, to produce the same substance, are under all possible circumstances accurately the same. It matters not, for instance, whether hydrochloric acid (HCl) is produced by the simple union of its components, hydrogen and chlorine, or by any more complex mode of formation; 1 part by weight of hydrogen will always unite with 35·5 parts by weight of chlorine, while the gaseous bulks of these two quantities of matter will be equal. Again, those quantities and volumes of the other elements which are capable of *replacing* the hydrogen or the chlorine respectively in the typical compound hydrochloric acid (HCl) which we have chosen, are equally constant, and when once accurately determined, serve for ever as indubitable facts upon which to build the superstructure of chemical reasoning: the annexed list shows this clearly:—

	Formula.	Proportion by Weight.		Proportion by Volume.	
Hydrochloric acid	HCl	$H = 1$	$Cl = 35{\cdot}5$	$H = 1$	$Cl = 1$
Chloride of sodium	$NaCl$	$Na = 23$	$Cl = 35{\cdot}5$	$Na = 1$	$Cl = 1$
Hydrobromic acid	HBr	$H = 1$	$Br = 80$	$H = 1$	$Br = 1$
Bromide of sodium	$NaBr$	$Na = 23$	$Br = 80$	$Na = 1$	$Br = 1.$

The term EQUIVALENT, or combining proportion, is applied to the quantities which thus enter into these most simple combinations; and in compounds more complex than these, the law of definite proportions still holds good; for if the elements exist in larger quantity, that amount is invariably found to be some multiple of the original combining proportional, or to bear some simple relation to it.

But it must be observed that certain acid elements combine with 2, others again with 3 equivalents of basic element: such are the elements oxygen, sulphur, selenium and tellurium, which combine in the proportion of 1 volume or 1 equivalent with 2 volumes or 2 equivalents of hydrogen, sodium, &c., and are consequently sometimes called *biatomic*, from their being thus equal to two combining proportions of chlorine or its congeners; while the members of a third class of acid elements, as nitrogen, phosphorus and arsenic, unite in the proportion of 1 volume or 1 equivalent with 3 volumes or 3 equivalents of basic element, and are said to be *triatomic*, that is, equal to 3 equivalents of chlorine, bromine, &c. The nature of the combinations which the second or biatomic class of acid elements forms, is exemplified in the following Table:—

	Formula.	Proportion by Weight.		Proportion by Volume.	
Water, or oxide of hydrogen	$H_2\ O$	$H_2 = 2$	$O=16$	$H_2 =2$	$O=1$
Oxide of cadmium	$Cd_2 O$	$Cd_2 =112$	$O=16$	$Cd_2 =2$	$O=1$
Hydrosulphuric acid ...	$H_2\ S$	$H_2 = 2$	$S=32$	$H_2 =2$	$S=1$
Sulphide of mercury ...	$Hg_2 S$	$Hg_2=200$	$S=32$	$Hg_2=2$	$S=1$.

When these combinations take place, if the body produced remains a gas, it is found to be condensed to $\frac{2}{3}$rds the volume of its gaseous constituents, *i. e.* the 3 volumes of which it was composed occupy, after combination, the space of only 2.

The combinations formed by the members of the third class of acid-radicals, those to which the name "triatomic" has been assigned, are shown below; thus—

	Formula.	Proportion by Weight.		Proportion by Volume.	
Ammonia	$H_3\ N$	$H_3 = 3$	$N=14$	$H_3 =3$	$N=1$
Phosphide of copper	$Cu_3 P$	$Cu_3=96$	$P=31$	$Cu_3=3$	$P=1$
Arsenide of nickel ...	$Ni_3 As$	$Ni_3 =88{\cdot}5$	$As=75$	$Ni_3=3$	$As=1$.

When it is possible to examine this third class of compound substances in the gaseous state, its members also are found to have suffered condensation, and that to one-half the gaseous bulk of their components: thus the 2 volumes of the condensed compound contain the 4 volumes of which it is composed.

In this manner we find three series of bodies remarkable in their relations of weight and volume.

1st series: suffers no condensation in combination,—

$$\overset{\text{2 vols.}}{\begin{array}{|c|c|}\hline \mathrm{H} & \mathrm{Cl} \\ \hline \end{array}} \qquad \overset{\text{remain}}{} \qquad \overset{\text{2 vols.}}{\begin{array}{|c|c|}\hline \mathrm{H} & \mathrm{Cl} \\ \hline \end{array}}.$$

2nd series: suffers a condensation to two-thirds,—

$$\overset{\text{3 vols.}}{\begin{array}{|c|c|c|}\hline \mathrm{H} & \mathrm{H} & \mathrm{O} \\ \hline \end{array}} \qquad \overset{\text{become}}{} \qquad \overset{\text{2 vols.}}{\begin{array}{|c|c|}\hline \mathrm{H_2} & \mathrm{O} \\ \hline \end{array}}.$$

3rd series: suffers a condensation to one-half,—

$$\overset{\text{4 vols.}}{\begin{array}{|c|c|c|c|}\hline \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{N} \\ \hline \end{array}} \qquad \overset{\text{become}}{} \qquad \overset{\text{2 vols.}}{\begin{array}{|c|c|}\hline \mathrm{H_3} & \mathrm{N} \\ \hline \end{array}}.$$

The different *saturating* power possessed by the three classes of these acid elements, and shown by the formulæ given above (HCl, H_2O, H_3N, &c.), is not confined to them alone, but is manifested, as will be seen presently, in numerous compound molecules, which present analogous features, and are capable of replacing the simple bodies just alluded to.

The term "salt" is generally applied to those of the above combinations in which the properties of the constituents are completely, or nearly completely masked and merged in those of the new substance, which is thus in every way dissimilar from its components; thus the combination of potassium and chlorine, or sodium and iodine, gives rise to substances in which no property of the component elements is retained; the metal in each case has lost its metallic character, and has no longer any tendency to combine with a further quantity of the acid element, while the salt-radical has entirely parted with its odour and its distinguishing chemical properties, and cannot be expelled from the combination into which it has entered by the application of the highest temperature. The compounds formed in either instance being soluble, are also found to have acquired the peculiar taste which is well known as "saline," and are no longer such powerful chemical agents as their uncombined constituents.

The remarks now about to be made apply chiefly to that class of bodies in which the opposed elements which constitute the salt are united simply in the relation of their saturating power, for to these the term "salt" or "saline combination" is almost exclusively applied; water (H_2O), for example, is not the only oxide of hydrogen; there is another, the peroxide of hydrogen (H_2O_2), in which it will be observed that the double biatomic molecule O_2 ($O_2 = H_4$) is only combined with the double monatomic molecule of hydrogen, H_2; the compound H_2O_2 cannot therefore be said to contain the elements hydrogen and oxygen in the simple relation of their saturating power, at least as that has been determined by such observations as those just detailed. Cases of combination of this nature will be presently adverted to.

With regard, however, to this simplest class of compounds now under consideration, the perfect neutralization of the chemical properties of their constituents only holds good, as was just now stated, when the intensity of the antagonism of the two bodies is nicely balanced; but regarded theoretically, the constitution of a salt does not depend upon the nice adjustment of this equilibrium, it simply requires the union of an acid with a basic element; and viewed in this light, the combinations of oxygen with metals, or of hydrogen with salt-radicals, are true saline compounds, although with the more basic metals the feebly acid character of the oxygen is more than counterbalanced, and the compound remains basic, while the intensely acid character of the more powerful salt-radicals overcomes the weak basic properties of the hydrogen, and such combinations are therefore found to be acid. To illustrate these facts, and to exhibit the differences incident upon the varying apportioning of basic and acid element, the following cases are given:—

	Class I.	Class II.	Class III.
Basic	?	K_2O	H_3N
Neutral	NaCl	H_2O	?
Acid	HCl	?	?

In the first of these classes the compound with preponderance of base is wanting, because the intensely powerful acid element is capable of completely neutralizing the most energetic basic element; in the second class, the acid compound is deficient, because the less powerful acid element is incapable of effecting more than the neutralization of a less energetic basic element, hydrogen; in the third class, the very weak acid element is incapable even of the neutralization of the basic constituent, hydrogen, and consequently both the acid and neutral compounds are absent; at least it is probable that such is the case, although the inertness or insolubility of the members of this series (Ag_3P, H_3As, &c.) does not allow accurate observations of their relations to neutrality to be made.

Hitherto we have been regarding the multiplication of saturating power on the part of the acid elements only, but the same thing occurs also in the case of many basic elements. Two instances, those of the metals iron and copper, will suffice to show this, the comparison being made in each case with salts of the same acid-radical, and in which the monatomic molecule of the metal is supposed to exist either singly or multiplied.

SALTS OF IRON.

	Chloride.	Oxide.	Phosphide.
Ferrous*.	$FeCl$	Fe_2O	Fe_3P?
Ferric	Fe_2Cl_3	$(Fe_2)_2O_3$	$(Fe_2)_3P_3$.

SALTS OF COPPER.

	Chloride.	Oxide.	Phosphide.
Cuprous	Cu_2Cl	$(Cu_2)_2O$	$(Cu_2)_3P$
Cupric	$CuCl$	Cu_2O	Cu_3P.

---

* It has been proposed by some chemists to assume, in the case of iron and of several other metals, two different atoms or equivalents, each conbining with the same weight of chlorine, &c., but themselves possessing a different weight. For instance, some have even said that the iron of a *ferrous* was not the same metal as the iron of a *ferric* salt: in the first case it would have the usual equivalent or atomic weight of 28, and in the second, the atomic weight 18·66, that is, ⅔rds of the first atom. The two molecules are respectively called ferrosum (Fe) and ferricum (fe), and are each equivalent to 1 atom of hydrogen, being each capable of combining with 1 atom of chlorine. Viewed

From the above Table it will be seen that the conventional expression for that salt which contains the greater number of equivalents of the basic, and the less number of equivalents of the acid element, is *-ous* salt, the other being termed the *-ic* salt.

But when we pass beyond the cases just cited, and examine the characters of compounds in which the basic element is combined with a yet larger quantity of the acid-radical, we find that the new compound is no longer neutral, but partakes of the acid character of the preponderating element. Thus, when in the union of chromium or iron with oxygen, the oxygen amounts to two equivalents, we find the new body possessing powerfully acid properties, and capable of uniting as a compound acid- (*i. e.* salt-) radical with hydrogen or the metals, thus—

$HCrO_2$ chromic acid.	$KCrO_2$ chromate of potassium.
$HFeO_2$ ferric acid.	$KFeO_2$ ferrate of potassium.

It must not be supposed that two equivalents is the largest quantity of oxygen that a compound acid-radical can contain: permanganic acid, for instance, is the hydrogen salt of a radical containing four equivalents of oxygen, thus—

HMn_2O_4 permanganic acid. KMn_2O_4 permanganate of potassium.

A precisely similar result occurs when, on the other hand, there is a preponderating number of equivalents of basic element in a compound. The compound radical ammonium, containing one equivalent of nitrogen and four of hydrogen, partakes in a striking manner of the basic properties of the hydrogen, which

in the light of this theory, the ferrous chloride remains FeCl, while the ferric chloride becomes feCl; and so on with the various oxides.

To the beginner this may perhaps be elucidated thus:—

FeCl and Fe_2Cl_3 are not comparable, but 3(FeCl) or Fe_3Cl_3 is the true chemical representative of Fe_2Cl_3.

Therefore, Fe_3 is equal in saturating power to Fe_2, for $Fe_3 = 28 \times 3$, and $Fe_2 = 28 \times 2$ are each equal to $Cl_3 = 35{\cdot}5 \times 3$:

Therefore, say some, the metals are different and have different equivalents, which may be obtained by dividing each formula by 3,—

$$\frac{Fe_3Cl_3}{3} = FeCl; \text{ and } \frac{Fe_2Cl_3}{3} = \tfrac{2}{3}(Fe)Cl;$$

then Fe=28, and $\frac{2}{3}$Fe or fe=18·66, are each equivalent to Cl=35·5.

constitutes so large a proportion of the compound; and it is found to play the part of a base almost as energetically as potassium or sodium, combining with the acid-radicals to form very stable salts, the salts of ammonium.

From the capability of the basic elements of combining with every acid element, and *vice versâ*, whether the opposing elements are unequal or equal in intensity of antagonism, results that large class of chemical changes known as "double decompositions." They arise in many instances from bringing together a pair of salts the constituents of which are not well apportioned to each other, but which, by an interchange of their basic and acid elements, would become exactly, or at least more nearly balanced in antagonism: let us take an extremely simple instance: —oxide of sodium or soda (Na_2O) is a salt in which the basic properties of the sodium preponderate vastly over the acid tendency of the oxygen; chloride of hydrogen or hydrochloric acid (HCl) is a salt in which the precise reverse obtains, as we have before seen; now, if these compounds be mixed, the opposed elements of each being much more nearly the exact counterpart of one another, unite, forming two new compounds which are far more stable than those formerly existing, since the mutual antagonism of their components is more perfect:—

$$Na_2O + 2HCl = H_2O + 2NaCl.$$

This apparent election, which bodies make when they are, as it were, at liberty to choose with what they will combine, has been variously termed "elective affinity," "chemical affinity," and "chemical attraction." In reality, it is in every case the effect of many causes,—the resultant of many forces; we cannot, however, enter now into the details of their action, except so far as to state that in many double decompositions much depends upon *insolubility*, much upon *volatility*, and much upon *mass*.

It has been lately shown that double decompositions are of far more frequent occurrence in chemistry than was formerly imagined; it was thought that in many cases, especially where the elements were concerned, direct combination took place when bodies of opposite chemical characters were presented to each other: thus, when chlorine and hydrogen are mixed in the sunlight, and hydrochloric acid (HCl) results from their union, it was imagined that a kind of combination occurred, differing from that mentioned just now, inasmuch as it consisted in a direct union of the molecules of hydrogen and chlorine. Recent experiments, however, appear to show that the molecular arrangement of the elements is not expressed truly when written H and Cl, but that their constitution is that of a binary molecule, a true salt, in fact, in which the hydrogen or chlorine, or whatever the element may be, is both base and acid; and that thus when HCl is formed by H and Cl uniting, the action is as follows:—

$$HH + ClCl = HCl + HCl.$$

Numerous instances might be adduced and proofs given, but are here unnecessary; let it suffice to say that this view seems to give one reason why elements in the nascent state are more powerful agents than when liberated. It is argued—since the element has not yet united with itself to form a twin atom, therefore its combining tendency is still wholly unsatisfied.

It will at once be seen that if this law of binary combination and double decomposition be one of those most deeply impressed upon matter, it is likely to prevail in the more complex chemical compounds. By chemical analysis it is found, that though among the large number of bodies possessing the general characters of salts many consist of but two elements, and those of the opposed classes, yet that there are many which have by no means so simple a constitution; these, however, participate in the same double decompositions as their congeners of a simpler form; and so, when their "elective affinity" is allowed full play, we find that they transfer to each other their basic and acid *compounds*, just as we have seen the simpler types of salts mutually interchange their basic and acid *elements*. The occurrence of basic compounds is rare; the bodies of this constitution belong almost exclusively to the domain of organic chemistry, and the student will for the present have little or nothing to do with them; with one, however, the compound base ammonium (NH_4), he will speedily become acquainted; it is a substance of great importance analytically, and is, moreover, a remarkable instance of the manner in which the basic element hydrogen overcomes the feebly acid properties of nitrogen, and thus confers on their combination a basic character. The acid compounds are far more numerous and important, and are either produced by the union of the acid elements among themselves, or by their combination with basic elements in such proportion as to allow of the preponderance of their own properties over those of the basic elements. It is singular also that many of these acid compounds result from the combination of the two acid elements, sulphur and oxygen, with the remaining bodies of their own class; the composition of a few such compounds is given below, with the names which, by long usage, have become attached to them and cannot be desirably removed, although they must be regarded as wholly apart from any theoretical considerations touching the nature and constitution of the bodies which they designate; the examples are given as existing in saline combination with hydrogen:—

HNO_3 Nitric acid.	$HClO$ Hypochlorous acid.	$HClO_3$ Chloric acid.
H_2SO_4 Sulphuric acid.	H_2CO_2 Carbonic acid.	$H_2C_2O_4$ Oxalic acid.
H_3PO_4 Phosphoric acid.	$H_3\mathrm{Cfdy}$* Hydroferricyanic acid.	$H_3\overline{Ci}$† Citric acid.

With regard to the nomenclature of these compounds, it may be as well remembered that (with one or two exceptions, as in the case of sulphocyanogen (CyS)), when the *compound acid portion* of a binary combination contains no oxygen or sulphur, the termination of its own name is altered into *-ide* when we wish to designate any compound which it forms with a basic element, thus:—

$CN\,CN$ Cyanogen.	$Cl\,Cl$ Chlorine.	SS Sulphur.	PP Phosphorus.
$K\,CN$ Cyanide of potassium.	NH_4Cl Chloride of ammonium.	Fe_2S Sulphide of iron.	Ag_3P Phosphide of silver.

---

* $\mathrm{Cfdy} = Fe_2C_6N_6$.

† $\overline{Ci} = C_6H_5O_7$.

An exception is here made when these acid bodies unite with the basic element hydrogen; and though it is chemically correct to call such a compound as HCl "chloride of hydrogen," yet conventionality demands that it be also termed "hydrochloric or chlorhydric acid;" and thus with all such compounds.

Now, if oxygen be present in the acid compound, a totally distinct nomenclature is adopted; these bodies combined with hydrogen constitute a very large section of the so-called acids, and receive either the termination -ic, as nitr*ic* acid (HNO_3), or -ous, as hypochlor*ous* acid (HClO). When the hydrogen in one of these groups has been replaced by another basic element, the designation that previously terminated in -ic now ends in -ate, and that in -ous in -ite; as nitr*ate* of potassium (KNO_3), and hypochlor*ite* of calcium (CaClO). From the following Table of the hydrogen and potassium salts of some compound acid-radicals which contain sulphur and oxygen, the student will perceive the usage and changes of these terms:—

Hyposulphurous acid	$H_2S_2O_3$	Hyposulphite of potassium	$K_2S_2O_3$
Sulphurous acid	H_2SO_3	Sulphite of potassium	K_2SO_3
Sulphuric acid	H_2SO_4	Sulphate of potassium	K_2SO_4

Here is a similar list, containing the hydrogen and potassium salts of a series of compound acid-radicals formed by the union of chlorine and oxygen:—

Hypochlorous acid ...	HClO	Hypochlorite of potassium...	KClO
Chlorous acid............	$HClO_2$	Chlorite of potassium.........	$KClO_2$
Chloric acid	$HClO_3$	Chlorate of potassium.........	$KClO_3$
Perchloric acid	$HClO_4$	Perchlorate of potassium ...	$KClO_4$

It will have been observed, that in the Table of acids given at page 45 there are three classes of those bodies, distinguished by containing a different amount of hydrogen, that is, of basic element: these classes are the groups of *mono*basic, *bi*basic, and *tri*basic acids which contain acid-radicals requiring these different amounts of basic element to satisfy their respective combining powers; and if the student will refer to what was said regarding the three series of acid *elements* at page 38, he will at once perceive that these three series of *compound* acid-radicals accurately correspond with them. This relation may be exhibited thus:—

		Series I.	Series II.	Series III.
Silver Salts of	Acid Elements	Monatomic. $AgCl$ Chloride of silver.	Biatomic. Ag_2S Sulphide of silver.	Triatomic. Ag_3P Phosphide of silver.
	Acid Compounds	Monobasic. $AgClO_3$ Chlorate of silver.	Bibasic. Ag_2SO_4 Sulphate of silver.	Tribasic. Ag_3PO_4 Phosphate of silver.

The difference between a ferrous and a ferric, between a cuprous and a cupric salt of an *elementary acid-radical*, has been already pointed out; it now only remains to transfer this distinction to the corresponding salts of the *compound acid-radicals*. We will take potassium, iron, and bismuth as the basic elements in our salts; and, for the compound acid-radicals, those existing in the nitric, sulphuric, and phosphoric acids. Now, potassium is monatomic, *i. e.* $K_1 = H_1$; and iron is sometimes sesquiatomic, *i. e.* $Fe_1 = H_{1\frac{1}{2}}$, or $Fe_2 = H_3$; while bismuth is triatomic, *i. e.* $Bi_1 = H_3$. Taking these values, we arrive at the following formulæ for the different salts of the same acids:—

Series I.	Series II.	Series III.
Monatomic.	Biatomic.	Triatomic.
KNO_3 Potassic nitrate.	K_2SO_4 Potassic sulphate.	K_3PO_4 Potassic phosphate.
$Fe_2(NO_3)_3$ Ferric nitrate.	$(Fe_2)_2(SO_4)_3$ Ferric sulphate.	Fe_2PO_4 Ferric phosphate.
$Bi(NO_3)_3$ Bismuthic nitrate.	$Bi_2(SO_4)_3$ Bismuthic sulphate.	$BiPO_4$ Bismuthic phosphate.

Here it is seen how the formula of the same description of salt varies, not only with the saturating power of the acid body, but also with the atomic function of the basic constituent.

A word in explanation of a term in general use, the term "basic salt:"—when an absolutely perfect double decomposition does not occur, the precipitate produced, instead of being a pure salt, is a compound one; this may be best illustrated by a hypothetical example, where M stands for a basic radical, such as one of the metals—

$$20MCl + 19KHO = \underbrace{19(MHO), MCl}_{\text{Basic salt.}} + 19KCl.$$

With regard to solvents;—the action of these agents is exceedingly obscure; they appear to fulfil an office intermediate between chemical union and mechanical mixture. The student had better regard them simply as agents for presenting bodies in a liquid form, and as rarely participating in the chemical actions which take place in their very midst: of course they do occasionally exert very powerful chemical actions; but these instances can be readily discriminated. The more stable the equilibrium of a body, the less chemical influence is it likely to exert; and thus water is far less likely to interfere than the acids, and is for this reason always employed wherever it is practicable, as the solvent to which the least objection can be raised.

CHAPTER V.

OF REAGENTS.

Reagents are those substances which by admixture we bring to act upon the bodies we desire to analyse, in such a manner as to produce certain phenomena which shall prove indubitably the presence of the substance sought for. If in such circumstances the expected effect is not produced, we must infer the absence of the object of our search.

It is obviously, therefore, of the greatest importance that the reagents which are employed in chemical analysis should, if not absolutely pure, at least be free from substances which would interfere with the indications which they are employed to give. The amount and the nature of the impurities which they contain should be accurately known.

Most of the reagents in common use are met with in commerce of sufficient purity to allow of their application in all but the more delicate operations of analysis. For certain special cases, however, as in legal investigations for the purpose of ascertaining the presence or absence of poison, too much care cannot be bestowed upon the preparation of absolutely pure reagents; and in such instances it is generally necessary for the chemist to ensure the purity of the materials he employs by preparing, or at least scrupulously purifying them himself.

The ordinary methods of purification are briefly these: Sublimation, Crystallization, Precipitation, and Distillation.

Sublimation can only be resorted to when it is desired to free a body solid at ordinary temperatures, but volatile at a higher degree of heat, from non-volatile impurities; iodine is usually purified in this way: many mercury and ammonium salts might also be thus freed from accompanying foreign matters which were not volatile. In the sublimation of many substances it is simply necessary to place the substance in a dish over which is fixed a tall beaker or bell-jar, which may be luted or otherwise attached to the dish below; if the dish containing the substance is now heated, the volatile substance (iodine, oxalic acid, &c., as the case may be) rises in vapour,—speedily however condensing on the cold surface of the receiver above.

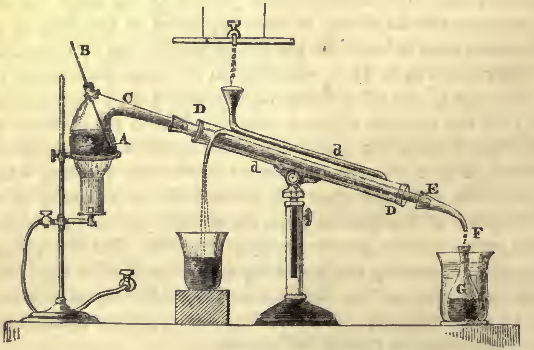
Crystallization is perhaps the most commonly adopted of all methods of purification. In general, substances dissolve more abundantly in hot than in cold solvents. If then at some given temperature a menstruum, as water, alcohol or æther, be saturated with any solid body (*i.e.* supplied with it until no more is dissolved), the solution perfectly transparent at that degree of heat, will, as soon as the temperature diminishes, deposit some of the dissolved matter in the solid form. In the same manner let a given bulk of a saturated solution of almost any substance be taken, and without increasing its temperature, let its volume be diminished to one half (as by slow spontaneous evaporation), then a considerable portion of the solid matter before held in solution will be found to have separated in the form of crystals. Upon these two facts is based the method of purification by crystallization.

Salts differ much as to their solubility in the same menstruum; and by taking advantage of the facts which experimenters have accumulated upon this point, we can separate different compounds with considerable accuracy by evaporating the solution containing the mixture, we will suppose of two salts, to that degree of concentration at which one of them will almost entirely separate, while the other will remain almost as wholly in solution. By the repetition of this process upon the already partially purified product of the first crystallization, greater purity is attained. But with many articles of commerce one carefully conducted crystallization is often found sufficient. The technical name for the liquid remaining after the separation of the crystals is "mother-liquor," while the successive products of the crystallizing process are spoken of as "crops" of crystals.

Precipitation is frequently employed when the substance constituting the impurity is known to form an insoluble compound on the addition of some reagent the introduction of which does not interfere with the efficiency of the reagent we seek to purify. Let it be supposed that chloride of ammonium (NH_4Cl) is the substance with which we wish to deal. Now the impurity which this salt commonly contains is chloride of iron ($FeCl$); to separate this the substance is dissolved in water, and a few drops of sulphide of ammonium, $(NH_4)_2 S$, are added to the solution; the black sulphide of iron $(Fe_2 S)$ is formed and precipitated, its removal being effected by passing the liquid through a filter, while the reagent added, so far from contaminating the chloride of ammonium by the decomposition, itself helps to form an additional quantity of that salt, the ammonium originally combined with the sulphur uniting with the chlorine of the chloride of iron $(NH_4)_2 S + 2FeCl = Fe_2 S + 2NH_4 Cl$: if any excess of the alkaline sulphide has been added, by boiling the solution it may be volatilized and thus removed. However, it is not often possible thus to remove the excess of the substances introduced in order to precipitate impurities; but care can then be taken that the foreign substances unavoidably brought in shall be such as do not interfere with the reactions which the purified substance is intended to exhibit. Sometimes, on the other hand, the pure substance is precipitated by an appropriate reagent, leaving the impurities in solution, being therefore just the reverse of the preceding process.

Distillation is always used to separate a liquid which vaporizes at a certain temperature from other liquid or solid matters which are not volatile at that temperature. Most liquids when heated to a certain point which is peculiar to each substance, boil and are converted into vapour, and in this condition of vapour they remain as long as that degree of heat is maintained, but no sooner does it diminish, than they again return to the liquid form of matter. The apparatus employed is generally the following:—A is the retort in which the liquid is placed, the temperature being indicated by the thermometer B, and regulated accordingly; the only way of escape for the vapour which rises from the boiling liquid is through the neck C into the apparatus D D, which is a glass tube passed through an outer tube of zinc or copper, *d d*, the space between these two tubes being occupied by cold water; the vapour is thereby cooled completely, and consequently reduced to the liquid state, in which condition it flows through the adapter E, and issues from the

Fig. 3.



point F into the receiver G. By this process of distillation several liquids of different degrees of volatility may be separated, the "distillates" being preserved apart, while non-volatile substances, whether solids or liquids, in suspension or solution, may be removed, since they remain in the retort when the volatile matters have passed over; this separation is of course more easily effected than that of volatile liquids from liquids of different volatility.

We here give a list of the reagents employed in analysis, separating, however, those commonly used from those employed for special purposes.

LIST OF REAGENTS EMPLOYED IN CHEMICAL ANALYSIS.

The reagents to which an asterisk is affixed are employed in the solid state: the remainder dissolved in water.

General Reagents.

BASIC ELEMENTS.

*Zinc (Zn).

SALTS OF POTASSIUM.

*Nitrate of potassium (KNO_3).
Chromate of potassium ($KCrO_2$).
*Cyanide of potassium (KCN).
Acetate of potassium ($K\bar{A}$).
*Hydrate of potassium (KHO).
Ferrocyanide of potassium (K_2Cfy).
*Carbonates of potassium and sodium ($K_2CO_3+Na_2CO_3$).

SALTS OF SODIUM.

*Carbonate of sodium (Na_2CO_3).
*Biborate of sodium or borax ($Na_2Bo_4O_7$).
Phosphate of sodium (Na_2HPO_4).

SALTS OF AMMONIUM.

Chloride of ammonium (NH_4Cl).
Hydrate of ammonium (NH_4HO).
Sulphydrate of ammonium (NH_4HS).
Carbonate of ammonium ($[NH_4]_2CO_3$).
Oxalate of ammonium ($[NH_4]_2\bar{O}$).

SALTS OF BARIUM.

Chloride of barium ($BaCl$).
Hydrate of barium ($BaHO$).

Special Reagents.

BASIC ELEMENTS.

*Iron (Fe).
*Copper (Cu).

SALTS OF POTASSIUM.

Iodide of potassium (KI).
Sulphocyanide of potassium ($KCNS$).
Silicate of potassium ($KSiO_2$?).
Sulphydrate of potassium (KHS).
Sulphate of potassium (K_2SO_4).
Acid metantimoniate of potassium ($K_2H_2Sb_2O_7$).
Ferricyanide of potassium (K_3Cfdy).

SALTS OF SODIUM.

Acetate of sodium ($Na\bar{A}$).
Hydrate of sodium ($NaHO$).
Sulphydrate of sodium ($NaHS$).
Sulphite of sodium (Na_2SO_3).
Phosphate of sodium and ammonium ($NaNH_4HPO_4$).

SALTS OF AMMONIUM.

Molybdate of ammonium (NH_4MoO_2).
Acetate of ammonium ($NH_4\bar{A}$).
Phosphate of ammonium ($[NH_4]_2HPO_4$)

SALTS OF BARIUM.

*Fluoride of barium (BaF).

SALTS OF CALCIUM.

Chloride of calcium ($CaCl$).
*Oxide of calcium (Ca_2O).
Sulphate of calcium (Ca_2SO_4).

SALTS OF IRON.

*Ferrous sulphate (Fe_2SO_4).
Ferric chloride (Fe_2Cl_3).

SALT OF COBALT.

Nitrate of cobalt ($CoNO_3$).

SALT OF SILVER.

Nitrate of silver ($AgNO_3$).

SALT OF LEAD.

Acetate of lead ($Pb\bar{A}$).

SALT OF PLATINUM.

Bichloride of platinum ($PtCl_2$).

SALT OF GOLD.

Terchloride of gold ($AuCl_3$).

SALTS OF HYDROGEN.

Hydrochloric acid (HCl).
Nitric acid (HNO_3).
Acetic acid ($H\bar{A}$).
Water (H_2O).
Hydrosulphuric acid (H_2S).
Sulphuric acid (H_2SO_4).
Oxalic acid ($H_2C_2O_4$).

ACID ELEMENT.

*Carbon (C).

TEST PAPERS.

Blue litmus paper.
Red litmus ,,
Turmeric ,,
Starch ,,
Acetate of lead ,,

ORGANIC BODY.

*Starch ($C_{12}H_{20}O_{10}$).

*Oxide of barium (Ba_2O).
*Carbonate of barium (Ba_2CO_3).

SALT OF MAGNESIUM.

Sulphate of magnesium (Mg_2SO_4).

SALTS OF COPPER.

Cuprous sulphate (Cu_4SO_4).
Cupric sulphate (Cu_2SO_4).

SALTS OF MERCURY.

Mercurous nitrate (Hg_2NO_3).
Mercuric chloride ($HgCl$).
Mercuric oxide (Hg_2O).

SALT OF BISMUTH.

Oxyhydrate of bismuth
(BiH_3O_3, Bi_2O_3).

SALT OF PALLADIUM.

Chloride of palladium ($PdCl$).

SALTS OF ETHYLE.

Oxide of ethyle ($[C_2H_5]_2O$).
Hydrate of ethyle (C_2H_5HO).

SALTS OF HYDROGEN.

Sulphurous acid (H_2SO_3).
Carbonic acid (H_2CO_3).
Tartaric acid ($H_2C_4H_4O_5$).
Hydrofluosilicic acid ($H_3Si_2F_9$).

ACID ELEMENTS.

Bromine (Br).
Chlorine (Cl).

ORGANIC BODIES.

*Sugar ($C_{12}H_{22}O_{11}$).
*Gelatine ?

BASIC ELEMENTS.

Iron (Fe).

The purest iron met with in commerce is in the form of pianoforte wire: it should be preserved in a closely-stoppered bottle, together with some caustic lime to prevent oxidation.

Zinc (Zn).

One chief impurity of this metal is lead, which, however, does not ordinarily interfere with its applications. The most detrimental impurity is arsenic, and the zinc employed in analysis should always be free from this substance: some specimens of commercial zinc are quite free from it. It should be either granulated or cut into small strips.

Copper (Cu).

The most convenient form in which to employ this metal is that of foil or turnings.

SALTS OF POTASSIUM.

Iodide of potassium (KI).

This salt is found of sufficient purity in commerce for ordinary operations: its chief contamination is carbonate of potassium (K_2CO_3), which may be separated by digesting the crude salt in hot strong alcohol, filtering, and crystallizing out the iodide. To make a solution for the purposes of testing, 1 part of salt may be dissolved in 10 parts of water.

Nitrate of potassium KNO_3).

Commercial nitre is sufficiently pure for ordinary use: its great impurities are chloride and sulphate of potassium, from which it may be freed by repeated crystallizations.

Chromate of potassium ($KCrO_2$).

The salt met with in commerce is pure enough for the purposes to which it is applied. As the bichromate of potassium is a salt of more common occurrence, it may be used for the preparation of the neutral chromate by adding to every 100 parts of bichromate dissolved in water, 47 parts of dry carbonate of potassium (K_2CO_3). The salt may then be crystallized. For use, 1 part of the crystals should be dissolved in 10 of water.

Cyanide of potassium (K[CN] *or* KCy).

The cyanide prepared by throwing a mixture of 8 parts of dried ferrocyanide of potassium with 3 of dried carbonate of potassium into a crucible heated to low redness, is sufficiently pure for ordinary analytical purposes. When so heated it decomposes thus,—

$$2(K_2FeCy_3)+K_2CO_3=5KCy+KCyO+2Fe+CO_2.$$

When its contents are in a state of tranquil fusion the crucible is removed from the fire and allowed to stand, so that the particles of iron may subside: the fused mass is then poured out upon an iron plate. It consists of cyanide and cyanate of potassium, and should be kept in a well-stoppered bottle. The cyanide may be obtained pure by digesting the mass in hot alcohol, in which the cyanate is nearly insoluble.

Sulphocyanide of potassium ($K[CNS]$ *or* $K\,[CyS]$ *or* KCsy).

This salt is prepared by fusing 46 parts of ferrocyanide of potassium, 17 of carbonate of potassium, and 32 of sulphur in a covered iron crucible or pan. The fused mass, when cold, is boiled with alcohol; the sulphocyanide crystallizes out on cooling. 1 part should be dissolved in 10 of water.

Silicate of potassium ($KSiO_2$?).

A solution of silicate of potassium made by fusing 1 part of pure quartz-sand (Si_2O_3) with 4 parts of carbonate of potassium, and dissolving the resulting mass in boiling water, is occasionally employed in analysis. The fused mass should be first pounded and washed with cold water.

Acetate of potassium ($K[C_2H_4O_2]$ *or* $K\bar{A}$).

The commercial salt is sufficiently pure for all ordinary analytical purposes. 1 part should be dissolved in 4 of water.

Hydrate of potassium (KHO).

The salt met with in commerce contains many impurities, of which the principal are the chloride, sulphate, and silicate of potassium; these do not generally interfere with its use. But it also contains very frequently carbonate of potassium, alumina (Al_4O_3), and oxide of lead; the presence of these substances is often very troublesome in analytical processes. The last impurity is derived from the flint-glass bottles in which the solution of hydrate of potassium is often kept: German glass bottles should be used instead. To obtain the pure hydrate, it is only necessary to dissolve the commercial salt in alcohol, in which its impurities are insoluble, and then by evaporating the clear part of the solution in a silver dish, the hydrate is obtained perfectly pure, if care has been taken to preserve it from the carbonic acid of the air. The following is a method of preparing a solution of this substance:—10 parts of carbonate of potassium are dissolved in 100 parts of water and the solution heated to boiling in a silver or bright iron vessel provided with a lid: 8 parts of good freshly burnt lime (Ca_2O) are slaked in another covered vessel, and the hydrate formed added by degrees to the boiling solution of carbonate of potassium, the mixture being constantly stirred. The change may be represented thus:—

$$K_2CO_3+2(CaHO)=Ca_2CO_3+2KHO.$$

The mixture is boiled for a few minutes, the lid of the vessel remaining on; the liquid is then allowed to rest until all the carbonate of calcium formed has settled, when the clear solution of potassa or hydrate of potassium is poured off into a well-stoppered bottle.

Sulphydrate of potassium (KHS).

This salt is prepared by passing sulphuretted hydrogen (H_2S) into a solution of hydrate of potassium until the liquid has a strong odour of the gas.

Sulphate of potassium (K_2SO_4).

The commercial salt is sufficiently pure for analytical purposes; it is sometimes, however, expedient to recrystallize it. For a solution for testing, 1 part is to be dissolved in about 12 of water.

Acid metantimoniate of potassium ($K_2 H_2 Sb_2 O_7$).

To prepare this salt, the neutral antimoniate is at first procured by throwing a mixture of 1 part of antimony (Sb) with 4 parts of nitre (KNO_3) into a red-hot crucible; when the mass is cold, the excess of nitre is removed from it by digesting the fused mass in tepid water; the insoluble residue still left is then *boiled* with water for some time, and is thereby dissolved: its solution is then evaporated to the consistence of a syrup, and solid hydrate of potassium added to convert the antimoniate into metantimoniate: the liquid is further evaporated until, upon a drop being taken out upon a glass rod, it readily crystallizes; it is then allowed to cool, when a crystalline mass is obtained containing the acid and neutral antimoniates of potassium. The crystals are then dried on filter-paper and preserved dry in a stoppered bottle for use. When required for testing, 1 part is dissolved in about 20 of water at a gentle heat, the solution cooled and filtered. During this process of solution the neutral salt is converted by the action of water into the acid metantimoniate, hydrate of potassium being produced at the same time.

Ferrocyanide of potassium ($K_2 [FeC_3 N_3]$ *or* $K_2 [FeCy_3]$ *or*
$K_2 Cfy + 1\frac{1}{2} aq$)*.

This salt is met with in great purity in commerce: its solution becomes somewhat alkaline on keeping. 1 part of salt should be dissolved in 12 parts of water.

Carbonates of potassium and of sodium ($K_2 CO_3 + Na_2 CO_3$).

The separate salts are mixed in equivalent proportions. The mixture fuses at a lower temperature than either of its constituents.

Ferricyanide of potassium ($K_3 [Fe_2 C_6 N_6]$ *or* $K_3 [Fe_2 Cy_6]$ *or* $K_3 Cfdy$).

The commercial salt is of sufficient purity. This substance is prepared by passing chlorine gas into a solution of 1 part of ferrocyanide of potassium ($K_2 Cfy$) in 9 parts of water until a drop of the liquid no longer produces a blue precipitate or colour in a solution of perchloride of iron ($Fe_2 Cl_3$). It should be crystallized several times: the crystals are of a fine deep red colour: 1 part of them should be dissolved in 10 of water for use as a test.

SALTS OF SODIUM.

Acetate of sodium ($Na[C_2 H_4 O_2]$ *or* $Na\overline{A}$).

This salt is met with in commerce of sufficient purity for ordinary analytical operations. Being much cheaper than acetate of potassium, it is generally employed in its stead, although it cannot be so advantageously used in experiments where free oxalic acid is present, since the oxalate of sodium which is then formed is comparatively insoluble. 1 part is to be dissolved in 4 of water.

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* The symbol $aq = H_2O$, and is generally employed to denote water of crystallization.

Hydrate of sodium ($NaHO$).

This salt is frequently substituted for hydrate of potassium, on account of its greater cheapness. It is subject to the same impurities as the hydrate of potassium, and may be freed from them in a similar manner.

Sulphydrate of sodium ($NaHS$).

This salt is also used instead of the sulphydrate of potassium, and may be prepared in a similar manner.

Sulphite of sodium ($Na_2SO_3+10\,aq$).

This salt may be prepared by passing sulphurous acid gas (SO_2) (produced by boiling copper turnings in a flask with concentrated sulphuric acid, and passing the gas through water in a wash-bottle) into an aqueous solution of carbonate of sodium, until carbonic acid gas is no longer evolved. The solution should be evaporated with as little exposure to the air as possible, on account of the great tendency of the sulphite to pass into sulphate, and finally allowed to crystallize. The solution for testing should contain about 1 part of sulphite in 5 parts of water.

Carbonate of sodium (Na_2CO_3).

The commercial salt usually contains an admixture of sulphate and chloride of sodium, from which it is difficult to purify it. An easy method of preparing pure carbonate is by precipitating a comparatively pure specimen of a sodium salt with oxalic acid or a soluble oxalate. The oxalate of sodium is nearly insoluble, and by washing the precipitate obtained as before mentioned with water, only a small quantity of oxalate is lost, whilst the impurities are washed away. By ignition of this oxalate the pure carbonate is obtained, thus—

$$Na_2C_2O_4=Na_2CO_3+CO.$$

Biborate of sodium *or* borax ($Na_2Bo_4O_7+10\,aq$).

The commercial salt may be employed for ordinary analytical operations, It can be purified by crystallization.

Phosphate of sodium ($Na_2HPO_4+12\,aq$).

For ordinary purposes the commercial phosphate may be employed; it contains sulphate of sodium, from which it may be purified by crystallization. For use as a test 1 part is to be dissolved in 10 parts of water.

Phosphate of sodium, ammonium and hydrogen, *or* microcosmic salt *or* phosphorus salt ($NaNH_4HPO_4+4aq$).

This salt is prepared by boiling a solution of 6 parts of phosphate of sodium (the reagent just described) in 2 parts of water, and adding 1 part of powdered chloride of ammonium (NH_4Cl). Chloride of sodium separates and is removed by filtration, while the filtrate on concentration yields crystals of microcosmic salt.

SALTS OF AMMONIUM.

Chloride of ammonium (NH_4Cl).

The chief impurity of this salt as met with in commerce is chloride of iron; this may be readily separated by precipitation, a few drops of sulphydrate of ammonium (NH_4HS) being added to a solution of chloride of ammonium, and any black precipitate of sulphide of iron produced being filtered off; hydrochloric acid is then added in quantity just sufficient to decompose any excess of sulphide of ammonium, and the liquid boiled till all odour of the sulphuretted hydrogen has left it: when the trifling excess of hydrochloric acid has been saturated with ammonia, the solution is evaporated and the salt crystallized. 1 part should be dissolved in about 8 parts of water.

Molybdate of ammonium (NH_4MoO_2).

In the preparation of this salt molybdic acid is at first prepared; this is done by roasting native sulphide of molybdenum (MoS) in a platinum crucible at a low red heat, with constant stirring, as long as sulphurous acid (SO_2) is evolved. The impure molybdic acid thus obtained is then dissolved with the aid of heat in ammonia. Much of its impurity is left undissolved, while more separates when the solution is evaporated to crystallize. By crystallization the bimolybdate is formed ($[NH_4]_2Mo_4O_7$).

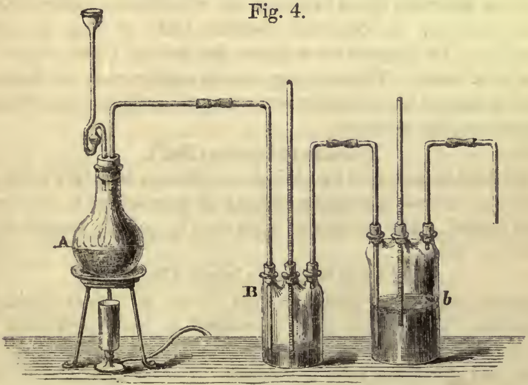
Acetate of ammonium ($NH_4C_2H_3O_2$ *or* $NH_4\overline{A}$).

This salt may be best prepared by neutralizing acetic acid with carbonate of ammonium.

Hydrate of ammonium (NH_4HO).

Commercial ammonia may be advantageously used in analysis; or it may be prepared by taking equal weights of freshly burnt lime (Ca_2O) and powdered chloride of ammonium (NH_4Cl), introducing them into a flask A, and adding a little water: the evolved gas is passed through a *small* quantity of water contained in the first wash-bottle, represented in the annexed figure by B; it is then conducted into a bottle, *b*, or a series of bottles similarly fitted with tubes, and half-full of distilled water. The following equation represents the change:—

Fig. 4.



$$NH_4Cl + CaHO = NH_4HO + CaCl;$$

but although NH_4HO represents the hydrate of ammonium corresponding to the hydrate of potassium (KHO), and although for convenience and analogy sake we speak of this hydrate, yet it is more correct to regard the substance so called as a solution of the gas ammonia (NH_3) in water (H_2O); for it will be seen that $NH_4HO = NH_3 + H_2O$.

Sulphydrate of ammonium (NH_4HS).

This salt is prepared by passing hydrosulphuric acid (H_2S) into a solution of hydrate of ammonium until the liquid is fully saturated and the gas escapes unabsorbed. The sulphide of ammonium ($[NH_4]_2S$) is obtained by dividing a solution of hydrate of ammonium into two equal parts, and after having saturated one part with hydrosulphuric acid, adding the reserved part to it.

Carbonate of ammonium ($[NH_4]_2CO_3$).

The commercial carbonate is a sesquicarbonate, but when dissolved in hot water the solution is said to contain the neutral carbonate. The common preparations of this salt are of sufficient purity for almost every analytical purpose.

Oxalate of ammonium ($[NH_4]_2C_2O_4 + aq$ *or* $[NH_4]_2\bar{O} + aq$).

This salt may be prepared by exactly neutralizing a solution of oxalic acid by carbonate or hydrate of ammonium: 1 part of crystals should be dissolved in 24 parts of water for use as a solution for testing.

Phosphate of ammonium ($[NH_4]_2HPO_4$).

This salt may be prepared by decomposing the acid phosphate of calcium by carbonate of ammonium.

SALTS OF BARIUM.

Chloride of barium ($BaCl + aq$).

This salt is generally found in commerce of sufficient purity for ordinary analytical purposes. It sometimes contains lead: it may be purified by crystallization. To prepare the solution for testing, 1 part should be dissolved in 10 of water. This salt may also be readily made by dissolving the carbonate of barium (a commonly occurring mineral) in hydrochloric acid, and crystallizing the product.

Fluoride of barium (BaF).

This salt may be prepared by adding hydrofluoric acid (HF) to a solution of chloride of barium containing hydrate of ammonium as long as a precipitate is formed. The precipitate must then be quickly washed with water on a filter and dried.

Oxide of barium *or* baryta (Ba_2O).

This compound is best prepared from nitrate of barium purified by recrystallization. The nitrate, finely powdered, is introduced little by little into a crucible maintained at a bright red heat. After cooling, the crucible is broken, and the fused mass is separated from foreign matters and preserved from the air. The decomposition is as follows:—

$$2BaNO_3 = Ba_2O + N_2O_4 + O.$$

Hydrate of barium ($BaHO + 4\frac{1}{2}$ aq).

This salt may be prepared by dissolving the oxide in boiling water, filtering the solution into a bottle or flask, and closing the latter by a cork to exclude the air, which, from the carbonic acid gas which it contains, would soon convert the hydrate into the carbonate of barium. The above solution on cooling deposits the hydrate in large crystals, which may always, by a second or sometimes a third crystallization, be obtained perfectly pure. This substance may also be prepared by heating to redness in a crucible a mixture of 6 parts of finely powdered sulphate of barium ($Ba_2 SO_4$) with 1 part of powdered charcoal and 1½ of flour, and boiling the resulting mass with water for a long time in a loosely-corked flask: the solution is to be filtered whilst hot with the same precaution as in the first process. The decompositions which occur are these:—

$$(\alpha) \quad Ba_2 SO_4 + 2C = Ba_2 S + 2CO_2$$

$$(\beta) \quad Ba_2 S \quad + 2(H_2 O) = H_2 S + 2(BaHO).$$

As it is important that this reagent should be quite free from the salts of the alkalies, the second process is a very convenient method, since, from the great insolubility of the sulphate of barium, it may be easily washed free from all soluble impurities, among which the alkaline salts are the most usual and most deleterious. For testing, a cold saturated solution of the crystallized hydrate may be employed.

Carbonate of barium ($Ba_2 CO_3$).

This salt occurs in a state of comparative purity as a mineral: for analytical purposes, however, it should always be precipitated by carbonate of sodium or ammonium from the pure chloride of barium (BaCl); the precipitate is to be thoroughly washed, and then stirred with distilled water so as to form a pasty mass; in this condition it should be preserved for use in a stoppered bottle. This salt, like the preceding, should be absolutely free from soluble salts.

SALTS OF CALCIUM.

Chloride of calcium (CaCl).

This may be preparad in the purest form by dissolving the finest white marble ($Ca_2 CO_3$) or precipitated carbonate of calcium, or, better still, small crystals of Iceland spar, in hydrochloric acid (HCl), the hydrochloric acid not being in sufficient quantity to dissolve the whole of the carbonate.

Oxide of calcium ($Ca_2 O$).

Freshly burnt quicklime just from the kiln should be taken, the white pieces selected and preserved in a well-stoppered bottle.

Sulphate of calcium ($Ca_2 SO_4 + 2$ aq).

This salt may be prepared by precipitating pure chloride of calcium with sulphuric acid ($H_2 SO_4$), washing the precipitate thoroughly, and then digesting the sulphate of calcium formed, with repeated agitation, in cold water. It is almost insoluble, and therefore the saturated solution may be used.

SALT OF MAGNESIUM.

Sulphate of magnesium ($Mg_2 SO_4 + 7$ aq).

The commercial salt (Epsom salts) is of sufficient purity for all ordinary analytical purposes. 1 part should be dissolved in 10 parts of water.

SALTS OF IRON.

Protosulphate of iron *or* ferrous sulphate ($Fe_2 SO_4 + 7$ aq).

The commercial salt is of sufficient purity for employment in analysis. The solution is made by agitating the crystals with cold water, out of contact with the air.

Sesqui- *or* perchloride of iron, *or* ferric chloride ($Fe_2 Cl_3$).

This salt may be easily prepared by dissolving pianoforte wire (the purest form in which iron occurs commercially) in hydrochloric acid, boiling the solution, and adding nitric acid (HNO_3) drop by drop until the original greenish-brown colour of the solution has changed to a bright yellow, or until a drop of the solution taken out on a glass rod is no longer precipitated blue on the addition of ferricyanide of potassium (K_3 Cfdy). Excess of ammonia solution is then added, and the precipitate produced thoroughly washed with hot water; it is then dissolved in hydrochloric acid, care being taken that enough acid is not added to dissolve the whole.

SALT of COBALT.

Nitrate of cobalt ($CoNO_3 + 3$ aq).

This salt may be purchased in a state fit for use: it is troublesome to prepare from cobalt ore. 1 part is to be dissolved in about 10 of water.

SALT OF COPPER.

Protosulphate of copper *or* cupric sulphate ($Cu_2 SO_4 + 5$ aq).

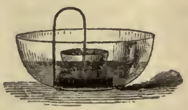
The commercial salt is always contaminated with ferric sulphate; for analytical purposes the metallic copper obtained by electrolysis may be dissolved in hot sulphuric acid ($H_2 SO_4$); or the pure hydrate, oxide, or carbonate may be taken, and heated with diluted sulphuric acid. The salt should be crystallized from its solution. 1 part should be dissolved in 10 parts of water.

SALT OF SILVER.

Nitrate of silver ($AgNO_3$).

This is best obtained by dissolving pure silver in nitric acid (HNO_3) which has been diluted with about its own bulk of water, evaporating the solution to dryness, and gently fusing the residue. The fused mass may be dissolved in water when cold, and then crystallized. It is thus obtained quite free from acid. If silver coin (*i. e.* silver alloyed with copper) be employed, it is necessary, after dissolving it in nitric acid, to precipitate the silver as chloride by the addition of hydrochloric acid, to filter it, and then to wash it till it no longer contains a trace of the soluble copper salt. The pure chloride of silver is now to be placed in a small dish of porous earthenware, placed in a larger dish or basin; both vessels are then to be so far

Fig. 5.



filled with water, to which a few drops of hydrochloric acid have been added, that their contents do not mix. A piece of zinc is to be laid under the inner vessel, and connected with the chloride of silver by means of a bent platinum wire, when the desired action will at once commence, and after the lapse of a short time the whole of the chloride of silver will have been "reduced" to the metallic state: the change may be represented by the two equations—

$$(1)\ HCl + Zn = ZnCl + H$$

$$(2)\ AgCl + H = HCl + Ag.$$

The small dish is now to be removed, and the finely divided silver which it contains to be repeatedly washed with dilute hydrochloric acid, and, finally, with pure water. When quite free from hydrochloric acid, the silver is to dissolved in nitric acid, crystallized and fused as mentioned above*. For use, 1 part of the fused salt is dissolved in 20 parts of water.

SALT OF LEAD.

Acetate of lead ($PbC_2H_3O_2$ *or* $Pb\bar{A}+1\frac{1}{2}$ aq).

This salt is met with in commerce of sufficient purity: 1 part should be dissolved in 6 parts of water.

SALTS OF MERCURY.

Protonitrate of mercury *or* mercurous nitrate (Hg_2NO_3).

This salt is obtained by leaving metallic mercury in contact with nitric acid (HNO_3) without applying heat. In order to preserve it in the state of mercurous nitrate, some metallic mercury must always be kept in its solution.

Perchloride of mercury *or* mercuric chloride ($HgCl$).

The commercial salt is sufficiently pure. 1 part is to be dissolved in 16 parts of water.

Peroxide of mercury *or* mercuric oxide (Hg_2O).

This salt may be purchased tolerably pure. It should volatilize when heated without leaving a residue.

SALT OF BISMUTH.

Oxyhydrate of bismuth *or* mixed oxide and hydrate of bismuth (BiH_3O_3, Bi_2O_3).

The commercial basic nitrate of bismuth may be used instead of the basic hydrate (for the conversion of metallic sulphides soluble in alkalies into oxides by boiling it with such alkaline solutions): it must be free from arsenic (As).

The metal bismuth may be purified from arsenic by fusing it with nitrate of potassium (KNO_3); it may then be dissolved in dilute nitric acid, and the

---

* By this fusion a portion of nitrite is said to be formed;—this may be separated by dissolving the fused mass in cold water, evaporating and crystallizing afresh.

solution diluted with water till a precipitate begins to form; from this precipitate the solution is filtered, and the filtrate evaporated until it is of sufficient concentration to crystallize. The crystals are then digested with water containing a little nitric acid, excess of ammonia solution added, and the precipitate of basic hydrate washed thoroughly and dried.

Salt of Palladium.

Protochloride of palladium *or* palladious chloride ($PdCl$).

The metal palladium is dissolved in nitro-hydrochloric acid, the solution evaporated to dryness on the water-bath, by which means palladic chloride is first formed, but this salt ($Pd_2 Cl_3$) is converted into palladious chloride ($PdCl$) with evolution of chlorine at the temperature employed: after the first evaporation, hydrochloric acid should be added, and the liquid again evaporated; water is then to be poured on the salt, and the whole carried to dryness once more on the water-bath.

Salt of Tin.

Protochloride of tin ($SnCl$).

This salt is obtained by dissolving the granulated metal in hydrochloric acid (the concentrated acid diluted with its own bulk of water); the mixture is to be heated, care being taken to stop the action before all the tin and hydrochloric acid have been consumed: the solution of the chloride is then to be decanted clear from the residual metal, and poured into a bottle containing a few fragments of pure tin: a little dilute hydrochloric acid should also be added.

Salt of Platinum.

Per- *or* bichloride of platinum *or* platinic chloride ($PtCl_2$).

This salt is prepared in precisely the same manner as the palladious chloride.

Salt of Gold.

Terchloride of gold *or* auric chloride ($AuCl_3$).

This salt may be prepared as the palladious chloride if the metallic gold is pure. If, however, the gold contains copper (Cu) or silver (Ag), the nitro-hydrochloric solution is at once evaporated to dryness on the water-bath, and redissolved in water, by which means the whole of the silver remains as chloride. The aqueous solution is then slightly acidified with hydrochloric acid and boiled with a solution of oxalic acid; the gold is thus precipitated in the metallic form, while the copper remains in solution; if, however, any copper still contaminates the gold in the form of oxalate of copper, it may be removed by treating the metal with ammonia solution.

Salts of Ethyle.

Oxide of ethyle *or* ether ($[C_2 H_5]_2 O$).

This is obtained of sufficient purity in commerce for the ordinary analytical operations. If, however, ether free from water is required, it is obtained "anhydrous" by digestion with, and distillation from, caustic lime (Ca_2O). For most purposes this is, however, unnecessary. The specific gravity of anhydrous ether is 0·73.

Hydrate of ethyle *or* alcohol ($[C_2H_5]HO$).

This is to be obtained of great purity as "rectified spirit," having the specific gravity of 0·83; this, like commercial ether, contains water, from which it, too, may be freed by distillation with caustic lime. By other subsequent distillations with ignited carbonate of potassium (K_2CO_3), or anhydrous sulphate of copper (Cu_2SO_4), it may be rendered quite free from water. It is then termed "absolute," and has a specific gravity of 0·795. For all ordinary purposes the alcohol recently introduced by the Excise, and known as "methylated spirit," may be employed. This spirit is simply alcohol intentionally and avowedly mixed with methyle alcohol to the extent of 10 per cent. This is done in order to preclude its use as a beverage, without interfering with its applicability to most manufacturing and chemical purposes.

SALTS OF HYDROGEN.

Chloride of hydrogen *or* hydrochloric acid (HCl).

Nitric and sulphuric acids and salts of iron are common impurities of commercial hydrochloric acid: it may, however, always be obtained of great purity in commerce. Its specific gravity should be 1·2. 1 part, by measure, of acid diluted with 2 parts of water is often used in analysis as dilute hydrochloric acid.

Nitrate of hydrogen *or* nitric acid (HNO_3).

The commercial acid generally contains a little hydrochloric and sulphuric acid (H_2SO_4); it may, however, be obtained pure. The diluted acid should have the specific gravity of 1·12, and is made by mixing 1 volume of strong acid with 2 of water.

Acetate of hydrogen *or* acetic acid ($HC_2H_3O_2$ *or* $H\bar{A}$).

This acid as obtained in commerce is of sufficient purity for most analytical operations. It should have a specific gravity of 1·048. It occasionally contains sulphuric acid.

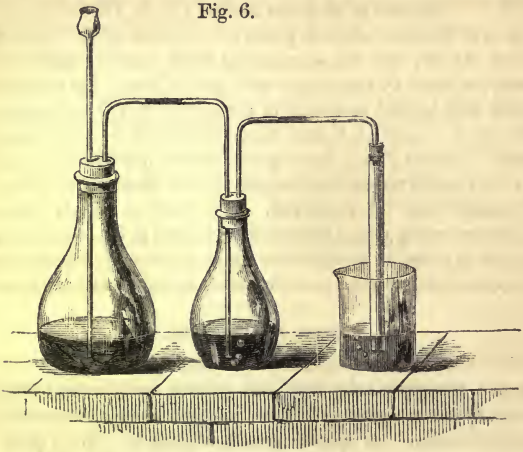
Oxide of hydrogen *or* water (H_2O).

This substance, as it commonly occurs, holds various salts in solution, of which the principal are the chlorides, sulphates, and carbonates of potassium, sodium, calcium, and magnesium: from these impurities it may be separated by distillation.

Sulphide of hydrogen *or* hydrosulphuric acid *or* sulphuretted hydrogen (H_2S).

This substance may be easily prepared by acting upon almost any metallic sulphide with hydrochloric acid or with sulphuric acid; in practice, however, the protosulphide of iron (Fe_2S) is almost invariably employed: the evolved gas is washed by passing it through a wash-bottle containing a small quantity of water, and it may be afterwards dried by passing it through a tube containing chloride of calcium in small fragments. The solution of this gas in water may be prepared by passing the gas into distilled water as long as it is dissolved, which may be ascertained by observing whether the bubbles as they pass through the liquid are dissolved, or whether they escape without diminution: a saturated solution of this gas is much employed in analysis.

Fig. 6.



Sulphurous acid (H_2SO_3).

This acid is not known to us in the separate state, but only as a solution of the compound called sulphurous acid gas (SO_2) in water (H_2O). Sulphurous acid gas is evolved when charcoal (C), copper (Cu), or mercury (Hg) are boiled with concentrated sulphuric acid. The following changes occur:—

$$2(H_2SO_4)+C=2(H_2SO_3)+CO_2$$

$$2(H_2SO_4)+2Cu=H_2SO_3+Cu_2SO_4+H_2O:$$

but the sulphurous acid splits thus—

$$H_2SO_3=H_2O+SO_2.$$

Sulphurous acid gas may be washed, and water may be saturated with it, just as in the case of ammonia gas.

Sulphuric acid (H_2SO_4).

The common impurities of the commercial acid are lead (Pb) and arsenic (As); both are separated by passing a stream of sulphuretted hydrogen through the diluted acid. For ordinary purposes a good specimen of commercial acid suffices, but for special cases, such as the detection of poisons in medico-legal investigations, it is necessary to employ an acid which is absolutely pure. The dilute acid employed in analysis is prepared by mixing 1 part of the concentrated acid (oil of vitriol) with 5 parts of water; the greater part of the lead is separated by this dilution.

Carbonic acid (H_2CO_3).

This acid is not known to us in the separate state, but only as a solution of carbonic acid gas (CO_2) in water (H_2O), for $H_2CO_3=CO_2+H_2O$. The gas (CO_2) can be easily prepared by decomposing any carbonate by an acid in an apparatus similar to that figured on page 64. Carbonate of calcium (marble) and hydrochloric acid (HCl) are usually employed:—

$$Ca_2CO_3+2HCl=H_2CO_3+2CaCl;$$

but the carbonic acid is immediately decomposed into water and carbonic acid gas, which may be passed into water, in which a portion will dissolve, or into the solution to be submitted to its action.

Oxalic acid ($H_2C_2O_4$ *or* $H_2\bar{O}$).

The commercial substance is of sufficient purity for ordinary operations. It may be purified by sublimation. 1 part of crystals should be dissolved in 20 of water.

Sulphindigotic acid.

The solution of indigo in oil of vitriol, or strong sulphuric acid, is called by this name. It is used in a very dilute state as a chemical test.

Tartaric acid ($H_2C_4H_4O_5$ *or* $H_2\bar{T}$).

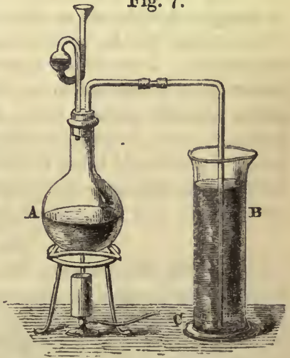
This acid is met with of sufficient purity for almost all analytical purposes. It may be purified by recrystallization.

Hydrofluosilicic acid ($H_3Si_2F_9$).

This acid is prepared as follows:—A mixture of 1 part of sand (Si_2O_3) and 1 part of fluoride of calcium (CaF) is introduced into the flask A; 6 parts of concentrated sulphuric acid are then added, and heat applied by means of a sand-bath. A glass delivery-tube passes through 4 parts of water placed in the jar B, and dips beneath the surface of the mercury, C, at the bottom of the vessel. The following actions take place:—Hydrofluoric acid (HF) is generated by the action of the sulphuric acid on the fluoride of calcium (CaF), and in its turn this hydrofluoric acid acts upon the sand present, producing gaseous fluoride of silicon; thus—

$$2(CaF)+H_2SO_4=2(HF)+Ca_2SO_4;\ \text{and}$$
$$6(HF)+Si_2O_3=3(H_2O)+\underbrace{2(SiF_3)}_{\text{Fluoride of silicon.}}$$

Fig. 7.



The fluoride of silicon escapes through the mercury, C, into the superincumbent layer of water, and by the latter it is instantly decomposed, silicic acid being again formed and precipitated, while the hydrofluosilicic acid remains dissolved in the water; thus—

$$6(SiF_3)+4H_2O=2(HSiO_2)+2(H_3Si_2F_9).$$

The use of the mercury in preventing the access of water to the mouth of the delivery-tube is obvious: the liquid should be filtered through a linen cloth to separate the gelatinous silicic acid, and the filtrate preserved in a bottle of German glass.

Acid Elements.

Carbon (C).

The charcoal selected for blowpipe examinations should be made of sound beechwood, and should be free from bark or knots. If the pieces are about 1½ inch in diameter, they should be sawn into pieces of about 4 inches in length, and each piece should be divided longitudinally, the flat surfaces of the section being well adapted for blowpipe experiments.

Bromine (Br).

This salt-radical may be obtained in commerce of sufficient purity.

Chlorine (Cl).

Chlorine may be easily prepared by one of the methods given on p. 19; if required dry it may be passed over fragments of fused chloride of calcium ($CaCl$) in a long tube, or over pieces of pumice-stone soaked in oil of vitriol.

Test Papers.

Vegetable blues, or at least most of them, possess the peculiar property of becoming red when moistened with an acid, *i.e.* the hydrogen salt of a simple or compound acid-radical, while their original colour is restored by an alkaline solution, that is, by the solution of a substance whose basic properties are definite. Some of the most delicate vegetable blues even assume a new colour when submitted to an alkaline liquid, becoming a brilliant green, whilst vegetable yellows, when dipped into alkaline solutions, become red-brown, but are not influenced by acids beyond the restoration of their original colour (boracic acid being an exception, for it behaves like an alkali). These indications, although very valuable, must not be too implicitly relied on, since certain salts which are theoretically neutral produce changes of colour.

Blue litmus paper.

The litmus of commerce should be dissolved in water, and very dilute sulphuric acid added to the clear blue solution until the colour has been changed to a reddish violet; the blue colour is then restored by the addition of a small quantity of the original solution: white writing-paper, not highly glazed, is then to be painted with the blue liquid, on one side only, and the coloured pieces, when dry, are to be cut into narrow strips for use, and preserved in a well-stoppered bottle.

Red litmus paper.

This may be prepared by using the blue liquid just mentioned, after having slightly reddened it with a drop of very dilute sulphuric acid.

Dahlia paper.

If the richly-coloured petals of the purple dahlia, or those of the heartsease, are boiled with alcohol, a red solution is obtained, which is of far greater delicacy than that produced by common litmus; it will become green also by the action of alkalies. Paper may be coloured with it as with the litmus solutions.

Turmeric paper.

An alcoholic extract of turmeric-root is of an orange-yellow colour, and becomes reddish brown when submitted to the action of alkaline solutions.

Manganese paper.

Strips of paper dipped in a moderately strong solution of manganous sulphate ($Mn_2 SO_4$) are occasionally employed for the detection of ozone.

Acetate of lead paper.

Strips of paper steeped in a solution of acetate of lead ($PbC_2 H_3 O_2$) are very useful in the detection of sulphuretted hydrogen ($H_2 S$).

Starch paper.

Strips of paper dipped in solution of starch made by boiling starch in water, and kept somewhat moist, are very useful in the detection of bromine and iodine.

ORGANIC BODIES.

Those forms of these bodies found in commerce may be safely employed, selecting, of course, the uncoloured variety of Starch ($C_{12} H_{20} O_{10}$); the purest white Sugar ($C_{12} H_{22} O_{11}$), and that kind of Gelatine known as isinglass.

CHAPTER VI.

DETECTION OF THE BASIC RADICALS IN THEIR COMPOUNDS.

WE have now introduced to the notice of the student the characteristic features of the basic and acid elements, existing as elements in the uncombined state, and have remarked upon the peculiar properties which they manifest, and by means of which their identity can always be safely established. The consideration, however, of the laws of chemical combination will have rendered it apparent that, from the extremely energetic properties which have been impressed upon these classes of elementary matter, it must be a comparatively rare occurrence to find them existing in nature in the isolated or uncombined condition; and therefore, if we are provided with no other means of recognizing them than those which apply to that state, these bodies must frequently elude us. Such means are not, however, wanting; and it will be seen from the observations which follow, and from the details which will occupy this and the next chapter, that the tests which we can apply to prove the existence of these bodies in their compounds, are, if possible, still more copious and conclusive than those which serve to assure us of their presence when they exist in the elementary state.

In the present chapter we shall devote ourselves exclusively to the detection of the *basic radicals in their compounds*; reserving the description of the methods of distinguishing the acid radicals of compound bodies for a subsequent chapter.

The principal means at our disposal for the recognition of a basic radical, is by the addition of some reagent to produce a saline combination which shall contain it, and which shall be at the same time easily identified by some remarkable physical or chemical characters. The majority of those compounds, the formation of which is held to be most conclusive proof of the presence of a basic radical, are such as present some *striking peculiarity of colour, or of insolubility in certain menstrua, or of colour and insolubility combined*; but there are others again which are *gases of well-marked properties*; and these are equally recognizable, and no less certain criteria of the presence of the body sought for.

The great mass of the basic radicals with which the student will have to do being elementary, no proof can be obtained of their presence from any decompositions which they might undergo; the compound basic radicals, as ammonium, strychnine, morphine, and quinine, being of complex constitution, may be thus recognized.

Without further remark we will now proceed to state at length the various tests for the basic radicals when in combination, pausing only to give a synoptical view of the subdivisions to be adopted, the members of each of which will be found identical with those given at page 3, as the subdivisions of the basic elements. In Subdivision III., however, three organic bases have been introduced.

1. Salts, the solutions of which are not precipitated by carbonate of ammonium; by a mixture of the chloride, hydrate, and sulphide of ammonium; or by the passage of hydrosulphuric acid gas through their acid solution:—

Salts of Potassium, Sodium, Lithium, and Ammonium.

2. Salts, the solutions of which are precipitated by carbonate of ammonium; but not by a mixture of chloride, hydrate and sulphide of ammonium, nor by the passage of hydrosulphuric acid gas through their acid solution:—

Salts of Barium, Strontium, Calcium, and Magnesium.

3. Salts, the solutions of which are precipitated by carbonate of ammonium, and also by a mixture of chloride, hydrate and sulphide of ammonium; but not by the passage of hydrosulphuric acid gas through their acid solution:—

Salts of Yttrium, Erbium, Terbium, Thorinum, Cerium, Lanthanium, Didymium, Zirconium, Glucinum, Aluminium, Chromium, Uranium, Iron, Manganese, Cobalt, Nickel, Zinc, Morphine, Quinine, Strychnine.

4. Salts, the solutions of some of which are precipitated by carbonate of ammonium, and by a mixture of chloride, hydrate and sulphide of ammonium; but all of which, without exception, are precipitated by the passage of hydrosulphuric acid gas through their acid solution:—

Salts of Cadmium, Copper, Silver, Mercury, Lead, Bismuth, Palladium, Tin, Antimony, Arsenic, Platinum, Rhodium, Ruthenium, Iridium, Osmium, Gold, Tungsten, Molybdenum, Vanadium.

SUBDIVISION I.

SALTS OF POTASSIUM, SODIUM, LITHIUM, AND OF THE COMPOUND METAL AMMONIUM.

The number of these combinations is of course only limited by the number of acid-radicals in existence, each of the above basic bodies (and the same observation is true of most of the basic radicals) having the property of forming salts with every acid radical. The stability of these combinations varies with the accurate opposition of the combining substances to each other; if they are unequally matched, then a ready decomposition is effected, if a more appropriate combination can afterwards occur. Since the metals of this subdivision are the most powerfully basic bodies with which we are acquainted, the inequality of power, if there be any, is always on the side of the acid-radical, and such compounds are invariably decomposed when brought into contact with an acid-radical of more intense properties. The metallic chlorides (MCl), bromides (MBr), iodides (MI), and sulphates (M_2SO_4) are among the more stable; while the nitrates (MNO_3), oxides (M_2O), sulphides (M_2S), hydrates (MHO), sulphydrates (MHS), and carbonates (M_2CO_3), are examples of the more easily decomposable salts of these metals. The decompositions take place as follows:—

$$M_2O + 2HCl = H_2O + 2MCl$$
$$M_2CO_3 + H_2SO_4 = H_2CO_3 + M_2SO_4$$
$$MHO + HBr = H_2O + MBr.$$

These observations also apply to the corresponding salts of almost every basic radical known.

The salts of the metals of this group are remarkable for their great solubility in water; and especially is it to be noted that their oxides, sulphides, carbonates*, sulphates, oxalates, and phosphates are soluble in that menstruum. The application of this statement will be seen when the salts of the other metals are considered, since many of their combinations with the acid radicals mentioned above are insoluble in water.

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* The rare metal lithium presents a remarkable exception here, its carbonate and phosphate being insoluble.

There are certain conventional expressions applied to the salts of this group with which the student should familiarize himself:—

1. Their hydrates (MHO) are termed "the alkalies," or "the caustic alkalies;" and the hydrates of potassium and sodium are called "the fixed caustic alkalies," in contradistinction to the hydrate of ammonium, which is very volatile.

2. Their salts in general are called "salts of the alkalies," or "alkaline salts;" and such expressions as "the sulphates of the alkalies," or "an alkaline acetate," are frequently employed.

There is a very striking family resemblance among the salts of this group of metals in many of their physical and chemical properties; many of the combinations of the different members of the group, with the same acid-radical, crystallize in the same form, or are *isomorphous*: they are all colourless also, unless combined with a coloured acid-radical; and in peculiarity of taste, and absence of actively poisonous properties, they possess a great similarity.

Since the great object of analysis is continually to subdivide larger into smaller groups, until at last each individual member is isolated, we will at once divide this group into two sections, by availing ourselves of the following properties of the different members:—

SECTION I.—SALTS OF POTASSIUM, SODIUM, AND LITHIUM.

Not volatilized by exposure in a dish to the heat of a naked flame, *i. e.* by ignition.

SECTION II.—SALTS OF AMMONIUM.

Readily volatilized by ignition.

We have comparatively slender means at our disposal for the detection of all these metals, on account of the great solubility of most of their salts in all menstrua; for it must be remembered that our recognition of substances depends for the most part upon the formation of some insoluble salt of well-defined physical peculiarities of colour or form. The few salts which are insoluble present, however, such striking features, as almost to defy mistake.

SECTION I.—*Bodies not volatilized by ignition.*

SALTS OF POTASSIUM, SODIUM, AND LITHIUM.

SALTS OF POTASSIUM.

Solution for the reactions:—chloride of potassium (KCl) in water.

The metal potassium combines with oxygen in two proportions, forming a protoxide K_2O, and a peroxide K_2O_2; oxygen is, however, the only acid-radical with which potassium is known thus to combine; every other salt which it forms contains the basic and acid-radicals, either in the same relative proportion as they occur in the protoxide K_2O, or in those in which they occur in the (proto-)chloride KCl, they are therefore termed proto-salts; and all may be referred to the two types of MCl and M_2O. The potassium salts are white, unless the acid-radical contained in them, or an associated basic radical, is coloured; they are good examples of the taste known as saline, and are not usually poisonous, unless taken in very large quantities; they are often employed in medicine.

When heated before the blowpipe they frequently decompose, if their acid-radical is a compound; and this decomposition is the more readily effected when they are heated in the presence of some powerful chemical agent, such as charcoal, which forms the usual support for substances undergoing the blowpipe examination.

This body, although inert generally at low temperatures, becomes at high temperatures a very powerful chemical agent, and by its influence under such circumstances, a sulphate, for instance, would be converted into a sulphide, thus—

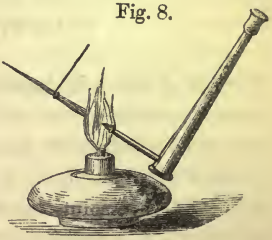
$$K_2SO_4+2C=K_2S+2CO_2:$$

or again, a nitrate would yield a carbonate by the joint effect of the heat and the carbonic acid produced by the combustion of the charcoal, thus—

$$4KNO_3+5C=2K_2CO_3+3CO_2+4N.$$

Some salts, nevertheless, generally those which contain the elementary acid-radicals, but also a few others, as the cyanide and the carbonate, resist this method of decomposition. All potassium salts, however, when so heated, fuse, and, with but few exceptions, sink into the charcoal. They impart also a violet tinge to the blowpipe flame playing over them,—the cause of this is the volatilization of a small portion of the salt, and its subsequent decomposition by the carbonaceous constituents of the flame, with separation of potassium. Potassium, it will be remembered, when combining with oxygen, inflames, burning with a violet light; to the trace of potassium-vapour produced in this experiment, and its immediate reoxidation on contact with the highly-heated air surrounding the flame, the reaction in this case is due. A good method of performing this experiment is to dip a loop of platinum wire (perfectly clean and imparting by itself no colour to the blowpipe flame) into a solution of the potassium salt to be tested: the blowpipe flame should be as blue as possible, with no white streaks which would interfere with the observation of the colour: the woodcut shows the arrangement. If a potassium salt be mixed with good alcohol, and the mixture repeatedly stirred, upon setting it on fire the characteristic violet flame will be produced.

Fig. 8.



Almost the only insoluble salts which potassium forms, and by means of which it may be recognized, are the following:—the chloroplatinate, perchlorate, carbazotate, and acid tartrate.

The Chloroplatinate is produced by the action of hydrochloroplatinic acid ($HPtCl_3$) [the so-called bichloride of platinum ($PtCl_2$), with 1 equivalent of hydrochloric acid (HCl)] on solutions of potassium salts: it is a yellow crystalline precipitate; the crystals are octahedral, and belong to the regular system. The test, as is the case with most other liquid tests, is applied by simply mixing it with the solution to be tested; and if the precipitation of the insoluble salt does not occur immediately, it is well to agitate the liquid by stirring, or by shaking the test-tube containing it. In the present instance, to hasten the change, a few drops of hydrochloric acid should be added at the same time as the test-liquid; the presence of alcohol also renders the precipitate more insoluble. If so small a quantity of potassium should be present as to give no precipitate under these circumstances, the chloroplatinate of potassium may yet be obtained by evaporating the solution to which the reagent has been added just to dryness, and then digesting it with alcohol. The chloroplatinate being far more insoluble in that menstruum than in water, remains as a yellow residue if but a minute trace only of potassium be present.

The formula of the precipitate is $KPtCl_3$, in which the K is the basic and the $PtCl_3$ the acid radical. The double decomposition which produces it is as follows:—

$$KCl + HPtCl_3 = HCl + \underset{\text{yell. ppt.}}{KPtCl_3}.$$

1 part of this salt dissolves in 1·44 parts of cold water, but it is more soluble in hot water: 1 part requires about 3775 parts of rectified spirit for its solution.

THE PERCHLORATE is produced by the action of perchloric acid ($HClO_4$) in solutions of potassium salts, if the latter are not too dilute: it is a white crystalline precipitate; the crystals are right rhombic prisms. Its formula is $KClO_4$. 1 part dissolves in 65 parts of water at 15° C., and in a less quantity of boiling water. It is quite insoluble in alcohol.

THE CARBAZOTATE is produced by the action of carbazotic acid* ($HC_6H_2X_3O$) on solutions of potassium salts: it is a yellow precipitate which is crystalline, the crystals belonging to the rhombic system. Its formula is $KC_6H_2X_3O$. 1 part requires 260 parts of water at 15° C. for its solution. It is insoluble in alcohol.

The Acid Tartrate is produced by excess of tartaric acid

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* $X = NO_2$, a radical which, in the *nitro-substitution compounds*, is found to replace H.

($H_2C_4H_4O_6$ *or* $H_2\bar{T}$) added to solutions of potassium salts: it is then precipitated rapidly, particularly if they be shaken or stirred. The delicacy of this test is much increased if a solution of the acid tartrate of sodium is added, instead of tartaric acid, to a neutral solution of the potassium salt. It is a white crystalline precipitate, the form of the crystals being that of the oblique prism with a rhombic base, and belonging to the monoclinic system.

The formula of the precipitate is $KHC_4H_4O_6$ *or* $KH\bar{T}$; the reaction producing it is as follows:—

$$KCl+H_2\bar{T}=HCl+\underset{\text{white ppt.}}{KH\bar{T}}.$$

It is important that excess of tartaric acid should be present, and not excess of the potassium salt, as in the latter case the neutral tartrate, $K_2\bar{T}$, would be formed, and this is a perfectly soluble salt. The neutral tartrate is also produced by dissolving the acid tartrate in potash (KHO) solution, thus,—

$$KH\bar{T}+KHO=KK\bar{T}+H_2O.$$

1 part of acid tartrate of potassium dissolves in 240 parts of water at 10° C.: it is insoluble in alcohol. It dissolves in strong acids.

THE SILICOFLUORIDE is produced by the action of hydrofluosilicic acid ($H_3Si_2F_9$); a very slight gelatinous film at first appears in the liquid, but gradually thickens to a precipitate. Its formula is $K_3Si_2F_9$. It dissolves very sparingly in cold, but more readily in hot water.

THE ACID METANTIMONIATE is soluble.

The tests most commonly employed for the detection of potassium are, the violet colour of the blowpipe flame, and the formation of the chloroplatinate and the acid tartrate.

SALTS OF SODIUM.

Solution for the reactions:—chloride of sodium (NaCl) in water.

The metal sodium resembles potassium very closely. It forms two compounds with oxygen, a protoxide (Na_2O), and a peroxide (Na_2O_3); but among the numerous salts which this metal forms with other acid-radicals, none are found corresponding to the peroxide. The salts of sodium are therefore all regarded as formed after the types protochloride (MCl), and protoxide (M_2O), and so are called proto-salts. They are white, unless associated with a coloured acid-radical; they possess in general no poisonous properties; one indeed, the chloride (NaCl), appears to be quite necessary to the well-being of the animal organism.

When heated on charcoal before the blowpipe, sodium salts, like potassium salts, fuse and sink into the charcoal, and suffer similar decompositions. They impart to the blowpipe flame a brilliant yellow tinge, which is much more intense than the violet colour produced by potassium salts, the latter being less volatile than those of sodium. Thus, in a mixture of salts tested in this manner, the potassium flame is entirely masked by the sodium, unless the salt of the former metal is present in greatly preponderating quantity: if the sodium salt is mixed with even 20 or 30 times its weight of the potassium compound, the yellow colour, though weakened, is still distinctly perceptible. The same colour is observed when alcohol is inflamed after digestion with sodium salts.

The only insoluble salt by means of which sodium can be recognized, is the acid metantimoniate; but the test is not delicate, and is difficult of application.

THE CHLOROPLATINATE and the PERCHLORATE are soluble.

THE CARBAZOTATE is soluble; but a slight precipitate occurs in very concentrated solutions.

THE ACID TARTRATE is soluble; but a slight precipitate occurs in very strong solutions.

THE SILICOFLUORIDE is much more soluble than the corresponding potassium compound.

The Acid Metantimoniate is produced by the action of metantimoniate of potassium ($K_2H_2Sb_2O_7 + 6aq$). This reagent is liable to decomposition* by keeping its solution; it should

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* Metantimoniate of potassium ($K_2H_2Sb_2O_7$) passes readily into antimoniate of potassium ($KSbO_3$) by losing H_2O; thus—

$$K_2H_2Sb_2O_7 = 2KSbO_3 + H_2O.$$

therefore be dissolved only just before applying the test. The precipitate separates in crystalline grains, but does not appear immediately if the solution be dilute: the deposition is facilitated by agitation.

Its formula is $Na_2H_2Sb_2O_7+6aq$.

It is almost insoluble in cold water, but slightly soluble in boiling water. It is quite insoluble in alcohol. In carbonate of potassium solution it dissolves, but not in other potassium salts.

The tests employed in practice for the detection of sodium are, the colour of the blowpipe flame, and the formation of the acid metantimoniate: the former of these is very delicate; the latter, however, is little used.

SALTS OF LITHIUM.

Solution for the reactions:—chloride of lithium ($LiCl$) in water.

Lithium differs in many respects from the two preceding metals; it forms two combinations with oxygen, but the salts of lithium are all proto-salts; of these we may take the chloride ($LiCl$) and the oxide (Li_2O) as types. The lithium salts are white when the acid-radical is colourless.

They are more fusible than the potassium or sodium salts, and impart a very distinct carmine colour to the blowpipe flame; the presence of a large quantity of a potassium salt does not materially interfere with this reaction, but a small quantity of a sodium compound gives rise to a yellow flame.

The insoluble salts by which lithium may be recognized are these:—the carbazotate, the carbonate, the phosphate, and the silicofluoride.

THE CHLOROPLATINATE and the PERCHLORATE are soluble.

THE CARBAZOTATE is produced by the action of carbazotic acid.

The Carbonate is produced by the action of a very soluble neutral carbonate, *e.g.* carbonate of potassium (K_2CO_3), of sodium (Na_2CO_3), or of ammonium ($[NH_4]_2CO_3$), upon rather concentrated solutions of salts of lithium: it is crystalline.

Its formula is Li_2CO_3. 1 part requires 100 parts of cold water for its solution, but less of boiling water. By most acids it is decomposed and dissolved: it is insoluble in alcohol.

THE ACID TARTRATE is soluble.

The Phosphate is produced by the action of phosphate of sodium (Na_2HPO_4) on solutions of lithium salts: the precipitation takes place especially on ebullition. If the solution is then evaporated to dryness, and the residue treated afresh with water, a perfect separation of the lithium is effected. This salt is a white powder.

Its composition is said to be variable: some analyses give the formula $LiNaHPO_4$.

It is nearly insoluble in water containing phosphate of soda, scarcely soluble in cold water, but more so in hot. It dissolves in dilute nitric acid.

THE SILICOFLUORIDE is insoluble.

The distinguishing features by which lithium salts are recognized are practically these,—the carmine-coloured blowpipe flame, and the very insoluble phosphate of lithium and sodium.

SECTION II.—*Bodies readily volatilized by ignition.*

SALTS OF AMMONIUM.

Solution for the reactions:—chloride of ammonium (NH_4Cl) in water.

Ammonium (NH_4) is the first compound metal with which the student has to deal. It is not known in the separate state, but the salts in which it exists are very numerous: they are all proto-salts, 1 equivalent of NH_4 being equal to 1 equivalent of H; in other words, the basic radical ammonium is monatomic. All these salts are colourless, unless their constituent acid-radical is coloured; they are not actively poisonous unless their acid-radical has very poisonous properties.

When heated, ammonium salts entirely volatilize, and in so doing impart no colour to the flame (the chloride indeed tinges the flame blue, but this is due to the chlorine).

They may, however, be immediately recognized by their behaviour when warmed gently with hydrate of potassium (KHO); a double decomposition occurs, thus,—

$$NH_4Cl + KHO = KCl + NH_4HO.$$

The hydrate of ammonium thus produced decomposes into water (H_2O) and *ammonia* gas (NH_3). This gas has a most peculiar pungent odour, termed ammoniacal, but better known as that of hartshorn, or spirits of sal-volatile. The pungent odour is sufficient to reveal the presence of this gas, which may also be detected by holding over the mouth of a test-tube from which it is issuing, a stout rod moistened with concentrated hydrochloric or acetic acid, when dense white fumes will be seen about the rod, instead of the ordinary almost transparent vapour of the acid; this effect is due to the formation of an ammonium salt,

$$NH_3 + HCl = \underset{\text{White fume.}}{NH_4Cl.}$$

The principal insoluble salt by which this metal is recognized is the chloroplatinate.

The Chloroplatinate is produced by the action of chloroplatinic acid ($HPtCl_3$) on solutions of ammonium salts. It is a yellow crystalline precipitate, resembling the corresponding potassium salt in being octahedral, and belonging to the regular system.

Its formula is $NH_4 PtCl_3$.

It is very insoluble in cold water, but more so in hot; it is still more insoluble in alcohol, 1 part requiring 1405 parts of rectified spirit for its solution. It is more soluble in dilute acid than in pure water.

THE PERCHLORATE and the CARBAZOTATE are soluble.

THE ACID TARTRATE is only produced by tartaric acid ($H_2\bar{T}$), when added to very concentrated solutions of ammonium salts, especially of the hydrate. It is a white crystalline precipitate of the same form as the corresponding potassium compound.

Its formula is $NH_4 H \bar{T}$.

It is as readily soluble in the hydrate of ammonium ($NH_4 HO$) as the potassium salt is in hydrate of potassium (KHO), the very soluble neutral tartrate being thereby formed. It is rather insoluble in cold water, but dissolves freely in boiling water; it is more insoluble in alcohol, and more soluble in acids.

THE SILICOFLUORIDE is soluble.

The tests to be actually employed for the detection of ammonium obviously are, the volatility of the salt, its ammoniacal odour when heated with solution of hydrate of potassium (KHO), or when mixed with moist hydrate of calcium ($CaHO$), and its precipitation by chloroplatinic acid.

REACTIONS.	K.	Na.	Li.	NH_4.
Chloroplatinate...	yellow crystalline	—	—	yellow crystalline
Perchlorate	white	—	—	—
Carbazotate	yellow crystalline	—	yellow crystalline	—
Carbonate	—	—	white	—
Acid tartrate	white crystalline	—	—	white crystalline
Phosphate	—	—	white	—
Silicofluoride	white gelatinous	—	white gelatinous	—
Acid metantimoniate	—	white granular	—	—
Colour imparted to blowpipe flame	violet	yellow	carmine	—

In order to avoid too much verbal recapitulation, and to show the student the method of consecutively applying the tests above mentioned when searching either for one or more of the basic radicals which the subdivision contains, the Table on the following page is annexed. Tables, it must be remembered, are not guides to be followed blindly, but only indications of the kind of course which the student should pursue in analysis; the best can after all be but descriptions of one series of methods, of which several may be equally good for the attainment of the same end; and the student should bind himself to no one formula, but seek frequently to vary his method of analysis by adopting other sequences of experiments. Greater scope will be afforded him in the succeeding subdivisions than in the present one for so doing; and in the Tables which will be appended to each, we shall not always select that which is believed to be the best method of distinguishing a substance, if a slightly inferior one is more striking. Tables, nevertheless, which contain the most accurate methods are of great value, and a complete series of such will be found in the second part of the present volume: they will be constructed upon the supposition that all the substances occurring in their respective subdivisions are present, whilst in those appended to each subdivision it will be assumed that one member only is to be detected.

Analysis of Subdivision I.

The salt may be one of POTASSIUM, SODIUM, LITHIUM, or AMMONIUM.

<table>
<tr><td colspan="4">Ignite the substance; if nothing volatilizes, we infer the</td></tr>
<tr><td rowspan="3">absence of Ammonium, and confirm it by gently warming a fresh portion of the original substance with solution of hydrate of potassium.</td><td colspan="3">presence of
Potassium, Sodium, or Lithium.
Dissolve a portion of the ignited salt in a few drops of water, add one drop of hydrochloric acid and a few drops of bichloride of platinum, and stir; if no precipitate is produced, even after the addition of alcohol, and the lapse of some time, we infer the</td></tr>
<tr><td rowspan="2">absence of Potassium.</td><td colspan="2">presence of
Sodium or Lithium.
Dissolve the rest of the ignited salt in water, add solution of phosphate of sodium, and evaporate to dryness on a water-bath; redissolve in a small quantity of cold water; if an insoluble residue is left, we infer the</td></tr>
<tr><td>absence of Sodium.</td><td>presence of Lithium.</td></tr>
</table>

SUBDIVISION II.

SALTS OF BARIUM, STRONTIUM, AND CALCIUM; AND OF MAGNESIUM.

One great distinction between this and the first subdivision may be at once pointed out; it is this: that a far smaller number of the salts of these metals is soluble in water; and among the insoluble, or nearly insoluble salts, are found the sulphates, carbonates, oxalates, and phosphates, nearly all of which are easily soluble in the first group, nearly all almost insoluble in the present. It is, however, especially to be remembered, that among the soluble salts of this subdivision the oxides and sulphides are ranked, because this constitutes a distinguishing feature between the first two and the last two subdivisions. If we desire to separate the metals of this group from those of the preceding one, we have only to form their carbonates, oxalates, or phosphates;

the metal is thus precipitated in an insoluble combination, and being collected on a filter, the clear liquid passing through will contain the salts of the first subdivision. The way in which these insoluble salts are formed, is by adding a soluble salt of the required acid-radical to the solution which we wish to precipitate; now almost the only soluble salts of the acid-radicals in question are the hydrogen salts (the so-called acids), and the salts containing the metals of the first subdivision (the alkaline salts); of these, for reasons which will soon be obvious, we prefer to employ the ammonium salts, and of the ammonium salts the neutral carbonate $(NH_4)_2CO_3$ is the most advantageous. Any salt thus chosen as the precipitant of an entire group is commonly called the group-test or group-reagent; in fact, we find in every subdivision that there is a certain reagent which precipitates every member of the group, to which this name of group-reagent has been applied. Afterwards other reagents are used, some of which exercise their action on several members, some on individuals only. Subdivision I. has no such general reagent; the entire group is not precipitated by any single substance, we are therefore obliged to resort to particular or special tests.

Certain conventional expressions are attached to the compounds of this subdivision also. Their oxides and hydrates are called "the alkaline earths," and their other salts "the salts of the alkaline earths."

The three first members of the subdivision bear a very strong resemblance to each other; their salts are for the most part colourless, except in those cases where the acid-radical is coloured. The compounds of barium are very poisonous, but those of strontium and calcium are not so. The fourth member, magnesium, differs in many respects from the others, many of its salts are far more soluble in water; this difference is strikingly exhibited in the case of its sulphate, which is an extremely soluble salt, while the sulphates of the other three metals are almost insoluble.

The second subdivision is as readily broken up into two parts or sections as the first, although by different means.

SECTION I.—SALTS OF BARIUM, STRONTIUM, AND CALCIUM.

Precipitated by carbonate of ammonium ($[NH_4]_2CO_3$), and not redissolved by the addition of chloride of ammonium (NH_4Cl).

SECTION II.—SALTS OF MAGNESIUM.

Precipitated by carbonate of ammonium ($[NH_4]_2CO_3$), and redissolved by the addition of chloride of ammonium (NH_4Cl).

Since so many insoluble salts occur in this group, there is less difficulty in recognizing its different members than in the case of the preceding subdivision.

The group-test is carbonate of ammonium ($[NH_4]_2CO_3$).

SECTION I.—*Precipitated by Carbonate of ammonium* ($[NH_4]_2CO_3$), *and not redissolved by Chloride of ammonium* (NH_4Cl).

SALTS OF BARIUM, STRONTIUM, AND CALCIUM.

SALTS OF BARIUM.

Solution for the reactions:—chloride of barium ($BaCl$) in water.

Barium forms two combinations with oxygen, a protoxide (Ba_2O) and a peroxide (Ba_2O_2). The protoxide is the type of a large number of barium salts; these are white unless the acid-radical in them introduces colour into the compound; those which are soluble are extremely poisonous.

When heated before the blowpipe, especially in the presence of a reducing agent such as charcoal, they are frequently converted into oxide; in these cases the oxide remains infusible, and becomes somewhat incandescent; but if the salt resists decomposition, as do the chloride, bromide, and iodide, it remains as a fused mass upon the charcoal. A platinum wire moistened with a solution of a barium salt imparts a yellowish-green tinge to the blowpipe flame; this may also be observed with insoluble salts if they are previously moistened with an acid,—hydrochloric acid for instance. Barium salts impart no colour to the borax-bead.

The principal insoluble salts by means of which barium may be recognized are these:—the chromate, hydrate, sulphate, carbonate, phosphate, and silicofluoride.

The Chromate is produced by the action of chromate of potassium ($KCrO_2$) on solutions of barium salts; in very dilute solutions it appears only after standing. It is a pale yellow precipitate. Its formula is $BaCrO_2$. It is almost absolutely insoluble in water, but is dissolved by most acids.

THE HYDRATE is produced by the action of the hydrates of potassium (KHO) or of sodium ($NaHO$) in moderately concentrated solutions of barium salts. The hydrate of ammonium (NH_4HO) produces no precipitate. It is to be observed that the salts of potassium and sodium may generally be employed indifferently as reagents, as they almost invariably act in the same manner; the salts of ammonium can only in certain instances be substituted for those of potassium or sodium, as in most cases they exercise an action peculiar to themselves. Many substances in fact are soluble in ammonium salts, but not in the salts of the fixed alkalies. The hydrate of barium is a white amorphous precipitate.

The formula of the hydrate is $BaHO + 4\frac{1}{2}aq$. Whenever H_2O is written as *aq*, it is always to be understood to signify "water of crystallization," or water loosely combined with the substance: this water need never be taken into account in writing the equation which represents the reaction; in the present case, for instance, the change which takes place is simply a mutual transference of acid and basic radical between the acting substances, and may be represented thus:—

$$BaCl + KHO = KCl + \underset{\text{White ppt.}}{BaHO}.$$

The hydrate of barium is comparatively soluble in water, 1 part dissolving in 35 parts of water at 13° C., and in 2 parts at 100° C. It is immediately dissolved by those acids whose barium salts are soluble, and it is decomposed by most others.

The Sulphate is produced by the action of sulphuric acid (H_2SO_4), or of soluble sulphates on solutions of barium salts: in very dilute solutions it becomes evident only after standing for a few seconds. It is a white pulverulent precipitate, which glistens somewhat in the light.

Its formula is $Ba_2 SO_4$.

It is one of the most insoluble substances known, 1 part dissolving in 43,000 parts of water: its solubility is not perceptibly increased by the presence of chloride of ammonium or chloride of sodium, nor by acids, although there are circumstances in which certain salts of citric acid prevent the formation of the precipitate of sulphate of barium.

The Carbonate is produced by the action of the neutral carbonate of potassium or ammonium (K_2CO_3 *or* $[NH_4]_2CO_3$) on solutions of barium salts. It is a white precipitate.

The formula is Ba_2CO_3.

This salt is slightly soluble in solutions of ammonium salts (especially in chloride of ammonium); it is almost perfectly insoluble in water, 1 part dissolving in 15,420 parts of water at the boiling temperature: it is readily decomposed by most acids; but dissolves in solution of carbonic acid (H_2CO_3), forming the soluble acid carbonate of barium ($BaHCO_3$), thus:—

$$Ba_2CO_3 + H_2CO_3 = 2(BaHCO_3).$$

The Oxalate is produced by the action of the oxalate of potassium or ammonium ($K_2C_2O_4$ *or* $[NH_4]_2C_2O_4$) on solutions of barium salts. It is a white pulverulent precipitate.

Its formula is $Ba_2C_2O_4$.

It is slightly soluble in a solution of chloride of ammonium, and dissolves in 200 parts of water (either cold or boiling). It is readily dissolved by most acids, but not by acetic acid ($H\bar{A}$ *or* $HC_2H_3O_2$).

The acid oxalate is produced by the action of oxalic acid ($H_2C_2O_4$) on solutions of barium salts; it appears, after standing for a few minutes, as a white crystalline precipitate: the crystals are very acute rhombohedrons. Its formula is $BaHC_2O_4$. 1 part of this salt dissolves in 336 parts of water at 15°·5 C.; it is more soluble in hot water, but less so in alcohol. It is dissolved readily by most strong acids.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium (K_2Cfy) on concentrated solutions of barium salts. It is a dense pale yellow and crystalline precipitate. Its formula (disregarding its water of crystallization) is $KBaCfy$; thus being in reality a ferrocyanide of potassium and barium. It is soluble in 36·38 parts of water at 14° C., and in 11·85 parts of boiling water.

THE PHOSPHATE is produced by the action of phosphate of sodium (Na_2HPO_4) on solutions of barium salts. It is a white pulverulent precipitate. Its formula is Ba_2HPO_4. It dissolves easily in solutions of many ammonium salts, from which it is reprecipitated by the hydrate of ammonium (NH_4HO). 1 part dissolves in 20,570 parts of water at 20° C.; it is readily dissolved by most acids, even by acetic acid.

The Silicofluoride is produced by the actîon of hydrofluosilicic acid ($H_3Si_2F_9$) on solutions of barium salts. It is a white, transparent and gelatinous precipitate, the separation of which is promoted by shaking and stirring the liquid, and by the addition of alcohol to it.

Its formula is $Ba_3Si_2F_9$.

1 part of this salt is soluble in 3802 parts of water at the ordinary temperature, or in 733 parts of water acidulated with hydrochloric acid: it is more soluble in hot water; nearly insoluble in alcohol.

The special tests employed for the detection of the various members of the preceding subdivision produce no precipitates with solutions of barium salts.

The special tests for barium which the student should particularly remember are these:—the yellowish-green blowpipe flame, the insolubility of the chromate and of the sulphate, and the production of the nearly insoluble silicofluoride.

SALTS OF STRONTIUM.

Solution for the reactions:—nitrate of strontium ($SrNO_3$) in water.

Strontium, like barium, forms two combinations with oxygen, a protoxide (Sr_2O) and a peroxide (Sr_2O_2). The protoxide may be regarded as the type of the large number of salts which this metal forms. Salts of strontium resemble barium salts in most of their chemical characters, but differ from them in being destitute of poisonous properties.

When heated before the blowpipe, strontium salts are for the most part converted into the oxide, which remains infusible, and becomes somewhat incandescent when the blowpipe flame is directed upon it. The chloride, bromide and iodide resist decomposition under these circumstances, and remain fused, and not decomposed even on charcoal. A wire moistened with a solution of any strontium salt imparts a fine crimson colour to the flame, which, unlike the similar colour imparted by lithium, does not disappear after long heating. The borax-bead is colourless and transparent.

The principal insoluble salts by which strontium is recognized are the hydrate, the sulphate, the carbonate, the oxalate, and the phosphate.

THE CHROMATE is soluble.

THE HYDRATE is produced by the action of hydrate of potassium (KHO) on rather concentrated solutions of strontium salts: the hydrate of ammonium (NH_4HO) produces no precipitate. It is white and flocculent.

Its formula is $SrHO + 4\frac{1}{2}aq$.

It is less soluble in water than the corresponding barium salt; 1 part requiring 50 parts of cold water, or 2·4 parts of boiling water for its solution. It is dissolved by those acids whose strontium salts are soluble, and decomposed by most others.

The Sulphate is produced by the action of sulphuric acid (H_2SO_4) or of soluble sulphates on solutions of strontium salts, unless they are extremely dilute. It is a white pulverulent precipitate.

Its formula is Sr_2SO_4.

It is somewhat more soluble than the corresponding barium salt. A solution of chloride of ammonium does not dissolve it; but in a solution of chloride of sodium it is gradually but completely taken up, although it is reprecipitated by the addition of sulphuric acid (H_2SO_4). 1 part dissolves in 6895 parts of water at 14° C., and in 9638 parts of boiling water.

The Carbonate is produced by the action of the neutral carbonates of potassium or ammonium (K_2CO_3 *or* $[NH_4]_2CO_3$) on solutions of strontium salts: it is a white precipitate.

Its formula is Sr_2CO_3.

This salt is more soluble in solutions of ammonium salts, especially chloride of ammonium, than is the corresponding barium compound. It dissolves in 18,045 parts of water at the ordinary temperature, but in a much less quantity of boiling water; it is readily decomposed by most acids; but in solutions of carbonic acid gas (CO_2) it dissolves without decomposition, in the same manner as the carbonate of barium, forming the analogous compound, namely, the acid carbonate of strontium ($SrHCO_3$).

The Oxalate is produced by the action of oxalic acid ($H_2C_2O_4$), or of soluble oxalates, even in dilute solutions of strontium salts. It is a white precipitate.

Its formula is $Sr_2C_2O_4$.

This salt is very soluble in hot aqueous solutions of chloride or nitrate of ammonium; it is very sparingly soluble in cold water, but dissolves in 19·2 parts of boiling water; it is dissolved readily by most strong acids, but not by acetic acid ($HC_2H_3O_2$, or $H\bar{A}$).

THE FERROCYANIDE is soluble.

THE PHOSPHATE is produced by the action of phosphate of sodium (Na_2HPO_4) on solutions of strontium salts. Its formula is Sr_2HPO_4. It dissolves readily in most ammonium salts, but is reprecipitated by the addition of hydrate of ammonium (NH_4HO). It is insoluble in water, but dissolves in most acids.

THE SILICOFLUORIDE is soluble, especially in the presence of acids.

The special tests of the first subdivision are without well-defined action on salts of strontium.

The special tests for strontium which the student should particularly remember are these:—the blowpipe flame, the action of sulphates on soluble strontium salts, and the absence of the reaction with chromates and silicofluorides; by means of this last test this metal is usually distinguished from barium, the reactions of which in most other respects are so similar to its own.

SALTS OF CALCIUM.

Solution for the reactions:—chloride of calcium ($CaCl$) in water.

Calcium, like the two preceding metals, forms two combinations with oxygen, a protoxide (Ca_2O), and a peroxide (Ca_2O_2): it combines with almost every acid-radical to produce salts; which, like those of barium and strontium, are all proto-salts. They are colourless, except in cases where the acid-radical introduces colour. They are devoid of poisonous properties.

These salts resemble those of the two preceding metals in their behaviour when heated before the blowpipe on charcoal, being for the most part decomposed into the oxide (lime). This oxide remains infusible, and is remarkably incandescent, the light which it emits increasing with the intensity of the heat, and reaching its maximum only when the lime is subjected to the highest temperature at our disposal—such, for instance, as that produced by the oxyhydrogen blowpipe. The light thus obtained has been utilized, and is known as the "lime light." The chloride, bromide, and iodide of calcium resemble the corresponding salts of barium and strontium in remaining undecomposed before the blowpipe flame on charcoal. A platinum wire, moistened with a solution of a calcium salt, tinges the flame of an orange-red colour; the colour, however, imparted by a *pure* salt of calcium is a very pure red, the orange tint which it generally has being in fact owing to the presence of a trace of sodium; the red of pure calcium salts may even be mistaken for the crimson of strontium compounds; actual comparison, nevertheless, shows the difference. The red colour may be observed even with the insoluble salts of calcium, by heating them before the blowpipe after they have been moistened with a strong acid, such as hydrochloric acid. The borax-bead is colourless.

The principal insoluble salts of calcium are the hydrate, the sulphate, the carbonate, the ferrocyanide, and the phosphate.

THE CHROMATE is soluble.

THE HYDRATE is produced by the action of hydrate of potassium (KHO) on solutions of calcium salts; the hydrate of ammonium (NH_4HO) produces no precipitate. The hydrate is a white bulky precipitate.

Its formula is CaHO.

This salt dissolves in about 730 parts of water at the ordinary temperature, but at temperatures about the boiling-point, in from 1310 to 1350 parts, thus presenting the peculiarity of being less soluble in hot than in cold water. It dissolves readily in most acids.

THE SULPHATE is produced by the action of sulphuric acid (H_2SO_4) or soluble sulphates on solutions of calcium salts, unless they are very dilute. It is a white, somewhat crystalline precipitate.

Its formula is Ca_2SO_4+2aq.

The solubility of this salt in water is increased by the presence of chloride of ammonium, or of other ammonium salts, and also by sodium salts, especially the chloride of sodium; from its solution in water containing this latter compound it is not reprecipitated, as the sulphate of strontium is, by the addition of sulphuric acid (H_2SO_4). Sulphate of calcium is far more soluble in water than the corresponding salts of barium and strontium, 1 part requiring about 460 parts of water, either at the ordinary temperature or that of boiling water, for its solution.

The Carbonate is produced by the action of the neutral carbonate of potassium or ammonium (K_2CO_3 *or* $[NH_4]_2CO_3$) on solutions of calcium salts. It is a bulky white precipitate, but when seen under the microscope, is found (as is the case with many other precipitates) to be crystalline. It is a substance which is said to be dimorphous, for it is capable of assuming two distinct crystalline forms not belonging to the same system: the occurrence of these forms is determined by the temperature at which the salt is produced; if precipitated in the cold, the crystals assume forms belonging to the rhombohedral system; if at the temperature of boiling water, they belong to the right prismatic system.

Its formula is Ca_2CO_3.

When recently precipitated, it dissolves with comparative ease in concentrated solutions of chloride of ammonium and other ammonium salts; it is also soluble to a slight extent in solutions of chloride of sodium. In water it is very slightly soluble, 1 part requiring 10,600 parts at the ordinary temperature, and 8834 parts of water at 100° C. for its solution. It is decomposed by most acids, and dissolved by solution of carbonic acid gas (CO_2), with formation of the acid carbonate ($CaHCO_3$).

The Oxalate is produced by the action of oxalic acid ($H_2C_2O_4$), or soluble neutral oxalates, on solutions of calcium salts; when extremely dilute, appearing after the lapse of a few seconds. It is a granular precipitate.

The formula of the salt dried at 100° C. is $Ca_2C_2O_4 + aq$.

It is insoluble in chloride of ammonium and in water; it is also insoluble in acetic acid ($H\bar{A}$), but dissolves in the stronger acids, nitric and hydrochloric, readily.

The Ferrocyanide is produced by the action of ferrocyanide of potassium (K_2Cfy) on solutions of calcium salts, especially on standing, and more quickly still by boiling. It is a dense white precipitate. Its composition is that of a ferrocyanide of potassium and calcium; it is $KCaCfy + 1\frac{1}{2}aq$. This salt is more insoluble in the presence of chloride of ammonium and other salts; it dissolves in 795 parts of water at 15° C., and in 145 parts of boiling water: it is soluble in dilute, but insoluble in concentrated hydrochloric acid.

THE PHOSPHATE is produced by the action of the phosphate of sodium ($Na_2 HPO_4$) on solutions of calcium salts. It is a bulky white precipitate. Its composition is probably Ca_2HPO_4. It is somewhat soluble in solutions of ammonium salts, and also in solutions of chloride of sodium.

THE SILICOFLUORIDE is soluble.

The special tests of the preceding subdivision are without well-defined action on the salts of calcium.

The special means of distinguishing calcium from strontium and barium which the student should remember are these:—the blowpipe flame and remarkable incandescence; the comparative insolubility of the ferrocyanide, and the comparative solubility of the sulphate, as serving to distinguish calcium from both strontium and barium; and the solubility of the chromate and silicofluoride as distinguishing it from barium.

SECTION II.—*Precipitated by Carbonate of ammonium* ($[NH_4]_2CO_3$), *and redissolved by Chloride of ammonium* (NH_4Cl).

SALTS OF MAGNESIUM.

SALTS OF MAGNESIUM.

This metal resembles the three preceding in forming one class of salts only, namely, proto-salts. These salts, although resembling those of barium, strontium, and calcium in many respects, yet differ from them in many chemical characters. They are white, unless when combined with a coloured acid-radical, and act powerfully as purgatives when taken into the animal system.

When heated on charcoal they are for the most part decomposed, and the oxide formed is as infusible and highly incandescent as lime: the chloride, bromide, iodide, &c., if perfectly free from water, are not decomposed; but if water be present, they too decompose by fusion thus—

$$2MgCl + H_2O = Mg_2O + 2HCl:$$

this decomposition will be found to obtain among many of the succeeding metals. Magnesium salts impart no colour to the blowpipe flame; but when strongly heated in the oxidizing flame, after having been moistened with solution of nitrate of cobalt ($CoNO_3$), the mass is found on cooling to have acquired a very pale pink colour. The borax-bead is transparent and colourless.

The principal insoluble salts by means of which this metal is recognized are—the hydrate, the carbonate, the ferrocyanide and the phosphate.

THE CHROMATE is soluble.

The Hydrate is produced by the action of the hydrate of potassium (KHO). It is a bulky white precipitate. The hydrate of ammonium (NH_4HO) exerts a very peculiar action upon solutions of magnesium salts, which must be here explained, as it is the type of a reaction which will be found to occur frequently between hydrate of ammonium and the salts of other metals.

This reaction has its foundation in the fact that salts of ammonium containing strong acid-radicals, as Cl and SO_4, form double salts with magnesium salts, and that from these double salts the magnesium cannot be precipitated by the addition of hydrate of ammonium in excess. The hydrate of ammonium acts in the first place by ordinary decomposition upon a magnesium salt, producing the hydrate of magnesium; but in so doing a salt of ammonium must be simultaneously formed, corresponding to the original magnesium salt; thus—

$$MgCl+NH_4\,HO=NH_4Cl+\underset{\text{Precipitate.}}{MgHO.}$$

The chloride of ammonium thus produced then unites with another equivalent of chloride of magnesium (supposing more to be present); and upon the double salt so formed (MgCl, NH_4Cl) any excess of hydrate of ammonium will exert no decomposing action. Hydrate of ammonium, therefore, when added in excess to a solution of a magnesium salt, can never precipitate more than one-half of the magnesium; and for every two equivalents present, the following will be the decomposition:—

$$2MgCl+2NH_4HO=\underset{\substack{\text{Soluble double}\\ \text{salt.}}}{MgCl,\ NH_4Cl}+\underset{\text{Precipitate.}}{MgHO}+NH_4HO.$$

It is obvious from this, that if excess of ammonium salt is subsequently added, even that portion of the hydrate of magnesium formed will be perfectly dissolved, because

$$MgHO+2NH_4Cl=NH_4\,HO+MgCl,\ NH_4Cl.$$

The hydrates of barium, strontium, and calcium being more soluble than the hydrate of magnesium, also produce the hydrate when added to magnesium salts.

The formula of the salt dried at 100° C. is MgHO.

It dissolves readily in salts of ammonium and in 55,368 parts of cold or boiling water; it is easily decomposed and dissolved by almost every acid.

THE SULPHATE is extremely soluble.

The Carbonate is produced by the action of neutral carbonate of potassium (K_2CO_3) on solutions of magnesium salts. The neutral carbonate of ammonium does not produce an immediate precipitate, but after boiling the solution or allowing it to stand, a portion of the magnesium is precipitated. It is a bulky white precipitate.

The formula of this salt is variable, on account of its not being the neutral carbonate, but a mixed carbonate and hydrate; it is sometimes $2(MgHO), 3(Mg_2CO_3)+3aq$, and sometimes $MgHO, 2(Mg_2CO_3)+2aq$. The reaction which results in its formation is not so simple as those previously given; it is as follows:—

$$8(MgCl)+4(Na_2CO_3)+4(H_2O)=2(MgHO),$$
$$3(Mg_2CO_3), 3aq+8NaCl+CO_2.$$

The precipitate is increased by boiling, because then the carbonic acid escapes which has been keeping a portion of the magnesium in solution as acid carbonate ($MgHCO_3$), which, in common with the other acid carbonates of this subdivision, and all salts of similar composition, is perfectly soluble in cold water, but is decomposed directly the temperature is raised, with precipitation of neutral carbonate and evolution of carbonic acid gas.

The formula of the salt produced by very great excess of neutral carbonate of ammonium ($[NH_4]_2CO_3$), is $MgNH_4CO_3+2aq$; the precipitation of the magnesium is said to be complete. This precipitate is quite soluble in pure water if cold, but from the solution when boiled, neutral carbonate of magnesium is precipitated, the neutral carbonate of ammonium volatilizing at the same time; thus—

$$2(MgNH_4CO_3)=\underset{\text{Precipitate.}}{Mg_2CO_3}+\overrightarrow{(NH_4)_2CO_3}.$$

Both the above-described precipitates are instantly dissolved by solutions of ammonium salts. The first of them is somewhat soluble in excess of cold solutions of its precipitants, and in most other sodium and potassium salts, as chloride, sulphate, and nitrate. It requires 2493 parts of cold, and 9000 of boiling water for its solution. Both salts are readily decomposed and dissolved by almost every acid, but are dissolved with formation of the acid salt by solutions of carbonic acid gas (CO_2).

THE OXALATE is soluble, unless the oxalic acid or soluble oxalate employed is added to very concentrated solutions of magnesium salts, or the mixture allowed to stand for some time; the precipitate is easily dissolved by ammonium salts and acids.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium (K_2Cfy) after long standing or by rapidly boiling: its precipitation is also immediately induced by the action of chloride of ammonium (NH_4Cl).

Its formula is $Mg_2Cfy+6aq$; but when an ammonium salt is present, the salt appears to be $MgNH_4Cfy$.

It is insoluble in chloride of ammonium, but is dissolved immediately by hydrochloric acid.

THE PHOSPHATE is produced by the action of phosphate of sodium (Na_2HPO_4) on solutions of magnesium salts, and is slowly precipitated. It is white and crystalline. Its formula is Mg_2HPO_4+7aq. It is insoluble in ammonium salts: it dissolves in 322 parts of cold water, but is less soluble in boiling water: it is said to decompose on boiling. In acids it is immediately soluble.

If hydrate of ammonium (NH_4HO) be present in a solution of magnesium salt when the phosphate of sodium is added, the latter salt becomes one of the most delicate tests for the presence of magnesium, which is then completely precipitated from its solutions in ammonium salts (the double salts before mentioned), from which no other reagent in common use will separate it.

The Phosphate of Magnesium and Ammonium thus produced crystallizes in regular six-sided prisms, with dihedral summits, belonging to the right prismatic system.

Its formula is $Mg_2NH_4PO_4+6aq$.

It dissolves in 7548 parts of solution of chloride of ammonium, and in 15,627 parts of chloride of ammonium solution containing hydrate of ammonium; it requires 44,330 parts of water containing hydrate of ammonium for its solution; and it dissolves in 15,293 parts of pure water at the ordinary temperature, but is far more soluble in boiling water, and very readily soluble in most acids.

THE SILICOFLUORIDE is soluble.

The special reagents of the first subdivision exert no well-defined action on solutions of magnesium salts.

The special means of recognizing magnesium are these:—its incandescence and blowpipe reaction with nitrate of cobalt ($CoNO_3$): its precipitation by carbonate of potassium (K_2CO_3) in common with the other members of the present subdivision, and the immediate re-solution of this precipitate by the addition of an ammonium salt, while its immediate precipitation from such solutions by the addition of hydrate of ammonium and phosphate of soda is a yet more striking feature. From barium, strontium, and calcium, the excessive solubility of its sulphate will serve to distinguish it; and from calcium it is also distinguished by the immediate solubility of its ferrocyanide in hydrochloric acid.

REACTIONS.	Ba.	Sr.	Ca.	Mg.
Chromate	yellow	—	—	—
Hydrate......................	white	white	white	white
Sulphate	white	white	white	—
Carbonate	white	white	white	white
Oxalate	white	white	white	—
Ferrocyanide..............	—	—	pale yellow	yellowish white
Phosphate	white	white	white	white
Silicofluoride..............	white	—	—	—
Colour imparted to the blowpipe flame	green	crimson	red	—

We now give a Table exhibiting the general method of distinguishing the members of this subdivision, on the supposition that it is our object to analyse a solution in which only one of these basic radicals exists. It must be borne in mind that this table, like that given on page 81, is meant only to indicate the general plan of procedure in such cases.

Analysis of Subdivision II.

The salt may be one of BARIUM, STRONTIUM, CALCIUM, or MAGNESIUM.

<table>
<tr><td colspan="4">Dissolve in water, or in a few drops of hydrochloric acid; add a considerable quantity of solution of chloride of ammonium; warm the liquid gently, and add solution of carbonate of ammonium until no more precipitate is produced.</td></tr>
<tr><td rowspan="3">The absence of any precipitate indicates the presence of
Magnesium,
which remains in solution as
$MgCl, NH_4Cl$.
Its presence must be confirmed by the addition of a few drops of phosphate of sodium, and of hydrate of ammonium, which will produce a crystalline precipitate, either immediately or after the lapse of a few minutes.</td><td colspan="3">The formation of a precipitate indicates the presence of
Barium, Strontium, or Calcium.
Filter and wash with water; redissolve the precipitate in a few drops of hydrochloric acid, and add hydrofluosilicic acid with simultaneous agitation.</td></tr>
<tr><td rowspan="2">The formation of a transparent gelatinous precipitate indicates the presence of
Barium.</td><td colspan="2">The absence of any precipitate indicates the presence of
Strontium or Calcium.
Add a solution of ferrocyanide of potassium.</td></tr>
<tr><td>The formation of a precipitate, especially on warming, indicates
Calcium.</td><td>The absence of a precipitate indicates
Strontium,
the presence of which must be confirmed by the addition of a drop of dilute sulphuric acid, or by the blowpipe flame.</td></tr>
</table>

SUBDIVISION III.

SALTS OF YTTRIUM, THORINUM, CERIUM, LANTHANIUM, DIDYMIUM, ZIRCONIUM, GLUCINUM, ALUMINIUM, CHROMIUM, URANIUM, TITANIUM, TANTALUM, NIOBIUM, AND PELOPIUM, IRON, MANGANESE, COBALT, NICKEL AND ZINC; AND OF THE COMPOUND BASES MORPHINE, QUININE, AND STRYCHNINE.

It was remarked in the prefatory observations to the last subdivision, that the present group was distinguished from the former, as that again was from the one preceding it, by the increased number of insoluble salts which its members formed. In addition to the carbonates, oxalates and phosphates, which are as a general rule insoluble in water and in neutral saline solutions, both in this and the second subdivision we find that the hydrates and sulphates of the metals and basic radicals belonging to this group are almost equally insoluble. A well-marked distinction is thus seen between the members of the present subdivision and those of the two preceding ones; and their separation may be readily effected by taking advantage of this difference.

To the oxides of the first eight of the above metals the conventional expression "the earths" is frequently applied, and their salts are spoken of in general as "the salts of the earths," while to the last three the term "alkaloids" is applied, and their salts are called "the salts of the alkaloids."

The really important members of this group, to the reactions of which only the beginner need at first attend, are the salts of aluminium, chromium, uranium, iron, manganese, nickel, cobalt and zinc; the remainder, viz. the salts of yttrium, thorinum, cerium, lanthanium, didymium, zirconium and glucinum, are of very rare occurrence. They form a kind of link between the second and third subdivisions, resembling the salts both of magnesium and of aluminium in many particulars. Neither need the reactions of the compound bases, morphine, quinine, and strychnine, be studied by the beginner; it may be remembered, however, that they are all decomposable by ignition. One characteristic of certain oxides of this group deserves to be mentioned: they are, after ignition, soluble only in hot sulphuric acid.

There are several reactions by means of which this group may be divided into smaller sections: this division is perhaps most easily, and, for practical purposes, most effectively accomplished by the action of excess of hydrate of ammonium in the presence of chloride of ammonium. The group divides thus:—

SECTION I.—SALTS OF YTTRIUM, THORINUM, CERIUM, LANTHANIUM, DIDYMIUM, ZIRCONIUM, GLUCINUM, ALUMINIUM, CHROMIUM, URANIUM, TITANIUM, TANTALUM, NIOBIUM, AND PELOPIUM.

Not volatilized by heat, but precipitated as hydrates by excess of hydrate of ammonium (NH_4HO) in the presence of chloride of ammonium (NH_4Cl); *ferric* salts behave in a similar manner.

SECTION II.—SALTS OF MANGANESE, COBALT, NICKEL, AND ZINC.

Non-volatile, and not precipitated by the addition of excess of hydrate of ammonium (NH_4HO) in the presence of chloride of ammonium (NH_4Cl); *ferrous* salts behave in a similar manner.

SECTION III.—SALTS OF THE COMPOUND BASES, MORPHINE, QUININE, AND STRYCHNINE.

Volatilized and destroyed by heat.

The group-test is a soluble sulphide—a salt chosen because it precipitates every member of this group, but produces no precipitate in either of the preceding groups. Of the soluble sulphides, sulphide of ammonium ($[NH_4]_2S$) is selected, for reasons which will be evident presently.

SECTION I.—*Salts not volatilized by heat, but precipitated as hydrates by excess of Hydrate of ammonium* (NH_4HO) *in the presence of Chloride of ammonium* (NH_4Cl)

SALTS OF YTTRIUM, THORINUM, CERIUM, LANTHANIUM, DIDYMIUM, ZIRCONIUM, GLUCINUM, ALUMINIUM, CHROMIUM, URANIUM, TITANIUM, TANTALUM, NIOBIUM, AND PELOPIUM.

SALTS OF YTTRIUM.

The salts of this metal are but of rare occurrence in nature; and it has been shown that they consist of a mixture of the salts of three metals, to which the names Yttrium, Erbium, and Terbium have been assigned; their separation is, however, very difficult, on account of the small quantity in which they occur, and the great similarity of their chemical characters; the mixed salts are therefore generally called the salts of yttrium, and recognized by the reactions given below: these salts are believed to be proto-salts.

The colour of the salts is white, unless the acid-radical introduces colour. The taste of pure yttrium salts is at first sweet, and then astringent. Heated before the blowpipe, the oxide is generally produced, and remains infusible. The oxide of erbium is said to be of an orange-colour, while the salts of terbium are said to acquire a reddish colour on drying. Yttrium salts give *no peculiar reaction with borax* before the blowpipe, nor do they impart any colour to the flame; with *nitrate of cobalt*, oxide of yttrium (Y_2O) gives a *greyish-blue colour.*

The principal insoluble salts which this metal forms are these,—the hydrate, the double sulphate of yttrium and potassium, the carbonate, the oxalate, the ferrocyanide and the phosphate.

THE CYANIDE is soluble.

The Hydrate is a white powder, and is produced when the hydrates of potassium or ammonium are added to solutions of yttrium salts: it is also formed by the action of the sulphides of potassium or ammonium, its precipitation being accompanied by the evolution of hydrosulphuric acid, according to the following equation:—

$$2YCl+(NH_4)_2S+2H_2O=2YHO+2NH_4Cl+H_2S.$$

The composition of the precipitate is not always exactly YHO; for occasionally it contains a little of the original salt of yttrium employed, if that salt were the sulphate or nitrate. This hydrate is insoluble in excess of the precipitants; it dissolves somewhat in salts of ammonium, and if boiled with them dissolves entirely, displacing the ammonium. It is insoluble in water, but soluble in acids.

THE DOUBLE SULPHATE OF YTTRIUM AND POTASSIUM forms when a saturated solution of sulphate of potassium is added to a somewhat concentrated solution of a salt of yttrium. It is a crystalline powder. Its formula is said to be $YKSO_4$. It is soluble in 10 parts of the precipitant, in 16 parts of cold water, and in a less quantity of a solution of an ammonium salt, or of acids.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium on solutions of yttrium salts; it is also formed by exposure of the hydrate to the air. It is a white powder, occasionally crystalline. Its composition is Y_2CO_3+3aq.

The Oxalate is produced by the action of oxalic acid or oxalate of ammonium. It is a white powder. Its composition is $Y_2C_2O_4+3aq$. The three salts (those of yttrium, erbium, and terbium) of which this precipitate is composed are of different degrees of solubility in acids, the yttrium salt being more soluble than the others: a method of separation has been founded on this fact. It is insoluble in water, also in oxalic and in dilute hydrochloric acid, but is soluble in nitric or concentrated hydrochloric acid. The action of oxalate of potassium on yttrium salts produces the double oxalate of yttrium and potassium YKC_2O_4.

THE FERROCYANIDE is produced by the addition of ferrocyanide of potassium to any salt of yttrium except the acetate. The precipitate is at first white, changing to a pearl-grey. Its composition is Y_2Cfy. It is insoluble in excess of the precipitant, in water, and in acetic acid, but soluble in hydrochloric acid.

THE PHOSPHATE is formed by the addition of phosphate of sodium to salts of yttrium. It is a white powder. Its formula is probably Y_2HPO_4. It is very slightly soluble in water, but dissolves in hydrochloric or nitric acids: on boiling these solutions the salt Y_3PO_4 is deposited, while this precipitate, by exposure to the air, becomes converted into a mixture of Y_2CO_3 and Y_2HPO_4. Y_3PO_4 occurs in nature as the mineral Xenotime.

The Silicofluoride is insoluble in water, but soluble in hydrochloric acid.

The other reagents of the preceding groups produce no characteristic precipitates with solutions of yttrium salts.

The characteristic reactions by means of which the metal yttrium is distinguished, are—the absence of colour in the borax bead, and the insolubility of the hydrate in the hydrates of potassium or ammonium, coupled with the great solubility of its double sulphate.

SALTS OF THORINUM.

The salts of thorinum are even rarer than those of yttrium. The mineral Thorite is the chief source of this metal. Its salts are believed to be protosalts: they are white, unless the acid-radical introduces colour. When these salts are heated before the blowpipe, the oxide (Th_2O) is generally produced, and remains infusible; it imparts no tinge to the flame, and *gives with borax a colourless bead.* It yields no characteristic reaction with nitrate of cobalt.

The principal insoluble salts which this metal forms are these,—the hydrate, the sulphate of thorinum and potassium, the carbonate, the oxalate, the ferrocyanide and the phosphate.

THE CYANIDE is soluble.

The Hydrate is formed by the action of the hydrates or sulphides of potassium or ammonium on solutions of thorinum salts. It is a white gelatinous precipitate. Its formula is probably ThHO. It is soluble in excess of the precipitants, and in water. It is readily dissolved when moist by hydrochloric and nitric acids, but with difficulty when dry.

The Double Sulphate of Thorinum and Potassium is most perfectly precipitated by adding a boiling concentrated solution of sulphate of potassium to a solution of sulphate of thorinum. It is a white crystalline powder. The formula of the salt is $ThKSO_4$. It dissolves slowly in cold water, but very easily in hot water; it is, however, perfectly insoluble in a cold saturated solution of sulphate of potassium, and is thereby distinguished from the corresponding salt of yttrium. The sulphate of thorinum is insoluble in hot water, but redissolves on cooling; this reaction is not observed with the double sulphate.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium. It is produced also by exposing the hydrate to the air. Its formula is that of a basic carbonate. It is soluble in excess of the precipitant, and in acids with decomposition.

THE OXALATE is precipitated by the addition of oxalic acid. It is a heavy white precipitate. Its formula has not been ascertained. It is insoluble in water or oxalic acid, and but sparingly soluble in other dilute acids. The oxalate of potassium produces a double salt of potassium and thorinum.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium, and is precipitated as a heavy white powder. Its composition has not been ascertained. It is insoluble in water, but soluble in acids.

THE PHOSPHATE is produced by the action of phosphate of sodium, and is precipitated in white flakes. Its composition has not been ascertained. It is insoluble in water and in phosphoric acid.

The special reagents of the first and second groups produce no characteristic effects in solutions of thorinum salts. Chromate of potassium produces a yellow precipitate.

The reactions characteristic of thorinum salts are—the absence of colour in the borax bead, the insolubility of the hydrate in the hydrates of potassium or ammonium, and the great insolubility of its double sulphate in a saturated solution of sulphate of potassium.

SALTS OF CERIUM.

The salts of this metal are met with in many minerals; they are nevertheless of rare occurrence. Like yttrium, it is always accompanied by two other metals; these are lanthanium and didymium; and although the salts of the two latter elements have not been examined very minutely, yet sufficient is known about them for us to furnish a slight account of each. The reactions which follow must therefore be understood to be those of cerium, although, from the great similarity in the chemical properties of the three metals, the descriptions of salts of cerium will apply to a considerable extent to the salts of lanthanium and didymium also.

Cerium forms two classes of salts,—the cerous or protosalts (such, for instance, as the protochloride [$CeCl$], and the protoxide [Ce_2O]), and the ceric or sesqui- or per-salts (such, for instance, as the sesquichloride [Ce_2Cl_3] and the sesquioxide [$(Ce_2)_2O_3$]): the proto-salts are generally colourless, the others frequently red or yellow. The proto-salts when heated before the blowpipe are converted into sesquioxide, which, if pure, is an infusible powder of a lemon-yellow colour, but if containing didymium, of a brownish red. It does not tinge the flame, nor does it give any reaction with nitrate of cobalt: but *with borax* on the platinum wire it forms a glass which is *orange or dark yellow while hot, and a paler yellow when cold*; this is the effect of the oxidizing flame, the colour being of course due to the presence of sesquioxide of cerium. If the bead be subsequently brought into the reducing flame, it is decolorized by reason of the reduction of the sesquioxide into the protoxide.

CEROUS SALTS.

The principal insoluble cerous salts are the hydrate, the double sulphate of cerium and potassium, the carbonate, the oxalate, the ferrocyanide, and the phosphate.

THE CYANIDE is produced by the action of cyanide of potassium. It is a white gummy precipitate which rapidly decomposes, cerous hydrate and hydrocyanic acid being formed.

The Hydrate is produced by the action of the hydrates or sulphides of potassium or ammonium: it is a white powder which rapidly absorbs oxygen from the air, becoming thus converted into the sesquihydrate. Its formula is probably $CeHO$. It is insoluble in excess of its precipitants, but readily soluble in acids.

The Double Protosulphate of Cerium and Potassium is produced by adding a saturated solution of sulphate of potassium to a solution of a cerous salt. It is a granular and crystalline white precipitate. Its composition is probably $Ce_2 KSO_4$. It is insoluble in excess of its precipitant, very slightly soluble in cold water, but readily dissolved by boiling water and by acids.

THE CARBONATE is precipitated by the carbonate of potassium or of ammonium, and is also produced by the exposure of the hydrate to the air. The precipitate at first appears in the form of white amorphous flakes, but after some days changes beneath the liquid into shining crystalline scales. Its composition is $Ce_2 CO_3 + 3aq$. It is slightly soluble in excess of its precipitants, insoluble in water and carbonic acid, but it is dissolved by other acids, thereby suffering decomposition.

THE OXALATE is produced by the action of oxalic acid or oxalate of potassium or of ammonium, and is a curdy white precipitate, becoming slowly crystalline. Its composition is $Ce_2 C_2 O_4 + 3aq$. It is insoluble in water or oxalic acid, but dissolves in hydrochloric or nitric acid.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium: it is a white precipitate. Its composition is not known. It is insoluble in water, but soluble in nitric acid.

THE PHOSPHATE is produced by the action of phosphate of sodium. Its formula is not known: it occurs as a white powder. It is insoluble in water and in phosphoric acid, but easily soluble in hydrochloric or nitric acid. A phosphate, probably $M_3 PO_4$, occurs impure in nature as the minerals Edwardsite and Phosphocerite.

The special reagents of the first and second subdivisions produce no characteristic reactions with cerous salts.

CERIC SALTS.

The principal insoluble salts of this series are the hydrate, the double sulphate of cerium and potassium, and the phosphate.

The Hydrate is produced by the action of the hydrates or sulphides of potassium or ammonium. When pure, it is of a sulphur-yellow colour. Its composition is probably $Ce_2 H_3 O_3$. It is of course easily soluble in acids; and when hydrochloric acid is employed, protochloride of cerium is formed, and chlorine evolved.

The Double Sesquisulphate of Cerium and Potassium is formed by adding a saturated solution of sulphate of potassium to a solution of a ceric salt (the sesquisulphate of cerium, which is soluble, is the best for the purpose). It is an orange-yellow crystalline salt, insoluble in excess of the precipitant. Its formula has not been determined. It is dissolved with difficulty by cold water, but is more readily soluble in hot water.

THE OXALATE is produced by the action of oxalate of ammonium. It is a yellow crystalline powder. Its composition has not been determined. It is insoluble in water, but soluble in a solution of chloride of ammonium.

The action of the special tests of the first and second subdivisions upon ceric salts have not been ascertained.

The best methods of recognizing cerium are—its blowpipe reactions, the insolubility of cerous hydrate in potassa, and the change of colour which it undergoes; together with its coloured salts and very insoluble double sulphates.

SALTS OF LANTHANIUM.

The salts of this metal are invariably associated with those of cerium, occurring, in some cases, as in the mineral Monazite (the phosphate of cerium and lanthanium), in equivalent proportion to the cerium present. Practically speaking, lanthanium only forms proto-salts: one member of a higher series, the peroxide, is known; but it decomposes into the protoxide with great facility. The protoxide is peculiar in this respect, that even after strong ignition it dissolves readily in acids. The salts of lanthanium have a sweet astringent taste.

THE PROTOXIDE is produced when lanthanium salts are heated before the the blowpipe. It is a white infusible powder, which, however, under some conditions, assumes a brown tint, supposed to be due to the formation of peroxide. It gives no reaction with nitrate of cobalt; *with borax it yields an opalescent glass.*

The principal insoluble salts of lanthanium are the hydrate, the sulphate, the carbonate, the oxalate, and the phosphate.

THE CYANIDE is unknown.

The Hydrate is produced by the action of soluble hydrates or sulphides. It separates as a very viscid precipitate. Its composition has not been ascertained. It is insoluble in excess of the precipitants, but it readily dissolves, with decomposition of course, in acids. Boiled with chloride of ammonium solution, it dissolves, displacing the ammonium.

The Sulphate possesses the same peculiar property as the cerous sulphate and the sulphate of thorinum, viz. that of being less soluble in hot than in cold water. By this character, lanthanium is separated from didymium, the sulphate of the latter metal exhibiting the same peculiarity in a far less marked degree. The salt is crystalline. Its formula seems to be La_2SO_4+3aq. It is comparatively soluble in water, 1 part dissolving in 6 parts of water at 3° C., in 42·5 parts at 23° C., and in 115 parts at 100° C.

The Double Sulphate of Lanthanium and Potassium is formed only by the action of sulphate of potassium upon concentrated solutions of salts of lanthanium. It is a red or yellow precipitate. Its composition is $LaKSO_4$. It is somewhat soluble in water.

The Carbonate is formed by the addition of the carbonates of potassium or ammonium, and also by the exposure of the hydrate to the air. When precipitated in the cold, it appears in a gelatinous form, but when from a hot solution, in crystalline scales. The formula has not been determined. It is insoluble in excess of the precipitants, and in water, but dissolves readily in acids, with decomposition.

The Oxalate is produced by the action of oxalate of ammonium. It is a white powder. Its formula is unknown. It is insoluble in water and in saline solutions.

The Phosphate is produced by the action of phosphate of sodium. It is a white precipitate. Its composition is unknown. It is soluble in acids.

The action of the special tests of the two preceding subdivisions upon salts of lanthanium has not been ascertained.

SALTS OF DIDYMIUM.

The salts of this metal, like those of lanthanium, occur constantly associated with those of cerium. Didymium appears to form only one class of salts, which are considered as proto-salts, and are remarkable for their beautiful colours, being either pink, rose, or violet. The oxide is pure white; but the brown colour which it generally has, is by some attributed to the presence of a higher oxide. The oxide presents the same peculiarity as the oxide of lanthanium, viz. that of dissolving either in strong or weak acids after lengthened ignition.

The oxide is produced when didymium salts are heated before the blowpipe; it is infusible and of a dark brown colour in the oxidizing flame, and greyish-white in the reducing flame: it imparts no tinge to the flame. *With borax, it gives a glass of a fine amethyst colour in both flames.*

But little is known with respect to the pure salts of didymium; the hydrate, the double sulphate of didymium and potassium, the carbonate, and the oxalate are insoluble.

The Cyanide is not known.

The Hydrate is produced by the action of hydrate of potassium, the hydrate of ammonium precipitating a basic salt: the sulphide of ammonium produces the hydrate of didymium only after heating the mixture. It is of a violet colour according to some accounts; according to others, the precipitated hydrate is pale rose-red, and gelatinous. Dried at 100° C., its formula is DiHO. It is insoluble in water, but soluble in chloride of ammonium on ebullition, displacing the ammonium. It is readily soluble in acids.

The Sulphate resembles the sulphates of cerium and lanthanium in being more soluble in cold than in hot water; being, however, far more soluble in hot water than those sulphates, this forms a good means of separating this metal from lanthanium*. The greatest difference between the solubility of

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* Cerium is always separated previously by other means. Didymium, however, generally accompanies all lanthanium and cerium salts, even if

the sulphates of didymium and cerium is said to be at 40° C. Its formula is Di_2SO_4+aq, after boiling. It forms fine red crystals. The sulphate of didymium dissolves in 5 parts of water at a temperature between 15° and 20° C.; and such a solution begins to deposit crystals at 53° C., and continues to do so as the temperature rises, until, at 100° C., 1 part only is held in solution by 50·5 parts of water.

The Double Sulphate of Didymium and Potassium is produced by the action of sulphate of potassium. The salt has the formula $DiKSO_4+aq$ after boiling, and is of an amethyst colour. It is totally insoluble in excess of the precipitant, but soluble in 63 parts of water.

THE CARBONATE is produced by the action of soluble carbonates, and is also formed by the exposure of the hydrate to the air. Its formula (dried *in vacuo*) is Di_2CO_3+2aq; at 100° C. it loses three-fourths of its water and some carbonic acid gas. It is a rose-red powder.

THE OXALATE is produced by oxalate of ammonium. It is precipitated either as an almost white powder, or in rose-coloured crystals. Its formula is $Di_2C_2O_4+4aq$. It is completely insoluble in water, and almost so in oxalic acid, and even in the mineral acids when somewhat diluted.

The action of the special tests of the first and second groups upon salts of didymium has not been ascertained.

SALTS OF ZIRCONIUM.

The combinations of this metal are of rare occurrence: it is found in nature as silicate, forming the minerals Zircon and Hyacinth. It is thought that the salts of the so-called zirconium are a mixture of the salts of several metals, like the yttrium and cerium groups; yet, owing to the close resemblance of these metals to one another, and their great rarity, no method has yet been devised for separating them. Zirconium salts are believed to be sesqui-salts.

The salts of zirconium are white, unless their acid-radical is coloured. When heated before the blowpipe they are for the most part converted into the oxide, which remains infusible, and *incandesces in the most brilliant and characteristic manner*; moistened with *nitrate of cobalt*, and intensely heated, the mass becomes of a *dirty violet colour*; the oxide imparts no tinge to the blowpipe flame, and yields *a colourless glass with borax*, which becomes slightly opaque when cold.

The principal insoluble salts by which this metal is recognized are these,—the hydrate, the double sulphate of zirconium and potassium, the carbonate, the oxalate, and the phosphate.

THE CYANIDE is unknown.

The Hydrate is produced by the action of the hydrates or sulphides of ammonium or potassium. It is a semigelatinous precipitate. Its formula

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they have been very carefully purified. Its presence can be detected by an examination with the prism.

is probably $Zr_2H_3O_3$. It is insoluble in excess of the precipitants and in water, but is easily soluble in acids if it has been precipitated and washed in the cold; if, however, it has been precipitated from a hot solution, or the mass has been washed with boiling water only, it dissolves in none but concentrated acids, and then after long digestion. It is not soluble in boiling solutions of ammonium salts.

The Double Sulphate of Zirconium and Potassium is produced by the action of a saturated solution of sulphate of potassium. It is a white crystalline precipitate, the formula of which has not yet been determined. It appears to be very slightly soluble in water, but soluble in acids if it has not been boiled during precipitation, nor washed with hot water: if that has been done, it partakes of the peculiarity of the hydrate.

The Carbonate is produced by the action of the carbonates of potassium or ammonium, and also by the carbonate of calcium. It is a white powder. Its composition is uncertain; it is most probably a basic salt. It is slightly soluble in excess of its precipitants. Its solubility in acids varies as in the case of the hydrate.

The Oxalate is produced by the action of oxalic acid not in excess, or by oxalate of ammonium. It is a white flaky powder. Its composition seems variable. It is insoluble in water, and in excess of oxalic acid, even with the aid of heat, but is easily dissolved by hydrochloric acid.

The Ferrocyanide is stated by some authors to be insoluble, by others not; by some it is said to be soluble in excess of ferrocyanide of potassium.

The Phosphate is produced by the action of phosphate of sodium: it is a white precipitate, insoluble in water.

Most of the special reagents of the first and second groups produce no marked reactions with salts of zirconium; the behaviour of the others has not been ascertained.

The tests to be relied upon for zirconium are—its brilliant incandescence and reaction with nitrate of cobalt, with the insolubility of its hydrate in potassa, and the formation of its very insoluble double sulphate.

SALTS OF GLUCINUM.

The salts of this metal are of rare occurrence; its chief source is the beryl, in which it occurs together with aluminium, combined with the radical of silicic acid; it is frequently termed beryllium. The salts of this metal are believed to be sesqui-salts.

Glucinum salts are colourless, unless the acid-radical is coloured. The taste of the soluble salts is sweet. When heated before the blowpipe they generally leave the oxide, which is infusible, imparts no colour to the flame, becomes of *a bluish-grey colour* on treatment *with nitrate of cobalt,* and *with borax* yields a *transparent colourless glass,* which becomes slightly opaque on cooling.

The principal insoluble salts by which glucinum is recognized are these,—the hydrate, the carbonate, and the phosphate.

The Cyanide is unknown.

The Hydrate is produced by the action of the hydrates or sulphides of potassium or ammonium. It is a gelatinous precipitate. Its formula is $G_2 H_3 O_3$. It is insoluble in water, but readily soluble in acids and in hydrate of potassium; it dissolves also in salts of ammonium when boiled with them, the glucinum taking the place of the ammonium. From its solution in hydrate of potassium, it is not reprecipitated by boiling, unless much water is at the same time added, it then precipitates completely; the addition of chloride of ammonium will also reprecipitate it, exerting the same action as in the case of aluminium.

The Carbonate is produced by the action of the carbonates of potassium or ammonium, or by the exposure of the hydrate to the air; glucinum is also completely separated from its salts by boiling their solutions with carbonate of barium. It is white, occasionally granular, but sometimes bulky. It is a basic salt. It is soluble in excess of its precipitants, but more readily in carbonate of ammonium, from which solution it is reprecipitated by ebullition: it dissolves also when boiled in solutions of ammonium salts, producing carbonate of ammonium. It is readily soluble in acids, except carbonic acid.

The Ferrocyanide is produced by the action of ferrocyanide of potassium, and is precipitated as a gelatinous mass after some time.

The Phosphate is produced by phosphate of sodium. It is a white precipitate. Its formula is unknown. It is insoluble in water, but soluble in acids, including phosphoric acid.

The special tests of the first and second subdivisions, and also those of the present group, such as oxalates and sulphates, produce no precipitates with solutions of salts of glucinum.

Salts of glucinum are recognized by the absence of blowpipe reactions, taken together with the solubility of its hydrate in potassa, and of its carbonate in carbonate of ammonium.

SALTS OF ALUMINIUM.

Solution for the reactions:—chloride of aluminium ($Al_2 Cl_3$) in water.

This metal is at present known to form only one series of salts; and they are sesqui-salts having the general formula $M_2 R_3$.

They are colourless, unless the acid-radical, or an associated basic radical, introduces colour. Their taste is astringent and somewhat sweet.

When heated before the blowpipe they are, for the most part, converted into the sesquioxide, which remains infusible and incandesces strongly: *this residue, when moistened with nitrate of* *cobalt, and intensely heated, is seen on cooling to have acquired a fine blue colour.* The salts of aluminium, when *fused with borax on platinum wire, dissolve, forming a colourless bead, which re-remains so on cooling*; they impart no colour to the flame.

The insoluble salts, by the formation of which this metal is recognized, are these,—the hydrate, the carbonate, the phosphate, while the chromate and silicate, also insoluble, are occasionally employed for its separation or detection.

The Cyanide cannot be produced by ordinary means; cyanide of potassium added to solutions of salts of aluminium precipitates hydrate of aluminium.

The Chromate is only precipitated after long standing.

The Hydrate is produced in a great variety of ways: it constitutes the precipitate when the salts of aluminium are thrown down by the soluble hydrates, sulphides, or carbonates; it is also obtained by other means, such as a prolonged washing of the chromate of aluminium, or by the addition of the insoluble carbonates of the metals barium or calcium to the solution of a salt of aluminium: the sesquichloride (Al_2Cl_3) is the best for this purpose. It is a white gelatinous precipitate, which dries into a transparent horny mass.

Its composition, when recently thrown down, is that of a basic salt, especially when produced from the salt $(Al_2)_2(SO_4)_3$ by the action of the soluble hydrates: such a basic salt might be represented by the formula $(Al_2)_2(SO_4)_3$, $n(Al_2H_3O_3)$; and it has been found that by long-continued washing the sulphate of aluminium is removed, and pure hydrate of aluminium left upon the filter. To obtain the pure hydrate of aluminium, it is, however, simpler to redissolve the first precipitate produced in hydrochloric acid, and to reprecipitate by hydrate of ammonium. Its formula, when pure, is $Al_2H_3O_3$.

This salt dissolves easily in hydrate of potassium, forming a new compound termed aluminate of potassium, in which the aluminium is supposed to enter into the composition of the acid-radical: the salt is formed thus—

$$KHO + Al_2H_3O_3 = KAl_2O_2, H_2O + H_2O.$$

It is obtained combined with water of crystallization, in a crystalline form, as KAl_2O_2+aq, or, more probably, $Al_2KH_2O_3$: it is not decomposed at the boiling temperature, a property which it will be seen constitutes a distinction between this metal and chromium. The hydrate is reprecipitated by the addition of chloride of ammonium to the alkaline solution of the so-called aluminate, thus—

$$Al_2KH_2O_3+NH_4Cl=Al_2H_3O_3+KCl+NH_3;$$

and also by exact neutralization, thus—

$$KAl_2O_2, H_2O+HCl=Al_2H_3O_3+KCl.$$

The hydrate of aluminium is but triflingly soluble in hydrate of ammonium, and even this slight solubility is prevented by the presence of chloride or carbonate of ammonium. It is not appreciably dissolved by sulphide of ammonium, unless a large quantity of water be present. It is insoluble in pure water, but is of course readily dissolved by acids—partially even by carbonic acid. It is slightly soluble in alkaline carbonates.

The Silicate is produced by the action of silicate of potassium upon aluminium salts. It is a bulky gelatinous precipitate: its formula is probably $Al_2(SiO_2)_3$.

The Sulphate is soluble.

The Double Sulphate of Aluminium and Potassium is produced by the action of a strong hot solution of sulphate of potassium on a hot solution of sulphate of aluminium; crystals of the double sulphate (also termed alum) are deposited as the solution cools. Alum is occasionally found native, and is prepared commercially on a large scale. 1 part of alum dissolves in 10 parts of cold, and 3 parts of boiling water.

The Carbonate is said to be produced by the action of carbonate of ammonium on salts of aluminium; if so, the precipitate rapidly alters, and will be found, after washing with hot water, to be nearly pure hydrate of aluminium.

The Oxalate is insoluble in water, but soluble in oxalic acid.

The Ferrocyanide does not appear to exist; for the greenish precipitate usually produced by the action of ferrocyanide of potassium on aluminium salts seems to be hydrate of aluminium containing some cyanide of iron: the colour of the precipitate becomes gradually blue. With some salts, this precipitate does not occur till heat has been applied.

The Phosphate is produced by the action of phosphate of sodium; it is a salt bearing a great resemblance to the hydrate.

Its composition is probably $Al_2 PO_4$, but it generally contains a somewhat larger proportion of the phosphoric-acid radical.

It is insoluble in water and salts of ammonium, but soluble in acetic and other acids, and in hydrate of potassium.

The Silicofluoride is soluble.

The other reagents of the first and second groups give no characteristic reactions with salts of aluminium.

The chief reactions employed for the recognition of aluminium salts are these,—the reaction of the sesquioxide with nitrate of cobalt, and the formation of the insoluble hydrate, silicate, and phosphate.

SALTS OF CHROMIUM.

The metal chromium forms numerous combinations with oxygen, which, however, do not represent entire series: they are these,—Cr_2O, Cr_6O_4, Cr_4O_3, Cr_2O_2, CrO_2, and Cr_2O_4. Two only of these oxides correspond to series of salts,—the protoxide (Cr_2O) and the sesquioxide ($[Cr_2]_2O_3$): the former, or chromous salts, are generally of a red colour, often inclining to blue, and are much more soluble in hot than in cold water, while the latter, or chromic salts, are of a fine green or blue colour when seen by reflected light, but red by transmitted light. The chromous salts resemble ferrous salts, as will shortly be seen, in the property of dissolving large quantities of nitric oxide gas (N_2O_2), forming dark brown solutions. On account of their great tendency to pass into a higher state of oxidation, chromous salts are among the most powerful reducing agents known. Both the chromous and chromic salts, if heated before the blowpipe, leave a green residue of sesquioxide, which remains infusible: they impart no colour to the flame, nor do they yield any characteristic reaction with nitrate of cobalt; but when *dissolved in borax,* the sesquioxide produces *a green bead when cold, in whichever flame it has been heated.*

The metal chromium is recognized by a peculiar reaction, which no metal hitherto treated of presents. It forms at least one combination with oxygen, possessing acid properties and playing the part of an acid radical: with this compound the student has already become familiar in the guise of a reagent, viz. the chromate of potassium. The formation of this substance forms one of the best tests of the presence of chromium: it is produced by the action of powerful oxidizing agents on any chromium salt of a lower degree of oxidation. The most common and convenient method of producing it is to fuse the sesquioxide of chromium with nitrate of potassium, a body which readily decomposes and parts with its oxygen; the change may be thus represented—

$$4(KNO_3)+(Cr_2)_2O_3=\underset{\text{Chromate of potassium.}}{4(KCrO_2)}+N_2O_3+N_2O_4.$$

The chromates are remarkable for their brilliant colours; chromate of potassium is a *yellow* salt, and if dissolved in water and added to a solution of nitrate of silver, a fine *crimson* precipitate of chromate of silver is produced, which is very characteristic. The full details of the reactions of chromic acid will be found in Chapter VII.

CHROMOUS SALTS, OR PROTO-SALTS OF CHROMIUM.

Solution for the reactions:—protochloride of chromium ($Cr Cl$) dissolved in water.

These are comparatively unimportant, because their existence is very transient, owing to the readiness with which they absorb oxygen and pass into chromic salts. The protochloride is the most easily obtained, and it forms the following characteristic compounds when acted on by reagents:—the chromate, the hydrate, and the sulphide.

THE CYANIDE is produced by the action of cyanide of potassium: it is a white precipitate. Its formula is $CrCy$. It is insoluble in excess of the precipitant, but oxidizes rapidly, forming a mixture of the chromic oxide and cyanide.

THE CHROMATE is produced by the action of chromate of potassium; it is a brown precipitate. Its formula is probably $CrCrO_2$, which is equal to Cr_2O_2, the formula of the so-called binoxide: this salt, if long washed with water, is converted into chromic acid and sesquioxide of chromium.

The Hydrate is produced by the action of hydrate of potassium. It is a yellow powder, if guarded from the action of the air; but on access of air it becomes brown. Hydrate of ammonium gives a greenish white precipitate in the presence of chloride of ammonium, soluble in excess of the hydrate, producing a blue solution, changing to red by exposure to the air. The composition of the hydrate is CrHO. It is insoluble in water or in dilute acids, but dissolves slowly in strong acids. The hydrate is generally precipitated as a more or less brown powder, hydrogen escaping and an oxide (Cr_3O_2) being formed.

The Sulphide is produced by the action of sulphide of potassium. It is a black precipitate, soluble in excess of the precipitant. It always contains some uncombined sulphur.

THE CARBONATE appears to be produced by the action of carbonate of potassium. If precipitated in the cold, it separates as a dense yellow powder, but from a hot solution as brilliant brownish yellow crystals. The substance becomes green by exposure to the air.

THE FERROCYANIDE is produced by ferrocyanide of potassium. Its formula is probably Cr_2Cfy. It is a yellowish green precipitate.

THE PHOSPHATE is a blue precipitate, produced by the action of phosphate of sodium. It becomes green by exposure to the air, and is readily dissolved by acids.

The action of the other tests hitherto employed has not been ascertained upon this series of salts.

Chromous salts may be recognized by their peculiar hydrate and sulphide.

CHROMIC SALTS, OR SESQUI-SALTS OF CHROMIUM.

Solution for the reactions :—chromic sulphate ($[Cr_2]_2[SO_4]_3$) in water.

These are the salts of chromium which are usually met with. Those insoluble salts which characterize the series are the chromate, the hydrate, the carbonate, the ferrocyanide, and the phosphate.

THE CYANIDE is produced by the action of cyanide of potassium: it is a light bluish-grey precipitate.

Its formula is Cr_2Cy_3.

It is insoluble in excess of the precipitant, but soluble in excess of chromium salt: it dissolves in dilute acid without decomposition, but is decomposed when dissolved in hydrate of potassium.

THE CHROMATE is produced by the action of chromate of potassium. It is a yellowish-brown precipitate.

The formula is $Cr_2(CrO_2)_3$.

It is a very unstable compound, and is perfectly decomposed, even by long washing with water, into chromic acid and sesquioxide of chromium, which remains upon the filter.

This salt is insoluble in excess of the precipitant, but soluble in acids, and also in hydrate of potassium, with decomposition into chromic acid and a sesqui-salt of chromium.

The Hydrate is produced by the action of the hydrates or sulphides of potassium or ammonium, and also by the addition of the insoluble carbonates of the alkaline earths to solutions of the sesqui-salts of chromium. It is a bulky precipitate, the colour of which varies with the precipitant: when produced by hydrate of potassium, it is green; when by hydrate of ammonium, bluish-green inclining to bluish-grey. It is thought that these differences in colour are due to varying amounts of water in the precipitate.

The composition of the hydrate dried at 100° C. is $Cr_2H_3O_3$; but if the precipitate has been dried over sulphuric acid, other compounds are obtained, as, for instance,

$$2(Cr_2H_3O_3)+aq, \text{ and } Cr_2H_3O_3+aq;$$

if a current of dry air is the only desiccator, the formula of the precipitate is $2(Cr_2H_3O_3)+7aq$. It frequently retains traces of its precipitants.

This salt resembles the hydrate of aluminium in being perfectly soluble in excess of hydrate of potassium, from which solution it is reprecipitated either by neutralization or by the addition of chloride of ammonium; but it differs from hydrate of aluminium in being reprecipitated from its solution in hydrate of potassium, either by long standing or by boiling: the precipitate which thus separates has the formula $Cr_2H_3O_3+3aq$. Hydrate of ammonium also dissolves this salt to a certain extent, the amount dissolved increasing with the strength of the reagent; with a very strong solution of hydrate of ammonium, a pink solution is formed, from which the hydrate of chromium is thrown down on boiling as a dull violet precipitate. Chloride of ammonium does not affect the solubility of this salt. It is readily soluble in the acids, except after its precipitation from its hydrate of potassium solution by boiling.

THE SULPHATE is soluble.

THE DOUBLE SULPHATE OF CHROMIUM AND POTASSIUM is a very soluble salt, and crystallizes well in octohedra, if its solution has not been heated above 50° C.

Its formula is $KCr_2(SO_4)_2 + 12\,aq.$

It dissolves in 6 parts of water at the ordinary temperature.

The Carbonate is produced by the action of the carbonates of potassium or ammonium: it is a pale green or a bluish-green precipitate.

Its composition is that of a mixed carbonate and hydrate, and appears to be uncertain.

It dissolves slightly in excess of its precipitants, forming a greenish-blue solution with carbonate of potassium, and a pink solution with carbonate of ammonium: from both it is reprecipitated by boiling. It also dissolves readily in hydrate of potassium and in acids.

The Oxalate is produced, by the action of oxalate of ammonium on chromic chloride, as a pale green precipitate.

Its composition is unknown; it is probably a basic salt, for the neutral salt $(Cr_2)_2\overline{O}_3$ is very soluble.

It dissolves readily in many acids.

The Ferrocyanide and the Ferricyanide are not precipitated by their respective reagents.

The Phosphate is produced by the phosphate of sodium as a bluish-green precipitate.

Its composition is unknown.

Its behaviour with reagents is almost identical with that of the the hydrate.

The other special reagents of the first and second groups, as well as those of the present group, yield no precipitates with sesqui-salts of chromium.

The chief means for the recognition of the metal chromium are these,—the production of the sesquioxide by the ignition of most chromous and chromic salts, and the formation of the chromate of potassium described above from the salts of either series; the borax bead, and the precipitation and behaviour of the chromic hydrate.

SALTS OF URANIUM.

This metal forms a great number of combinations with oxygen: many of these, however, are probably combinations of oxides one with another; for corresponding series of salts are not found. Uranium forms two series of salts, the uranous corresponding to the chloride UCl, and the uranic represented by the chloride U_2Cl_3: the salts of the first series are generally of a greenish, while those of the latter are for the most part of a yellowish colour.

Most salts of uranium when heated before the blowpipe are converted into uranous oxide U_2O, which remains as a black infusible residue: they impart no colour to the blowpipe flame, nor do they give any characteristic reactions with nitrate of cobalt; but when heated *with borax*, *the glass in the outer flame becomes red or yellow while hot*, *and yellow or colourless when cold*, the depth of colour depending on the amount of salt present, while *in the reducing flame the colour changes to a bottle-green.*

URANOUS SALTS, OR PROTO-SALTS OF URANIUM.

Solution for the reactions:—protochloride of uranium ($U\,Cl$) in water.

The principal insoluble salts of this series are these,—the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide and the phosphate.

The Cyanide and Chromate do not appear to exist. Cyanide of potassium produces a black precipitate of U_2O with evolution of hydrocyanic acid; and chromate of potassium produces a yellowish-brown precipitate, which appears to be a mixture of uranic chromate and uranous chromite.

The Hydrate is produced by the action of the hydrates of potassium or ammonium, also by carbonates of calcium on solutions of uranous salts; it separates in reddish-brown gelatinous flakes, which turn black by boiling, the change being due, it is thought, to loss of water. If not washed free from its precipitant, it rapidly absorbs oxygen from the air, and is converted into the yellow compound known as the uranate of potassium or ammonium (p. 118).

Its composition is not known.

It dissolves easily in acids, but, after ignition, is soluble only in concentrated sulphuric acid.

The Sulphide is produced by the action of sulphide of ammonium. It is a black precipitate, which becomes grey by washing with water, and appears to be thus converted into a mixture of uranous hydrate and sulphur.

Its composition is not known.

It dissolves in acids, especially in nitric acid.

The Sulphate is soluble, and it forms no insoluble double sulphate.

The Carbonate is produced by the action of carbonate of potassium or ammonium. It is a green precipitate.

Its composition is probably that of a mixed carbonate and hydrate.

It dissolves in a large excess of its precipitants, especially in carbonate of ammonium, forming a green solution.

The Oxalate is produced by the action of oxalic acid; it is a greenish-white precipitate, which does not oxidize by exposure to the air.

The formula of the air-dried salt is $U_2C_2O_4+3aq$.

It is insoluble in water, and but slightly soluble in hydrochloric acid.

The Ferrocyanide is produced by the action of ferrocyanide of potassium; it is a light brown precipitate.

Its formula is U_2Cfy.

It dissolves slightly in hydrochloric or nitric acid.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium: it is a brownish-red precipitate, which appears only after the lapse of some time.

THE PHOSPHATE is produced by the action of phosphate of sodium; it is green and gelatinous.

Its formula is U_2HPO_4+aq.

It dissolves in concentrated hydrochloric acid, and is reprecipitated by the addition of water.

The other special reagents of the two former subdivisions are not known to yield any characteristic precipitates with uranous salts.

The chief methods employed for the detection of uranous salts are these,—the formation of the hydrate, the carbonate, and the phosphate.

URANIC OR URANYLIC SALTS.

Solution for the reactions:—the nitrate of uranyle (U_2O, NO_3) in water.

This series of salts is one of the most remarkable that have yet been mentioned. The oxide, which is taken as its representative, has the formula $(U_2)_2O_3$; but when the other salts of the series are examined, it is found that they do not correspond to the typical formula, but are all at total variance with it: thus the nitrate is U_2ONO_3, not $U_2(NO_3)_3$, the ordinary composition of a sesquinitrate; and the sulphate is $(U_2O)_2SO_4$, instead of $U_4(SO_4)_3$; and these are not imaginary formulæ, but the simplest expressions for the salts of this series, legitimately derived from uranic oxide or uranic chloride by double decomposition, assuming of course that in the nitrate and sulphate the same acid-radicals exist as are found in other nitrates and sulphates. The idea was then conceived, that uranic oxide was not a sesquioxide, but a protoxide of the compound basic radical uranyle U_2O; uranic oxide then becomes $(U_2O)_2O$, the chloride U_2OCl, and the sulphate $(U_2O)_2SO_4$: this view harmonizes with the composition of uranic salts in general, and is commonly adopted; its probability is confirmed by the composition of certain compounds of antimony and other metals.

The chief insoluble salts of this radical are these,—the cyanide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

THE CYANIDE is produced by the action of cyanide of potassium. It is of a fine yellow colour. It dissolves in excess of the precipitant and in nitric acid.

THE CHROMATE is produced by chromate of potassium. It is a yellow precipitate.

The Hydrate is obtained by the decomposition of the oxalate in sunlight, or by evaporating the alcohol solution of the nitrate. It cannot be produced by the action of the hydrates of potassium or ammonium on neutral solutions of uranylic salts, since the yellow precipitates which these salts occasion are always combinations of potassium or ammonium with uranyle and oxygen: they are sometimes called uranates. The composition of the potassium compound is $K(U_2O)_2O$; that of the ammonium compound is unknown. They are insoluble in excess of their precipitants: the ammonium compound is slightly soluble in water, soluble in carbonate of ammonium, but insoluble in chloride of ammonium; the potassium compound dissolves in the acid carbonate of potassium.

The Sulphide is produced by the action of the sulphides of potassium or ammonium. It is a brownish-black precipitate, which subsides very slowly. Its composition is probably U_4S_3.

It is soluble in excess of the precipitants, and slightly soluble in water, yielding a brown solution: it dissolves in acids with decomposition.

The Sulphate is soluble, and it forms no insoluble double sulphate.

The Carbonate produced by the action of the carbonates of potassium or ammonium is a compound analogous to the hydrate just described. A similar compound salt is also produced by the action of carbonate of calcium. They are yellow precipitates.

The composition of the carbonate of potassium precipitate is K_2CO_3, U_2OCO_3; that of the ammonium compound is similar: both are readily soluble in excess of their precipitants.

The Oxalate is produced by the action of oxalic acid: oxalate of potassium and oxalate of ammonium generally produce a compound salt. It occurs as a yellow powder or in yellow crystalline grains.

Its composition, when air-dried, is $(U_2O)_2\bar{O}+3aq$; when dried at 100° C. it is $(U_2O)_2\bar{O}+aq$.

It dissolves easily in warm solutions of oxalate of potassium or ammonium, and, on cooling, crystallizes out as the double salt. It dissolves in 125 parts of water at 14° C, and in 30 parts of boiling water: it is more soluble in strong acids.

The Ferrocyanide is produced by ferrocyanide of potassium. It is a dark brownish-red precipitate.

Its composition is probably $(U_2O)_2Cfy$. It dissolves in the carbonates of sodium and ammonium.

The Ferricyanide is produced by ferricyanide of potassium. It is a brownish-red precipitate. It dissolves in carbonate of ammonium.

The Phosphate is produced by phosphate of sodium. It is a light yellow precipitate.

Its composition is $(U_2O)_2HPO_4+3aq$.

It scarcely dissolves at all in water, but easily in carbonate of ammonium.

The special reagents of the first and second groups are not known to yield any characteristic reactions with uranic salts.

The chief means employed for the detection of uranic salts are these,—the blowpipe reactions, and the formation of the so-called hydrate and ferrocyanide.

SALTS OF TITANIUM.

The body titanium forms three oxides; one only, however, is of sufficient importance to be considered analytically, and that is possessed of the properties of an acid-radical. This oxide, the so-called titanic acid, dissolves in hydrochloric and other acids; and from its being precipitated from that solution by alkaline hydrates or carbonates, in excess of which it is insoluble, its reactions are frequently considered in this group: we shall, however, treat of it in the third subdivision of the acid-radicals.

SALTS OF TANTALUM, NIOBIUM, AND PELOPIUM.

These three rare bodies are known to form but one oxide each, which plays the part of an acid-radical. They have been placed in this group for the same reason as has been adduced under TITANIUM; they, however, exhibit a difference in their behaviour with hydrate of potassium, being soluble in excess of that reagent. They will be considered in the third subdivision of acid-radicals.

SALTS OF IRON.

The metal iron resembles uranium and chromium in forming a large number of oxides; many of these are, however, believed to be combinations of oxides among themselves, since they yield those oxides as products of decomposition. Thus the oxide Fe_6O_4 may be decomposed into salts of the ferrous and ferric series, by the action of the ferrocyanide and the ferricyanide of potassium, whence it is argued by some that its real composition must be $Fe_2O, (Fe_2)_2O_3$. The truly important oxides of iron are Fe_2O, $(Fe_2)_2O_3$, and FeO_2: the two former represent series of salts, the ferrous and ferric series respectively, while the latter has the properties of a compound acid-radical, and as such will be treated of in the next chapter. Ferrous salts are generally white if anhydrous, but when containing water of crystallization they are usually of a pale bluish-green. Ferric salts also are often white when anhydrous, and of a reddish-brown or reddish-yellow colour when crystallized with water. The soluble salts of iron in general have a nauseous metallic taste.

All salts of iron when heated before the blowpipe are converted in the oxidizing flame into $(Fe_2)_2O_3$, which is brown while hot, and red when cold; and if this sesquioxide be heated carefully in the reducing flame, it is converted into the black oxide Fe_6O_4: both of these compounds remain infusible. Iron salts give no characteristic reaction with nitrate of cobalt before the blowpipe, and impart no colour to the flame; but when *fused with borax,* they produce a bead which *in the oxidizing flame is red while hot, and yellow after cooling, and in the reducing flame is slightly yellow while hot, and bottle-green or colourless when cold.*

The production of a ferrate ($MFeO_2$) does not form the same characteristic test for iron as the analogous chromium compound does for chromium. Ferrate of potassium ($KFeO_2$) is obtained by the action of oxidizing agents on sesquioxide of iron. Its aqueous solution is of a magnificent wine-red colour; but the salt is very unstable, giving off oxygen and depositing sesquioxide of iron.

FERROUS SALTS, OR PROTO-SALTS OF IRON.

Solution for the reactions:—ferrous sulphate (Fe_2SO_4) in water.

The chief insoluble salts of this series are these,—the cyanide, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate. The great tendency which these salts have to pass into ferric salts is a serious obstacle in observing their reactions, which are in consequence usually more or less mixed with the reactions due to ferric salts.

In making the solution for the reactions, the salt should be washed two or three times with water, to dissolve away the outer coating; and, when finally dissolved, access of air should be prevented by stopping the mouth of the test-tube with the thumb.

The Cyanide is produced by cyanide of potassium acting upon pure ferrous salts, as a light reddish-brown precipitate.

Its composition is thought to be FeCy.

It dissolves in acids. It is also very soluble in cyanide of potassium, uniting with it to form a compound which was formerly regarded as a double salt having the formula 2(KCy), FeCy:

this compound was, however, noticed to differ from other double salts, inasmuch as the iron existing in it could not be precipitated even by so powerful a reagent as an alkaline sulphide; nor could it by any means be detected until the constitution of the body was broken up, and its cyanogen ($Cy=CN$) destroyed by the action of some powerful oxidizing agent: fusion (*e.g.*) with nitrate or chlorate of potassium would restore the iron to the state in which it could be easily recognized. This, coupled with the fact that in ordinary decompositions the substance $2(KCy)FeCy$ divided itself into K_2 and $FeCy_3$, led to the supposition that it was in reality a true salt containing a compound acid-radical, $FeCy_3$, which was thenceforth called "ferrocyanogen;" and to its salts the name of "ferrocyanides" was applied. It is a good instance of the way in which metamorphoses take place among complex molecules.

The Chromate does not appear to exist. Chromate of potassium gives a yellowish-brown precipitate with ferrous salts, which appears to be a mixture of the chromic and ferric sesquioxides. This precipitate is partially soluble in nitric acid, yielding a green solution.

The Hydrate is produced by the action of the hydrates of potassium or ammonium on neutral solutions of ferrous salts, also by the carbonates of the second subdivision, but only on boiling. The hydrate of ammonium precipitates only half the metal present in the solution of a ferrous salt, the ammonium salt formed combining with the remaining half of the unchanged ferrous salt, and producing a double salt undecomposable by the excess of hydrate of ammonium present: this has been already observed in the case of the salts of magnesium (p. 93); it occurs thus:—

$$2(FeCl)+2(NH_4HO)=\underset{\text{ppt.}}{FeHO}+FeCl,NH_4Cl+NH_4HO.$$

When absolutely free from ferric salt, this precipitate is white; but as ordinarily prepared, it is of a greenish colour. It absorbs oxygen very rapidly from the air, and is converted into red ferric hydrate.

The formula is FeHO.

It is insoluble in excess of its precipitants; but the presence of ammonium salts prevents its precipitation by these reagents, especially by the hydrate of ammonium. Ammonium salts also dissolve it when once precipitated, although imperfectly. It is readily soluble in acids.

The Sulphide is produced by the action of the sulphides of potassium or ammonium; it is also produced by the passage of hydrosulphuric acid gas into a solution containing a ferrous salt dissolved in an ammonium compound, and containing hydrate of ammonium, while in neutral or acid solutions of ferrous salts hydrosulphuric acid yields no precipitate, except in rare cases, such as the neutral ferrous acetate ($Fe\bar{A}$), in which partial precipitation occurs. It is a black precipitate.

Its formula is Fe_2S; but it probably contains some water.

It is insoluble in excess of its precipitants. It is slightly soluble in water, forming a green solution, from which it is reprecipitated by the addition of sulphide of ammonium. It dissolves in hydrochloric and nitric acids, but is less soluble in acetic acid.

THE SULPHATE is soluble, 1 part of the crystals, which have the formula Fe_2SO_4+7aq, dissolving in 2 parts of cold, and in three-fourths of boiling water.

THE DOUBLE SULPHATE OF IRON AND POTASSIUM ($KFeSO_4+3aq$) is also soluble.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium (but not by carbonate of calcium); it is a white precipitate, which becomes green and then reddish-brown by exposure to the air, from a gradual conversion at first into the hydrate of the magnetic oxide (Fe_6O_4) and afterwards into ferric hydrate.

Its formula is $2(Fe_2CO_3)+aq$.

It is insoluble in excess of its precipitants; but ammonium salts prevent its precipitation by these reagents: it is soluble in carbonic and other acids, in most cases suffering decomposition.

THE OXALATE is produced by oxalic acid after a time, and immediately by oxalate of potassium or ammonium: it is a yellow powder.

Its formula is $Fe_2C_2O_4+2aq$.

It is scarcely soluble in cold water, and dissolves but sparingly in boiling water: it behaves similarly with oxalic acid. It dissolves in concentrated hydrochloric acid, but not in concentrated sulphuric; in warm dilute sulphuric acid it is, however, soluble.

The Ferrocyanide is produced by ferrocyanide of potassium; it is a white precipitate, which rapidly becomes blue by exposure to the air.

Its formula is KFe_3Cfy_2 *or* $KFeCfy, Fe_2Cfy$. By exposure to the air, or by the action of nitric acid or chlorine, it is converted into Prussian blue (Fe_4Cfy_3), according to the equation

$$3(KFe_3Cfy_2)+4Cl=2([Fe_2]_2Cfy_3)+3KCl+FeCl.$$

It is nearly insoluble in water.

The Ferricyanide is produced by the action of ferricyanide of of potassium (K_3Cfdy); it is a blue precipitate.

Its formula is Fe_3Cfdy.

It is insoluble in water and in hydrochloric acid.

THE PHOSPHATE is produced by the action of phosphate of sodium; it is a white precipitate, which acquires a dirty bluish-green colour by exposure to the air.

Its formula is Fe_2HPO_4.

It is soluble in hydrate of ammonium, but insoluble in other ammonium salts, and in water: it is dissolved by acids.

The other special reagents of the present and of the two preceding groups produce no characteristic reactions in solutions of ferrous salts.

Ferrous are distinguished from ferric salts by their hydrate and ferro- and ferricyanide.

FERRIC SALTS, OR SESQUI-SALTS OF IRON.

Solution for the reactions:—sesquichloride of iron (Fe_2Cl_3) dissolved in water.

These salts are produced by the action of many powerful salt-radicals upon ferrous salts: thus chlorine and bromine convert a ferrous into a ferric salt with the utmost rapidity—

$$2(FeCl)+Cl=Fe_2Cl_3 \textit{ or } 3(Fe_2\,SO_4)+Cl_3=Fe_4(SO_4)_3+Fe_2\,Cl_3;$$

and even the oxygen of the air effects the same change, although more slowly. Certain acids containing an easily decomposable acid-radical, act in a similar manner, and, as a more complex substance is concerned, the change is accompanied by a decomposition of the acid itself; thus:—

$$2(FeNO_3)+2(HNO_3)=(Fe_2[NO_3]_3)+NO_2+H_2O.$$

The converse operation, namely, the conversion of a ferric into a ferrous salt, is effected by the introduction of some substance possessing a tendency to combine with and remove a portion of the acid-radical present: basic elements are generally employed for this purpose; and metallic iron may itself be used, thus—

$$Fe_2Cl_3+Fe=3(FeCl);$$

or *nascent* hydrogen may be employed, *i. e.* hydrogen at the moment of its liberation, before the molecule H has united with another molecule to form the gas H H. Nascent hydrogen is applied either by passing some readily decomposable and gaseous hydrogen-compound into the ferric salt, as thus, by sulphuretted hydrogen—

$$2(Fe_2Cl_3)+H_2\,S=4(FeCl)+2HCl+S,$$

or by decomposing water with some substance having a powerful affinity for oxygen, as sulphurous acid, which acts by being converted into sulphuric acid during the decomposition,—

$$2(Fe_2Cl_3)+H_2\,O+H_2\,SO_3=4(FeCl)+2(HCl)+H_2\,SO_4,$$

or by decomposing an acid by a metal such as zinc, in the presence of a ferric salt,—

$$2(Fe_2Cl_3)+H_2\,SO_4+2Zn=4(FeCl)+2(HCl)+Zn_2\,SO_4.$$

The term "reduction" is applied to any such transformation from a higher state of combination to a lower one.

The principal insoluble ferric salts are these,—the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, and the phosphate. Ferricyanide of potassium produces a characteristic reaction, but no precipitate.

THE CYANIDE is not produced by its appropriate reagent, cyanide of potassium precipitating from ferric salts ferric hydrate, with evolution of hydrocyanic acid.

THE CHROMATE is produced by the action of chromate of potassium: it is a brown precipitate.

Its composition is not known.

It is decomposed by water, especially at the boiling temperature, into chromic acid and sesquioxide of iron.

The Hydrate is produced by the action of the hydrates of potassium and ammonium, by the carbonates of the second group, and also by the carbonates of manganese, zinc, and copper, which, though themselves insoluble in solutions of ferric salts, nevertheless decompose them completely at ordinary temperatures after standing some time. The hydrate is a precipitate of a fine red-brown colour.

Its formula, when recently precipitated, is $Fe_2 H_3 O_3$; dried at 100° C., its composition is $(Fe_2)_2 O_3 + 2aq$: and if kept for some time under water it becomes $(Fe_2)_2 H_3 O_3$, *or* $(Fe_2)_2 (HO)_3$; a similar formula expresses the constitution of the oxalate, and of the ferrocyanide (Prussian blue). When precipitated by hydrate of potassium, the hydrate contains a portion of the precipitant, while the carbonates of the second subdivision precipitate a basic salt.

It is insoluble in excess of its precipitants, and in solutions of ammonium salts, but readily soluble in acids, and also to a large extent in sesquichloride of iron.

The Sulphide is produced by the action of the sulphides of potassium or ammonium when a solution of a ferric salt is added to a solution of the reagent; if the contrary course be adopted, a mixture of sulphur with ferrous sulphide is precipitated. The sulphide is black.

Its composition is $(Fe_2)_2 S_3$; but it probably contains water.

It is insoluble in excess of its precipitants, but soluble to a trifling extent in water, forming a green solution: it dissolves in most acids, but not in acetic acid.

THE SULPHATE AND DOUBLE SULPHATE are soluble.

THE CARBONATE can scarcely be said to exist, the precipitate produced by the action of the carbonates of potassium or ammonium being chiefly the hydrate, and containing only a minute and variable amount of carbonic acid. The precipitate thus produced has, however, a peculiar property, viz. of dissolving in concentrated solutions of its precipitants; it then yields a red solution, from which it is reprecipitated by boiling, or by dilution with water. This solubility is probably due to the formation of a soluble double compound containing the two metals present.

THE OXALATE is produced by the action of the oxalates of potassium or ammonium (not added in excess, lest a soluble double oxalate should be formed). It is a lemon-yellow powder.

Its formula is $Fe_4\bar{O}_3$, *or* $(Fe_2)_2\bar{O}_3$. $Fe^4, C^6 O^{12}$

It is nearly insoluble in water, but soluble in oxalic acid, yielding a solution which, in the light, gradually decomposes, evolving carbonic acid gas, and depositing crystals of ferrous oxalate.

The Ferrocyanide is produced by ferrocyanide of potassium; it is commonly called Prussian blue. The solution to be tested should be neutral; if alkaline, it should be made acid with acetic acid; and if it contains a strong acid, an alkaline acetate should be added.

Its formula is Fe_4Cfy_3, *or* $(Fe_2)_2Cfy_3$.

It is insoluble in water and in dilute hydrochloric acid, but is decomposed by sulphuric, nitric, and concentrated hydrochloric acids, and, in common with all cyanogen compounds, by hydrate of potassium. It is soluble in oxalic acid, and also in neutral tartrate of ammonium.

The Ferricyanide, or, as some think, the cyanide (Fe_2Cy_3), is produced by the action of ferricyanide of potassium: no precipitate is formed, for the salt is soluble in water; but the colour, a deep green with a tinge of brown, is characteristic: this is best seen in very dilute solutions; in concentrated ones it may be mistaken for a precipitate.

The Phosphate is produced by the action of phosphate of sodium: it is a white flocculent precipitate.

Its composition is said to be $Fe_2\,PO_4+2aq$.

It is insoluble in ammonium salts, with the exception of the hydrate and carbonate; it also dissolves to a slight extent in carbonate of sodium. It is soluble in 1500 parts of boiling water, and readily dissolves in weak acids, except cold acetic acid.

The other special reagents of the present and two preceding groups give no characteristic reactions with solutions of ferric salts.

The principal means employed for the recognition of ferric salts are these,—the borax bead, and the formation of the reddish-brown hydrate and of the beautiful blue ferrocyanide, together with the peculiar reaction of ferricyanide of potassium.

SECTION II.—*Non-volatile Salts, not precipitated by excess of Hydrate of ammonium* (NH_4HO) *in the presence of Chloride of ammonium* (NH_4Cl).

SALTS OF MANGANESE, COBALT, NICKEL, AND ZINC.

SALTS OF MANGANESE.

Manganese resembles the three preceding metals in forming a great number of combinations with oxygen; but the majority of these compounds, like those previously described, are supposed to be formed by the union of the oxides among themselves. The two oxides Mn_2O and $(Mn_2)_2O_3$ are the only oxides of manganese which represent series of salts; and of these series the former is by far the more important, and its members more numerous. Manganese, like iron, forms a combination with oxygen, having in its salts the formula MnO_2, and playing the part of an acid-radical: manganese also combines with oxygen to form another acid-radical with the formula Mn_2O_4, and which is also known in combination with basic radicals in the form of the permanganates. Manganous salts are either colourless or of a pale rose tint: this colour has been said to be due to the presence of cobalt; and it is also stated that it is owing to the presence of a manganic salt, and that, if this impurity be removed by sulphurous acid or an appropriate reducing agent, the salt is decolorized. Manganic salts are red.

Salts of manganese, when heated before the blowpipe, for the most part decompose, leaving the brown oxide (Mn_6O_4), which remains infusible, imparts no tinge to the blowpipe flame, nor gives any characteristic reaction with nitrate of cobalt. *Fused with borax,* all manganese salts colour the bead of *a hyacinthine-red colour in the oxidizing flame,* due, probably, to the formation of a sesquiborate ($Mn_2[BO_2]_3$), while, *in the reducing flame,* the glass becomes *pink, and finally colourless,* by reason of the reduction of the salt to the state of protoborate: this is much facilitated by the addition of a little metallic tin.

There are other means of recognizing the metal, both in manganous and manganic salts, besides the precipitation of certain insoluble compounds and the production of the characteristic borax bead; these are the formation of the manganic and of the permanganic acids,—tests as sensitive for the detection of manganese as chromic acid for the recognition of chromium. These acids of manganese are obtained by exposing any manganese salt to the action of a substance capable of yielding oxygen; a mixture of carbonate of sodium and nitrate of potassium is generally employed: the most minute trace of the metal confers upon the fused mass, when cold, a bluish-green tint, which is quite characteristic. The formula of manganic acid is $HMnO_2$, and of manganate of potassium $KMnO_2$. Permanganic acid is even more readily formed, and is a test of great delicacy: the manganese salt is dissolved in concentrated nitric acid, the solution boiled, and then a few grains of peroxide of lead (Pb_2O_2) added; upon allowing the excess of peroxide to settle down, the supernatant liquid will be seen to have acquired a most beautiful reddish-violet colour, if but a very minute trace of manganese were present. The formula of permanganic acid is HMn_2O_4.

Manganic acid is readily converted into permanganic, and *vice versâ,* as the following equations show. Manganate of potassium with nitric acid is thus decomposed:—

$$5(KMnO_2)+4(HNO_3)=2(KMn_2O_4)+MnNO_3+3(KNO_3)+2(H_2O);$$

while permanganate, with alkalies, yields the manganate, thus,—

$$2(KMn_2O_4)+2(KHO)=4(KMnO_2)+O+H_2O.$$

MANGANOUS SALTS, OR PROTO-SALTS OF MANGANESE.

Solution for the reactions:—sulphate of manganese (Mn_2SO_4) in water.

The chief insoluble salts by means of which this series may be distinguished are these,—the cyanide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Cyanide is produced by the action of cyanide of potassium: it is a dirty-yellow bulky precipitate, becoming brown by exposure to the air.

Its formula is MnCy.

It is soluble in excess of the precipitant, and in strong acids with decomposition. Manganicyanogen is formed with difficulty.

The Chromate is produced by the action of chromate of potassium after the lapse of some time, or more rapidly by boiling the solution. It is a dark brown precipitate.

Its formula, when dried at 100° C., is $MnCrO_2+aq$.

It is slightly soluble in water, and soluble in acids.

The Hydrate is produced by the action of the hydrates of potassium or ammonium on neutral solutions of manganous salts; the latter, as in the cases of magnesium and iron (pp. 93 and 121), only precipitates half the amount of metal present as hydrate, the remaining half forming with the ammonium salt produced in the first decomposition a soluble compound not precipitable by excess of hydrate of ammonium. One result of this action is, that, if a sufficient quantity of an ammonium salt be added to a solution of a manganous salt, the subsequent addition of hydrate of ammonium produces no precipitate whatever. This solution of the manganous salt in a salt of ammonium, or the precipitated hydrate (which is white), rapidly absorbs oxygen from the air, becoming converted into the manganic hydrate.

The formula of the hydrate is MnHO.

It is insoluble in excess of its precipitants, but perfectly soluble in ammonium salts, if no manganic hydrate be present.

The Sulphide is produced by the action of the sulphides of potassium or ammonium; it is also produced by passing hydrosulphuric acid gas into an ammoniacal solution of a manganous salt; but if the solution of the manganous salt be acid or neutral, this gas produces no precipitate, or only the faintest turbidity if the solution be quite neutral. It is a buff or flesh-coloured precipitate when quite pure, and very pale when precipitated from dilute solutions: by contact with the air it becomes brown.

Its formula is $Mn_2 S$, but it probably contains some water.

It is insoluble in excess of its precipitants, but readily soluble in most acids, even in acetic acid (if concentrated), with decomposition.

The Sulphate ($Mn_2 SO_4 + 7aq$) is soluble. It occurs in pink crystals.

The Double Sulphate of Manganese and Potassium ($KMnSO_4 + 3aq$) is also soluble.

The Carbonate is produced by the action of the carbonates of potassium or ammonium; it is only formed by the action of the carbonates of the second group on boiling. It is a pinkish-white precipitate, which does not become brown by exposure to the air.

Its formula, dried at 88° C., is $2(Mn_2CO_3) + aq$.

It is insoluble in excess of its precipitants, but when recently precipitated dissolves in solution of chloride of ammonium. It dissolves in 7680 parts of water, and in 3840 parts of solution of carbonic acid gas (CO_2): in acids it dissolves with decomposition.

The Oxalate is produced by the action of oxalic acid, or of the oxalates of potassium or ammonium, not added in excess, lest a compound and soluble oxalate should be formed. It is a nearly white powder, crystalline, and usually showing a faint tint of rose.

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Its formula, when dried at 100° C., is $Mn_2C_2O_4 + 2aq$.

It dissolves in 900 parts of cold, and in a less quantity of boiling water. It is somewhat soluble in an excess of the alkaline oxalates, and also in solutions of ammonium salts. Oxalic acid dissolves it slightly, but abundantly on heating; the stronger acids dissolve it more easily.

The Ferrocyanide is produced by the action of ferrocyanide of potassium. It is a white precipitate.

Its formula is Mn_2Cfy.

It is insoluble in most ammonium salts. It dissolves in hydrochloric acid.

The Ferricyanide is produced by the action of ferricyanide of potassium: it is a brownish-yellow precipitate.

Its formula is $Mn_3Fe_2Cy_6$.

It is insoluble, or nearly so, in ammonium salts, and also in hydrochloric acid.

The Phosphate is produced by the action of phosphate of sodium: it is a white precipitate, which does not become brown on exposure to the air.

The composition of this salt appears to vary with the method of precipitation, although the same precipitant (Na_2HPO_4) be used. If excess of the precipitant be employed, adding it to a cold neutral solution of the manganous salt, a salt of the formula $Mn_3PO_4+3\frac{1}{2}aq$ is precipitated; but if the solution of the manganous salt be kept in excess and were acid, the precipitate, which slowly forms, has the composition $Mn_2HPO_4+3\,aq$.

The other special reagents of the present and two preceding groups produce no characteristic reactions with manganous salts.

The chief means for the detection of manganous salts are these,—the blowpipe reaction, the formation of the hydrate, the sulphide, the carbonate, and the ferricyanide.

MANGANIC SALTS, OR SESQUI-SALTS OF MANGANESE.

The manganic salts are extremely soluble; and their solutions are generally of a rose-red colour. They are but little known, owing to their excessive instability, being easily resolved, in most instances into the corresponding manganous salt and salt-radical.

The chief insoluble salts are the hydrate and phosphate.

The Hydrate is obtained by precipitating solutions of manganic salts ($[Mn_2]_2[SO_4]_3$ for example) by the action of carbonate of calcium, also by exposing manganous hydrate to the air, or to chlorine; it is always, however, mixed with $MnHO$. It is a bulky brown powder.

Its formula is $Mn_2H_3O_3$.

The Phosphate is only obtained by heating the sesquioxide $(Mn_2)_2O_3$ with phosphoric acid: it is a peach-coloured powder.

Its formula is $Mn_2(PO_4)_3+aq$.

It is insoluble in all acids except hydrochloric.

SALTS OF COBALT.

There are many points of resemblance between this metal and the three preceding. It corresponds in particular very closely to iron in the number and chemical properties of the oxides which it forms. One oxide (Co_2O) is, however, the only one that can be said to represent a series of salts, the sesqui-salts, typified by the sesquioxide $([Co_2]_2O_3)$, being very readily decomposed into proto-salts and salt-radicals. The remaining oxides are generally believed to be compounds of these two. The cobaltous or proto-salts are generally of a pink or violet colour; and such of the cobaltic or sesqui-salts as are known are dark red or brown.

The salts of cobalt, when heated before the blowpipe, generally yield a dark green powder of protoxide, which remains infusible, imparts no colour to the blowpipe flame, and is not affected by nitrate of cobalt: *fused with borax,* however, they produce *a fine blue bead, in both the reducing and oxidizing flames.*

COBALTOUS SALTS, OR PROTO-SALTS OF COBALT.

Solution for the reactions:—nitrate of cobalt $(CoNO_3)$ in water.

The principal insoluble cobaltous salts are these,—the cyanide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Cyanide is produced by the action of cyanide of potassium: it is a dirty pale-red precipitate, approaching to brown.

Its composition, when dried over sulphuric acid, is $CoCy+aq$.

It is soluble in excess of its precipitant, being converted completely, on boiling the solution, into cobalticyanide of potassium ($K_3Co_2Cy_6$ *or* K_3Cocy). Dilute acids produce no precipitate in this solution; for the hydrocobalticyanic acid formed by their action is very soluble in water. If the solution of cobalticyanide of potassium be strongly acidulated with nitric acid, evaporated to dryness, and fused, the cobalticyanide is decomposed, the black oxide (Co_2O) is left, and may be tested before the blowpipe. The cyanide is soluble in hydrate of ammonium and most other ammonium salts, especially on heating; but it is insoluble in water, and in dilute acids.

THE CHROMATE is produced by chromate of potassium. It is reddish brown.

It is thought to be a basic salt.

The Hydrate is produced by the hydrates of potassium or ammonium; the latter exerts the same action as has been explained in the cases of magnesium, iron, and manganese, precipitating only half the metal as hydrate, the other half remaining dissolved by the ammonium salt produced at first. When freshly precipitated it is blue; it then changes to violet or a dirty red, and finally to green; this happens more rapidly if the liquid be boiled: if exposed to the air it becomes green, and partially converted into cobaltic hydrate.

The composition of the blue precipitate is that of a basic salt, while the formula of the red one is $CoHO$.

It is insoluble in excess of hydrate of potassium, but soluble in the more stable ammonium salts; and therefore, if hydrate of ammonium be added to an acid solution of a cobaltous salt, no precipitate is produced, because such an ammonium salt is at the same instant formed. The hydrate is readily soluble in acids.

The Sulphide is produced by the action of the sulphides of potassium or ammonium, also by passing sulphuretted hydrogen into an ammoniacal solution of a cobaltous salt. If, however, the latter solution be neutral, the gas precipitates it but imperfectly, except in the case of a salt containing a weak acid-radical, as that existing in the acetate. Acid solutions of cobaltous salts are not precipitated at all by sulphuretted hydrogen, except in the instances just alluded to; but even then the acetic acid must not be too concentrated, lest it retain some of the cobalt in solution. The sulphide is also produced by the addition of recently precipitated sulphide of manganese (Mn_2S) to solutions of cobaltous salts. It is a black precipitate.

Its formula is Co_2S, together with some water.

It is but very triflingly soluble in excess of its precipitants. It is almost absolutely insoluble in acetic acid, and is only slowly dissolved by the acids (H_2SO_4, HCl, and HNO_3) in the cold; but in nitrohydrochloric acid it easily dissolves.

THE SULPHATE (Co_2SO_4+7aq) is soluble. The double sulphate of cobalt and potassium ($KCoSO_4+3aq$) is also soluble.

THE CARBONATE is produced by the action of a neutral or acid carbonate of potassium or ammonium, but not by the carbonates of the second group, except at the boiling temperature. It is a peach-coloured precipitate.

Its formula is $Co_2CO_3, 3(CoHO)$. It contains also some water.

It is extremely soluble in excess of carbonate of ammonium, and slightly soluble in concentrated solutions of the carbonates of potassium or sodium. It immediately dissolves in acids, suffering decomposition.

THE OXALATE is produced by the action of oxalic acid or oxalate of potassium. It is a rose-coloured powder.

Its formula when dried in the air is $Co_2C_2O_4+2aq$.

It dissolves readily in hydrate and carbonate of ammonium, and slightly in other ammonium salts. It is almost insoluble in water, but soluble in 40,000 parts of boiling oxalic acid solution.

THE FERROCYANIDE is produced by ferrocyanide of potassium. It is a pale blue precipitate, which becomes a greyish-red after some time, and, by careful heating, assumes a green colour.

The formula of the dry salt is Co_2Cfy.

It is partially soluble in hydrate of ammonium and in the carbonate, but is insoluble in hydrochloric acid. It dissolves without decomposition in sulphuric acid, with which, indeed, it combines to form a crystalline compound.

The Ferricyanide is produced by ferricyanide of potassium. It is a dark-red precipitate.

Its formula is Co_3Cfy_2.

It is insoluble in hydrate of ammonium and in hydrochloric acid.

THE PHOSPHATE is produced by the action of phosphate of sodium. It is a blue precipitate.

Its formula appears to be Co_3PO_4.

It dissolves readily in hydrate of ammonium, and slightly in many other ammonium salts; it is also soluble in phosphoric and most other acids.

The other special tests of the present and two preceding groups give no characteristic reactions with cobaltous salts.

Cobaltous salts may be detected by their blowpipe reaction, and the formation of their hydrate, sulphide, and ferricyanide.

COBALTIC SALTS, OR SESQUI-SALTS OF COBALT.

The chief insoluble salt of this series is the hydrate; but the phosphate and the ferrocyanide are also known, and are insoluble. Many soluble salts of this series may be formed by dissolving the sesquihydrate in acids; but they are all extremely unstable, decomposing with great rapidity into the corresponding proto-salts. The acetate is almost the only stable cobaltic salt.

The Hydrate is formed by saturating water, in which some cobaltous hydrate or carbonate is suspended, with chlorine, or by exposing an ammoniacal solution of a cobaltous salt to the air until it has assumed a brown colour, and then precipitating it with hydrate of potassium.

Its formula is $Co_2H_3O_3$.

It dissolves in most acids, generally with evolution of oxygen and formation of the proto-salt. It is insoluble in hydrate of ammonium.

The Sulphide is produced by the action of hydrosulphuric acid, or sulphide of ammonium, on a solution of the acetate. It is a black precipitate.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium. It is a dark red precipitate. By excess of the precipitant it is resolved into the green protoferrocyanide (Co_2Cfy) and ferricyanide of potassium.

THE PHOSPHATE is produced by the action of phosphate of sodium. It is a brown precipitate.

The action of the other special tests of the present and two preceding groups upon the sesqui-salts of cobalt has in many cases not been ascertained.

SALTS OF NICKEL.

The salts of this metal are almost as closely allied to those of cobalt as are the salts of erbium and terbium to those of yttrium, or the salts of didymium and lanthanium to those of cerium; they have, however, been made the subjects of more complete investigation, on account of their occurring in far greater abundance. Nickel is only known to form two combinations with oxygen, a protoxide, Ni_2O, and a sesquioxide, $(Ni_2)_2O_3$, although the existence of a higher oxide has been alleged. The protoxide alone represents an important series of salts, the only representatives of the sesqui-salts being the oxide and the hydrate. The proto-salts of nickel are generally of a yellow colour when anhydrous, and when hydrated, green.

When heated before the blowpipe, the salts of nickel leave a residue of a greenish-grey or dull black appearance, which is infusible, and imparts no colour to the flame: it is not affected by nitrate of cobalt solution; but when fused *with borax* on the platinum wire, it produces a bead which, *in the reducing flame, is opaque and grey,* from particles of reduced metal diffused through it, whilst *in the oxidizing flame it becomes of a transparent brownish orange-red*: if, however, a small fragment of nitrate of potassium be added to the grey nickel bead produced in the inner flame, and the bead be again carefully heated in the oxidizing flame, a glass of a red-purple colour is produced.

NICKELOUS SALTS, OR PROTO-SALTS OF NICKEL.

Solution for the reactions:—protosulphate of nickel (Ni_2SO_4) in water.

The principal insoluble salts are these,—the cyanide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Cyanide is produced by the action of cyanide of potassium. It is a pale greenish precipitate.

Its formula is $NiCy$.

It is readily soluble in excess of its precipitant, a double salt ($NiCy, KCy$) being formed; it is, however, reprecipitated as $NiCy$ upon the addition of hydrochloric or sulphuric acid, since no compound is formed similar to those produced by iron and cobalt under similar circumstances. Hydrate of potassium decomposes the cyanide of nickel, with formation of cyanide of potassium and protoxide of nickel. The cyanide dissolves quickly in hydrate or carbonate of ammonium, and more or less perfectly in most ammonium salts. It is insoluble in water and in acids.

THE CHROMATE is produced by the action of chromate of potassium on certain proto-salts of nickel, and is generally precipitated only, or chiefly, on heating the mixed solutions. It is a reddish-yellow powder.

Its formula is probably $NiCrO_2$.

It is insoluble in water.

The Hydrate is produced by the action of hydrate of potassium, hydrate of ammonium producing only a slight precipitate, since the hydrate of nickel is soluble, not only in the ammonium salt produced, but in the precipitant itself. It is a precipitate of a pale green colour.

Its formula is $NiHO$.

It is insoluble in excess of hydrate of potassium. Ammonium salts readily dissolve it, forming a fine bluish-purple solution.

The Sulphide is produced by the action of the sulphides of potassium or ammonium, or by the passage of hydrosulphuric acid gas into an ammoniacal solution of a proto-salt of nickel, by which means sulphide of ammonium is formed. Hydrosulphuric acid occasions only a trifling turbidity in *neutral* solutions of nickel salts containing energetic acid-radicals. If, however, the acid-radical of the salt is weak, as are many of those derived from the organic kingdom, then the gas precipitates more of the nickel; this is the case with the acetate of nickel. Acid solutions of nickel salts are not precipitated at all by hydrosulphuric acid, except in the cases of the weak acids before mentioned. The recently precipitated sulphides of manganese and cobalt, when introduced into solutions of nickel salts, also cause the precipitation of the nickel as sulphide. It is a black precipitate.

Its formula is Ni_2S.

It is insoluble in excess of sulphide of potassium, but somewhat soluble in excess of sulphide of ammonium; that is, in excess of the ordinary yellow sulphide ($[NH_4]_2S + nS$), which contains sulphur. Colourless sulphydrate of ammonium (NH_4HS) does not dissolve it. From the solution, which is brownish-yellow, neutralization with acetic acid reprecipitates it. It is insoluble in water, almost insoluble in acetic acid, slightly soluble in hydrochloric acid, but dissolves at once on the addition of nitric acid. In most acids it is soluble at the boiling temperature.

THE SULPHATE ($Ni_2SO_4 + 7aq$) and the double sulphate ($KNiSO_4 + 3aq$) are soluble.

THE CARBONATE is produced by the action of the acid or neutral carbonates of potassium or ammonium on solutions of nickel salts, and also by allowing the hydrate to absorb carbonic acid gas from the air. It is also produced by the carbonates of the second subdivision, but only at the boiling temperature. It is a pale green precipitate.

Its formula is that of the mixed hydrate and carbonate. When precipitated at the boiling temperature, it is sometimes of the formula $Ni_2CO_3, 6NiHO$, after drying in the air, or *in vacuo*.

It is soluble in excess of carbonate of ammonium, forming a greenish-blue solution. It is but very slightly soluble in a concentrated solution of carbonate of sodium. It is readily soluble in most acids.

THE OXALATE is produced by the action of oxalic acid, but by the alkaline oxalates only after the lapse of some time. It is a greenish-white precipitate.

Its formula is $Ni_2C_2O_4 + 2aq$.

It dissolves readily in hydrate or carbonate of ammonium, but less easily in other ammonium salts. It is insoluble in water, slightly soluble in solution of oxalic acid; but it dissolves with comparative rapidity in the stronger acids.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium. It is a green precipitate.

Its formula is Ni_2Cfy; but it generally retains a portion of its precipitant.

It is soluble in hydrate of ammonium, forming a red solution; but the ammonium salts in general do not dissolve it.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium; it is a reddish-brown precipitate.

THE PHOSPHATE is produced by the action of phosphate of sodium; it is a pale green precipitate.

Its formula is probably Ni_2HPO_4.

It is insoluble in water, but soluble in strong acids.

The other special reagents of the present and of the first and second groups, give no characteristic reactions with protosalts of nickel.

The means usually employed for the recognition of the proto-salts of nickel are these,—the blowpipe reaction, the precipitation of the hydrate, of the cyanide, of the sulphide, and of the ferro- and ferricyanides.

SESQUI-SALTS OF NICKEL.

These salts are, as has been stated, unstable in the extreme. The only insoluble salts known are the sesquioxide ($[Ni_2]_2O_3$) and the hydrate ($Ni_2H_3O_3$). When the hydrate is dissolved in acids, proto-salts of nickel are immediately formed. The sesquioxide may be obtained by moderately heating the protonitrate. It is also formed when hydrate of nickel comes in contact with a hypochlorite,—

$$4(NiHO)+CaClO=(Ni_2)_2O_3+CaCl+2H_2O.$$

If the solution decanted from the precipitated oxide be boiled, a further precipitation occurs; but the precipitate is now the hydrate ($Ni_2H_3O_3$).

SALTS OF ZINC.

Solution for the reactions:—sulphate of zinc (Zn_2SO_4) in water.

The metal zinc differs from the preceding metals in many of its chemical characters: it forms only one series of salts, proto-salts, of which the chloride (ZnCl) or the oxide (Zn_2O) may be taken as representatives. Two other combinations of zinc and oxygen are supposed to exist, the suboxide (Zn_4O), and the peroxide (Zn_2O_2); but their existence is somewhat problematical at present.

Most zinc salts, when heated before the blowpipe on charcoal, leave the white infusible residue of protoxide (Zn_2O), which *incandesces strongly*, and when removed from the flame appears slightly yellow while hot, and becomes white on cooling. The metal itself being volatile below a white heat, if the oxide be reduced to the metallic state by exposure to the inner flame of the blowpipe, it volatilizes, and, passing through the highly heated air which surrounds the blowpipe flame, oxidizes again, and is deposited on a more distant and cooler part of the charcoal as an "incrustation." The oxide, *if moistened with a solution of nitrate of cobalt, and again strongly heated in the oxidizing flame,* is found, after cooling, to have assumed *a green colour.* Zinc salts impart no colour to the flame; and when fused with borax on a platinum wire, the bead, if saturated with zinc, remains clear in the outer flame, but in the reducing flame becomes milk-white; and if very intensely heated, the zinc salt is reduced to the state of metal, and alloys with the platinum. The metal zinc itself burns in the blowpipe flame with an intense bluish or greenish white light.

The principal insoluble salts are the cyanide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

THE CYANIDE is produced by the action of cyanide of potassium; it is a white precipitate.

Its formula is ZnCy.

It is soluble in excess of its precipitant, and in excess of the hydrates of potassium or ammonium, and in most ammonium salts; it is insoluble in water, but dissolves in acids, even in acetic.

THE CHROMATE is produced by the action of the chromate of potassium on solutions of zinc salts. It is a precipitate of a fine yellow colour.

Its composition appears to vary.

It is soluble in hydrate of potassium,—chromate of potassium and hydrate of zinc being formed, both of which are dissolved by the excess of the precipitant.

The Hydrate is produced by the action of the hydrate of potassium or ammonium; it is a white gelatinous precipitate. The ammonium salt does not precipitate the whole of the zinc.

Its formula is ZnHO.

It is soluble in excess of its precipitants, and in ammonium salts; it is dissolved by most acids.

The Sulphide is produced by the action of the sulphides of potassium or ammonium on solutions of zinc salts, or by passing sulphuretted hydrogen gas into an alkaline solution of zinc, while from neutral solutions of zinc this gas precipitates but a small part of the metal present, and from acid solutions none at all; the acetate of zinc, however, is an exception, being completely thrown down by hydrosulphuric acid, whether a neutral solution, or one acidified with acetic acid be taken. It is a white precipitate.

The formula of this precipitate is $ZnHS_{\frac{1}{2}}O_{\frac{1}{2}}$; *i.e.* it is a hydrate in which half the oxygen is "replaced" by sulphur: the hydrate has, it will be remembered, the formula ZnHO. In order to avoid fractions, the formula of the so-called sulphydrate of zinc may be thus written,—Zn_2H_2SO, *or* Zn_2S,H_2O.

It is insoluble in excess of its precipitants, slightly soluble in acetic acid, but readily soluble in stronger acids.

THE SULPHATE (Zn_2SO_4+7aq) and the double sulphate ($KZnSO_4+3aq$) are soluble.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium, but is only partially precipitated, except after boiling the solution, because, the precipitate being a mixed hydrate and carbonate, some carbonic acid is liberated, which retains a portion of the carbonate of zinc in solution.

Its formula is Zn_2CO_3, 3ZnHO.

It is somewhat soluble in excess of carbonate of sodium, more so in carbonate of ammonium, and readily dissolves in the common ammonium salts. It dissolves in 44,642 parts of water, but separates when the solution is heated, and does not redissolve on cooling. It is readily soluble in most acids, and to some extent even in carbonic acid.

THE OXALATE is produced by the action of oxalic acid or oxalate of potassium on solutions of zinc salts. It is a white precipitate.

Its formula, when dried in the air, is $Zn_2C_2O_4+2aq$.

It dissolves readily in hydrate or carbonate of ammonium, but less easily in other ammonium salts; it is scarcely soluble in water, but dissolves in hydrochloric acid.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium; it is a white precipitate.

Its formula is $Zn_2Cfy + 1\frac{1}{2}aq$.

It is partially soluble in excess of its precipitant, soluble in hydrate of ammonium and other ammonium salts, and slightly soluble in dilute acids.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium: it is a precipitate of an orange-brown colour.

Its formula is Zn_3Cfy_2.

It dissolves readily in hydrate of ammonium and other ammonium salts.

THE PHOSPHATE is produced by the action of phosphate of sodium; it is a white semigelatinous precipitate, changing to a crystalline powder.

Its composition is Zn_2HPO_4 when the precipitant has been added in excess; but if the solution of the zinc salt preponderate, its formula is Zn_3PO_4.

These precipitates are soluble in the hydrate and other salts of ammonium; they are insoluble in water, but soluble in acids.

The other special reagents of the two preceding groups exert no characteristic action on solutions of zinc salts.

The chief means employed for the recognition of zinc salts are these,—the blowpipe reactions on charcoal and with nitrate of cobalt, together with the formation of the hydrate and sulphide.

SECTION III.—*Salts of the compound bases, which may be volatilized and destroyed by ignition.*

SALTS OF MORPHINE, QUININE, AND STRYCHNINE.

In addition to the elementary basic radicals which this third group contains, we here introduce a few of that large class of compound basic bodies of which so great a number exists, but of which few are of sufficiently frequent occurrence to warrant consideration in an analytical work. They occur in nature, or in natural products. Morphine is found in *opium*, the inspissated juice of the *Papaver somniferum*; quinine in the bark of the *Cinchona lancifolia* and the allied trees; and strychnine in the seeds of the *Strychnos nux-vomica* and other species of *Strychnos*: and in those substances these bases exist associated with other bases, one or two of which will be noticed in conjunction with them. They are bodies of great medicinal importance; and as toxicological cases frequently arise in which these substances are concerned, the student ought to be fully acquainted with their reactions. Being all entirely constituted of the four elements carbon, hydrogen, nitrogen, and oxygen, they are all volatile, or decompose, leaving a residue of carbon, upon the application of heat, and may thus be readily distinguished from every other member of the group with which, by the action of reagents, they may occasionally be confounded. Another peculiarity which they present, is the ready solubility of their salts in alcohol. These compound bases combine directly with acids to form salts without the disengagement of hydrogen, as is the case with certain elementary basic radicals which have been described. On this account, these substances can scarcely be considered as basic *radicals*; for the sake of convenience we will term them basic *bodies*.

SALTS OF MORPHINE.

Solution for the reactions:—hydrochlorate of morphine ($C_{17}H_{20}NO_3Cl + 3aq$) in water.

The very complex basic body morphine, combines with acids to form perfectly stable salts: all these salts are, however, formed after one type—that of a proto-salt; and their general formula is consequently MR.

Morphine, like quinine and strychnine, may be regarded as an *ammonia*, and like ordinary ammonia (NH_3), when combining with acids, becomes a salt of ammonium (NH_4): thus

$$\underbrace{\mathrm{NH_3}}_{\text{ammonia.}}+\mathrm{HCl}=\underbrace{\mathrm{NH_4Cl}}_{\substack{\text{hydrochlorate of}\\\text{ammonia, or chloride}\\\text{of ammonium.}}};\qquad \underbrace{\mathrm{C_{17}H_{19}NO_3}}_{\text{morphine.}}+\mathrm{HCl}=\underbrace{\mathrm{C_{17}H_{20}NO_3Cl}}_{\substack{\text{hydrochlorate of morphine,}\\\text{or chloride of morphine-}\\\text{ammonium.}}}$$

Salts of morphine are generally very soluble in water and alcohol, but insoluble in ether. They are without colour, unless their acid-radical introduces it; their taste is bitter, and they are poisonous. When heated they carbonize, *i. e.* suffer complicated decomposition, one of the results of which is the separation of carbon; this residual carbon will burn entirely away if free access of air be allowed, the heat being still maintained. With other agents also, as sulphuric acid, peroxide of lead, &c., characteristic products of decomposition are obtained, by means of which morphine may be recognized:—

α. When powdered morphine, or a concentrated solution of a morphine salt, is projected into a concentrated solution of ferric sulphate, which must be neutral, or but slightly acid, the latter is coloured of a deep blue. This colour disappears by the addition of acid or alcohol, or upon the application of heat.

β. The addition of nitric acid to a salt of morphine, or its concentrated solution, gives a reddish orange-colour, which passes into a yellow.

Among insoluble morphine salts are the following:—the chloroplatinate, the carbazotate, the hydrate, the ferrocyanide, the ferricyanide, and the phosphate.

Morphine is always associated with another base, narcotine (among others), which may be thus distinguished:—its hydrate is insoluble in hydrate of potassium, but soluble in ether, while concentrated nitric acid dissolves narcotine without coloration, becoming yellow, however, on heating.

The Chromate and Cyanide are unknown.

The Chloroplatinate is produced by the addition of chloroplatinic acid to a solution of a salt of morphine. It is a yellow, curdy precipitate.

Its composition is $C_{17}H_{20}NO_3PtCl_3$.

It is somewhat soluble in water, and may be crystallized.

The Carbazotate is unknown.

The Hydrate is produced by the action of a very dilute solution of hydrate of potassium (not in excess) upon solutions of morphine; it is also produced by the carbonates and acid carbonates of the alkalies. It is a white precipitate.

Its composition is $C_{17}H_{20}NO_3HO$.

It is easily soluble in the hydrates of potassium and calcium (lime-water), in the hydrate and chloride of ammonium, but is scarcely soluble in cold water; boiling water dissolves about $\frac{1}{500}$th of its weight of the hydrate. In cold alcohol it is but slightly soluble, but it dissolves more readily at the boiling temperature. It is insoluble in ether. Most acids dissolve it.

The Sulphydrate is unknown.

The Sulphate is very soluble.

The Carbonate is produced only when a solution of carbonic acid gas, made under pressure and saturated with morphine, is considerably cooled without the pressure being removed.

The Oxalate is hardly known.

The Ferrocyanide is not well known; but it appears to be soluble.

The Ferricyanide is produced by the action of ferricyanide of potassium upon solutions of morphine salts. It is a yellow crystalline precipitate.

The Phosphate is produced by phosphate of sodium as a crystalline precipitate very soluble in water.

The action of many of the special reagents of the present and two preceding groups upon morphine salts has not been ascertained.

Morphine is generally recognized by the reactions with ferric sulphate and nitric acid.

SALTS OF QUININE.

Solution for the reactions:—sulphate of quinine ($[C_{20}H_{25}N_2O_2]_2SO_4+7aq$) in dilute sulphuric acid.

The compound basic body quinine unites with most acids to form salts of great stability. They are all formed upon the type MR, the chloride, or rather the hydrochlorate, having the formula $C_{20}H_{25}N_2O_2Cl$, which is equivalent to QuHCl, Qu being the symbol for 1 equivalent of the basic body, or *ammonia*-quinine ($C_{20}H_{24}N_2O_2$).

Salts of quinine are not usually very soluble in water. Some of their acid solutions exhibit the very remarkable phænomenon of *fluorescence* or *epipolic dispersion*,—a magnificent blue luminosity seen upon the surface of the liquid when viewed in reflected light, and which is owing to a change effected in the *actinic* rays by the dissolved quinine salt. The hydrochlorate of quinine does not exhibit this curious property. Quinine salts are, for the most part, extremely soluble in alcohol, while some dissolve also in ether: generally they are without colour, and very bitter in taste. When heated, they generally leave a residue of carbon, unless with an acid-radical (as in the chlorate) containing much oxygen: such salts, indeed, usually explode. Peculiar products of decomposition may be obtained by the action of many reagents; and by these and other methods this body may be recognized.

Among these reactions are the following:—

a. If to a solution of a quinine salt, freshly prepared chlorine water be added, and then a few drops of hydrate of ammonium, a green colour is obtained; and if too much of the hydrate has not been added, the addition of a few drops more of chlorine water will convert the green tinge into a violet, and finally into a deep red.

β. Concentrated nitric acid dissolves quinine and many salts of quinine, forming a colourless solution, which becomes only faintly yellow on heating.

Among the insoluble salts of quinine are the hydrate and the sulphate.

Quinine is invariably associated to a large extent with cinchonine, which may be distinguished from quinine by the insolubility of its hydrate in dry ether. Addition of chlorine water causes no coloration in a solution of a cinchonine salt, while the subsequent addition of ammonia produces a yellowish-white precipitate.

THE CHROMATE AND CYANIDE are unknown.

THE CHLOROPLATINATE is produced by the action of chloroplatinic acid: it is a pale yellow flocculent precipitate, which becomes orange and crystalline by agitation.

Its formula is said to be $C_{20}H_{25}N_2O_2, H(PtCl_3)_2 + aq$.

THE PERCHLORATE is soluble, and the CARBAZOTATE is unknown.

The Hydrate is produced by the action of the hydrates and carbonates of potassium or ammonium, and by the sulphydrate of ammonium: it is a white curdy precipitate.

Its formula is $C_{20}H_{25}N_2O_2, H, O + 2aq$.

It is but slightly soluble in hydrate or carbonate of potassium, but dissolves more readily in hydrate of ammonium; it dissolves in 350 parts of cold, and in 400 parts of boiling water; it is extremely soluble in alcohol, and somewhat so in ether. It is dissolved by most acids.

THE SULPHYDRATE is not known.

THE SULPHATE is the commonest salt of quinine: it is comparatively insoluble in cold water, requiring 265 parts of water at 15° C., and 24 parts of boiling water, for solution; it is extremely soluble in alcohol, and somewhat so in ether; it is dissolved by most acids.

THE CARBONATE is only obtained by allowing a carbonic acid solution of hydrate of quinine to evaporate spontaneously.

THE OXALATE is obtained by adding oxalate of ammonium to a solution of the acetate of quinine: it is a white precipitate, and is but slightly soluble in cold water or alcohol, but soluble in boiling alcohol.

THE FERROCYANIDE is produced when alcoholic solutions of hydroferrocyanic acid ($H_2 Cfy$) and of quinine are mixed, and separates as an orange crystalline precipitate.

Its composition is $C_{20} H_{25} N_2 O_2, H_3, Cfy_2 + 2aq$.

THE FERRICYANIDE is produced by the action of a concentrated solution of ferricyanide of potassium on a solution of hydrochlorate of quinine containing some free hydrochloric acid, and is precipitated as a golden-yellow crystalline powder.

It is easily soluble in water.

THE PHOSPHATE is a white crystalline body, very soluble in hot phosphoric acid.

SALTS OF STRYCHNINE.

Solution for the reactions:—hydrochlorate of strychnine ($C_{21} H_{23} N_2 O_2, Cl$) in water.

The compound basic body strychnine combines with most acids to form very stable salts, which are formed upon the type MR.

Most salts of strychnine are soluble in water; they are colourless unless their acid-radical introduces colour; they are intensely bitter and exceedingly poisonous: when heated they usually carbonize, and yield with some reagents characteristic products.

Strychnine may be recognized—

α. By dissolving the base of its salt in a drop of concentrated sulphuric acid, and adding to the solution one drop of a solution of chromate of potassium, when a purplish-blue colour is produced, which changes to red. The presence of sugar and of quinine is said to interfere with this test, but not when applied as follows:—the sulphuric acid solution of strychnine, to which a few drops of nitric acid has been added, is mixed with a few grains of peroxide of lead ($Pb_2 O_2$), when the liquid becomes successively blue, violet, and greenish-yellow*.

β. Concentrated nitric acid dissolves strychnine, forming a solution colourless in the cold, but which becomes slightly yellow on heating. If to this solution a small quantity of peroxide of lead be added, the same changes of colour may be witnessed as in the preceding experiment.

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* These and similar experiments, where a transparent colouration is produced, should be performed upon a fragment of white porcelain.

Among the insoluble salts of strychnine are these,—the chromate, the chloroplatinate, and the hydrate.

Strychnine is associated in nature, to a certain extent, with another base, brucine, which may be readily distinguished from it by being soluble in absolute alcohol. The action, too, of nitric acid upon the two bodies differs: it dissolves brucine, and colours the solution intensely red; when heated, this colour changes to yellow; and if stannous chloride or sulphide of ammonium be then added, the colour again changes and becomes a most intense violet.

THE CHROMATE is produced by the action of chromate of potassium: it is a brownish-yellow precipitate, slightly soluble in cold water or alcohol, but much more soluble in boiling water.

THE CYANIDE does not exist.

THE CHLOROPLATINATE is produced by the action of chloroplatinic acid on hydrochlorate of strychnine.

Its composition is $C_{21}H_{23}N_2O_2, PtCl_3$.

It is almost insoluble in water and in weak and boiling alcohol, also in ether.

THE PERCHLORATE is comparatively insoluble in water, but far more soluble in alcohol.

THE CARBAZOTATE is unknown.

The Hydrate is produced by the action of the hydrate or carbonate of potassium, and of the hydrate of ammonium on solutions of strychnine salts (not too dilute): it is a white precipitate, which appears crystalline under the microscope.

Its composition probably is $C_{21}H_{23}N_2O_2, HO$.

It is insoluble in hydrate or carbonate of potassium, but soluble in hydrate of ammonium. It is almost insoluble in water, 1 part requiring 6667 parts of water at 10° C. for solution, and 2500 parts of boiling water; nevertheless its cold aqueous solution, when diluted with 100 times its volume of water, possesses a marked degree of bitterness. It is very soluble in alcohol, but insoluble in absolute alcohol or ether. It dissolves in most acids.

THE SULPHYDRATE is unknown.

THE CARBONATE is said to be produced when a strychnine salt is precipitated by an alkaline carbonate.

THE OXALATE and THE SULPHATE are soluble.

THE FERROCYANIDE is produced by mixing saturated solutions of ferrocyanide of potassium and of a strychnine salt, and is a precipitate composed of nearly colourless needles.

Its composition is $(C_{21}H_{23}N_2O_2)_2 Cfy + 4aq$.

It is but slightly soluble in cold water or alcohol, but far more soluble in these liquids at the boiling temperature.

THE FERRICYANIDE appears to be soluble.

THE PHOSPHATE is soluble; THE SILICOFLUORIDE does not exist, being resolved, at the moment of its formation, into hydrofluate of strychnine and silicic anhydride (Si_4O_3).

The other special reagents of the present and two preceding groups are

TABLE OF

REACTIONS.	Al_2 (see page 109)	Cr_2 (see page 113)	U_2 (see page 117)	Fe (see page 120)
Cyanide	*	blue-grey	yellow	reddish brown
Chromate	yellow	yellow-brown	yellow	yellow-brown
Hydrate	white	green	yellow	greenish white
Sulphide	†	†	black	black
Carbonate	white	blue-green	yellow	greenish white
Oxalate	—	pale green	yellow	yellow
Ferrocyanide ...	*	—	red-brown	pale blue
Ferricyanide ...	—	—	brown-red	deep blue
Phosphate	white	green	light-yellow	greenish white
BLOWPIPE REACTIONS.	Incandescent residue, which, if moistened with $CoNO_3$ and again heated, becomes blue.	The borax-bead is green in the inner, and emerald-green in the oxidizing flame.	The borax-bead is yellow in the oxidizing, green in the reducing flame.	The borax-bead is reddish-brown in the oxidizing flame, and bottle-green in the reducing flame.

NOTE.—† means that the precipitate formed by the reagent

* means that a precipitate occurs, not of the salt

not known to give any characteristic reactions with solutions of strychnine salts.

Strychnine is usually detected by its reaction with chromic acid.

REACTIONS.

Fe_2 (see page 125)	Mn (see page 129)	Co (see page 132)	Ni (see page 136)	Zn (see page 140)
*	dirty yellow	dirty pink.	pale green	white
brown	brown	reddish brown	reddish yellow	yellow
red	white	olive	green	white
black	buff	black	black	white
red	white	peach-colour	pale green	white
yellow	white	rose	greenish white	white
deep blue	white	pale blue	greenish white	white
green solution	brown-yellow	dark red	greenish yellow	orange-brown
white	white	blue	pale green	white
Ferric salts give the same blowpipe reactions as ferrous salts.	With Na_2CO_3 a green mass. The borax-bead is grey in the inner, and amethyst in the outer flame.	The borax-bead in either flame is deep blue.	The borax-bead is red-brown in the outer, and grey in the inner flame.	With $CoNO_3$ the oxide assumes a green colour; with carbonate of sodium on charcoal, a yellow incrustation, white when cold.

added is similar in composition to that above it.

indicated opposite in the first column, but of the hydrate.

In the Table which we append to this group we have purposely
unfrequently, but are generally asso-

Analysis of

The metals of more common occurrence only being included,
IRON (ferrous or ferric), MANGANESE,

<table>
<tr><td colspan="4">Dissolve in hydrochloric acid; boil with a few drops of nitric acid, and ammonia.</td></tr>
<tr><td colspan="4">A precipitate may contain
Uranium, Aluminium, Chromium, or Iron.
The precipitate is washed, and digested with carbonate of ammonium in the cold, then filtered; if not wholly dissolved, we infer the</td></tr>
<tr><td rowspan="3">absence of Uranium, confirmed by adding acetic acid and ferrocyanide of potassium.
*</td><td colspan="3">presence of
Aluminium, Chromium, or Iron.
Redissolve in hydrochloric acid, and add excess of hydrate of potassium; if the precipitate at first formed is finally entirely dissolved, we infer the</td></tr>
<tr><td rowspan="2">absence of Iron.
*</td><td colspan="2">presence of
Aluminium or Chromium.
Boil the solution. If no precipitate is produced, we infer the</td></tr>
<tr><td>absence of Chromium.
*</td><td>possible presence of
Aluminium,
which may be ascertained by observing whether the addition of chloride of ammonium produces a precipitate.</td></tr>
</table>

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* If a precipitate is in any case obtained, the reactions

omitted to mention the rarer metals, since they not only occur ciated also with but few other bodies.

Subdivision III.

the salt may be one of URANIUM, ALUMINIUM, CHROMIUM, NICKEL, COBALT, or ZINC.

<table>
<tr><td colspan="5">add some quantity of solution of chloride of ammonium, and excess of</td></tr>
<tr><td rowspan="4"></td><td colspan="4">No precipitate will indicate the presence of
Manganese, Nickel, Cobalt, or Zinc.
Add sulphide of ammonium, wash any precipitate which may form thoroughly, dissolve it in nitro-hydrochloric acid, and add excess of hydrate of potassium; the formation of any precipitate will indicate the</td></tr>
<tr><td rowspan="3">absence of Zinc. This may be confirmed by observing that hydrosulphuric acid produces no precipitate in this solution.</td><td colspan="3">presence of
Manganese, Nickel, or Cobalt.
Redissolve in HCl, and add excess of carbonate of ammonium; the formation of no precipitate indicates the</td></tr>
<tr><td rowspan="2">absence of Manganese.
*</td><td colspan="2">presence of
Nickel or Cobalt.
Acidify with acetic acid, add cyanide of potassium in excess, boil the solution, and add slight excess of hydrochloric acid; the formation of no precipitate indicates the</td></tr>
<tr><td>absence of Nickel.
*</td><td>possible presence of
Cobalt,
which may be ascertained by evaporating to dryness, and observing whether the residue colours the borax-bead blue in both flames.</td></tr>
</table>

must be referred to, and confirmatory tests chosen.

SUBDIVISION IV.

SALTS OF CADMIUM, COPPER, SILVER, MERCURY, LEAD, BISMUTH, PALLADIUM, TIN, ANTIMONY, ARSENIC, PLATINUM, RHODIUM, RUTHENIUM, IRIDIUM, OSMIUM, GOLD, TUNGSTEN, MOLYBDENUM, AND VANADIUM.

The metals of this subdivision bear a very great resemblance to those of the last group, both in the number and the composition of the insoluble salts which they form: two members, indeed, of the present subdivision, cadmium and copper, differ in but few particulars from the general chemical characters of iron, nickel, cobalt, and zinc; but some metals of this class form insoluble chlorides and iodides, as copper and mercury (cuprous and mercurous chlorides), and also silver, lead, and platinum (argentic, plumbic, and platinous chlorides). As a general rule, however, the salts of the present and of the preceding subdivision correspond very closely in relative solubility and insolubility,—the chlorides, sulphates, silicofluorides, &c. of the fourth subdivision being soluble like those of the third, while the chromates, hydrates, carbonates, sulphydrates, sulphides, &c. are insoluble, at least for the most part, and thus resemble the similar salts of the third group. The great characteristic which enables us to arrange the metals whose names are given above into a distinct group, is the precipitation of their sulphides by hydrosulphuric acid gas, not only from neutral, but also from acid solutions,—the ready solubility of the sulphides of the former subdivision in acids being, it will be remembered, one of its distinguishing features. But, in addition to this, a new peculiarity manifests itself in the deportment of the sulphides of the present group, by means of which its further division into sections is effected. The peculiarity alluded to, is the solubility of a great number of these sulphides in alkaline sulphides, and the insolubility (under the same conditions) of the remainder.

A new feature is also to be observed in the members of this group, namely, their ready decomposition with precipitation of metal by the introduction of a sheet or bar of certain metals into their solutions: the metals zinc and iron are especially active in this respect, they simply act by assuming the place of the precipitated metal, thus—$CuCl + Fe = FeCl + Cu$.

The salts of the metals contained in this subdivision are sometimes called "salts of the heavy metals."

The first six metals of this subdivision are of frequent occurrence; and of the remainder, tin, antimony, platinum, and gold are the most important. The most abundant are copper, silver, lead, mercury, and tin; but others, such as cadmium, bismuth, and antimony, as well as some of quite the rarer ones, such as tungsten, molybdenum, and vanadium, exercise so very important an influence upon the commoner metals when alloyed with them, as to demand such attention from the student as may enable him to recognize these rarer bodies by their reactions: it is equally, if not more important, that he should be able accurately to recognize the presence of platinum and gold, on account of the great value set upon those metals.

It has just been mentioned that by the action of an alkaline sulphide, such as sulphide of ammonium (in which agent some of the sulphides of the present group are insoluble, while the remainder are soluble), we can separate this extensive subdivision into two sections; we shall adopt this method of arrangement, and here give a list of the members of each section. Another reaction is advantageously made use of for the still further subdivision of the former of these sections, namely, the formation of the insoluble argentic, mercurous, and plumbic chlorides by the addition of hydrochloric acid; the other chlorides of the group being soluble, are thus separated from these three bodies, and are subsequently precipitated in the form of sulphides.

SECTION I.—SALTS OF CADMIUM, COPPER, SILVER, MERCURY, LEAD, BISMUTH, AND PALLADIUM.

Salts of metals which form sulphides insoluble in sulphide of ammonium ($[NH_4]_2 S$).

SECTION II.—SALTS OF TIN, ANTIMONY, ARSENIC, PLATINUM, RHODIUM, RUTHENIUM, IRIDIUM, OSMIUM, GOLD, TUNGSTEN, MOLYBDENUM, AND VANADIUM.

Salts of metals which form sulphides soluble in sulphide of ammonium ($[NH_4]_2 S$).

The tests employed for the recognition of the members of this group are the following:—hydrochloric acid or a soluble chloride, iodide of potassium, cyanide of potassium, chromate of potassium, the hydrates of potassium and ammonium, sulphydrate and sulphide of ammonium, the carbonates of potassium and ammonium, oxalic acid and oxalate of potassium, sulphuric acid or a soluble sulphate, ferrocyanide and ferricyanide of potassium, phosphate of sodium, and hydrosulphuric acid.

The group test is hydrosulphuric acid ($H_2 S$) in an acid solution.

SECTION I.—*Salts of metals which form sulphides insoluble in Sulphide of ammonium* ($[NH_4]_2 S$).

SALTS OF CADMIUM, COPPER, SILVER, MERCURY, LEAD, BISMUTH, AND PALLADIUM.

SALTS OF CADMIUM.

Solution for the reactions:—chloride of cadmium ($CdCl$) in water.

Cadmium is a metal which presents so many features analogous to those of zinc, the last member of the preceding subdivision, that its most fitting place is at the beginning of the present group.

Cadmium, like many of the succeeding metals, appears to form an oxide containing half as much oxygen as the common oxide (Cd_2O), and the formula of which consequently is Cd_4O; the former oxide (Cd_2O) only is the representative or starting-point of the large number of salts which this metal yields.

Salts of cadmium, when heated before the blowpipe on platinum foil and in the oxidizing flame, undergo no change excepting the separation of the red-brown oxide, which remains infusible; but if heated on a reducing surface such as charcoal affords, and in the inner flame of the blowpipe, these compounds are reduced to the metallic state, while the metal volatilizes, becoming oxidized as it passes through the flame into the air, and then condenses on a distant part of the charcoal as a red-brown incrustation of oxide (Cd_2O). It imparts no colour to the blowpipe flame; when heated, however, with borax on a platinum wire and in the oxidizing flame, a transparent bead is produced, which, if saturated with the cadmium salt, becomes milk-white on cooling. In the reducing flame the metal is reduced, and if sufficiently heated, volatilized; before this is effected, however, the wire will probably be spoilt from the cadmium having formed a fusible alloy with the platinum. It yields no characteristic reaction with nitrate of cobalt. The salts of cadmium are white, unless the acid-radical introduces colour.

The chief insoluble salts by means of which cadmium is recognized are the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

A bar or plate of metallic iron introduced into the solution of a cadmium salt, does not precipitate the metal; but a bar of zinc removes the cadmium from its solution, the zinc combining with the acid-radical.

THE CHLORIDE is soluble. THE IODIDE is readily soluble.

THE CHROMATE is yellow.

THE CYANIDE, according to some chemists, is soluble; according to others, cyanide of potassium produces a precipitate with sulphate of cadmium ($Cd_2 SO_4$), soluble in excess of the precipitant and in warm ammonia-water, but insoluble in solutions of other ammonium salts.

The Hydrate is produced by the action of hydrate of potassium, and is partially precipitated also by hydrate of ammonium: it is a white precipitate.

Its formula is CdHO.

It dissolves readily in hydrate of ammonium and in many other ammonium salts, and readily in acids, suffering decomposition.

The Sulphide is produced by the action of hydrosulphuric acid or the sulphides of potassium and ammonium on solutions of cadmium salts; it is precipitated even from solutions acidified by dilute mineral acids, and of course also separates from neutral or alkaline solutions. It is a brilliant rich yellow precipitate.

Its formula is Cd_2S.

It is very slightly soluble in hydrate of ammonium, but dissolves easily in concentrated hydrochloric or nitric acids, and even in dilute hydrochloric at the boiling temperature, although precipitable from its acid solution by hydrosulphuric acid gas.

THE SULPHATE is soluble.

THE CARBONATE is produced by the action of the neutral or acid carbonates of potassium or ammonium: it is a white precipitate.

Its formula, dried at 100° C., is Cd_2CO_3.

It is insoluble in water, and in excess of its precipitants, but readily soluble in solutions of ammonium salts, and with decomposition, in acids.

THE OXALATE is produced by the action of oxalic acid or alkaline oxalates on solutions of cadmium salts: it is a white crystalline powder.

Its formula, dried at 100° C., is $Cd_2C_2O_4+2aq$.

It dissolves in the hydrate and in most other ammonium salts; it is nearly insoluble in water, and in solution of oxalic acid.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium: it is a yellowish-white precipitate.

Its formula is Cd_2Cfy.

It is soluble in hydrate of ammonium, but does not completely dissolve in other ammonium salts.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium: it is a pale yellow precipitate.

Its formula is Cd_3Cfdy.

It dissolves readily in hydrate of ammonium and in most other ammonium salts.

THE PHOSPHATE is produced by the action of phosphate of sodium: it is a white precipitate.

Its formula is probably Cd_3PO_4.

It is insoluble in water.

The other reagents of the present and three preceding subdivisions produce no characteristic reactions in solutions of cadmium salts.

The chief methods employed for the detection of cadmium are these,—the formation of the red-brown incrustation on charcoal, and the precipitation of the hydrate, readily soluble in ammonia, and of the brilliant yellow sulphide, insoluble in alkaline sulphides.

SALTS OF COPPER.

The metal copper presents some analogy with cadmium, differing, however, from it, among other characters, in forming two distinct and well-defined series of salts, the cuprous and cupric salts, of which the oxides Cu_4O and Cu_2O, and the chlorides Cu_2Cl and $CuCl$ may be considered as representatives.

Salts of copper when heated are converted into the oxide (Cu_2O), and before the blowpipe on charcoal may be reduced to the metallic state with the flame alone, although the reduction of the oxide may be much more readily effected if it be heated with carbonate of sodium. In this and in all cases in which it is sought to reduce a metal in order to ascertain whether the operation has been successful or otherwise, it is better to remove the mass from the charcoal, to powder it finely in a mortar, to stir up the powdered mass with water, and to allow the mixture to rest in order that the metallic particles may settle. Lastly, the liquid is to be poured off while it still holds the impurities present in suspension, and the agitation with fresh quantities of water, and decantation, to be repeated until the metallic particles are at length obtained perfectly pure and free from the charcoal, &c. which at first obscured their presence and rendered it doubtful. By this process, also, the malleability or brittleness of the metal under examination can be ascertained; for if, under the pestle, the globule of metal flattens out into a lamina, it may be pronounced malleable; and if, on the contrary, it is found to have been broken into minute fragments or powder, it must be considered brittle. Copper salts, when heated upon charcoal, give no incrustation, since neither copper nor its oxides are perceptibly volatile at the temperature employed; nevertheless many copper salts are sufficiently volatile to impart a pure green colour to flame. Nitrate of cobalt gives no reaction with cupric oxide. When heated *with borax* on a platinum wire, salts of copper give *in the oxidizing flame* a bead which is of a *fine green colour while hot, and blue when cold,* whilst, *in the reducing flame,* it becomes *at first colourless,* on account of the reduction of the cupric to the cuprous salts, or, if fully saturated, *a brick-red bead* is obtained on cooling. Copper salts are poisonous. Cuprous salts are either colourless or red; cupric salts are green, or if anhydrous, white: the former are converted into the latter on exposure while moist to the air, or to the action of such oxidizing substances as nitric acid, &c.

The metals iron, zinc, and cadmium precipitate copper from cupric salts; the two latter, however, precipitate a copper containing zinc or cadmium. Tin and lead also precipitate copper from some cupric salts; and bismuth also, at the boiling temperature, precipitates a very impure metal. The presence of copper is frequently ascertained by immersing metallic iron in a solution of a copper salt.

CUPROUS SALTS.

DI- OR SUB-SALTS OF COPPER.

Solution for the reactions:—cuprous chloride (Cu_2Cl) in hydrochloric acid.

The principle insoluble salts by means of which the cuprous salts are recognized are these,—the hydrate, the sulphide, the ferrocyanide, and the ferricyanide.

Many of the cuprous salts, such as the oxalate and the phosphate, either do not exist, or split, at the moment of their formation, into metallic copper and the corresponding cupric salt.

The Chloride is obtained by the action of stannous chloride (SnCl) on a solution of cupric chloride (CuCl), when the following reaction takes place:—

$$2CuCl + SnCl = \underset{\text{cup. chlor.}}{Cu_2Cl} + SnCl_2.$$

This salt may also be prepared by boiling metallic copper with an acid solution of cupric chloride. It is a white powder, which may, however, be crystallized from its hydrochloric acid solution. It slowly becomes green on exposure to the air.

The formula of this salt is Cu_2Cl.

It is nearly insoluble in water, but easily soluble in hydrochloric acid, yielding a brown solution, from which a large volume of water precipitates the greater part of the salt; it dissolves also in hydrate of ammonium, giving a colourless solution which rapidly becomes blue on exposure to the air, a cupric salt being formed, and oxygen absorbed.

The Iodide is produced by the action of iodide of potassium on solution of cuprous chloride; also, it is said, by precipitating a cupric salt with iodide of potassium, iodine being liberated, thus—

$$Cu_2SO_4+2KI=K_2SO_4+Cu_2I+I.$$

It is a brown-red powder.

Its formula is Cu_2I.

It is somewhat soluble in hydrochloric acid.

THE CHROMATE is unknown.

THE CYANIDE is produced by the action of cyanide of potassium on solutions of cuprous salts: it is a white curdy precipitate.

Its formula is Cu_2Cy.

It dissolves in the hydrate and in many other ammonium salts; it dissolves also in strong hydrochloric acid, but is insoluble in warm dilute sulphuric acid.

The Hydrate is produced by the action of hydrate or carbonate of potassium upon solutions of cuprous salts: it is an orange-yellow powder.

Its formula is that of an oxyhydrate, in which the oxide $(Cu_2)_2O$ predominates.

It is soluble in hydrate of ammonium, yielding a colourless solution if the air be excluded; it is said to dissolve in almost all acids, even in the weakest, without suffering a profound change, for such solutions still afford cuprous salts by double decomposition. This hydrate is, however, only thus soluble in acids when moist, but when anhydrous, is at once decomposed by them.

The Sulphide is produced by the action of hydrosulphuric acid on acid, neutral, or alkaline solutions of cuprous salts; it is a black precipitate.

Its formula is Cu_4S *or* $(Cu_2)_2S$.

It dissolves with difficulty in strong boiling hydrochloric acid, but is at once decomposed by cold nitric acid into cupric nitrate and cupric sulphide; after ebullition with nitric acid, of course, all the copper exists in the form of cupric nitrate.

THE SULPHATE does not exist. THE CARBONATE is not known.

THE OXALATE is produced by the action of oxalic acid or oxalate of potassium: it is a white powder, which changes after a time to a blue-green.

Its formula is not known. It dissolves readily in the hydrate and carbonate of ammonium, but to a slight extent only in other ammonium salts.

The Ferrocyanide is produced by the action of ferrocyanide of potassium on solutions of cuprous salts: it is a white flaky precipitate, which becomes reddish brown from conversion into the corresponding cupric salt.

Its formula is $(Cu_2)_2 Cfy$.

It is soluble in the hydrate, but not in other ammonium salts.

The Ferricyanide is produced by the action of ferricyanide of potassium upon solutions of cuprous salts. It is a red-brown precipitate.

Its formula is $(Cu_2)_3 Cfdy$.

It dissolves readily in the hydrate, but is insoluble in other ammonium salts.

The other special tests of the present and three preceding groups exert no characteristic or well-defined action on solutions of cuprous salts.

The means usually employed for the detection of cuprous salts are these,—the formation, and behaviour with ammonia water of the insoluble chloride, and the precipitation of the iodide, hydrate, and sulphide.

CUPRIC SALTS.

Solution for the reactions:—cupric sulphate (Cu_2SO_4) in water.

The chief insoluble salts by means of which copper, in this form of combination, is recognized are these,—the chromate, the cyanide, the hydrate, the oxide, the sulphide, the carbonate, the oxalate, the ferrocyanide, and the phosphate.

The Chloride is soluble.

The Iodide does not exist. A cupric salt, with iodide of potassium, yields cuprous iodide and free iodine.

The Chromate is produced by the action of chromate of potassium upon solutions of cupric salts. It is a dull yellowish brown precipitate.

Its formula is probably $CuCrO_2$.

It dissolves in hydrate of ammonium, forming a green solution, and is readily soluble also in dilute nitric acid.

The Cyanide is produced by the action of cyanide of potassium on solutions of cupric salts. It is a brownish yellow precipitate, which decomposes spontaneously, at ordinary temperatures, into cyanogen gas (CN) and a combination of cuprous and cupric cyanide ($Cu_2Cy, CuCy$).

Its formula is $CuCy + aq$.

It is readily dissolved by excess of its precipitant.

The Hydrate is produced by the reaction of equivalent quantities of a cold solution of hydrate of potassium or ammonium, and of a cold solution of a cupric salt. If the precipitant be deficient in quantity, a green basic salt is precipitated. The hydrate is a flocculent blue precipitate.

Its formula is $CuHO$.

This precipitate is somewhat soluble in excess of hydrate of potassium, from which solution it is completely reprecipitated by ebullition, in the form of the black or cupric oxide (Cu_2O); it is also readily soluble in hydrate of ammonium, forming a deep blue solution. The state in which the copper exists in this ammoniacal solution is very remarkable. The metal is believed to have replaced part of the hydrogen in the compound molecule NH_4, and to constitute a new compound basic radical, known as cuprammonium (NH_3Cu). Other similar compound radicals have been obtained, in the form of salts; and in them two or more equivalents of the hydrogen in ammonium have been replaced by copper. When the cupric *sulphate* is treated with hydrate of ammonium, it is the *sulphate* of cuprammonium* that is formed; and so with other salts.

The Oxide is produced by the action of a boiling solution of hydrate of potassium on solutions of cupric salts, or by boiling the hydrate with hydrate of potassium. It is a granular-black precipitate.

Its formula is Cu_2O.

It is readily soluble in hydrochloric, sulphuric, or nitric acid.

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* The formula of this salt is $\left(N\left[N\begin{array}{c}H_3\\ \left(\begin{array}{c}H_3\\ Cu\end{array}\right)\end{array}\right]\right)_2$, $SO_4 + aq$; for it is to be observed that these compound ammoniums are rendered still more complex by the cuprammonium itself replacing 1 eq. of hydrogen in ordinary ammonium (NH_4).

The Sulphide is produced by the action of hydrosulphuric acid on solutions of cupric salts, whether alkaline, neutral, or acid. It is precipitated in black flakes, which, when exposed to the air, absorb oxygen, passing into cupric sulphate.

Its formula is Cu_2S.

It is insoluble in the hydrates of potassium, sodium, or ammonium, and in the sulphides of potassium and sodium, but dissolves slightly in sulphide of ammonium; it is soluble in cyanide of potassium. Concentrated boiling hydrochloric acid dissolves it slowly, with evolution of hydrosulphuric acid,—while nitric acid decomposes it more readily, with separation of sulphur, and formation of sulphuric acid and of cupric nitrate.

The Sulphate is soluble.

The Carbonate is produced by the action of carbonate of potassium on solutions of cupric salts; it is a greenish blue precipitate, which, by boiling, is converted into cupric oxide.

Its formula is that of a mixed carbonate and hydrate, Cu_2CO_3, $CuHO$.

It is slightly soluble in excess of its precipitant, forming a bluish solution; in excess of carbonate of ammonium it dissolves perfectly, forming a deep blue solution (containing a salt of cuprammonium): the carbonate dissolves also in other ammonium salts; it is soluble in cyanide of potassium, is insoluble in water, but dissolves readily in acids, with decomposition.

The Oxalate is produced by the action of oxalic acid, or of the alkaline oxalates, not added in excess (to avoid the formation of soluble double salts), on cupric salts. It is a pale blue precipitate.

Its formula is $Cu_2C_2O_4+aq$ when dried at 100° C.

It dissolves in excess of alkaline oxalates, in hydrate or carbonate of ammonium, but is insoluble, or but slightly soluble, in other ammonium salts. It is insoluble in water or in oxalic acid, but soluble in hydrochloric acid.

The Ferrocyanide is produced by the action of ferrocyanide of potassium: it is a flocculent precipitate of a fine brownish red colour.

Its formula is Cu_2Cfy.

It is insoluble in ammonium salts, also in water and in most acids; but it is soluble in concentrated sulphuric acid, and reprecipitable from the solution by water.

The Ferricyanide is produced by the action of ferricyanide of potassium on cupric salts: it is a greenish-yellow precipitate.

Its formula is believed to be Cu_3Cfdy.

It dissolves in hydrate and carbonate of ammonium; but it is insoluble, or nearly so, in other ammonium salts.

The Phosphate is produced by the action of phosphate of sodium: it is a greenish blue precipitate.

Its formula is probably $Cu_3 PO_4$.

It dissolves but slightly in ammonium salts, is insoluble in water, but dissolves in almost all acids.

The other special tests of the present and three preceding groups are without well-defined action on solutions of cupric salts.

The means chiefly employed for the recognition of cupric salts are the precipitation of the black oxide, the sulphide, and the ferrocyanide. The blue colour of the ammoniacal cupric compounds is also very characteristic of these salts of copper.

SALTS OF SILVER.

The salts of silver bear some resemblance to those of copper,—the principal points of resemblance being the formation of two series of salts, and the existence of similar relations in the case of both metals to the compound basic radical ammonium. The di- or sub-salts of silver, or argentous salts, are not by any means so numerous or well-defined as the cuprous salts; and indeed the argentous oxide (Ag_4O) is almost the only well-known member of the series,—a series which is quite unimportant in an analytical point of view, and which we do little more than mention. The argentic salts will be described at length; and of them the argentic oxide (Ag_2O) and the argentic chloride ($AgCl$) may be considered typical. Silver salts are poisonous, but are occasionally employed in medicine: their taste is generally nauseous and metallic; some, however, are excessively sweet.

Salts of silver, when heated before the blowpipe on charcoal, are reduced very readily to the metallic state, and still more readily in the presence of carbonate of sodium; they furnish no incrustation upon the charcoal, nor do they impart any colour to the flame. When heated with borax, an opalescent or milk-white bead is produced: in the reducing flame the glass becomes grey from the reduced silver disseminated through it; the borax afterwards becomes clear, the metal running into a globule, which then alloys with the platinum wire. With this and many subsequent metals this experiment is not usually tried, as it furnishes no decisive result except the destruction of the platinum wire; if the experiment be performed, it may be done on charcoal.

Iron, zinc, cadmium, lead, and tin precipitate metallic silver from most soluble salts of that metal, and very generally, when placed in contact with insoluble silver salts, equally effect their reduction, the silver appearing as a grey, brown, or black mass, usually spongy (see p. 60). Copper reduces silver in the form of minute spangles, while mercury forms an alloy with it. Other metals, as bismuth, antimony, and arsenic, also reduce silver, but less effectively. Many salts also, the metal of which has a tendency to pass into another and higher stage of combination, exert a similar action: ferrous sulphate and stannous chloride are examples of these salts:—

$$3(AgNO_3) + \underset{\textit{Ferrous}\text{ sulphate.}}{6(Fe_2\,SO_4)} = 3Ag + \underset{\textit{Ferric}\text{ nitrate.}}{(Fe_2)_2\,(NO_3)_3} + \underset{\textit{Ferric}\text{ sulphate.}}{2([Fe_2]_2\,[SO_4]_3)};$$

$$AgNO_3 + \underset{\textit{Stannous}\text{ chl.}}{2SnCl} = Ag + SnNO_3 + \underset{\textit{Stannic}\text{ chl.}}{SnCl_2}$$

ARGENTOUS SALTS.

DI- OR SUB-SALTS OF SILVER.

Of these the chloride and the oxide are almost the only examples known. The argentous chloride ($Ag_2\,Cl$) is said to be produced by dissolving the corresponding oxide ($Ag_4\,O$) in hydrochloric acid; and by some it is asserted to be the grey violet or blue compound produced by exposing argentic chloride

(AgCl) to the action of light while in the moist state: the latter is said to undergo the following decomposition:—

$$2AgCl = Ag_2Cl + Cl.$$

ARGENTIC SALTS, OR SILVER SALTS.

Solution for the reactions:—nitrate of silver ($AgNO_3$) in water.

The chief insoluble salts which serve for the recognition of the compounds of silver are these,—the chloride, the chromate, the cyanide, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Chloride is produced by the action of hydrochloric acid or any soluble chloride on solutions of argentic salts; it is a heavy white curdy precipitate, becoming violet and finally black by exposure to light. It fuses without decomposition, to a yellowish red liquid.

Its formula is $AgCl$.

It is soluble in cyanide of potassium, in the chlorides of the alkaline and some other metals, also in the alkaline hyposulphites; it dissolves easily in hydrate of ammonium, which, if concentrated, deposits crystalline films of a compound containing chloride of silver and ammonia. It is somewhat soluble in concentrated hydrochloric acid, but absolutely insoluble in water. In a solution of mercuric nitrate ($HgNO_3$) it dissolves.

THE IODIDE is produced by the action of hydriodic acid or a soluble iodide on solutions of argentic salts. It is a yellow curdy precipitate, which becomes of a deeper colour when heated, and may be fused at a higher temperature.

Its formula is AgI.

It is dissolved to a considerable extent by a concentrated solution of the chlorides or iodides of potassium or sodium, but is insoluble in water or acids. In hydrate of ammonium it is less readily soluble than the chloride or bromide of silver.

THE CYANIDE is produced by the action of cyanide of potassium on solutions of argentic salts: it is a curdy white precipitate.

Its formula is AgCy.

It is soluble in excess of its precipitant, and in the hydrate and other salts of ammonium; it dissolves sparingly in boiling dilute nitric acid, and is decomposed by the concentrated acids, especially on boiling.

The Chromate is produced by the action of chromate of potassium on argentic salts: it is a granular precipitate, of a fine dark crimson.

Its formula is $AgCrO_2$.

It is soluble in excess of its precipitant, also in hydrate of ammonium; it is insoluble in water, but is dissolved by most acids.

The Hydrate or Oxide is produced by the action of the hydrates of the alkaline metals or of barium: it is a precipitate of an olive-green colour, changing rapidly to a brown.

The precipitate at first produced is believed to be the hydrate, which rapidly decomposes into water and the oxide, thus—

$$2(AgHO) = H_2O + Ag_2O.$$

It is readily soluble in cyanide of potassium and in hydrate of ammonium, and sufficiently soluble in water to impart to it a perceptible metallic taste and an alkaline reaction; it dissolves readily in most acids. Care should be taken, after experimenting, to precipitate the ammoniacal solution of argentic oxide which has been obtained, with hydrochloric acid (with formation of argentic chloride), since *fulminating silver* is occasionally deposited from it, although it generally decomposes with separation of metallic silver. The three formulæ, NAg_3, $NAgH_2$, and $NAgH_3$, have been assigned by different chemists to the body termed fulminating silver.

The Sulphide is produced by the action of hydrosulphuric acid on alkaline, neutral, or acid solutions of silver salts: it is a black precipitate.

Its formula is Ag_2S.

This salt is insoluble in cyanide of potassium and in hydrate of ammonium, which are the solvents for most silver salts; it is also insoluble in alkaline sulphides, in water, and in dilute acids: it dissolves in concentrated sulphuric and nitric acids.

The Sulphate is produced by the action of the alkaline and other soluble sulphates, and of sulphuric acid, upon strong solutions of silver salts: it is a white crystalline precipitate.

Its formula is Ag_2SO_4.

This is by no means an insoluble salt, 1 part dissolving in 87 parts of water; it is more soluble in nitric acid, and still more so in concentrated sulphuric acid, from which solution it is partly precipitated by the addition of water.

The Carbonate is produced by the action of the neutral or acid carbonate of potassium: it is a white precipitate, which rapidly assumes a yellowish buff colour.

Its formula is Ag_2CO_3.

This salt readily dissolves in cyanide of potassium, and is also soluble in the hydrate and carbonate of ammonium. It is insoluble in water, but easily soluble in most acids.

The Oxalate is produced by the action of oxalic acid on solutions of argentic salts: it is a white precipitate.

Its formula is $Ag_2C_2O_4$; but it contains a little water (2 per cent.) mechanically retained.

It dissolves in the hydrate and carbonate of ammonium, and in warm solutions of other ammonium salts; it is scarcely soluble in water, but dissolves in nitric acid.

The Ferrocyanide is produced by the action of ferrocyanide of potassium: it is a white precipitate.

Its formula is Ag_2Cfy.

It dissolves in cyanide of potassium and in hydrate of ammonium, but is insoluble in other ammonium salts; it dissolves partly with decomposition in concentrated sulphuric or nitric acids, but is not acted on by other acids, not even by hydrochloric.

The Ferricyanide is produced by the action of ferricyanide of potassium on argentic salts, or by the action of nitric acid on the ferrocyanide: it is an orange-yellow precipitate.

Its formula is Ag_3Cfdy.

It dissolves in a large proportion of cyanide of potassium, and easily in hydrate or in a hot solution of carbonate of ammonium, but not in other ammonium salts.

The Phosphate is produced by the action of phosphate of sodium (Na_2HPO_4) on solutions of argentic salts: it is a brilliant lemon-yellow precipitate.

Its formula is Ag_3PO_4.

It is insoluble in water, but dissolves in cyanide of potassium, also in hydrate of ammonium, but less easily in other ammonium salts; in most acids it dissolves readily.

The other special tests of the present and three preceding subdivisions exert no characteristic action upon solutions of argentic salts.

The reactions usually employed for the detection of argentic salts are these,—the formation of the insoluble chloride, chromate, oxide, and phosphate, and the general solubility of these salts in hydrate of ammonium.

SALTS OF MERCURY.

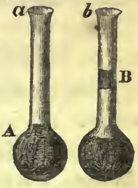
Salts of this metal possess some features in common with those of silver, but at the same time are characterized by such peculiarities of their own as to render their detection very easy. Mercury, like copper and silver, enters into a compound ammonium; and it also forms, like those metals, two series of salts, the mercurous and mercuric: the salts of both these series are generally colourless when neutral, unless the acid-radical is coloured, and of a yellow tint when basic. The mercurous salts are both more numerous and more important than the corresponding compounds of the two preceding metals. The formula of mercurous oxide is Hg_4O, and of mercurous chloride Hg_2Cl, while mercuric oxide is represented by the expression Hg_2O, and mercuric chloride by $HgCl$.

The metal itself being volatile, all its salts are necessarily either volatile or decomposable by heat; and consequently the ordinary blowpipe examination, by which metallic compounds are often recognized, fails in this instance. This volatility furnishes, however, the best method for the detection of mercury when the following plan is adopted. The mercury salt is mixed with about three or four times its bulk of dry carbonate of sodium (Na_2CO_3), and the mixture introduced into a narrow tube (*a*) made of hard glass free from lead, and having a small stout bulb at its lower end; the mixture should occupy about the space shown at A in the figure. The bulb and its contents are then heated strongly before the blowpipe, when the following decompositions take place:—

$$2(HgCl)+Na_2CO_3=2(NaCl)+Hg_2CO_3, \text{ and}$$
$$Hg_2CO_3=2Hg+CO_2+O.$$

The mercury condenses about B in figure *b*, as distinct metallic globules if an appreciable quantity of mercury were present, or, if the quantity were very minute, as a grey sublimate, the particles of which may be easily collected into obvious globules by cutting the tube off below B, and inserting and turning round, in the tube cut off, a splinter of wood.

Fig. 9.



At B is a metallic mirror on the interior of the tube. At A is a dirty white powder.

Mercury compounds may also be recognized when in solution by adding to the liquid a few drops of hydrochloric acid to originate the action; and then by immersing in the mixture a few fragments of copper foil, and boiling, the mercury is deposited upon the copper, thus—

$$HgCl+Cu=CuCl+Hg.$$

In the foregoing experiment the presence of nitric acid should be avoided, as it would dissolve all the mercury which would otherwise be liberated. The strips of copper used, when quite dry, may be placed in a narrow tube and strongly heated, when the mercury will volatilize and condense in the upper part of the tube in the form of the usual grey sublimate.

Mercurous salts in solution are not acted on by iron, but are decomposed with separation of metallic mercury by zinc, cadmium, copper, lead, and bismuth, though at the commencement of the action a white or yellow precipitate is formed, consisting of a basic salt. Tin, antimony, and arsenic act less perfectly, while ferrous sulphate and stannous chloride act upon mercurous salts as they do upon those of silver. Upon solutions of mercuric salts the metals above mentioned act much in the same manner, but more slowly, usually at first reducing the mercuric to the mercurous salt.

The salts of mercury exert a very deleterious action upon the animal œconomy; they are employed in medicine.

MERCUROUS SALTS, OR DI- OR SUB-SALTS OF MERCURY.

Solution for the reactions:—mercurous nitrate (Hg_2NO_3) in water.

The principal insoluble salts of this series are these,—the chloride, the chromate, the oxide, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Chloride is produced by the action of hydrochloric acid or soluble chlorides on solutions of mercurous salts. It is a dense white precipitate.

Its formula is Hg_2Cl.

It is insoluble in the hydrates of potassium and ammonium, but is decomposed by them with formation of oxide; it is very triflingly soluble in the chlorides of the alkaline metals. It does not perceptibly dissolve in cold hydrochloric or nitric acid; but it is dissolved by these acids after long boiling. It is easily soluble in nitrohydrochloric acid or in chlorine water, with formation of mercuric chloride.

THE IODIDE is produced by the action of hydriodic acid or iodide of potassium upon solutions of mercurous salts, or by triturating an insoluble mercurous salt (Hg_2Cl for instance) with those reagents. It is a dull-green powder.

Its formula is Hg_2I.

With excess of its precipitant it decomposes into mercuric iodide (HgI) and mercury; many other bodies which exert no solvent action act similarly. Boiling concentrated solutions of the chlorides of sodium and ammonium dissolve mercurous iodide to a slight extent. It is almost insoluble in water and acids.

THE CYANIDE does not exist.

The Chromate is produced by the action of chromate of potassium on mercurous salts; it is a precipitate of a bright red colour, turning black by exposure to light.

Its composition is that of a basic salt; if boiled in nitric acid it is converted into the neutral chromate Hg_2CrO_2.

It dissolves sparingly in ammonium salts; it is slightly soluble in cold water, but more so in boiling water; it also perceptibly dissolves in nitric acid.

The Oxide is produced by the action of hydrate of potassium* on solutions of mercurous salts: it is a precipitate of a brownish-black colour.

Its formula is Hg_4O, which, like other oxides of the same type, is perhaps more intelligible when written $(Hg_2)_2O$.

This salt is decomposed either by ebullition with its precipitant, or with solutions of many other salts, or even with water only, into mercuric oxide (Hg_2O) and mercury.

The Sulphide is produced by the action of hydrosulphuric acid upon alkaline, neutral and acid solutions of mercurous salts; it is a black precipitate.

Its formula is Hg_4S, which may be written $(Hg_2)_2S$.

When boiled with water or with solutions of various salts, it exhibits a similar tendency to that shown by the oxide, in dividing into mercuric sulphide (Hg_2S) and metallic mercury. It is insoluble in sulphide of ammonium, but decomposed by sulphide of potassium into mercuric sulphide, which dissolves, and metallic mercury, which separates; it also behaves in a similar matter with hydrate of potassium. In dilute acids and in concentrated nitric acid it is insoluble; but it is dissolved by nitrohydrochloric acid.

THE SULPHATE is produced by the action of sulphuric acid or sulphate of sodium on mercurous salts (such as the nitrate): it is a heavy white crystalline precipitate.

Its formula is $(Hg_2)_2SO_4$.

---

* When hydrate of ammonium acts upon solutions of mercurous salts, a black compound is formed similar in constitution to the compounds containing copper or silver formed in the same way. In the case of the mercurous salts, however, the compound ammoniums are generally insoluble; if mercuric nitrate be employed, the following reaction takes place:—

$$3(Hg_2NO_3)+3(NH_4HO)=2(NH_4NO_3)+3H_2O+NH(Hg_2)_3, NO_3.$$

It dissolves in dilute nitric acid, from which solution it is precipitated by dilute sulphuric acid: it is very sparingly soluble in water; in hot concentrated sulphuric acid it dissolves, but crystallizes on cooling.

The Carbonate is produced by the action of carbonate of potassium; it is a yellow precipitate.

It formula is $(Hg_2)_2CO_3$.

This salt decomposes spontaneously into mercurous oxide ($[Hg_2]_2O$) and the gas CO_2; it is slightly soluble in excess of its precipitant and in many acids.

Carbonate of ammonium produces in mercurous solutions a grey or black precipitate, which probably has a similar constitution to that of the hydrate of ammonium products.

The Oxalate is produced by the action of oxalic acid or oxalate of potassium: it is a white precipitate.

Its composition is $(Hg_2)_2C_2O_4 + aq$.

It is scarcely soluble either in hot or cold water; it is insoluble in oxalic, and in dilute nitric or sulphuric acid, but dissolves slightly in the two latter acids when they are concentrated and warm.

The Ferrocyanide is produced by the action of ferrocyanide of potassium: it is a dense white precipitate.

Its formula is not known.

The Ferricyanide is produced by the action of ferricyanide of potassium: it is a reddish-brown precipitate.

Its composition is not known.

The Phosphate is produced by the action of phosphate of sodium: it is a white precipitate.

Its formula is not well ascertained; but it seems to be a mixture of the mercurous and mercuric salts.

It is somewhat soluble in chloride of ammonium solution: it is insoluble in water and in phosphoric and tartaric acids.

The other special tests of the present and three preceding groups do not give characteristic reactions with mercurous salts in solution.

The tests usually employed for the detection of mercurous salts are these,—the precipitation of the chloride, the chromate, the oxide, and the sulphide, and the reactions mentioned in the preliminary remarks—although these are applicable to the detection of mercury in any form.

MERCURIC SALTS.

Solution for the reactions:—mercuric chloride ($HgCl$) in water.

The principal insoluble salts by which mercury in this form is recognized are these,—the iodide, the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

THE CHLORIDE is soluble.

The Iodide is produced by the action of hydriodic acid or iodide of potassium upon solutions of mercuric salts. It is a magnificent scarlet precipitate, known as *geranium-colour*: a modification of this salt exists, which possesses a fine yellow tint.

Its formula is HgI.

It is soluble in excess of iodide of potassium, and in mercuric salts, forming colourless solutions; it is very soluble in most ammonium salts, and in chloride of potassium, also in many acids. 1 part requires 150 parts of cold water for solution.

THE CYANIDE is soluble.

The Chromate is obtained by the action of chromate of potassium on solutions of mercuric salts: it is a fine yellow precipitate.

Its formula is that of a basic salt $Hg_2O, HgCrO_2$.

It is soluble in excess of many mercuric salts, and in most acids, even in acetic acid.

The Hydrate is produced by the action of hydrate of potassium* on solutions of mercuric salts: it is a yellow precipitate.

---

* Hydrate of ammonium exerts an action on mercuric salts analogous to that mentioned in the case of mercurous salts: it yields precipitates, gene-

Its formula is $HgHO, H_2O$, although, by many chemists, this precipitate is said to be the oxide (Hg_2O), into which compound the hydrate rapidly passes on drying, or by being kept.

The hydrate dissolves very sparingly in water, conferring upon it a perceptible metallic taste, and an alkaline reaction which may be detected by delicate test-papers (prepared with an alcoholic tincture of violets); it dissolves in those acids which do not form insoluble mercuric salts. Like the iodide, the mercuric oxide exists in two modifications, a yellow and a red, which may be distinguished not only by their physical properties, but by their behaviour with reagents: oxalic acid, for instance, combines with the yellow modification in the cold, while with the red modification it produces no action.

The Sulphide is produced by the action of hydrosulphuric acid on acid or neutral solutions of mercuric salts: the addition of a small quantity of this reagent produces a double salt, which is a white precipitate of the formula $HgNO_3, Hg_2S$, *or* $HgCl, Hg_2S$, *or* $Hg_2SO_4, 2Hg_2S$, according to the acid-radical present; by the addition of more of the precipitant, these salts become yellow, orange, brown, and finally black, from their conversion entirely into the black mercuric sulphide, which, indeed, like the iodide and the oxide, exists also in a red mofication.

Its formula is Hg_2S.

It is insoluble in sulphide of ammonium, but dissolves completely in sulphide of potassium. It is insoluble in hydrochloric or nitric acid, even at the boiling temperature, but dissolves readily in nitro-hydrochloric acid, with decomposition.

The Sulphate, if formed by the double decomposition of neutral aqueous solutions of (*e.g.*) mercuric nitrate and sulphate of sodium, is immediately decomposed by the water present, espe-

rally white, consisting of salts of compound ammoniums, the acid-radicals of which are those of the mercuric salts; thus, with mercuric chloride,—

$$2HgCl+2(NH_4HO) = N\genfrac{}{}{0pt}{}{H_2}{Hg_2}Cl+NH_4Cl+2H_2O.$$

This compound was formerly much employed in medicine, and was known by the name of "white precipitate."

cially on boiling the mixture, with formation of a lemon-yellow precipitate, formerly called *turbith mineral,* the composition of which is that of a basic sulphate ($Hg_2SO_4, 2[Hg_2O]$), which dissolves in 2000 parts of cold, or 600 of boiling water, but is very soluble in acids.

THE CARBONATE is produced by the action of carbonate of potassium, or the carbonates of the alkaline earths, on solutions of mercuric salts: it is a brownish-red precipitate.

Its formula is $Hg_2CO_3, 3(Hg_2O)$.

It dissolves sparingly in solution of carbonate of potassium, and is soluble in chloride of ammonium; it is also somewhat soluble in a solution of carbonic acid.

THE OXALATE is produced by the action of oxalic acid or oxalate of potassium upon mercuric salts: it is a white precipitate.

Its formula is $Hg_2C_2O_4 + aq$.

It is soluble in chloride of ammonium, and in some other ammonium salts, insoluble in water, alcohol, or ether; slightly soluble in hot dilute nitric and sulphuric acids, but more soluble in those acids when concentrated.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium: it is a white precipitate, which becomes blue on standing.

The composition of this precipitate is not accurately known; by some chemists it is stated to be simply cyanide of iron ($FeCy$).

THE FERRICYANIDE is produced by the action of ferricyanide of potassium on certain mercuric salts, as the nitrate. It is a yellow precipitate.

Its composition is not known.

THE PHOSPHATE is produced by the action of phosphate of sodium on certain mercuric salts, as the nitrate. It is a white precipitate.

The formula of the salt dried at 100° C. is $Hg_4P_2O_7$.

It is soluble in many ammonium salts, insoluble in water and alcohol, but dissolves in phosphoric and in hydrochloric acid.

The other special reagents of the present and three preceding groups exert no definite or characteristic action on solutions of mercuric salts.

The chief reactions made use of for the recognition of mercuric salts are these,—the formation of the scarlet iodide, of the chromate, the oxide, and the sulphide,—while the mercury they contain is readily detected by the same processes as those employed in the case of the mercurous salts.

SALTS OF LEAD.

The metal lead forms a link between those members of the present subdivision which have been already considered, and those which are to follow. It forms several combinations with oxygen, as the suboxide (Pb_4O), the (common) oxide (Pb_2O), and the peroxide (Pb_2O_2), together with some intermediate oxides. The peroxide partakes somewhat of acid characters. The suboxide of lead, like the suboxides of copper and mercury, decomposes under the influence of acids, forming salts of a higher series. There are no compounds of other acid-radicals with lead corresponding to the peroxide (Pb_2O_2); and the large class of lead salts may all be referred to the series of which Pb_2O is the oxide and $PbCl$ the chloride. The salts of lead are poisonous; many of them have a sweet taste.

In general, salts of lead, when heated before the blowpipe on charcoal, are converted into the oxide, which is of an orange-yellow colour when hot, and yellow when cold; usually, too, a portion of the salt is reduced to the metallic state, and this takes place immediately, and with the greatest ease, if the substance be heated in the reducing flame or with carbonate of sodium. In all cases an incrustation of the oxide (Pb_2O) is formed upon the charcoal at a little distance from the salt, since metallic lead volatilizes at a red heat, and the oxide at a white heat. Lead salts impart no colour to the flame, nor do they give any characteristic reaction with nitrate of cobalt. When fused with borax in the oxidizing flame, a clear yellowish glass is obtained, which remains transparent when cold, unless great excess of lead salt has been introduced; in the reducing flame metallic lead separates: this experiment should be performed on charcoal, to avoid the destruction of the platinum wire.

Salts of lead are decomposed by iron, the lead being deposited in an arborescent form; the same effect is produced more rapidly by zinc, cadmium, and tin.

PLUMBOUS SALTS, OR DI- OR SUB-SALTS OF LEAD.

The only salts of this series which seem to exist are the OXIDE (Pb_4O), and perhaps the SULPHIDE (Pb_4S): the former is produced by heating plumbic oxalate out of contact with the air, and the latter by igniting plumbic sulphate in a charcoal crucible. Dilute acids resolve plumbous oxide into plumbic salts and metallic lead.

PLUMBIC SALTS, OR LEAD SALTS.

Solution for the reactions:—plumbic nitrate ($PbNO_3$) in water.

The principal insoluble salts of this series are the chloride, the iodide, the chromate, the sulphide, the carbonate, the oxalate, the sulphate, the ferrocyanide, and the phosphate.

The Chloride is produced by the action of hydrochloric acid, or soluble chlorides, on solutions of lead salts: it is a white precipitate, which crystallizes in the form of six-sided prisms.

Its formula is $PbCl$.

It is very soluble in the hydrate of potassium, and somewhat so in solutions of alkaline hyposulphites and of acetate of sodium: it dissolves in 135 parts of water at 12°·5 C.; but in water containing certain salts, as chloride of calcium, it is less soluble: it is much more soluble in boiling than in cold water. It is very sparingly soluble in alcohol; of hydrochloric acid, cold and dilute, 1 part of plumbic chloride requires 1636 parts for solution, while in dilute nitric acid it is but very slightly soluble. Concentrated hydrochloric acid dissolves this salt abundantly.

Several compounds of chloride with oxide of lead are known; they are prepared by precipitating hot solution of chloride of lead with the hydrates of ammonium or calcium. They vary much in composition: the formulæ $2PbCl, Pb_2O$; $2PbCl, 7Pb_2O$; and $PbCl, Pb_2O$ have been assigned to three of these compounds.

When a hot solution of chloride of lead is acted on by lime-water (CaHO) a mixed chloride and hydrate is produced, having the formula PbCl, PbHO.

The Iodide is produced by the action of hydriodic acid, or a soluble iodide, on solutions of lead salts: it is a golden-coloured crystalline precipitate.

Its formula is PbI.

It is soluble in chloride of ammonium solution, especially on boiling; and it also dissolves in concentrated solutions of most soluble chlorides or iodides; it is insoluble, however, in hydrate of ammonium and other ammonium salts generally. 1 part dissolves in 1235 parts of cold, or 194 parts of boiling water. It is slightly soluble in ether, and dissolves somewhat more easily in nitric acid.

The Chromate is produced by the action of chromate of potassium on solutions of lead salts: it is a pale yellow, lemon-yellow, or orange precipitate.

Its formula is $PbCrO_2$.

This salt is slightly soluble in excess of its precipitant, and dissolves readily in hydrate of potassium; in chloride of ammonium solution it is insoluble; in water also it is insoluble, but is decomposed by hydrochloric and sulphuric acids; in dilute nitric acid it dissolves slowly without decomposition.

THE CYANIDE is produced by the action of hydrocyanic acid, or soluble cyanides, upon many lead salts: it is a white precipitate.

Its formula is PbCy.

It is soluble in hot solutions of chloride of ammonium and of some other ammonium salts; it is insoluble, or nearly so, in water, but is decomposed by nitric or sulphuric acid, with evolution of hydrocyanic acid.

The Hydrate or Oxide is produced by the action of the hydrates of potassium or ammonium on solutions of lead salts: it is a white precipitate, which, under the microscope, appears crystalline, the forms of the crystals varying with the method of preparation.

Its composition is $2(PbHO), Pb_2O$; but it is generally a basic salt containing a portion of the acid-radical of the original salt.

This salt is soluble in excess of hydrate of potassium, especially on heating, but not in excess of hydrate of ammonium; it is slightly soluble in water, but the presence of saline compounds diminishes its solubility to a great extent; it dissolves easily in those acids which do not form insoluble lead salts. The hydrate of lead is converted into the oxide (Pb_2O) by exposure to a gentle heat.

The Sulphide is produced by the action of hydrosulphuric acid on acid, neutral, and alkaline solutions of lead salts. It is a black precipitate, although, under certain circumstances, and especially by the action of pentasulphide of sodium ($Na_2 S_5$), a bright red precipitate is obtained, which may, however, be a higher sulphide than the ordinary black precipitate.

The composition of the black sulphide is $Pb_2 S$.

It is insoluble in alkaline sulphides, and in hydrate or cyanide of potassium; in cold dilute acids it is insoluble; but in strong boiling nitric acid it dissolves, with separation of sulphur, and in the fuming concentrated nitric acid it is converted into plumbic sulphate ($Pb_2 SO_4$). It dissolves in boiling concentrated hydrochloric acid.

The Sulphate is produced by the action of sulphuric acid, or soluble sulphates, on solutions of lead salts: it is a white, crystalline, and heavy precipitate.

Its formula is $Pb_2 SO_4$.

It dissolves in hot solutions of the chloride and some other salts of ammonium; it is also soluble in a hot solution of hydrate of potassium. 1 part of this salt dissolves in 22,816 parts of water at 11° C., and in 36,504 parts of dilute sulphuric acid; in dilute acids it is but slightly soluble, dissolving, however, in larger proportion in concentrated acids, especially in sulphuric.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium on lead salts: it is a dense, white, crystalline precipitate.

Its formula is Pb_2CO_3 when precipitated in the cold; if the liquid be boiled, the salt is a mixed hydrate and carbonate.

It is very soluble in hydrate of potassium, and somewhat soluble in solutions of ammonium salts; 1 part requires 50,651 parts of water at 15° C. for its solution. It dissolves with decomposition in those acids which form soluble lead salts.

The Oxalate is produced by the action of oxalic acid or alkaline oxalates on solutions of lead salts: it is a white crystalline precipitate.

The formula of the salt dried at 140° C. is $Pb_2C_2O_4$.

It dissolves in hot solutions of chloride of ammonium and of many other ammonium salts, the hydrate and carbonate excepted; it is insoluble in water, very sparingly soluble in oxalic acid solution, dissolving more freely in nitric acid.

The Ferrocyanide is produced by the action of ferrocyanide of potassium on solutions of lead salts: it is a white precipitate.

Its composition is $Pb_2Cfy + 1\frac{1}{2}aq$.

It is partly soluble in hot hydrate of ammonium, and perfectly in hot chloride of ammonium; in water it is insoluble; by sulphuric acid it is decomposed and slowly dissolved.

The Ferricyanide is comparatively soluble: it occurs in transparent brownish-red crystals.

The Phosphate is produced by the action of phosphate of sodium: it is a white precipitate.

This precipitate is a mixture of the two phosphates Pb_3PO_4 and Pb_2HPO_4.

It dissolves in chloride of ammonium solution, but is reprecipitated by the addition of hydrate of ammonium; it dissolves in hydrate of potassium; it is insoluble in water, but soluble in nitric acid; it is decomposed by hydrochloric or sulphuric acid.

The other special reagents of the present and three preceding groups are without characteristic action on solutions of lead salts.

The tests usually employed for the detection and recognition of lead salts are these,—the formation of the chloride, iodide, chromate, sulphide, and carbonate, and the reactions of lead compounds before the blowpipe.

SALTS OF BISMUTH.

The salts of bismuth bear certain resemblances to those of lead, although, in many particulars, they differ much from them. Bismuth forms several combinations with oxygen:—the suboxide, the composition of which is not accurately known; the oxide which is usually met with, Bi_2O_3; an intermediate oxide; and, lastly, the oxide Bi_2O_5, which is frequently called anhydrous bismuthic acid. The formula of the bismuthic chloride ($BiCl_3$), and that of the corresponding oxide (Bi_2O_3) may be taken as typical of the salts of bismuth, which may be termed proto-salts, and in reality correspond to the general formulæ which we have found to represent the larger number of the series of salts already treated of; for the metal bismuth is here "triatomic," that is, it corresponds to 3 equivalents of a monatomic (or monobasic) element, such as hydrogen (or chlorine), and to 1 equivalent of a tribasic radical, such as the phosphoric acid-radical (PO_4). In combining with biatomic or bibasic bodies, 2 equivalents are equal or correspond to 6 equivalents of hydrogen, and therefore to 3 equivalents of the biatomic molecules,—oxygen or the sulphuric radical (SO_4). Bismuthic chloride then corresponds to 3 equivalents of hydrochloric acid, and the oxide to 3 equivalents of water,—a fact which is perhaps more clearly shown by the following formulæ:—

$\begin{matrix}Cl\\BiCl\\Cl\end{matrix}$	$\begin{matrix}HCl\\HCl\\HCl\end{matrix}$	$\begin{matrix} & O \\ Bi & \\ & O \\ Bi & \\ & O\end{matrix}$	$\begin{matrix}H_2O\\H_2O\\H_2O\end{matrix}$	$BiPO_4$	$\begin{matrix}H\\HPO_4\\H\end{matrix}$
1 eq. of bismuthic chloride.	3 eqs. of hydrochloric acid.	1 eq. of bismuthic oxide.	3 eqs. of water.	1 eq. of bismuthic phosphate.	1 eq. of phosphoric acid.

We have been thus particular in explaining the constitution of the salts of bismuth previously to giving the full details concerning those of them with which we are at present concerned, in order that the student may see at a glance the relations of their formulæ to those of the corresponding salts of other metals.

When heated before the blowpipe on charcoal and in the oxidizing flame, bismuth salts generally fuse to a brown mass, which, upon cooling, becomes pale-yellow; this is the oxide (Bi_2O_3); in the reducing flame, globules of metallic bismuth are speedily produced, more easily in the presence of carbonate of sodium: in all cases the surrounding charcoal becomes covered with an incrustation of the oxide. This incrustation is more conspicuous when carbonate of sodium has been mixed with the bismuth salt under examination, on account of the volatility of metallic bismuth being greater than that of the oxide. Bismuth salts impart no colour to the blowpipe flame, nor do they yield any characteristic reaction with nitrate of cobalt. When fused with borax, a clear glass is obtained in the oxidizing flame, which is yellow whilst hot, and colourless when cold, the colour deepening as the amount of bismuth is increased; in the reducing flame (the action of which should be tried on charcoal) the bismuth is reduced to the metallic state, and the bead remains clear and colourless.

Bismuth salts exhibit a peculiarity which has already been seen to exist with one salt of lead (the chloride [$PbCl$]), which forms an oxychloride under the influence of hydrate of ammonium. Bismuth salts in general, by the action of water, yield salts of a similar character and constitution, to which the name *oxy-salts* (oxychloride, oxynitrate, &c.) or *basic salts* (basic chloride, basic nitrate, &c.) has been applied: these compounds are very insoluble in water, but soluble in excess of acid. Thus water precipitates from neutral bismuth salts the corresponding basic or oxy-salts,—whilst in the solution an acid salt remains, or sometimes the original salt in small quantities together with a portion of free acid. Disregarding those small portions of the original salts which remain dissolved and precluded from decomposition by the acid produced in the reactions, the following equations represent the action of water upon the chloride and the sulphate of bismuth respectively:—

$$3BiCl_3+3H_2O=\underset{\text{oxychloride of Bism.}}{BiCl_3, Bi_2O_3}+6HCl;$$

$$2(Bi_2[SO_4]_3)+3H_2O=\underset{\text{oxysulphate of Bism.}}{Bi_2(SO_4)_3, Bi_2O_3}+3H_2SO_4;$$

and even the nitrate (nitrates are generally the most soluble of all salts) is decomposed in a similar manner, but a *mixed hydrate and nitrate* is in this case formed—

$$3(Bi[NO_3]_3)+6H_2O=\underset{\substack{\text{mixed hydrate and}\\ \text{nitrate of Bism.}}}{Bi(NO_3)_3, 2(BiH_3O_3)}+6HNO_3.$$

These precipitates, insoluble in water, are readily dissolved by acids.

The metal bismuth is precipitated from its salts quickly and completely by iron, zinc, cadmium, and tin, and appears as a dark grey powder: this reduction is also effected by lead and copper; but the action is slow unless accelerated by heat.

BISMUTH SALTS, OR BISMUTHIC SALTS.

Solution for the reactions:—chloride of bismuth ($BiCl_3$) in dilute hydrochloric acid.

In addition to the insoluble oxysalts of bismuth, the undermentioned are the chief compounds of this metal not dissolved by water,—the chromate, the hydrate, the sulphide, the carbonate, the oxalate, the ferrocyanide, and the ferricyanide.

The Chloride is soluble in slight excess of hydrochloric acid.

The Iodide is produced by the action of iodide of potassium on bismuthic salts: it is a brown crystalline precipitate.

Its formula is BiI_3.

It is soluble in hydriodic acid.

The Chromate is produced by the action of chromate of potassium upon solutions of bismuthic salts: it is lemon-yellow.

Its formula is $Bi(CrO_2)_3$.

It is insoluble in hydrate of potassium or ammonium, very slightly soluble in water, but soluble in dilute nitric acid.

The Hydrate is produced by the action of the hydrates of potassium or ammonium, and also by the carbonates of barium, calcium, &c., in the cold, on solutions of bismuthic salts: it is a white flocculent precipitate.

Its formula is that of the mixed hydrate and oxide (BiH_3O_3, Bi_2O_3).

It is insoluble in excess of its precipitants, but readily dissolves in acids.

The Sulphide is produced by the action of hydrosulphuric acid on not too acid, or on neutral solutions of bismuthic salts: it is a brown-black precipitate.

Its formula is Bi_2S_3.

It is insoluble in the hydrates, sulphides, or cyanides of potassium or ammonium, also in dilute acids; but it is dissolved with decomposition by concentrated nitric acid.

THE SULPHATE is soluble.

THE CARBONATE is produced by the action of the carbonates of potassium or ammonium: it is a white flocculent precipitate.

Its formula is that of a basic salt,—$Bi_2(CO_3)_3$, $2Bi_2O_3$.

It is somewhat soluble in excess of its precipitants, insoluble in water and in solution of carbonic anhydride (CO_2), although very soluble (with decomposition) in strong acids.

THE OXALATE is produced by the action of oxalic acid upon solutions of bismuthic salts, and is deposited on standing: it separates as a granular crystalline precipitate.

Its formula is $Bi_2(C_2O_4)_3+3aq$.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium on solutions of bismuthic salts: it is a white precipitate.

Its formula is not known.

It dissolves in nitric and hydrochloric acids, but is reprecipitated on the addition of water.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium: it is a light brown precipitate.

Its formula has not been ascertained.

THE PHOSPHATE is produced by the action of phosphate of sodium on solutions of bismuthic salts: it is a white precipitate.

Its formula would appear to be $BiPO_4$.

The other special reagents of the present and three preceding subdivisions give no characteristic reactions with solutions of bismuthic salts.

The chief means employed for the detection of bismuth in its salts is the precipitation of the oxychloride, which is formed whenever a solution of bismuthic chloride is mixed with a large quantity of water. This (and so are the precipitates produced in a similar way with other salts of bismuth) is a salt which may be distinguished from the precipitates formed under the same circumstances in solutions of antimony, by being insoluble in tartaric acid. The other chief insoluble salts by which bismuth is recognized are the chromate, the hydrate, and the sulphide; the blowpipe reactions on charcoal are also characteristic. The insoluble bismuth salts, as the chromate, hydrate, or carbonate, may be easily distinguished from the analogous salts of lead or silver by their being insoluble either in hydrate of potassium or hydrate of ammonium.

SALTS OF PALLADIUM.

The metal palladium being of far rarer occurrence than the previously described members of the present group, its salts have not been so completely studied. The characteristics which these salts present differ from those of the salts already given, and more closely resemble those exhibited by tin and platinum compounds. Palladium forms two series of combinations with acid-radicals, the palladious and the palladic: of the former, palladious chloride ($PdCl$) and palladious oxide (Pd_2O) may be considered typical, while, of the latter, palladic chloride ($PdCl_2$) and palladic oxide (Pd_2O_2) are representatives. Palladic salts have a great tendency to form compounds the acid-radical of which contains palladium united with chlorine, iodine, &c.; they yield these definite saline combinations with the chlorides and iodides of the metals of the first subdivision, as in the following instance:—

$$PdCl_2+KCl=KPdCl_3.$$

When heated before the blowpipe, palladium salts are reduced with the greatest ease either in the oxidizing or reducing flame, the heat alone being sufficient to decompose them with formation of metal; owing to the difficult fusibility, however, of this element, no globules are seen, but only a black powder: they impart no colour to the blowpipe flame, nor do they give any reaction with nitrate of cobalt; when fused with borax, they are readily reduced in either flame.

Palladium salts are reduced by the same metals as effect the reduction of silver salts, and also by ferrous sulphate.

PALLADIOUS SALTS, OR PROTO-SALTS OF PALLADIUM.

Solution for the reactions:—palladious chloride ($PdCl$) in water.

The principal insoluble salts of this series are the iodide, the cyanide, the chromate, the hydrate, the sulphide, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

The Chloride is soluble.

The Iodide is produced by the action of hydriodic acid or of iodide of potassium on solutions of palladious salts: in very dilute solutions a brownish red colour at first appears; but after some time a black precipitate separates, which is the iodide.

Its formula is PdI.

It is insoluble in water, alcohol, or ether; neither is it dissolved by hydriodic acid.

The Cyanide is produced by the action of cyanide of potassium, or mercuric cyanide, on solutions of palladious salts: it is a yellowish-white precipitate.

Its composition is said by some to be $PdCy$; when precipitated by mercuric cyanide the formula $2(PdCy, HgCy)+aq$ has been assigned to it.

It is extremely soluble in cyanide of potassium and in hydrate of ammonium. It is soluble in hydrochloric acid unless very dilute.

The Chromate is produced by the action of chromate of potassium, but is not accurately known.

The Hydrate is produced by the action of the hydrates of the alkaline metals on solutions of palladious salts; it is also produced by the carbonates of potassium and sodium.

Its composition is that of a basic salt.

It is soluble in the hydrates of potassium or ammonium; it also dissolves in strong acids with the aid of heat.

The action of hydrate of ammonium on palladious salts varies: with some, as the nitrate, it produces no precipitate; with others, especially the chloride, it gives a flesh-coloured precipitate, which is but slightly soluble in water, and less so in alcohol, but soluble in excess of its precipitants. This precipitate is $NH_3\,PdCl$, or $N\left.\begin{matrix}H_3\\Pd\end{matrix}\right\}Cl$, as it may be written,—*i. e.* the chloride of *pallad-ammonium.*

The Sulphide is produced by the action of hydrosulphuric acid on alkaline, neutral, or acid solutions of palladious salts: it is a brownish-black precipitate.

Its formula is $Pd_2\,S$.

It is insoluble in sulphide of ammonium, but soluble in hydrochloric acid.

The Sulphate is soluble.

The Carbonate does not exist; for the soluble carbonates precipitate palladious hydrate.

The Oxalate is produced by the action of oxalate of potassium on solutions of palladious salts.

Its composition is not accurately known. When, however, oxalic acid is added to an ammoniacal solution of a palladious salt, a double oxalate is produced, having the formula $PdNH_4C_2O_4+aq$ when crystallized in short rhombic prisms, and the formula $PdNH_4C_2O_4+4aq$ when occurring in long needles.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium on palladious salts, and is precipitated on standing: it is a yellowish brown precipitate.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium: it is a red-brown precipitate.

THE PHOSPHATE is produced by the action of phosphate of sodium: it is a brown precipitate.

This precipitate is said to be a basic phosphate.

The other special reagents of the present and three preceding groups exert no characteristic action upon palladious salts.

The formation of palladious iodide, hydrate, and sulphide, and the reduction of the metal before the blowpipe, are made use of in analysis to detect palladious salts: the blowpipe reaction is, of course, applicable also to the recognition of the palladium in palladic salts.

PALLADIC SALTS, OR PER-SALTS OF PALLADIUM.

Only a few representatives of this series exist; they are almost confined to the chloride ($PdCl_2$) and the oxide (Pd_2O_2); the former gradually gives off chlorine, especially on heating, and even when its aqueous solution is boiled, and is reduced to palladious chloride ($PdCl$). When combined with chloride of potassium, palladic chloride gives a salt which is very stable; but the palladium in it probably exists in the form of a compound acid-radical ($PdCl_3$): this salt crystallizes in brownish-red octahedra. The oxide (Pd_2O) may be obtained by acting on palladic chloride with the hydrate of potassium. The sulphide (Pd_2S_2) cannot be obtained by passing hydrosulphuric acid into a solution of palladic chloride; for, if formed at all, it is immediately decomposed into palladious sulphide (Pd_2S) and sulphur.

On account of the large number of important metals included in this Subdivision, we have not deferred giving the Table of Reactions until the end of the group, but have placed a synopsis of the reactions of the 1st Section on the following page; and for the same reason, an Analytical Table will also be found appended.

TABLE OF

REACTIONS.	Cd. (see page 154)	Cu. (see page 160)	Ag. (see page 165)
Chloride	—	—	white
Iodide	—	—	pale yellow
Cyanide	—	brownish yellow	white
Chromate	yellow	yellowish brown	crimson
Hydrate	white	blue	buff
Oxide	—	black	brown
Oxychloride	—	—	—
Sulphide	bright yellow	black	black
Sulphate	—	—	white
Carbonate	white	blue	white
Oxalate	white	pale blue	white
Ferrocyanide	white	brownish crimson	white
Ferricyanide	pale yellow	greenish yellow	orange yellow
Phosphate	white	greenish blue	yellow
BLOWPIPE REACTIONS.	With carbonate of sodium on charcoal, a reddish brown deposit, the metal being reduced and volatilized.	With carbonate of sodium on charcoal, malleable globules; with borax in the oxidizing flame, a green, and in the reducing flame a red bead.	With carbonate of sodium on charcoal, malleable globule.

REACTIONS.

Hg_2. (see page 170)	**Hg.** (see page 173)	**Pb.** (see page 177)	**Bi.** (see page 183)	**Pd.** (see page 186)
white	—	white	—	—
dull-green	yellow, changing to scarlet	bright yellow	—	black
—	—	white	—	yellowish white
orange-red	dull-red	yellow	yellow	—
—	yellow	white	white	yellowish brown
brownish black	yellow	—	—	—
—	white	white	white	—
black	black	black	brownish black	brownish black
yellowish white	white	white	white	—
—	brownish red	white	white	—
—	white	white	white	pale yellow
—	white	white	yellowish brown	—
reddish brown	yellow	—	light brown	reddish brown
white	white	white	white	brown
Mixed with carbonate of sodium and heated in a glass tube, the metal sublimes.	Same as the mercurous salts.	With carbonate of sodium on charcoal, malleable globule and yellow incrustation.	With carbonate of sodium on charcoal, a brittle globule and yellow incrustation.	With carbonate of sodium on charcoal, reduced to the metallic state.

We also give an Analytical Table for the 1st Section of this subdivision, on account of the great number and importance of the metals it contains.

Analysis of Subdivision IV.

SECTION I.—Salts of metals which form Sulphides insoluble in Sulphide of Ammonium.

The salt may be one of CADMIUM, COPPER, SILVER, MERCURY (mercurous or mercuric), LEAD, BISMUTH, or PALLADIUM.

<table>
<tr><td colspan="5">Ignite the substance; if it does not volatilize, we infer the</td></tr>
<tr><td rowspan="4">absence of Mercury, which may be further confirmed by heating the dry salt mixed with dry Na_2CO_3 in a small tube and observing the absence of globules.</td><td colspan="4">presence of
Cadmium, Copper, Silver, Lead, Bismuth, or Palladium.
Dissolve the ignited residue in a little nitric acid, dilute with water, and add dilute sulphuric acid; if no white precipitate is produced, we infer the</td></tr>
<tr><td rowspan="3">absence of Lead.</td><td colspan="3">presence of
Cadmium, Copper, Silver, Bismuth, or Palladium.
To the same solution add dilute hydrochloric acid; if no precipitate is produced, we infer the</td></tr>
<tr><td rowspan="2">absence of Silver.</td><td colspan="2">presence of
Cadmium, Copper, Bismuth, or Palladium.
Add hydrate of ammonium in excess; if no white precipitate is produced, we infer the</td></tr>
<tr><td>absence of Bismuth.</td><td>presence of
Cadmium, Copper, or Palladium.
If the solution is blue, we infer the presence of Copper;
if colourless, of Cadmium or Palladium.
Add hydrosulphuric acid; if a yellow precipitate is produced, we infer the presence of Cadmium;
if a brownish-black, of Palladium.</td></tr>
</table>

SECTION II.—*Salts of metals which form sulphides soluble in Sulphide of ammonium* ($[NH_4]_2S$).

SALTS OF TIN, ANTIMONY, ARSENIC, PLATINUM, RHODIUM, RUTHENIUM, OSMIUM, GOLD, TUNGSTEN, MOLYBDENUM, AND VANADIUM.

SALTS OF TIN.

The chemical characteristics of the compounds of this metal resemble to a certain extent those of the preceding: it forms two series of combinations with chlorine and acid-radicals in general, —the stannous chloride and oxide ($SnCl$ and Sn_2O) being representatives of the first, and the stannic chloride and oxide ($SnCl_2$ and Sn_2O_2) typifying the second series. Stannic salts, however, are far more numerous and important than palladic salts; and so far from having, like them, a tendency to decompose into the acid-radical and the corresponding salt of the first series, they are actually produced easily from stannous salts,—half of the metal present being separated in the metallic state, while the portion of acid-radical previously united with this half combines with the residual elements: thus stannous oxide, under peculiar circumstances, passes into stannic oxide, thus—

$$2(Sn_2O) = 2Sn + Sn_2O_2.$$

Besides these two series there is a third, which is, however, unimportant, few members of it existing: it is intermediate between the stannous and stannic series, and has been called the stannoso-stannic series, while its members have been termed sesqui-salts.

When salts of tin are heated in the oxidizing flame of the blowpipe, they are converted into an intermediate oxide (Sn_4O_3), at least for the most part; several tin salts, however, as stannous chloride ($SnCl$), partially volatilize, while in the reducing flame tin salts yield their metal; but to effect this requires some skill in the operator, and may be taken as a test of proficiency in the use of the reducing flame: fluxes, such as carbonate of sodium or cyanide of potassium, should not be employed, since the operation is deprived of all difficulty by their aid. Tin salts impart no colour to the flame; *but with nitrate of cobalt the residual oxide*

(Sn_4O_3) *assumes a bluish-green colour.* When fused with borax in the oxidizing flame, they yield a colourless transparent glass, which, if surcharged with the tin salt, becomes opaque and crystalline: in the reducing flame, part of the tin present is reduced to the metallic state; this experiment should be performed on charcoal.

Although the salts of tin are placed together in the second section of the present subdivision, that is, among those metals the sulphides of which are capable of forming sulphur salts with the alkaline sulphides, yet, properly speaking, the stannous salts should belong to Section I., and the stannic salts to Section II., for the stannous sulphide (Sn_2S) does not dissolve as such in sulphide of ammonium, but only after its conversion into stannic sulphide by combination with the sulphur which sulphide of ammonium usually holds in solution; thus

$$Sn_2S+(NH_4)_2S+S=(NH_4)_2Sn_2S_3.$$

Stannous salts are reduced by iron under certain circumstances, readily by zinc and cadmium, slightly by lead. The same actions are observed with such stannic salts as are soluble.

STANNOUS SALTS, OR PROTO-SALTS OF TIN.

Solution for the reactions:—proto-chloride of tin ($SnCl$) in water.

The principal insoluble salts of this series are the iodide, the cyanide, the chromate, the oxychloride, the hydrate, the sulphide, the oxalate, the ferrocyanide, the ferricyanide, and the phosphate.

THE CHLORIDE is soluble.

The Iodide is obtained by the action of iodide of potassium in excess on solutions of stannous salts, especially after some time. It is a yellowish white precipitate; but from warm solutions it separates in fine reddish yellow crystals.

Its formula is SnI.

It dissolves sparingly in cold water, but more readily in hot; it is also soluble in a solution of stannous chloride.

THE CYANIDE is produced by the action of cyanide of potassium on solutions of stannous salts: it is a white precipitate, which is said to be stannous hydrate, not stannous cyanide. A portion of tin salt remains in the solution of cyanide of potassium.

THE CHROMATE is produced by the action of chromate of potassium in excess on solutions of stannous salts: if the stannous salt be in excess, a greenish white precipitate is obtained, which is thought to be chromic stannate (stannate of chromium), some of the oxygen contained in the chromic acid-radical being transferred from the chromium to the tin, to form stannic acid.

This precipitate dissolves in hydrochloric acid, forming a green solution.

THE OXYCHLORIDE is produced by precipitating stannous chloride with an insufficient amount of hydrate of potassium. It is a white precipitate.

Its composition is $2SnCl, Sn_2O, 3aq$.

It dissolves readily in most acids.

The Hydrate is produced by the action of the hydrate or carbonate of potassium or ammonium: it is a white precipitate.

Its formula is $SnHO$.

It is readily soluble in excess of hydrate of potassium, but not in excess of its other precipitants; it dissolves readily in acids. If the potassic solution of this salt be boiled, one of those curious metamorphoses occurs similar to those which have been noticed before, and which results in part of the tin present passing into a higher state of oxidation, at the expense of another part, which is reduced to the metallic state; thus—

$$4SnHO + 2KHO = K_2Sn_2O_3 + 2Sn + 3H_2O.$$

The Sulphide is produced by the action of hydrosulphuric acid on neutral or acid solutions of stannous salts; alkaline solutions are very partially precipitable. It is a brownish black precipitate.

Its composition is Sn_2S, or possibly, when recently precipitated, $SnHS$.

It dissolves in hydrate of potassium or sodium, but is reprecipitated from these solutions unchanged by hydrochloric acid; it is almost insoluble in protosulphide of ammonium ($[NH_4]_2S$) and in sulphydrate of ammonium (NH_4HS). When, however, the sulphide of ammonium has become converted into one of the higher sulphides, as $[NH_4]_2 S_2$, stannous sulphide dissolves in this reagent, producing sulpho-stannic acid, the ammonium salt of which is soluble, thus—

$$2SnHS + (NH_4)_2 S_2 = \underset{\text{sulpho-stannate of ammonium.}}{(NH_4)_2 Sn_2 S_3} + H_2 S.$$

If hydrochloric acid be added to this solution, stann*ic* sulphide $(Sn_2 S_2)$ is precipitated,—

$$(NH_4)_2 Sn_2 S_3 + 2HCl = 2NH_4 Cl + \underset{\text{yellow ppt.}}{Sn_2 S_2} + H_2 S.$$

Stannous sulphide dissolves in boiling hydrochloric acid, being converted into stannous chloride; boiling nitric acid decomposes it with formation of stannic oxide $(Sn_2 O_2)$.

THE SULPHATE is soluble.

THE CARBONATE does not exist.

THE OXALATE is produced by the action of oxalic acid on solutions of stannous salts; the alkaline oxalates produce double salts, which are soluble. It is a white crystalline precipitate.

Its formula is $Sn_2 C_2 O_4$.

It dissolves in hot solutions of chloride of ammonium and of other ammonium salts, and crystallizes out again on cooling; it is but slightly soluble in cold or hot water, or in oxalic acid, or in dilute cold mineral acids, but in hot hydrochloric or nitric acid it dissolves.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium on solutions of stannous salts. It is a white precipitate, becoming yellow by exposure to the air.

Its formula is $Sn_2 Cfy$.

It is insoluble in the chloride and many other salts of ammonium, in water and in acids, but it dissolves in hydrate of ammonium.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium. It is a white gelatinous precipitate.

Its composition is $Sn_3 Cfdy$.

It dissolves in hydrate of ammonium, but not in other ammonium salts.

THE PHOSPHATE is produced by the action of phosphate of sodium: it is a white precipitate.

It is insoluble in chloride of ammonium and in water, but dissolves in hydrochloric acid.

The other special reagents of the present and three preceding subdivisions are not known to yield any characteristic reactions with stannous salts.

The production of stannous hydrate and sulphide, and the reaction of the former salt when dissolved in hydrate of potassium and heated, are among the chief methods employed for the recognition of stannous salts.

STANNOSO-STANNIC SALTS, OR SESQUI-SALTS OF TIN.

These salts are thought by most chemists to be formed by the union of stannous and stannic salts.

THE OXIDE, or more properly, THE HYDRATE, is obtained by acting on stannous chloride with ferric hydrate,—ferrous chloride and stannoso-stannic hydrate being the products of the change, which may be more simply represented by assuming ferric oxide to be the ferric salt concerned—

$$(Fe_2)_2 O_3 + 4SnCl = (Sn_2)_2 O_3 + 4FeCl.$$

It is a yellowish-white precipitate, which dissolves in hydrochloric acid without decomposition, if protected from the air.

THE SULPHIDE, or more properly, THE SULPHYDRATE, is said to be obtained by passing hydrosulphuric acid through a solution of the hydrate in hydrochloric acid: it is a liver-coloured precipitate, having probably the formula $(Sn_2)_2 S_3$.

STANNIC SALTS, OR BI- OR PER-SALTS OF TIN.

Solution for the reactions: — stannic chloride ($SnCl_2$) in water.

This is the most stable series of the salts of tin, both of the preceding series possessing a great tendency to assume more acid-radical and pass into stannic salts. The decomposition of stannic salts under the influence of reagents is very peculiar, and wholly dependent upon the chemical nature of the substance presented to them: if the reagent be one possessing powerful basic properties, the stannic compound in combining with it assumes the functions of an acid-radical, thus—

$$2SnH_2O_2 + 2KHO = \underset{\text{stannate of potassium.}}{K_2Sn_2O_3} + 3H_2O.$$

If, again, the same salt, stannic hydrate, be acted upon by a reagent possessed of powerful acid properties, the metal unites with the acid-radical of the acid to form a salt in which the tin plays the part of a base, thus—

$$2SnH_2O_2 + 2H_2SO_4 = \underset{\text{stannic sulphate.}}{Sn_2(SO_4)_2} + 4H_2O.$$

These or similar peculiarities have been described in the case of aluminium, chromium, and palladium.

One important feature with respect to these salts is this:—there exist two modifications of them, which have been termed the stannic, and the metastannic salts; the hydrate, however, and those other salts in which a compound of tin and oxygen is presumed to play the part of the acid-radical, are the only instances in which this "dimorphism" is strongly marked.

The principal insoluble salts of this series are the cyanide, the chromate, the hydrate, the sulphide, the ferrocyanide, and the phosphate.

THE CHLORIDE is soluble.

THE IODIDE is not produced by iodide of potassium; but it separates in the form of orange or red crystals decomposable by water, when a solution of stannous chloride is boiled with iodine.

THE CYANIDE is not produced by cyanide of potassium, the white precipitate obtained being believed to be only stannic hydrate.

THE CHROMATE is produced by the action of chromate of potassium on solutions of stannic salts: it is a yellow precipitate.

The Hydrate occurs in two distinct varieties, according to the method of its production; in either form it is the hydrogen salt of a compound acid-radical, and yields salts with the hydrates of the first subdivision, which contain the alkaline metals.

The two modifications are called respectively stannic and metastannic acids.

1. STANNIC ACID is produced by the action of the hydrates or carbonates of potassium or ammonium, but it is precipitated in the purest form by the action of the carbonates of the second subdivision on solutions of stannic salts; it is also produced by decomposing stannic chloride with water. It is a white gelatinous precipitate.

Its formula is $H_2 Sn_2 O_3$, while its known salts may be represented by the formula $M_2 Sn_2 O_3$. Stannic hydrate when dried below 55° is, however, $H_2 Sn_2 O_3, H_2O$, or more simply, SnH_2O_2.

It dissolves readily in excess of hydrate of potassium or ammonium, or of carbonate of potassium; it remains dissolved, however, for a short time only, separating perfectly on standing. In many acids it dissolves readily, forming, by double decomposition, solutions of the ordinary stannic salts.

2. METASTANNIC ACID is produced by the action of concentrated nitric acid on metallic tin. The changes which accompany this formation of metastannic acid are very peculiar, nitrate of ammonium being one of the products; if the formula assigned to this acid be correct, the transformation may be thus represented,—

$$10Sn + 6HNO_3 + 6H_2O = H_{10} Sn_{10} O_{15} + 2NH_4 NO_3 + N_2O_3.$$

This substance is a white crystalline precipitate.

Its formula is $H_{10} Sn_{10} O_{15}$, while the salts which are known are represented thus,—$M_2 H_8 Sn_{10} O_{15}$.

It is soluble in hydrate of potassium, but insoluble in hydrate of ammonium. It does not dissolve in water, nor in dilute hydrochloric and nitric acids, but it is soluble in strong sulphuric acid. If this precipitate be boiled for some time with hydrochloric acid and then diluted with water, a clear solution is obtained containing metastannic chloride; upon boiling this diluted solution, metastannic acid is reprecipitated.

The Sulphide is produced by the action of hydrosulphuric acid on neutral or acid solutions of stannic salts: the precipitate is at first white, but with an excess of the precipitant, dull yellow.

Its formula is Sn_2S_2.

This salt is very soluble in the sulphides of potassium or ammonium, forming with these reagents a salt termed a sulpho-stannate, thus—

$$K_2S+Sn_2S_2=\underset{\substack{\text{sulpho-stannate}\\ \text{of potassium.}}}{K_2Sn_2S_3}.$$

The sulpho-stannates correspond perfectly to the ordinary stannates, the oxygen of those salts being replaced by an equivalent proportion of sulphur. Stannic sulphide dissolves in hydrate of potassium, but less readily in hydrate of ammonium; with the former reagent the action is as follows,—

$$6KHO+3Sn_2S_2=\underset{\substack{\text{stannate of}\\ \text{potassium.}}}{K_2Sn_2O_3}+\underset{\substack{\text{sulpho-stannate}\\ \text{of potassium.}}}{2K_2Sn_2S_3}+3H_2O.$$

In boiling hydrochloric acid, when strong, *stannic* sulphide dissolves, while it is decomposed by hot nitric acid with formation of metastannic acid. The sulphur-acid of tin corresponding to metastannic acid does not appear to exist.

The Sulphate is not known.

The Carbonate is not known.

The Oxalate is soluble.

The Ferrocyanide is produced by the action of ferrocyanide of potassium on solutions of certain stannic salts (as stannic chloride). It is a brownish yellow precipitate.

Its formula is Sn_2Cfy_2.

It is insoluble in hydrochloric acid, and also in the hydrate and other salts of ammonium.

The Ferricyanide is soluble.

The Phosphate is produced by the action of phosphate of sodium on solutions of stannic salts: it is a white precipitate, whose formula has not been ascertained.

The other special reagents of the present and three preceding groups exert no characteristic actions upon solutions of stannic salts.

The metamorphoses of the oxide and hydrate, and the precipitation, &c. of the sulphide, are among the most striking tests for stannic salts, some of which may also be recognized when in solution by the beautiful feathery crystalline deposit of metallic tin with which a piece of zinc immersed in the mixture becomes covered.

SALTS OF ANTIMONY.

The compounds which this body forms with salt-radicals bear considerable resemblance to those which the preceding metal yields, while, in general characters, antimony, like arsenic, is more closely allied, in many respects, to the acid elements, such as phosphorus or nitrogen, than to the basic elements, among which it is usually placed.

Antimony produces by combination with acid-radicals two series of compounds,—of the first of which, the oxide Sb_2O_3, and the chloride $SbCl_3$, may be taken as representatives; and of the second of which, the oxide Sb_2O_5, and the chloride $SbCl_5$, may be considered types: and between these two series, the same relation may be observed which has been seen to exist between the salts of tin,—the first or lower series having a tendency to pass into the second or higher stage of combination.

Most salts of antimony, when heated on charcoal in the oxidizing flame of the blowpipe, are converted into the oxide, which volatilizes and condenses upon the cooler and more distant part of the charcoal; some salts, however, such as the chloride, are volatilized unchanged. In the reducing flame, especially with reducing agents, such as carbonate of sodium or cyanide of potassium, globules of the metal are obtained, which are very brittle; they volatilize, oxidize, and condense upon the charcoal as oxide. The reduced metal, when volatilizing, imparts a greenish blue colour to the flame. Antimony salts, when moistened, after having been heated, with nitrate of cobalt, produce no characteristic colour. When heated with borax in the oxidizing flame, a clear glass is obtained, which is yellow while hot, and colourless when cold, and which, when subjected to the action of the reducing flame, becomes grey and cloudy, owing to the presence of reduced metal; this cloudiness, however, soon disappears, from the volatilization of the metal. This experiment should be performed on charcoal.

A remarkable feature which is to be observed with regard to antimony, is the property which it possesses of forming a compound with hydrogen: whenever a salt of antimony comes into contact with nascent hydrogen, this substance is invariably produced, according to the following equation,—

$$SbCl_3 + 6H = SbH_3 + 3HCl;$$

the change consists, however, of two stages, the first being the production of metallic antimony—

$$SbCl_3 + 3H = Sb + 3HCl,$$

and the second being the combination of this antimony with hydrogen by the action of 3 more equivalents—

$$Sb + 3H = SbH_3.$$

That this is really the case, is proved by the large amount of metallic antimony which is actually deposited; for the latter change does not take place so rapidly as the former. The best method of performing this experiment is to generate hydrogen in the ordinary apparatus (fig. 1, p. 15), taking care to employ specimens of zinc and of sulphuric acid perfectly free from arsenic (a very frequent impurity of these reagents), and then to introduce into the generating flask the solution to be examined for antimony: if this metal be present, antimoniuretted hydrogen is produced, which, after having been dried by passing through oil of vitriol in a second flask, may be kindled at a small jet made of a glass tube, and inserted in the cork of the washing-flask, care having been taken to allow sufficient time to elapse previously to the ignition of the gas, that all air may have been expelled from the apparatus, and therefore all risk of explosion avoided. The student should observe the following properties of the gas, remembering that none of them are presented by pure hydrogen:—

a. The gas kindled at the orifice will be seen to burn with a pale bluish-green flame, and to give rise, especially if the observation be made in a dark place, to a white smoke, which consists of antimonious oxide (Sb_2O_3); both constituents, indeed, of the gas combine with oxygen during the combustion, thus—

$$2SbH_3+6O=\underset{\substack{\text{white}\\\text{vapour.}}}{Sb_2O_3}+3H_2O.$$

β. If a cold porcelain surface be depressed into the flame burning at the jet, but not so as to extinguish it, a black spot of metallic lustre will be produced at the point of contact, which spot will be found volatilizable by further heating. This is metallic antimony, which has not been oxidized by the atmospheric oxygen present, on account of the reduction in the temperature effected by the cold porcelain.

γ. If the jet with a fine orifice be now removed, and a tube of hard glass of the form represented in fig. 11 be substituted for it, and, while the gas is passing, the middle of the wide part of the tube be heated by a spirit-lamp, the flame of which is urged by a blowpipe, there will speedily appear at the commencement of the narrow part or shoulder of the tube a mirror-like deposit, which, by the application of the flame, may be chased along the capillary tube, and finally driven out at its orifice. For the antimoniuretted hydrogen is decomposed at a high temperature into its constituents; and frequently so complete is this decomposition while the heat is maintained, that the gas issuing from the orifice, when kindled, will no longer stain a porcelain surface, being, in fact, pure hydrogen.

δ. Results closely analogous with those just mentioned are obtained with compounds of an element which, on account of its resemblance to antimony, and for the sake of convenient comparison, is introduced immediately after the metal we are now considering. Arsenic, the substance to which we refer, and which, like antimony, may be considered, strictly speaking, as one of the acid elements, forms a compound with hydrogen (AsH_3) perfectly corresponding with antimoniuretted hydrogen, and which when burning yields a spot or metallic stain if cooled by porcelain, and a metallic mirror when decomposed by heat. To distinguish, therefore, between the spot or mirror of arsenic and the spot or mirror of antimony, is a problem which the student should be able to solve with confidence; and the following reactions peculiar to antimony will enable him to do so:—

1. When *an antimony spot* on a fragment of porcelain is treated with a drop of concentrated nitric acid, the acid then completely removed by evaporation, and a drop of nitrate of silver solution added to the slight whitish residue on the porcelain, *no change of colour occurs.*

2. Again, if *an antimony spot* be moistened with a solution of hypochlorite of sodium (really a mixture, $NaClO + NaCl$), *it is scarcely at all dissolved.*

3. With respect to the mirror, if the tube containing *an antimony mirror* be detached from the apparatus in which the antimoniuretted hydrogen was being evolved, and connected similarly with another from which sulphuretted hydrogen is slowly evolved, and if, while the H_2S is traversing the tube, a gentle heat be applied to the mirror, it will become of *a reddish-yellow or brownish-black colour*, from formation of antimonious sulphide (Sb_2S_3). The sulphuretted hydrogen gas employed should be dry; and to effect its desiccation it may be passed through a bottle containing some oil of vitriol. Over the mirror, now converted into *a film of antimonious sulphide*, a slow current of dry hydrochloric acid gas (evolved by heating a concentrated solution of the acid, and dried by means of oil of vitriol) may now be transmitted, the apparatus employed being precisely similar to that last used. During the passage of the gas the antimonious sulphide disappears, being converted into *the volatile and colourless antimonious chloride* ($SbCl_3$), thus—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S;$$

the volatile chloride may be conducted into water, in which it is soluble; and then the solution may be tested by its most characteristic precipitant, a solution of sulphuretted hydrogen, which yields a fine orange-yellow precipitate of antimonious sulphide (Sb_2S_3).

A greater difference exists between the two series of salts which antimony forms, than has hitherto been observed in the case of any metal which has yet been brought before the notice of the student. Antimonious oxide (Sb_2O_3), and the chloride ($SbCl_3$), which may be taken as types of the first series, have a fair claim to be ranked among the bodies usually known as salts; antimonic oxide (Sb_2O_5) and the chloride ($SbCl_5$) are of a decidedly acid character, and yield, in the presence of powerful basic elements, salts in which the antimony forms part (or is presumed to form part) of a compound oxygenated acid-radical.

Antimonious salts are precipitated by iron, cobalt, zinc, cadmium, lead, and tin completely, in the form of a black powder; partially by copper or bismuth: when a trace of bismuth is present, the copper becomes coated with a violet-coloured film. Zinc precipitates the antimony from antimoniates rendered acid by HCl, in the form of a black powder.

ANTIMONIOUS SALTS, OR TER-SALTS OF ANTIMONY.

Solutions for the reactions:—antimonious chloride ($SbCl_3$) in dilute hydrochloric acid, and the double tartrate of antimonyle and potassium ($KSbO, C_4H_4O_6$) in water.

The metal in these salts is believed to be generally triatomic, from the usual composition of its salts—the chloride ($SbCl_3$), the sulphide (Sb_2S_3), and the sulphate ($Sb_2[SO_4]_3$), &c.: but there are certain salts, the composition of which can only be explained by supposing that antimony occasionally forms part of a basic radical containing oxygen, and termed *antimonyle* (SbO); and in this respect antimony resembles uranium, which forms (as the student will remember) a large series of salts of perfectly corresponding character, and presumed to contain the basic radical uranyle (U_2O). The salts of antimony whose existence favours this supposition are those which it forms with bibasic acids, such as oxalic and tartaric. The formulæ of such compounds are the following,—the oxalate (H, SbO, C_2O_4) and the tartrate ($H, SbO, C_4H_4O_6$).

The metal antimony presents many analogies with bismuth, and none more striking than the remarkable facility with which its salts are decomposed by water. If we regard antimonious salts as constituted similarly to bismuth salts, the bodies which result from their decomposition by means of water must be regarded as combinations of antimonious oxide with the salt originally employed, while the changes which occur may be represented in the same manner as in the case of bismuth salts.

If, for instance, antimonious chloride ($SbCl_3$) is mixed with a large quantity of water, an oxychloride, to which various formulæ have been assigned, is precipitated: its constitution has been thus represented, $2SbCl_3, 5Sb_2O_3$; it is known by the old name of *powder of Algaroth*. Many of the other salts of antimony are decomposed by water in a similar manner; but the nature of these salts and of their products of decomposition is ill understood.

The so-called oxy-salts of antimony are readily soluble in excess of the acid, the radical of which exists in the original salt, or, indeed, in excess of most other acids; and the peculiar feature which distinguishes them from the analogous compounds of bismuth, which they closely resemble, is that they are *soluble in excess of tartaric acid*, and that *the presence of the latter acid prevents their precipitation.*

The principal insoluble antimonious salts are the chromate, the oxide, the oxychloride, the sulphide, the oxalate, the ferrocyanide, and the phosphate.

THE CHLORIDE is soluble.

THE IODIDE is not produced by the action of iodide of potassium.

THE CYANIDE is not known.

The Chromate is produced by the action of chromate of potassium on solutions of antimonious salts: it is a brownish yellow precipitate.

Its formula is not known.

It is soluble in excess of the antimonious salt, forming a green solution.

The Oxide is produced by the action of the hydrates or carbonates of the first and second subdivisions upon solutions of antimonious salts, although the precipitation occurs less readily with such solutions as contain tartaric or other similar organic acid. The oxide is also produced by digesting any of the oxysalts mentioned above with solution of carbonate of potassium, or even by boiling certain of them (*e. g.* the oxysulphate or the oxynitrate) with water for some time. It is a white flocculent precipitate.

Its formula is Sb_2O_3.

It dissolves in excess of hydrate of potassium, but less perfectly in the carbonate; in hydrate of ammonium it is insoluble. It is readily soluble in acids, even in tartaric acid, but is not dissolved by nitric acid.

The Oxychloride is obtained, as already stated, when much water is added to a solution of antimonious chloride. Great reliance is placed on this reaction; to obtain it, the precipitate produced by the hydrate of potassium (the oxide Sb_2O_3) is dissolved in hydrochloric acid, and evaporated to a small bulk in order to ensure its conversion into the chloride ($SbCl_3$); this solution is then poured into a large quantity of water, when an immediate precipitation of the white oxychloride will occur.

The formulæ $2SbCl_3, 5Sb_2O_3$, and $4SbCl_3, 9Sb_2O_3$, have been assigned to this precipitate.

It dissolves in hydrochloric, tartaric, and most other acids, with the exception of nitric acid.

The Sulphide is produced by the action of hydrosulphuric acid upon acid or neutral solutions of antimonious salts: it is a precipitate of a fine orange colour, which is quite characteristic.

Its formula is Sb_2S_3.

It dissolves in the sulphides of potassium or ammonium, especially if these reagents contain excess of sulphur; it is also soluble in hydrate of potassium, but only to a slight extent in the hydrate or acid carbonate of ammonium. It is insoluble in dilute acids, but soluble in boiling concentrated hydrochloric acid; hot sulphuric acid dissolves it less easily, with evolution of hydrosulphuric acid, while hot nitric acid decomposes and oxidizes it.

THE SULPHATE is not well known; it would appear, however, that several varieties of this salt exist, many of which are insoluble (or nearly so) in water.

THE CARBONATE is not known.

THE OXALATE is produced by the action of oxalic acid on solutions of antimonious salts: it is a very bulky white precipitate, which separates completely only after standing.

Its formula is H, SbO, C_2O_4.

It is insoluble in cold water, but is decomposed by boiling water, which withdraws the acid constituent from it, and converts it into the oxide.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium on solutions of antimonious salts (if tartaric acid be absent): it is a white precipitate.

Its formula has not been ascertained; by some chemists it is believed to be an oxy-salt only.

It is insoluble in hydrochloric acid.

THE FERRICYANIDE is soluble.

THE PHOSPHATE is partially precipitated on the addition of phosphate of sodium; it occurs in white flakes.

Its composition appears to be uncertain.

The other special reagents of the present and three preceding subdivisions are not known to give any characteristic reactions with antimonious salts.

Antimonious compounds are often detected and recognized by the formation of the oxide, oxychloride, and sulphide.

ANTIMONIC SALTS, OR PENTA-SALTS OF ANTIMONY.

Solution for the reactions:—antimoniate of potassium ($KSbO_3$) in water.

These compounds, of which the oxide is Sb_2O_5, and the chloride $SbCl_5$, bear a striking resemblance to the stannic salts, although they partake even to a less extent of the characters of normal salts, and have a far greater tendency to become converted in the presence of basic elements into compound acid-radicals. They are, however, noticed among the saline combinations of the basic elements, to avoid the inconvenience which would result from placing them in a different section. The salts (if they may be so called) of this series do not present the same stability as the stannic salts: if, for instance, antimonic chloride ($SbCl_5$) be heated, it decomposes into antimonious chloride and chlorine, thus—

$$SbCl_5 = SbCl_3 + Cl_2.$$

The principal insoluble salts of this series are the hydrate and sulphide.

THE CHLORIDE is decomposed in the manner described below when introduced into water.

THE IODIDE, THE CYANIDE, and THE CHROMATE are unknown.

The Hydrate is produced by the action of water upon the penta-chloride of antimony, if the product be afterwards washed sufficiently. It is a bulky white precipitate. Like stannic hydrate, this occurs in two distinct forms, each of which has a tendency to appropriate oxygen, and then, as a compound acid-radical, to combine with hydrogen or metals. These two modifications are called antimonic and metantimonic acids respectively.

1. ANTIMONIC ACID is obtained by the method just described, or by dissolving metallic antimony in nitrohydrochloric acid containing excess of nitric acid.

The amount of hydrogen which it contains does not appear to have been accurately determined; but the formula $HSbO_3$ may be assigned to it with great probability, while the constitution of its salts is generally represented by the formula $MSbO_3$.

This acid is quite insoluble in hydrate of ammonium, and very slightly soluble in water or acids.

2. METANTIMONIC ACID is obtained by decomposing antimonious chloride with water, or by decomposing antimoniate of potassium by an acid.

The composition of the acid obtained by these methods is $H_4Sb_2O_7$: it is said to form two series of salts, represented by the formulæ $M_4Sb_2O_7$ for the neutral salts, and $M_2H_2Sb_2O_7$ for the acid salts.

Metantimonic acid is soluble in hydrate of ammonium; it also dissolves in a large quantity of water, from which solution it is reprecipitated by the addition of acids. In acids it is more soluble than antimonic acid.

The Sulphide is produced by the action of hydrosulphuric acid upon an acid solution of antimonic salts (tartaric acid prevents the precipitation, in the same way as it does that of antimonious chloride by water); it is also formed by passing hydrosulphuric acid gas through water in which antimonic or metantimonic acid is suspended: it is an orange-yellow precipitate.

Its composition is Sb_2S_5; but it generally contains the elements of water, which are evolved as water when the substance is dried. This body partakes of the characters of a hydrate, and, by the appropriation of sulphur from alkaline sulphides, becomes converted into a compound acid-radical united with the metal of the alkaline sulphide, and forming a salt which has been termed a sulphantimoniate. In these compounds we do not observe the difference which we find between antimonic and metantimonic acids: sulphantimonic acid does not appear to exist in more than one modification; and that is said to be tribasic. The sodium salt is well defined; it crystallizes in pale yellow tetrahedra with 9 eqs. of water, its formula being $Na_3SbS_4 + 9aq$.

The sulphide dissolves readily in the hydrates and sulphides of potassium, of ammonium, and of the second subdivision, especially on heating. From its solution in the hydrates of potassium or barium, a crystalline precipitate of antimoniate of potassium or barium is, however, deposited on standing. Carbonate of potassium also dissolves it on boiling. From these solutions it is reprecipitated by the addition of acids. It is insoluble in cold acids, but, when boiled with concentrated hydrochloric, dissolves, with evolution of hydrosulphuric acid, separation of sulphur, and formation of antimonious chloride.

THE SULPHATE, CARBONATE, OXALATE, FERROCYANIDE, FERRICYANIDE, AND PHOSPHATE do not exist.

The other special reagents of the present and three preceding subdivisions give no characteristic reactions with antimonic compounds.

Antimonic salts are recognized by the properties of the hydrate and of the sulphide.

SALTS OF ARSENIC.

The apology offered for introducing antimonic combinations among the reactions of the basic elements must be put forward again in the case of arsenic compounds. The combinations which this metal forms should be treated of among the compound acid-radicals; and indeed they must be again adverted to in the next Chapter: but so much inconvenience would arise from the total postponement of all consideration of these combinations until then, on account of many similarities which exist between arsenic and the basic elements, and because antimony serves to connect these, that the account of some of its reactions cannot be deferred.

Arsenic resembles antimony in its combinations with acid-radicals; it forms two series of such compounds: of the first the arsenious oxide (As_2O_3) and the arsenious chloride ($AsCl_3$) may be regarded as typical, while the second series is represented by the arsenic oxide (As_2O_5) and the arsenic chloride ($AsCl_5$). These two series, like the analogous antimony series, are mutually convertible by processes of oxidation and reduction; but from those bodies they differ in one important point, being endowed far more highly than the antimony compounds with the peculiar features of acid bodies: this feature is most strikingly manifested by the oxides, both of which yield salts containing, to one equivalent of arsenic, a larger proportion of oxygen than exists in the oxide. These salts are extremely stable; in contrast with this fact it will be remembered that the salts derived from antimonious oxide (Sb_2O_5) are *very easily decomposed*. These differences might have been expected from the close resemblance which arsenic bears to phosphorus and nitrogen; indeed it ought scarcely to be introduced among basic bodies, did not its resemblance in some points to antimony demand its comparison, for convenience sake, with that element.

The ordinary blowpipe experiments cannot be performed with the compounds of arsenic, on account of their volatility. To this there are a few exceptions: one is found in the arsenic oxide (As_2O_5), which sustains a temperature of 300° C. without change, but then decomposes into arsenious oxide (As_2O_3) and oxygen; and another exists in those salts in which the acid-radical AsO_4 enters, and which do not part with arsenic at a red heat. The extreme volatility of arsenic and its compounds furnishes us, however, with an admirable means of detecting this metal. When any compound of arsenic, which has been intimately mixed in a mortar with carbonate of sodium, or with carbonate of sodium and charcoal, is transferred to a narrow tube of hard glass about $\frac{1}{4}$ of an inch internal diameter, 6 or 8 inches long, and closed at one end, and then heated before the blowpipe, a metallic mirror of arsenic is invariably produced, even when that metal existed in minute quantity. The following equations are representations of the probable changes which occur. according as the experiment is varied:—

With arsenious oxide and carbonate of sodium,—

$$5As_2O_3+9Na_2CO_3=\underset{\text{mirror.}}{4As}+\underset{\substack{\text{arseniate of}\\ \text{sodium.}}}{6Na_3AsO_4}+\overset{\nearrow}{9CO_2};$$

with arseniate of sodium and charcoal,—

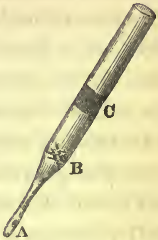
$$2Na_2HAsO_4+3C=\underset{\text{mirror.}}{2As}+2Na_2CO_3+\overset{\nearrow}{H_2O}+\overset{\nearrow}{CO};$$

with arsenious sulphide and cyanide of potassium,—

$$As_2S_3+3KCN=\underset{\text{mirror.}}{2As}+\underset{\substack{\text{sulphocyanide}\\ \text{of potassium.}}}{3KCNS}$$

Arsenic in the form of arsenious oxide (As_2O_3) may be readily detected by placing the smallest fragment of it in the finely drawn-out but strong point A of the tube in fig. 10, dropping in at a little distance above it a few splinters of charcoal, as at B, heating the charcoal red hot by the blowpipe flame, and then allowing the flame suddenly to impinge upon that part of the tube which contains the arsenious oxide: the latter substance readily volatilizes, and, in passing over the red-hot charcoal, parts with its oxygen, and condenses in the upper part of the tube, at or above C, as a black lustrous mirror of metallic arsenic.

Fig. 10.



At C is the metallic mirror on the inside of the tube.

At B small splinters of charcoal.

At A, a small lump of arsenious oxide.

The compounds of arsenic when heated in either flame of the blowpipe, give a most characteristic garlic odour, and volatilize, and for the most part oxidize also, depositing a white incrustation (As_2O_3) upon a more distant part of the charcoal. This oxide is frequently crystalline; and if an arsenic compound be gently heated in a tube open at both ends, and held obliquely over the lamp, crystals distinctly visible to the naked eye, and readily seen to be octahedra by the aid of a lens, condense towards the upper and cooler part of the tube. If the current of air be excluded, as would be the case were the tube closed at its lower extremity, most arsenical compounds would then volatilize unchanged: and thus, if the uncombined metal were present, a black mirror would be formed in the cool part of the tube; if one of the sulphides, a yellow or an orange sublimate; if the iodide, red crystalline scales would be deposited;—whilst it would condense as the oxide (As_2O_3), only if it so existed in the original substance, or were produced by the decomposition of the compound in which it occurred.

We now come to the consideration of the chief point in which arsenic resembles antimony, viz. the power which it possesses of combining in a similar manner with hydrogen. When arsenic compounds are exposed to the action of nascent hydrogen, they yield arseniuretted hydrogen (AsH_3), thus—

$$As_2O_3+12H=3H_2O+2AsH_3;$$

and, as has been described in the section on antimony, this change is most conveniently effected by adding to the flask in which hydrogen is being rapidly generated the solution of the arsenical compound. The gas cannot be dried by passing through oil of vitriol, which decomposes it at ordinary temperatures; but if required dry, it may be passed through a tube containing fragments of porous chloride of calcium. The test for arsenic by means of the formation of arseniuretted hydrogen is called Marsh's test, from its inventor. The student should observe the following properties of arseniuretted hydrogen, comparing them carefully with those of antimoniuretted hydrogen (see p. 200):—

α. The gas (which is colourless, has a specific gravity of 2·695, and at 40° C. condenses to a liquid, but has not yet been solidified) possesses a most peculiar odour, resembling that of garlic: it is excessively poisonous if inhaled, and has often been fatal to human life through incautiously breathing it. If the gas be kindled at a fine jet, it burns with a pale bluish white flame, giving rise to the formation of water and arsenious oxide; the latter may be seen as a white fume ascending in the current of heated air.

β. If a cold porcelain surface be depressed into the flame at the jet, a black lustrous spot of metallic arsenic will be produced, which is more readily volatilized by further heating than the corresponding antimony spot. It is caused by the cooling down of the burning gas below the temperature at which arsenic enters into combination with oxygen.

γ. If the jet be replaced by a tube similar to that represented in fig. 11, and the gas, as it passes through, be strongly heated ½ an inch or so from the shoulder of the tube, the flame being urged by the blowpipe, there appears after some little time a metallic mirror at that part where the tube has been narrowed in order to confine the reduced arsenic to the smallest possible space, and so to render the least trace obvious. This mirror is more volatile than that of antimony, and may be driven about the tube by the application of heat with the greatest ease: it is produced by a simple decomposition of the gas into its constituents.

δ. The results hitherto given as peculiar to or indicative of arsenic are, it will be remembered, the precise counterpart of those yielded by antimoniuretted hydrogen; and since we have already given the means of distinguishing the antimony mirror and spots with certainty, we now proceed to state the methods of infallibly recognizing arsenic.

1. *If an arsenic spot* be dissolved in concentrated nitric acid, the acid perfectly driven off at the temperature of 100° C., and the residual white film moistened with nitrate of silver solution, *its colour will change to yellow or red,* according to the degree of oxidation which the arsenic has undergone: if it has been converted into arsenious acid, the colour will be yellow; if into arsenic, red.

2. *An arsenic spot is immediately dissolved* when moistened with a solution of hypochlorite of sodium ($NaClO$).

3. *An arsenic spot remains undissolved* when moistened with a solution of sulphide of ammonium containing excess of sulphur (antimony dissolves at once).

To distinguish the arsenic mirror, the tube containing it is attached to an apparatus from which dry hydrosulphuric acid is being liberated; and the mirror, being warmed by a spirit lamp, is speedily converted into *the lemon-yellow tersulphide.* If the tube be now removed to another apparatus from which dry hydrochloric acid gas is being transmitted, and the gas be passed through it at the ordinary temperature, *no change occurs.* If the student will now refer to the behaviour of the antimony mirror under the same treatment (p. 202), he will see how marked is the difference.

But there is yet another means of discriminating between arsenic and antimony; it is the test of Fresenius and Babo.

An apparatus is taken similar to fig. 1 (p. 15), the tube (C) removed with its india-rubber connexion, and to the bent tube remaining is attached a tube drawn out as in the annexed figure:—

Fig. 11.

At A the heap of powder; at B the mirror; C is an opening at the extreme point.

In the generating-flask some fragments of limestone or marble, together with some water, are placed, and in the washing-bottle a little concentrated sulphuric acid. Hydrochloric acid is then poured down the funnel-tube of the generating flask; and the carbonic acid gas evolved is thoroughly dried by its passage through the oil of vitriol. The best arsenic combination to be acted upon in the present arrangement of apparatus is the arsenious (*or* ter-) sulphide (As_2S_3), a salt easily produced. The sulphide is dried at a temperature not exceeding that of boiling water, and mixed with about 12 times its bulk of a dry mixture (previously made) consisting of 3 parts of carbonate of sodium and 1 part of cyanide of potassium; the powder is now carefully introduced into the tube at A by means of a paper gutter, and the whole apparatus left for a few minutes, in order that it may become entirely filled with carbonic acid gas.

The arsenic tube is now very gently heated throughout its whole length, in order that every trace of moisture may be carried along and swept out of the apparatus by the advancing current of carbonic acid gas (carbonic anhydride), which should afterwards be allowed to pass at the rate of one bubble only per second. The part of the tube between B and A is now heated to redness with a spirit lamp, and the mixture itself also heated in the same manner with a lamp urged by the blowpipe. The arsenic, reduced by this means, condenses in the form of a mirror in the capillary tube at B; and it is said that a distinct mirror may be produced even when the quantity of arsenious sulphide operated upon does not amount to more than $\frac{1}{300}$th of a grain. *N antimony compound whatever yields a mirror under the same circumstances.*

By the action of metallic plates, aqueous solutions of arsenious oxide are but slowly reduced, while hydrochloric acid solutions deposit their metal more rapidly; zinc, cadmium, and tin reduce more quickly than copper, lead, bismuth, or antimony. Iron does not reduce the metal. These actions are not so complete with arsenic acid.

The combinations which arsenic in its basic capacity forms with salt-radicals are few in number, and can scarcely be termed salts, using that word in its ordinary restricted signification: these combinations of arsenic are, as we have stated before, of two series, the first being the series of arsenious combinations, or

ARSENIOUS SALTS, OR TER-SALTS OF ARSENIC.

Solution for the reactions:—arsenious oxide (As_2O_3) in hydrochloric acid.

In these salts the combining equivalent of arsenic is supposed to be triatomic, resembling in this respect the analogous antimonious salts. They do not, however, resemble the latter bodies either in forming those peculiar compounds with certain organic acids into which the antimony enters as a basic radical (SbO), nor in suffering the same decompositions by the action of water which antimonious salts experience.

THE CHLORIDE is decomposed by the action of water, yielding arsenious oxide and hydrochloric acid.

THE IODIDE is soluble in a considerable quantity of cold water.

THE CYANIDE and THE CHROMATE do not appear to exist.

The Oxide is obtained in commercial operations as a bye-product by heating the ores of metals containing arsenic in a current of air (roasting): in these processes the arsenic is oxidized and volatilized as the oxide (As_2O_3), which may then be collected and condensed in suitable chambers. This substance occurs in two well-defined varieties,—the *vitreous* and the *crystalline*. The first or glassy variety is produced when the oxide is fused under pressure, or sublimed and very slowly cooled; it is quite transparent, and breaks with a conchoidal fracture: the second variety is obtained by subliming the former modification and rapidly cooling the vapour, or by simply keeping the first variety for some time; it crystallizes in the regular system, either as octahedra or tetrahedra. On account of its powerful tendency to yield salts in which the arsenic is supposed to form part of a compound acid-radical, the oxide cannot be precipitated from arsenious salts by the addition of excess of the hydrates of potassium or ammonium, the following reaction taking place,—

$$2AsCl_3 + 10KHO = 6KCl + \underset{\text{arsenite of potassium.}}{K_4As_2O_5} + 5H_2O.$$

It is recognized as a compound acid-radical by the varied colours of the precipitates which its soluble combinations produce with different metallic salts: these are formed very readily by adding a solution of the desired metallic salt to a neutral solution of an alkaline arsenite, such as that of potassium ($K_4As_2O_5$) or of ammonium ($[NH_4]_4As_2O_5$). The arsenite of copper ($Cu_4As_2O_5$) is called *Scheele's green*, and the arsenite of silver ($Ag_4As_2O_5$) is *yellow*; and these salts are perhaps the most remarkable arsenites.

The composition of the arsenious oxide, or arsenious anhydride, is As_2O_3: it does not appear to form any compound with water, *i.e.* no hydrogen salt of the acid-radical As_2O_5; many of its salts, with other basic radicals, are considered bibasic, and the formula $M_4As_2O_5$ has been assigned to them.

Arsenious oxide is very soluble in the hydrates and carbonates of potassium and ammonium; in water it does not dissolve to any very great extent; its physical condition also influences its solubility. Thus 1 part of the opaque and crystalline variety dissolves in 7·72 parts of boiling water, whilst 1 part of the vitreous oxide requires 9·33 parts for solution: as the temperature decreases, the greater portion of the substance is deposited; for 80 parts of cold water are requisite to hold 1 part of the opaque oxide in solution, and 103 of cold water are required to dissolve 1 part of the vitreous variety. This substance is slightly soluble in alcohol. The presence of acids generally increases its solubility. Many arsenites dissolve in ammonium salts.

No Oxychloride exists.

The Sulphide is produced by the action of hydrosulphuric acid gas on neutral or acid solutions of arsenious salts (*e.g.* $AsCl_3$), or acidified solutions of arsenites: it is a precipitate of a very fine orange colour, which occurs native as Orpiment.

Its formula is As_2S_3.

It is very soluble in the hydrates, sulphides, and carbonates of potassium and ammonium. When dissolved in alkaline hydrates or carbonates, it yields a mixture of arsenite and sulpharsenite, perhaps thus—

$$2As_2S_3+5K_2CO_3=\underset{\text{arsenite.}}{K_4As_2O_5}+\underset{\text{sulpharsenite.}}{K_4As_2S_5}+K_2S+\overset{\nearrow}{5CO_2}.$$

When the sulphide is washed with cold water, a small quantity dissolves; but it is decomposed to a very slight extent even by boiling water, a trace only of arsenious acid passing into solution at the same time that a minute quantity of sulphuretted hydrogen escapes: this decomposition is shown more conspicuously if the sulphide be boiled with dilute sulphuric or hydrochloric acid,—boiling concentrated hydrochloric acid acting upon it with difficulty.

This substance partakes to a great extent of the features of the oxide just described, particularly in giving rise to a series of well-defined sulphur salts, known as the sulpharsenites: they belong to three distinct series, all produced from arsenious sulphide (As_2S_3), which we may here call the sulpharsenious anhydride. Thus we have these formulæ for the potassium salts of the three series—$K_4As_2S_5$, K_3AsS_3, and $KAsS_2$: the first series may perhaps be formed by the union of the second and third.

Some further observations will be offered on this subject when treating of the acid-radicals containing arsenic.

THE SULPHATE, THE CARBONATE, and THE OXALATE do not exist.

THE FERROCYANIDE is said to be produced by the action of ferrocyanide of potassium upon a solution of arsenious oxide (As_2O_3) in dilute hydrochloric acid.

Its composition is unknown.

It is decomposed by boiling nitric acid, but is insoluble in water.

THE FERRICYANIDE and THE PHOSPHATE do not appear to exist.

The other special reagents of the present and three preceding groups are not known to exert any characteristic or definite action upon arsenious combinations.

The formation of the oxide and the sulphide, together with the characteristic properties of certain "arsenites," are the chief means employed for the recognition of arsenic in arsenious compounds.

ARSENIC COMBINATIONS, OR PENTA-SALTS OF ARSENIC.

Solution for the reactions:—arsenic oxide (As_2O_5) in water.

These compounds are closely allied to the penta-salts of antimony, but partake more strongly of the acid character, and are, it would seem, confined to the forms of arsenic oxide (As_2O_5), and arsenic sulphide (As_2S_5), both of which may be considered anhydrous acids or anhydrides, and give rise to the salts termed "arseniates" and "sulpharseniates."

The Oxide (As_2O_5) is prepared by acting on arsenious oxide (As_2O_3) with nitric acid: it probably unites with the elements of water to produce arsenic acid (H_3AsO_4), which, since it easily yields up water on the application of heat, cannot be isolated. Arsenic acid forms, however, an extensive class of salts, the general formula for which is M_3AsO_4; these contain water of crystallization, and are isomorphous with the tribasic phosphates. The arseniates are frequently of very characteristic colours; the copper salt (Cu_2HAsO_4) is *greenish blue,* while the silver salt (Ag_3AsO_4) is *brownish red.*

The Sulphide is produced by the passage of hydrosulphuric acid through acid solutions of arseniates: it is a lemon-yellow precipitate.

Its formula is As_2S_5.

Athough quite insoluble in boiling water, it is very soluble in the hydrates, carbonates, and sulphides of potassium or ammonium, especially on the application of heat. When it dissolves in a soluble carbonate or hydrate, the solution contains a mixture of arseniate and sulpharseniate of the basic element introduced in the hydrate or carbonate employed. The following equation represents the action, assuming, for the sake of simplicity, the presence of oxide of potassium (K_2O) and the formation of arsenic salts with 3 equivalents of basic radical:—

$$4As_2S_5+12K_2O=\underset{\text{arseniate.}}{3K_3AsO_4}+\underset{\text{sulpharseniate.}}{5K_3AsS_4}.$$

This substance, like sulpharsenious anhydride, yields three series of salts, which are termed sulpharseniates, and to which the formulæ given below have been assigned: we take the potassium salts of the three series—$K_4As_2S_7$, K_3AsS_4, and $KAsS_3$; the first series may perhaps be formed by the union of the second with the third, for $K_3AsS_4+KAsS_3=K_4As_2S_7$.

The other reagents of the present and three preceding subdivisions do not appear to yield any characteristic reactions with a solution of arsenic acid; and, in fact, the other salts of the present series are not known to exist.

The chief means employed for the recognition of arsenic in the arsenic combinations are the precipitation and behaviour of the sulphide, and the formation of the coloured arseniates of copper and silver.

SALTS OF PLATINUM.

The metal platinum presents many features in common with palladium; it also resembles in some respects the metal tin. Platinum forms two series of combinations with salt-radicals:—the platinous salts, of which the chloride ($PtCl$) and the oxide (Pt_2O) are types; and the platinic salts, which may be represented by the chloride ($PtCl_2$) and the oxide (Pt_2O_2). As in the case of palladium, the platinous salts must be regarded as the normal saline combinations of platinum, since the platinic compounds have a great tendency to yield bodies in which the platinum constitutes part of the acid-radical contained in them. Like palladic salts, platinic salts pass very readily into the lowe series of combinations.

When heated before the blowpipe, either in the oxidizing or reducing flame, all platinum compounds are reduced to the metallic state with the greatest ease; but, owing to the infusibility of the metal, no globule, but only a black or grey powder is obtained; they impart no colour to the blowpipe flame, nor does the experiment with nitrate of cobalt yield any characteristic result. Fused with borax, platinum salts are merely reduced to the metallic state.

Platinic chloride ($PtCl_2$) readily combines with chloride of potassium to form a salt in which the platinum is supposed to form part of the salt-radical, and which is known as chloroplatinate of potassium ($KPtCl_3$); the platinic iodide, bromide, oxide, and sulphocyanide behave in a precisely similar manner, and yield perfectly analogous products. The formation of the chloroplatinates of potassium and ammonium forms one of the best means of recognizing platinum; they may always be produced by bringing the platinum into the higher stage of combination as a platinic salt, and then adding hydrochloric acid and chloride of potassium (or ammonium), when the precipitate $KPtCl_3$ (or $NH_4\,PtCl_3$) forms, either immediately, or upon agitation or addition of alcohol to the liquid.

Another test must be mentioned here as an important means of recognizing platinic salts: it is the action of stannous chloride, which when added to a platinic salt produces at first a reddish brown tint, and subsequently a gelatinous precipitate of the same colour; if the platinic solution be dilute, the colour of the liquid and precipitate is yellow. These precipitates are soluble in hydrochloric acid, giving brown solutions.

Platinic salts are reduced most quickly by iron, cobalt, zinc, cadmium, and copper, the platinum separating as a black powder, which aggregates into laminæ. Tin effects the reduction quickly, but forms a compound with the platinum. Nickel, lead, silver, bismuth, antimony, and arsenic act more slowly.

PLATINOUS SALTS, OR PROTO-SALTS OF PLATINUM.

Solution for the reactions:—platinous chloride ($PtCl$) in dilute hydrochloric acid.

The principal insoluble salts of this series are the chloride, iodide, cyanide, hydrate, sulphide, and carbonate.

The Chloride is obtained by heating platinic chloride, with constant stirring for some time, at the temperature of melting tin (228° C.). By the simple evaporation of the aqueous solution of platinic chloride at 100° C., this body is also to a certain extent produced. It is a greenish grey, or occasionally a brown powder. Its formula is PtCl. It is insoluble in water, but soluble in hydrochloric acid, and in a solution of platinic chloride. It does not dissolve in nitric or sulphuric acid.

THE IODIDE is produced by the action of iodide of potassium on platinous chloride in the presence of water, the substances being heated together. It is said to be obtained also when iodide of potassium acts upon solutions of platinous salts, which in these cases remain at first colourless, then become deep brown, and after some time deposit the iodide as a heavy rich black precipitate, leaving the supernatant liquid colourless. Its formula is PtI. It is acted upon by a hot solution of iodide of potassium, which forms iodoplatinate of potassium ($KPtI_3$) and leaves metallic platinum. The same change is slowly effected by hydriodic acid in the cold, with formation of iodoplatinic acid ($HPtI_3$). It is insoluble in water or alcohol, and even in concentrated nitric, sulphuric, or hydrochloric acid.

THE CYANIDE is produced by the action of cyanide of potassium on certain platinous salts, and by several other methods. It is a precipitate of a yellowish white colour. Its formula is PtCy. Its solubility in some menstrua varies with the method of its preparation; it is, however, always soluble in excess of cyanide of potassium, and, it would seem, also in hydrate of ammonium. It is insoluble in water and acids.

THE CHROMATE does not appear to exist.

THE HYDRATE is produced by the addition of warm hydrate of potassium, not in excess, to solutions of platinous salts, if not too dilute. It is a bulky black precipitate. Its formula is probably PtHO; but if precipitated by hydrate of sodium, the precipitate contains sodium. It is readily soluble in excess of its precipitants, forming green solutions, from which it may be reprecipitated by the addition of sulphuric acid, but which, if boiled, yield precipitates of metallic platinum. Boiling hydrochloric acid gives rise to the formation of chloroplatinic acid and metallic platinum.

The Sulphide is produced by the action of hydrosulphuric acid or soluble sulphides on solutions of platinous salts: it is a brownish black precipitate. Its formula is Pt_2S. It dissolves in large excess of sulphide of ammonium, forming a brownish red solution. It is not altered by boiling hydrate of potassium; the concentrated acids (nitrohydrochloric included) scarcely attack it even at the boiling temperature; but fuming nitric acid dissolves it after long ebullition, yielding

THE SULPHATE, a very soluble salt.

THE CARBONATE is precipitated slowly when carbonate of potassium acts upon solutions of platinous salts; carbonate of ammonium cannot be substituted for the potassium salt. It is a reddish brown precipitate, the formula of which is unknown.

THE OXALATE, THE FERROCYANIDE, THE FERRICYANIDE, and THE PHOS-

PHATE are not produced by their respective reagents, and if existing at all are soluble.

The other special reagents of the present and three preceding subdivisions are not known to give any characteristic reactions with platinous salts.

The chief means employed for the recognition of this series of salts is the behaviour of the chloride, and also the precipitation of the iodide and the sulphide.

PLATINIC SALTS, OR BI-SALTS OF PLATINUM.

Solution for the reactions: — platinic chloride ($PtCl_2$) in water.

The principal insoluble salts of this series are the iodide, the cyanide, the chromate, the hydrate, and the sulphide.

THE CHLORIDE ($PtCl_2$) is soluble.

The Iodide is produced by the action of iodide of potassium on solutions of platinic salts, and separates after standing, or more readily upon warming the mixed solutions: it is a precipitate of a brown colour.

Its formula is PtI_2.

It dissolves in alcohol with partial decomposition, giving a yellowish green solution; it is not decomposed by concentrated sulphuric acid in the cold. It dissolves readily in hydriodic acid.

THE CYANIDE is scarcely known, but appears to be soluble in cyanide of potassium, insoluble in acids.

THE CHROMATE is produced by the action of chromate of potassium on solutions of platinic salts: it is a deep red precipitate, the formula of which has not been ascertained.

The Hydrate is produced in a pure condition only when the hydrates of potassium or sodium, not in excess, are added to a solution of platinic nitrate; these precipitants throw down from most other platinic salts, potassium or sodium salts of one or other of the platinic acids. It is also produced by the action of the carbonates of the second subdivision. It is a black precipitate.

Its formula is PtH_2O_2.

This salt is soluble in excess of its precipitants, and from these solutions it is reprecipitated on the addition of acetic acid. It dissolves in the stronger acids.

The Sulphide is produced by the action of hydrosulphuric acid gas or soluble sulphides on neutral or acid solutions of all platinic salts; if the platinic solution be alkaline, partial precipitation only occurs. The chloroplatinates also yield platinic sulphide. It is a precipitate of a brownish black colour.

Its formula is $Pt_2 S_2$.

It is soluble in large excess of alkaline sulphides, especially if they contain ter- or penta-sulphides; it is insoluble in hydrochloric or nitric acid, but dissolves in nitro-hydrochloric.

THE CARBONATE does not appear to exist.

THE OXALATE exists, but is soluble.

THE SULPHATE, THE FERROCYANIDE, THE FERRICYANIDE, and THE PHOSPHATE do not appear to exist.

The other special reagents of the present and three preceding subdivisions give no characteristic reactions with platinic salts.

The formation of the insoluble chloroplatinates of potassium and ammonium, as described on p. 220, constitutes the best test for the presence of the bi-salts of platinum.

SALTS OF RHODIUM.

The metal rhodium is found associated with platinum in certain ores of the latter metal. It forms two series of combinations with salt-radicals, only one of which corresponds with a series of the platinum compounds, that is, the series of rhodious salts, of which the oxide is $R_2 O$, and the chloride RCl; the other series, the rhodic salts, is represented by the oxide ($[R_2]_2 O_3$) and the chloride ($R_2 Cl_3$).

Salts of rhodium are reduced to the metallic state when heated before the blowpipe in either flame, although, as the temperature is lowered, the finely-divided metal recombines with oxygen. They impart no colour to the flame, nor do they give any reaction with solution of nitrate of cobalt; with borax they are reduced. Most salts of rhodium have a pink or red colour.

Besides the two series of salts mentioned above, there is another series of more complicated character, derived from the rhodic salts. Of this series the salt $K_2 R_2 Cl_5 + aq$ may be taken as a representative: this salt, however, as also that of ammonium ($[NH_4]_2 R_2 Cl_5 + aq$) is comparatively soluble in water; and therefore the addition of chloride of potassium or ammonium to rhodic chloride, although giving rise to the formation of these salts—the chlororhodiates of potassium or ammonium—does not constitute so good a test for the presence of this metal as of platinum. The chlororhodiates are insoluble in alcohol. A salt of the formula $K_3 R_2 Cl_6 + 6aq$ also exists.

The addition of a solution of stannous chloride to concentrated solutions of rhodic salts produces a brownish yellow precipitate, with more dilute solutions a yellow precipitate, and with even the most dilute a yellow colouration.

Rhodic salts are reduced to the metallic state by iron, zinc, copper, and mercury, but not by silver.

RHODIOUS SALTS, OR PROTO-SALTS OF RHODIUM.

These salts are but little known; all those which have been examined, or nearly all, are insoluble in water and acids, and are generally produced by decomposing rhodic salts.

THE CHLORIDE, OXIDE, SULPHIDE, and SULPHATE are insoluble salts.

RHODIC SALTS.

These salts, although not corresponding in constitution with platinic salts, resemble them in one remarkable feature, viz. the power which the chloride and oxide possess of uniting with more chlorine or oxygen, and then, as a compound acid-radical, of assuming a basic constituent.

The chief insoluble salts of this series are the iodide, the hydrate, and the sulphide.

THE CHLORIDE is soluble.

The Iodide is produced by the addition of iodide of potassium, which darkens the solution, and produces, after a time, a slight yellow precipitate.

THE CYANIDE and CHROMATE are not produced by the appropriate reagents.

The Hydrate is produced by the action of hydrate of potassium on solutions of rhodic salts; more slowly by carbonate of potassium. It is a yellow precipitate. Hydrate of calcium produces a reddish brown precipitate. Its formula is said to be $R_2 H_3 O_3 + aq$. It is soluble in excess of hydrate of potassium, and dissolves slowly in acids.

The hydrate or carbonate of ammonium produces, after some time, in solutions of rhodic salts, a lemon-yellow precipitate of rhodiate of ammonium, which is soluble in hydrochloric acid.

The Sulphide is produced by the passage of hydrosulphuric acid gas, or the addition of soluble sulphides to warm neutral or acid solutions of rhodic salts, or to solutions of those salts in which the metal exists as part of the acid-radical. It is a brown precipitate. Its formula is probably $R_2 S_3$. It is soluble in sulphide, and to some extent in hydrate of potassium, but it is insoluble in excess of sulphide of ammonium; it dissolves in hydrochloric or nitric acid.

THE SULPHATE, THE CARBONATE, THE OXALATE, THE FERROCYANIDE, THE FERRICYANIDE, and THE PHOSPHATE, are not produced by their several reagents, or, if produced, are soluble.

The other special reagents of the present and three preceding groups are not known to give any characteristic reactions with rhodic salts.

The precipitation of the iodide, hydrate, and sulphide, and the reaction with stannous chloride, are the tests chiefly made use of for the detection of rhodic salts.

SALTS OF RUTHENIUM.

This metal is found associated with platinum, and is obtained from that portion of the ore which is insoluble in nitro-hydrochloric acid. It unites to some extent the peculiarities of platinum and rhodium, since it forms three series of salts, of which the representative oxides and chlorides are respectively Ru_2O and $RuCl$; $(Ru_2)_2O_3$ and Ru_2Cl_3; Ru_2O_2 and $RuCl_2$. The two latter series, like platinum and rhodium, yield other series of complicated constitution, in which the ruthenium is thought to constitute part of the acid-radical. In addition to these numerous compounds, this metal forms with oxygen another acid-radical, at present only known in the form of a potassium salt ($KRuO_2$). The colours of ruthenium salts are very varied.

Ruthenium has a greater tendency to combine with oxygen than any other of the metals resembling platinum, with the exception of osmium; consequently, when its salts are heated before the blowpipe, they are not reduced to the metallic state, the protoxide (Ru_2O) withstanding a white heat without parting with its oxygen. Ruthenium salts impart no colour to the flame, nor do they give any reactions with nitrate of cobalt or fused borax.

This metal possessing two series of salts both capable of furnishing compound acid-radicals containing ruthenium, yields similar precipitates with solutions of the chlorides of potassium or ammonium as do the corresponding compounds of the two preceding metals. Thus, with ruthenium salts two classes of these combinations are formed: if the ruthenium be introduced as sesquichloride, the chlorides of potassium and ammonium produce in concentrated solutions dark brown crystalline precipitates (either $K_2Ru_2Cl_5$, or $[NH_4]_2Ru_2Cl_5$), which are but slightly soluble in cold water, and insoluble in alcohol; if, on the other hand, the bichloride of ruthenium be employed, the addition of a solution of chloride of potassium gives rise, particularly in the presence of alcohol, to the precipitation of a rose-coloured crystalline salt ($KRuCl_3$).

RUTHENIOUS SALTS.

These salts are of trifling analytical importance; the chloride is almost the only soluble salt known, while the oxide, which does not dissolve in acids, is almost the only well-defined insoluble salt which has been examined.

SESQUI-SALTS OF RUTHENIUM.

These are better defined, more numerous, and more stable than ruthenious salts: they are produced by dissolving the sesqui-oxide in acids; the sesqui-oxide itself being obtained by heating the finely-divided metal before the blowpipe until it has acquired a bluish black colour.

The principal insoluble salts of this series are the hydrate and sulphide.

THE CHLORIDE is soluble.

THE CYANIDE* and THE CHROMATE do not appear to have been examined.

The Hydrate is produced by the action of the hydrates or carbonates of potassium or sodium on sesqui-chloride of ruthenium; it is also produced by a solution of phosphate of sodium, and even by one of borax, on heating. It is a blackish brown precipitate. Its formula is $Ru_2 H_3 O_3$. It is insoluble in excess of hydrate of potassium.

The Sulphide is produced by the passage of hydrosulphuric acid through a solution of the sesquichloride, or by the addition of sulphide of ammonium. Hydrosulphuric acid gives a result which is *characteristic of ruthenium*: if the gas be passed until the liquid appears nearly black, and the latter be then filtered, the filtrate will be found to have *changed from orange-yellow to a magnificent blue colour*; this change is said to be due to the reduction of the sesquichloride to the state of protochloride. The sulphide is black: its formula is probably $(Ru_2)_2 S_3$; it appears, however, always to contain an admixture of sulphur. It is not perceptibly soluble in excess of sulphide of ammonium.

THE SULPHATE and THE CARBONATE are not known, while THE OXALATE is not precipitated by oxalic acid, which only decolourizes the solution of the sesquichloride.

THE FERROCYANIDE does not appear to exist; ferrocyanide of potassium at first decolourizes the solution, and finally turns it bluish green.

The FERRICYANIDE and THE PHOSPHATE do not appear to exist.

The other special reagents of the present and three preceding subdivisions are not known to exert any characteristic actions upon the sesqui-salts of ruthenium.

RUTHENIC SALTS, OR BI-SALTS OF RUTHENIUM.

These salts are nearly as numerous and definite as the sesqui-salts of ruthenium. The chief salt from which they are obtained is the sulphate ($Ru_2 [SO_4]_2$), which is soluble in water, and is itself produced by digesting the sesqui-sulphide ($[Ru_2]_2 S_3$) in nitric acid.

The chief insoluble ruthenic salt is the hydrate.

THE CHLORIDE is not known, except in combination with chloride of potassium, &c.

THE CYANIDE and THE CHROMATE do not appear to have been obtained.

The Hydrate is produced by evaporating a solution of the sulphate to dryness in the presence of hydrate of potassium or carbonate of sodium. It is a yellowish brown gelatinous precipitate: its formula is thought to be $RuH_2 O_2$; it generally, however, retains a portion of its precipitant. It is soluble in acids, yielding solutions which are rose-coloured when concentrated, and yellow when dilute.

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* Mercuric cyanide colours a solution of sesquichloride of ruthenium blue, and produces a blue precipitate.

A Sulphide of a yellowish brown colour is produced when hydrosulphuric acid is passed through the aqueous solution of the salt $KRuCl_3$; but the liquid, unlike the solution of the sesquichloride, remains rose-coloured.

The Sulphate is soluble.

The Carbonate, Oxalate, Ferrocyanide, Ferricyanide, and Phosphate do not appear to have been examined.

The action of the other reagents upon solutions of ruthenic salts has not been ascertained.

SALTS OF IRIDIUM.

This metal also occurs associated with platinum, and is obtained from that portion of the ore which is insoluble; it is also found, combined with osmium, in separate grains, occurring in the platinum ore. In many respects it resembles ruthenium, and forms a corresponding number of combinations with salt-radicals, viz. iridious salts, represented by the oxide Ir_2O, and the chloride IrCl; sesqui-salts, represented by the oxide $[Ir_2]_2O_3$, and the chloride Ir_2Cl_3; iridic salts, represented by the oxide Ir_2O_2, and the chloride $IrCl_2$; and even a fourth series, represented by one or two members only, the composition of which does not, however, appear to have been accurately determined hitherto.

Salts of iridium, when exposed to a strong heat, are reduced to the metallic state; the metal, however, when exposed to a less elevated temperature, oxidizes. Its salts impart no colour to the blowpipe flame, are not affected by the nitrate of cobalt test, and yield no characteristic result by fusion with borax.

The sesqui- and bi-salts of iridium present the same tendency which the corresponding platinum, rhodium, or ruthenium compounds exhibit, to yield salts containing an acid-radical of which the rare metal forms a constituent. Thus, the addition of the chlorides of potassium or ammonium to sesquichloride of iridium, causes the precipitation of salts, the composition of which, disregarding the water of crystallization in all cases, is $K_3Ir_2Cl_6$, or $[NH_4]_3Ir_2Cl_6$, while the same reagents, if added to a solution of iridic chloride ($IrCl_2$), produce the salts $KIrCl_3$, or NH_4IrCl_3. These salts are comparatively soluble in water, but insoluble in alcohol. The colour of the former class of salts is olive-green; of the latter, a very dark red, approaching to black.

Iron, zinc, tin, and most other metals (excepting gold and platinum), partially precipitate iridium as a black powder.

IRIDIOUS SALTS, OR PROTO-SALTS OF IRIDIUM.

The salts of this series are better defined than ruthenious salts. The chloride (IrCl) appears to be insoluble in water, but soluble in hydrochloric acid, while with alkaline chlorides it unites to form the salts $KIrCl_2$, &c.

The hydrate, the oxide, and the sulphide appear to be well-defined insoluble salts.

The Cyanide and the Chromate do not appear to exist.

The Hydrate is produced by acting with the carbonates of potassium or sodium upon solutions of the salts $KIrCl_2$ or $NaIrCl_2$: it is a greenish grey precipitate. Its formula is probably IrHO. It dissolves in excess of its precipitants, yielding greenish yellow solutions; it also dissolves in acids, with a green colour.

The Oxide is produced by boiling the insoluble iridious chloride (IrCl) in solutions of hydrate of potassium: it is a black powder. Its formula is Ir_2O. It dissolves slightly in excess of hydrate of potassium; and the solution, if exposed to the air, passes through a purple to a *dark blue* colour. It is but slightly soluble in boiling acids.

The Sulphide is produced by the action of sulphuretted hydrogen on iridious salts: when so prepared it is of a brownish-yellow colour. Its formula is Ir_2S. It is more soluble in sulphide of potassium than is the corresponding platinous salt: it is slightly soluble in pure water, imparting to it a reddish brown colour; but this solubility is prevented by previously washing the sulphide with acidulated water, or a solution of chloride of ammonium. Nitric acid converts it into iridious sulphate.

THE SULPHATE is soluble.

THE CARBONATE, OXALATE, FERROCYANIDE, FERRICYANIDE, and PHOSPHATE do not appear to have been examined.

The other reagents of the present and three preceding groups are not known to exert any characteristic action upon solutions of iridious salts.

SESQUI-SALTS OF IRIDIUM.

These salts appear to be about as numerous as the preceding; the chloride and sulphate are soluble, while the hydrate and sulphide are insoluble.

The Hydrate is produced by the action of hydrate of potassium upon the sesquichloride: it is a bulky dark brown precipitate. This decomposition does not, however, invariably occur, even when the mixture is heated; but after a long time the liquid absorbs oxygen, becomes blue, and deposits iridic hydrate, IrH_2O_2. The brown sesquihydrate always contains potassium. It dissolves in acids, forming brown or dingy purple solutions.

THE SULPHIDE is produced by precipitating a sesqui-salt of iridium by hydrosulphuric acid gas: it is a brownish-black precipitate. Its formula is $(Ir_2)_2S_3$. It is somewhat soluble in solution of sulphide of potassium; in water also it dissolves slightly, colouring it yellow. Nitric acid converts it into the sesquisulphate.

THE SULPHATE is soluble.

The action of the other reagents of the present and three preceding groups upon sesqui-salts of iridium has not been ascertained.

IRIDIC SALTS, OR BI-SALTS OF IRIDIUM.

These salts are more easy of formation than those of the preceding series, inasmuch as they may be easily produced from any of the iridium salts of the two kinds previously described, by merely boiling their solutions in vessels exposed to the air, or still more readily by the action of nitric acid. The anhydrous iridic salts are generally black, or red if powdered; their solutions in water, red or dark brown when concentrated, and reddish yellow when dilute.

The principal insoluble iridic salts are the iodide, the hydrate, and the sulphide.

THE CHLORIDE is soluble.

The Iodide is produced by boiling iridic chloride with hydrochloric acid and iodide of potassium in solution: it is a black powder. Its formula is IrI_2. It is insoluble in water and in acids.

THE CYANIDE and THE CHROMATE are unknown.

The Hydrate is produced by the action of hydrate of potassium not only upon solutions of iridic salts with the aid of heat, but also upon any of the chlorides of iridium at the boiling temperature: it is a bulky precipitate of an indigo colour. Its formula is IrH_2O_2; but it always retains a portion of its precipitant. It is almost insoluble in dilute nitric or sulphuric acid; but it slowly dissolves in hydrochloric acid, the solution being at first blue, then green, and lastly of a reddish brown tint. Hydrate of ammonium produces a brown precipitate in solutions of iridic salts, but fails to precipitate the whole of the metal.

The Sulphide is produced by the action of hydrosulphuric acid gas upon solutions of iridic salts, which at first are decolourized; or by addition of sulphide of ammonium, not in excess, to solutions of iridic salts, or of salts in which the iridium forms part of the acid-radical: it is a brown precipitate. Its formula is Ir_2S_2. It is readily soluble in excess of sulphide of ammonium; it dissolves in sulphide of potassium also, and to a slight extent in water: by the action of nitric acid it is converted into iridic sulphate.

THE SULPHATE is soluble.

THE CARBONATE is said to be produced by the action of carbonate of potassium, not by carbonate of sodium, and is described as a reddish brown precipitate which gradually redissolves, leaving traces only of a brownish black powder.

THE OXALATE does not appear to exist; oxalic acid decolourizes solutions of iridic salts.

THE FERROCYANIDE does not appear to exist; ferrocyanide of potassium only decolourizes solutions of iridic salts.

THE FERRICYANIDE and PHOSPHATE do not seem to have been examined.

The other special reagents of the present and three preceding subdivisions are not known to yield any characteristic reactions with solutions of iridic salts.

The hydrate and sulphide are the most characteristic iridic salts; and by their formation the metal in this form of combination may be recognized.

PER-IRIDIC SALTS, OR TER-SALTS OF IRIDIUM.

Two only of these compounds are known,—the per-iridic chloride ($IrCl_3$) and the oxide (Ir_2O_3). The chloride is soluble in water, giving a red solution, while the oxide is a greenish-yellow precipitate, obtained by acting upon the salt K_3IrCl_6 ($3KCl, IrCl_3$) with hydrate of potassium,—the salt K_3IrCl_6 being formed by the union of chloride of potassium with per-iridic chloride. Per-iridic oxide is insoluble in water, and gives rise, under certain circumstances, to the salts termed iridiates ($MIrO_2$).

SALTS OF OSMIUM.

The metal osmium occurs alloyed with iridium, as already stated, in distinct grains, with platinum ores. In many of its chemical properties it is thought to resemble the arsenic, phosphorus, and nitrogen group of acid-radicals. It differs in many respects from the four preceding metals, and in no feature more remarkably than in the complete volatility of many of its compounds. Osmium forms no less than six compounds with oxygen, five of which exist in the isolated state. With other salt-radicals, such as sulphur, the combinations of this metal are not so numerous; five compounds with sulphur are known, and but four with chlorine. The first three series only appear to partake decidedly of what has been termed the normal saline character. The oxides and chlorides of these three series are the following:— Os_2O and $OsCl$; $(Os_2)_2O_3$ and Os_2Cl_3; Os_2O_2 and $OsCl_2$. There are then three series which appear to possess in a marked degree the acid character; two of these are represented by the following formulæ—Os_2O_3 and $OsCl_3$, Os_2O_5, while the third oxide, although termed osmic acid, or osmic anhydride, is scarcely known in combination with a basic radical, but generally appears as Os_2O_4. The colour of osmium salts is usually greenish, yellowish, brown, or black.

When heated in the air, osmium compounds oxidize to osmic anhydride (Os_2O_4), which is a volatile compound having a pungent odour somewhat resembling that of chlorine or bromine. This conversion into a volatile compound precludes the application of the ordinary blowpipe test.

Certain osmium salts present the usual characteristics of the allied rare metals, and yield, like them, salts in which the osmium forms part of the acid-radical. The best-defined of these salts is $KCl,OsCl_2$, or rather $KOsCl_3$, which crystallizes in regular octahedra of a dark brown colour, which dissolve in cold water, more readily in hot, and are reprecipitated on the addition of alcohol, in the form of a vermilion-coloured crystalline powder.

Osmium is precipitated from acid solutions of osmic anhydride (Os_2O_4) by iron, zinc, cadmium, and tin, as a blue or reddish black powder, partly suspended in the liquid, and giving it a blue or violet tint. On antimony, bismuth, lead, copper, mercury, and silver, osmium is deposited as a crust, without any blue colour. It is also reduced by ferrous sulphate, but not by stannous chloride.

OSMIOUS SALTS.

The Chloride ($OsCl$) is a green salt, soluble in water.

The Hydrate is precipitated by the action of hydrate of potassium on a solution of the salt $KOsCl_2$, and probably also by alkaline carbonates acting upon osmious salts. It is a greenish black precipitate, which dissolves slowly in acids, forming dull green solutions.

The Sulphide is produced by hydrosulphuric acid gas acting upon solutions of osmious salts: it is a brownish yellow precipitate, slightly soluble in water, and which, by the action of nitric acid, yields

The Sulphate, a soluble salt.

The other osmious salts are either unknown or soluble in water.

SESQUI-SALTS OF OSMIUM.

The existence of these salts appears to be doubtful.

OSMIC SALTS, OR BI-SALTS OF OSMIUM.

The Chloride ($OsCl_2$) is very soluble in water, giving a reddish yellow solution, from which the other osmic salts may be prepared.

The Hydrate is produced by the action of hydrate or carbonate of potassium on solutions of osmic chloride, osmic sulphate, or of the salt $KOsCl_3$: it is a black precipitate, which dissolves in excess of carbonate of potassium, forming a dark brown solution, from which it is reprecipitated by ebullition or on standing. It is insoluble in acids, excepting hydrochloric.

The Sulphide (Os_2S_2) is precipitated by the action of hydrosulphuric acid gas on solutions of osmic salts: it is a dark yellowish brown precipitate, which is slightly soluble in hydrate of potassium and in water, at least when recently precipitated, and before drying.

The Sulphate is soluble.

The other osmic salts are either unknown or soluble in water.

QUADROXIDE OF OSMIUM.

Osmic anhydride, or, as it is more commonly called, osmic acid, must be noticed here, as affording the principal means of recognizing osmium. The osm-iridium, or platinum to be tested for osmium, should be fused with three parts of nitre in a crucible, and the resulting dark red mass of osmiate of potassium just dissolved in water, the solution mixed with sulphuric acid which has been diluted with its own bulk of water, and then rapidly distilled. The body Os_2O_4 (osmic anhydride) condenses as a white crystalline mass in the receiver, or fuses beneath the watery portion of the distillate if the temperature be but slightly raised. It boils and evaporates below 100° C., subliming at a slight elevation of temperature, and then condensing upon a cooler part of the receiver. Its taste resembles that of oil of cloves, and its odour that of chlorine or iodine. It is extremely poisonous and corrosive. It colours all organic substances black, from the reduction of osmium upon them. It is soluble in water.

When an aqueous solution of this substance is mixed with excess of sulphurous acid gas (sulphurous anhydride), a dark blue liquid is finally produced, after the colour has passed through the stages of yellow, brown, and green. This blue compound is supposed to be an intermediate sulphate.

SALTS OF GOLD.

A considerable resemblance exists between gold and the immediately preceding metals; the compounds which it produces with salt-radicals are not, however, so numerous as those which the last five metals form. There are but two series of salts of gold, the aurous and auric salts; of these the former series is represented by the oxide Au_2O and the chloride $AuCl$, the latter by the bodies Au_2O_3 and $AuCl_3$. The latter series partakes to a great extent of the characteristics of the platinic, iridic, and similar compounds; but, in addition to these combinations, it seems probable that one member of a third series is known, per-auric oxide, Au_2O_5, which may be viewed as an anhydride.

When gold salts are heated before the blowpipe, they are reduced to the metallic state; and by an intense heat, especially with the aid of a flux (borax), or carbonate of sodium, the metal may be fused into a malleable globule, the peculiar colour of which is easily recognizable. Gold salts impart no colour to the flame, nor do they yield any characteristic reaction with nitrate of cobalt. When fused with borax, they are reduced.

Similarly to the metals recently considered, the second series of gold salts gives rise to compounds in which the gold is presumed to form part of the compound acid-radical contained in them. Thus, auric chloride ($AuCl_3$) forms with chloride of potassium a salt $KCl, AuCl_3$, or rather $KAuCl_4$, chloraurate of potassium,—while, if auric iodide be added to iodide of potassium, iodaurate of potassium ($KAuI_4$) is formed. These salts, however, being very soluble in water, do not enable us to employ their formation as a means of recognizing gold.

The reaction which auric chloride exhibits when treated with stannous chloride ($SnCl$), especially if the latter reagent contain a trace of stannic chloride ($SnCl_2$), is the most valuable and characteristic indication of the presence of gold. The solution to be tested should be acidified with a few drops of nitric acid, or a few drops of a solution of ferric chloride (Fe_2Cl_3) added to it, and then a small quantity of a solution of stannous chloride poured in: if gold be present, a reddish or purplish brown precipitate or cloud will be formed, marking the passage of the stannous solution as it mixes with the liquid under examination. It is better, in performing this experiment, to operate upon a considerable quantity of an extremely dilute gold solution (a drop or two of auric chloride in a beaker of water). This precipitate is called "*purple of Cassius*": when dry, and in fine powder, it has a dull blue tint. Its composition has been much discussed; but the formula $AuSn_3O_3+2aq$ seems a probable one. This compound may be prepared by placing an aqueous solution of auric chloride in contact with pure granulated tin. The purple of Cassius, when moist, is soluble in hydrate of ammonium, forming a solution of a magnificent reddish purple colour; boiled in hydrate of potassium, however, or in water, it remains unchanged. Boiling concentrated nitric or hydrochloric acids, or dilute sulphuric acid, act upon it but slowly, removing the tin.

Most metals precipitate gold from its solutious in the metallic state, either as a brilliant metallic deposit, or in the form of a brown powder. Some metals yield a purple powder containing gold, oxygen, and the metal used as the precipitant. Phosphorus, sulphur, and many reducing agents, separate metallic gold from its solutions.

One of the most characteristic tests for the presence of gold in a solution is the reduction of the metal effected by the addition of ferrous sulphate (Fe_2SO_4). If to a solution of gold containing 1 part of metal in 80,000 parts of water, a solution of ferrous sulphate be added, a bright blue tint is produced; even if the mixture be diluted to 320,000 parts, a pale violet colour is apparent.

AUROUS SALTS, OR PROTO-SALTS OF GOLD.

There appear to be no soluble salts of this series; the insoluble salts known are these,—the chloride, the iodide, the oxide, and the sulphide.

THE CHLORIDE is obtained in variable quantity whenever auric chloride is evaporated to dryness. The latter salt is completely converted into this compound, with loss of chlorine, if it be heated for some time to the melting-point of tin (228° C.), with continued stirring. It is a yellowish white powder. Its formula is AuCl. By water, especially on ebullition, it is resolved into auric chloride and metallic gold.

The Iodide is produced by adding a solution of iodide of potassium, not in excess, to a neutral solution of auric chloride: it is a lemon-yellow crystalline powder. Its formula is AuI. It is very soluble in excess of its precipitant. Water and acids are without action upon it in the cold; but upon raising the temperature, they decompose it into iodine and gold.

The Oxide is obtained by the action of boiling hydrate of potassium on a solution of auric chloride, or on the solid aurous chloride: it is a dark green powder. Its formula is Au_2O. It is slightly soluble in hydrate of potassium; hydrochloric acid converts it into auric chloride and metallic gold.

The Sulphide is obtained by passing hydrosulphuric acid gas through a boiling solution of auric chloride: it is a brownish black powder. Its formula is $Au_2 S$.

No other salts of this series are well known.

AURIC SALTS, OR PER-SALTS OF GOLD.

Solution for the reactions:—auric chloride ($AuCl_3$) in water.

The principal insoluble auric salts are the iodide, the hydrate, and the sulphide.

The Chloride ($AuCl_3$) is soluble.

The Iodide is produced when a solution of auric chloride is gradually added to a solution of iodide of potassium; the liquid becomes green and deposits a green precipitate, which redissolves on agitation.

Its formula is AuI_3; but it is speedily resolved into aurous iodide and iodine.

It is soluble in iodide of potassium solution.

The Cyanide is produced by adding cyanide of potassium, not in excess, to a solution of auric chloride: it is a yellow precipitate. Or it may produced by adding an excess of cyanide of potassium, and then acidifying with hydrochloric acid.

Its formula is probably $AuCy_3$.

It is insoluble, or nearly so, in dilute hydrochloric acid, but dissolves in excess of its precipitant, forming a salt to which the formula $KAuCy_4$ has been assigned, and which is much employed in electro-gilding.

The Hydrate is produced by the action of hydrate of potassium, not in excess, and of the ordinary temperature, upon a solution of auric chloride. It is a reddish yellow precipitate.

Its formula is unknown.

It dissolves in excess of its precipitant, forming aurate of potassium, probably $KAuO_2$. It is also soluble in hydrochloric acid, and in great excess of nitric or sulphuric acid.

Carbonate or hydrate of ammonium added (not in excess) to a tolerably concentrated normal solution of auric chloride produces a reddish yellow precipitate of the so-called aurate of ammonium, or fulminating gold: it detonates most powerfully after it has been carefully washed with hot water. Its constitution is obscure.

The Sulphide is obtained by the action of hydrosulphuric acid gas upon auric chloride at the ordinary temperature, or by the action of sulphide of ammonium. It is a black precipitate.

Its formula is Au_2S_3.

It dissolves in the sulphides of potassium and ammonium, and in hydrate of potassium, forming sulphaurates and aurates. From these solutions it is reprecipitated by acids in which it is insoluble. In nitro-hydrochloric acid, however, it dissolves.

The Carbonate does not exist.

The Oxalate does not exist. Oxalic acid acts upon solutions of auric salts in a peculiar manner; and this action constitutes *one of the most characteristic tests* for the presence of gold: when added to the gold solution (which should be previously evaporated in the presence of hydrochloric acid to ensure the absence of nitric acid), and the mixture boiled, the metal separates in the form of an orange-brown powder, or in minute spangles; for

$$2AuCl_3 + 3H_2C_2O_4 = 2Au + 6HCl + 6\overset{\nearrow}{CO_2}.$$

The Sulphate, the Ferrocyanide, the Ferricyanide, and the Phosphate do not appear to exist.

The other special reagents of the present and three preceding subdivisions give no characteristic reactions with auric salts.

The presence of gold is usually recognized by the formation of the malleable yellow globule, by the precipitation of the beautiful purple of Cassius, and by the reduction of the metal effected by ferrous sulphate or oxalic acid.

SALTS OF TUNGSTEN.

To this and the remaining metals of the present subdivision, many of the remarks made on the characteristics of arsenic apply. These elements do not yield true normal salts, but, uniting with several equivalents of acid-radicals, produce bodies which present the features of acid anhydrides; they are nevertheless noticed here, inasmuch as (like the analogous compounds of antimony and arsenic) they form certain insoluble combinations, such as hydrates and sulphides, which may occur among the salts of the other metals.

Tungsten forms three combinations with oxygen, two only of which are represented by combinations with other acid-radicals. These oxides are the binoxide (W_2O_2) with the corresponding chloride (WCl_2), and the teroxide (W_2O_3) with the corresponding ter-chloride (WCl_3); the remaining oxide is W_4O_5, and seems to be formed by the union of the two former.

Some of the salts of tungsten are volatile; but those which are not, when heated before the blowpipe, are usually converted into tungstic oxide, which is yellow when cold, but becomes darker on heating; in the reducing flame the oxide blackens, but does not fuse. When heated on platinum wire with carbonate of sodium, a dark yellow glass is obtained, which becomes paler, opaque, and crystalline, on cooling. Tungsten salts impart no colour to the flame. With nitrate of cobalt no reaction is obtained. Fused *with borax*, however, on platinum wire, *a clear colourless bead is formed in the oxidizing flame*; but this, if the tungstic oxide be increased in quantity, becomes slightly yellow, and even somewhat opaque while in the flame, and on cooling, milk-white. *In the reducing flame* with a moderate quantity of the oxide, the bead becomes *dark yellow while hot, and brownish yellow on cooling.* A more characteristic result is obtained if *microcosmic salt* be employed instead of borax; for *in the oxidizing flame* the bead becomes *pale yellow*, while *in the reducing flame* it is *clear blue.* If, however, iron were present, as in testing the mineral Wolfram (tungstate of manganese and iron), the bead would have been of a *bright red.*

With stannous chloride the salts of tungsten give a blue precipitate of the oxide W_4O_5. There are no tungsten compounds corresponding to the chloroplatinates, chloriridiates, and chloraurates.

TUNGSTOUS SALTS.

These compounds are but few in number, and, with the exception of the sulphide, unstable; they are also comparatively unimportant, as the analyst is almost entirely concerned with the tungstic series.

The chief insoluble salts of this series are the oxide and the sulphide.

The Chloride is a volatile liquid, decomposed by water.

The Iodide, the Cyanide, and the Chromate, are unknown.

The Oxide is produced both by decomposing the chloride (WCl_2) with water, and by acting on tungstic oxide (W_2O_3) with nascent hydrogen: the latter method at first produces the blue oxide. This oxide may also be obtained by heating tungstate of ammonium in a closed vessel: it is a brown or violet brown powder. Its formula is W_2O_2. It dissolves in hydrate of potassium, with evolution of heat and formation of tungstate of potassium (KWO_2). Hydrofluoric is the only acid which attacks it.

THE SULPHIDE is obtained by the action of heat on tungstic sulphide. It also occurs in nature. Its formula is W_2S_2. Nitrohydrochloric acid converts it into tungstic oxide and sulphuric acid.

THE SULPHATE, THE CARBONATE, THE OXALATE, THE FERROCYANIDE, THE FERRICYANIDE, and THE PHOSPHATE are unknown.

TUNGSTIC SALTS.

These compounds are chiefly recognized by the insoluble oxide and sulphide.

THE CHLORIDE is a volatile liquid, decomposed by water.

THE IODIDE, THE CYANIDE, and THE CHROMATE are unknown.

The Oxide is obtained by decomposing the salts in which tungsten occurs as part of the acid-radical: thus the native tungstate of calcium, or the artificial tungstate of sodium, yield the oxide when acted upon by hydrochloric acid. It is a yellow powder, becoming dull green when heated. Freshly precipitated it is gelatinous. Its formula is W_2O_3. This substance is soluble in the hydrates of potassium and ammonium, forming tungstates; from these solutions it is reprecipitated by nearly all acids, excess of which does not cause its re-solution (with the single exception of phosphoric acid). The organic acids, oxalic, citric, and tartaric, do not, however, effect the precipitation of tungstic oxide from tungstates, if added in excess. Tungstic oxide dissolves in the soluble sulphides of the alkaline metals.

The Sulphide is obtained by saturating a solution of an alkaline tungstate with hydrosulphuric acid, and the subsequent addition of hydrochloric acid. It is produced also when the oxide is dissolved in an alkaline sulphide, and the resulting solution reprecipitated by an acid. It is a liver-coloured precipitate. Its formula is W_2S_3. This compound is soluble in alkaline sulphides, forming a series of salts such as those described under antimony and arsenic: these solutions decompose in the air, finally yielding the tungstate and the sulphate of the alkaline metal. Tungstic sulphide dissolves in hydrate and carbonate of potassium, and less readily in hydrate of ammonium: in these cases it forms a mixture of sulphotungstate and tungstate, just as arsenic sulphide yields under the same conditions a mixture of sulpharseniate and arseniate. Tungstic sulphide is slightly soluble in water, colouring it yellow or brown; heat increases this solubility.

THE SULPHATE, THE CARBONATE, THE OXALATE, THE FERROCYANIDE, THE FERRICYANIDE, and THE PHOSPHATE are unknown.

The other special reagents of the first and three preceding subdivisions give no characteristic reactions with tungstic salts.

Tungstic salts are chiefly recognized by their oxide and sulphide; but the formation of the indigo-blue oxide by the action of nascent hydrogen is also characteristic, although not peculiar to this metal.

SALTS OF MOLYBDENUM.

This metal bears a considerable resemblance to the preceding; it forms, however, a larger number of compounds with oxygen and other salt-radicals, constituting several series, which are represented respectively by the oxides and chlorides Mo_2O and $MoCl$; Mo_2O_2 and $MoCl_2$; Mo_2O_3 and $MoCl_3$, while between the two latter oxides there exists one called the *blue oxide*, which is apparently intermediate or a compound of both ($Mo_{10}O_5$?).

Some molybdenum compounds, as the chlorides, sublime at a gentle heat; those which are fixed, usually yield the oxide Mo_2O_3 when heated in the air. When heated on platinum wire with carbonate of sodium, the oxide Mo_2O_3 gives a glass which is clear while hot, and becomes milk-white on cooling; if the bead be transferred to charcoal, and heated on it, it sinks in, and if the mass be levigated, a steel-grey powder of the metal is obtained. Molybdenum compounds impart no colour to the blowpipe flame, nor does nitrate of cobalt yield any decisive result. *With borax* the bead is *dark yellow or red in the oxidizing flame whilst hot*, and *colourless or of a bluish grey opaline appearance when cold*, according to the amount of molybdenum present; *in the reducing flame* the bead becomes *brown*, with but a minute trace of molybdenum, and *quite dark and opaque* if a little more be added. *With microcosmic salt* in the oxidizing flame the bead is *yellowish green when hot*, and *colourless when cold*, and if transferred to charcoal, becomes *opaque and bright green*; in the reducing flame the colour is of *as fine a green as that of chromium.*

The salts of molybdenum, in which that metal exists as a compound acid-radical combined with potassium, sodium, or ammonium (alkaline molybdates), yield with a small quantity of stannous chloride ($SnCl$) a blue colouration; with a larger quantity of the reagent, a blue precipitate; and with a still larger amount, a green precipitate: the blue and green precipitates dissolve in sulphuric acid, yielding blue or green solutions. There are no combinations of molybdenum known corresponding to the chloroplatinates and chloraurates.

MOLYBDOUS SALTS.

The soluble salts of this series are of a black or deep purple colour, or, if dilute, of a brownish green tint; the insoluble salts are dark grey or black. They are generally obtained from the oxide Mo_2O_3, by dissolving it in hydrochloric acid and adding zinc: the liquid becomes at first blue, then reddish brown, and finally black; the molybdous chloride ($MoCl$) formed, and present in the solution, is separated from the chloride of zinc by excess of hydrate of ammonium, which precipitates it as hydrate. Molybdous salts do not oxidize so readily as those of the next series.

The principal insoluble molybdous salts are the chromate, the hydrate, the sulphide, the ferrocyanide, and the phosphate.

THE CHLORIDE and THE IODIDE are soluble.

THE CYANIDE is unknown.

THE CHROMATE is produced by chromate of potassium.

The Hydrate is obtained by adding the hydrates of potassium or ammonium, or the carbonates of potassium or sodium, to solutions of molybdous salts: it is a brownish black precipitate. Its formula is probably MoHO. It is insoluble in excess of alkaline hydrates, slightly soluble in the carbonates of potassium, sodium, and ammonium. Recently precipitated, it dissolves slowly in acids; but after ignition, by which process it is converted into the oxide (Mo_2O), it is quite insoluble in acids.

The Sulphide is produced by the action of hydrosulphuric acid gas, as a brownish black, and by sulphide of ammonium as a yellowish brown precipitate. Its composition has not been ascertained. It dissolves readily in sulphide of ammonium.

THE SULPHATE, formed by dissolving molybdous hydrate in sulphuric acid, is soluble.

THE CARBONATE is not known.

THE OXALATE is a dark grey precipitate, slightly soluble in excess of oxalic acid.

THE FERROCYANIDE is produced by the action of ferrocyanide of potassium, as a dark brown precipitate.

Its composition is unknown.

It is soluble in excess of its precipitant, and also in excess of hydrate of ammonium, yielding dark brown solutions. From its ammoniacal solution it is reprecipitated upon the addition of chloride of ammonium.

THE FERRICYANIDE is produced by the action of ferricyanide of potassium, as a reddish brown precipitate.

THE PHOSPHATE is produced by the action of phosphate of sodium, as a dark grey precipitate, soluble in excess of molybdous chloride.

The action, on solutions of molybdous salts, of the other special reagents of the present and three preceding groups, has not been ascertained in all cases.

Molybdous salts are generally recognized by the formation of the insoluble hydrate and sulphide.

MOLYBDIC SALTS.

These salts are prepared by dissolving molybdic hydrate in the various acids. They may also be prepared by digesting excess of metallic molybdenum in a solution of per-molybdic oxide (Mo_2O_3) in that acid whose molybdic salt we desire to obtain. In the anhydrous state these salts are black; but when in solution, or combination with water, red or reddish brown.

The principal insoluble salts are the chromate, the hydrate, the sulphide, the ferrocyanide, and the phosphate.

THE CHLORIDE and THE IODIDE are soluble.

THE CYANIDE is unknown.

THE CHROMATE is produced by the action of chromate of potassium. It is precipitated in greyish yellow flakes, which are insoluble in water.

The Hydrate is obtained by the action of the hydrates of potassium or ammonium, or of the carbonates of potassium or sodium, on solutions of molybdic salts. It is a reddish brown precipitate, which becomes nearly black on drying. The formula is probably MoH_2O_2. It is insoluble in excess of the alkaline hydrates, but soluble in the carbonates; slightly soluble in water, to which it imparts a yellow or red tint. It is reprecipitated from its aqueous solution by chloride of ammonium and some other salts. It dissolves in acids.

The Sulphide is produced after some time, by the passage of hydrosulphuric acid gas through molybdic salts, as a brown precipitate, or by the addition of sulphide of ammonium, as a yellowish brown precipitate. Its formula is Mo_2S_2. It dissolves in sulphydrate of ammonium. It is easily soluble in nitric acid, while it is decomposed by sulphuric acid on ebullition, evolving the gas termed anhydrous sulphurous acid (SO_2), and yielding a blue solution.

THE SULPHATE and THE OXALATE are soluble.

THE CARBONATE does not appear to exist.

THE FERROCYANIDE is produced by ferrocyanide of potassium, as a dark brown precipitate insoluble in excess of its precipitant, but soluble in hydrate of ammonium; from this solution it is reprecipitated by chloride of ammonium.

THE FERRICYANIDE is produced by ferricyanide of potassium, as a dark brown precipitate insoluble in excess of its precipitant.

THE PHOSPHATE is produced by phosphate of sodium, as a brownish white precipitate.

The action, on bi-salts of molybdenum, of the other special reagents of the present and three preceding subdivisions, has not, in many cases at least, been well ascertained.

The hydrate and the sulphide are the most characteristic salts of the series.

Between the bi-salts and ter-salts of molybdenum, the characteristic BLUE OXIDE of molybdenum occurs: it is obtained by the oxidation of the lower, or the reduction of the higher oxides.

Its formula is doubtful.

It is soluble in water, but reprecipitated from its aqueous solution by chloride of ammonium.

TER-SALTS OF MOLYBDENUM.

The oxide of this series is commonly called molybdic acid; it is really anhydrous molybdic acid, or molybdic anhydride, and yields salts in which the molybdenum constitutes part of the acid-radical. Other ter-salts of molybdenum exist in addition to the oxide (Mo_2O_3): they are chiefly formed by dissolving the latter in acids.

The chief insoluble compounds of this series are the oxide, the sulphide, the ferrocyanide, and the ferricyanide.

THE CHLORIDE, THE IODIDE, and THE CYANIDE, if existing at all, are probably soluble.

THE CHROMATE is unknown.

The Oxide is produced by oxidizing one of the lower oxides or hydrates by nitric acid, or by roasting the native sulphide. It is a white crystalline body, which melts at a red heat to a yellow liquid. Its formula is Mo_2O_3. It dissolves in the hydrates of potassium and ammonium, forming the molybdates $KMoO_2$, and NH_4MoO_2. There are several series of molybdates—basic, normal, and acid; the alkaline molybdates only, such as those just mentioned, are readily soluble in water. The oxide (Mo_2O_3) dissolves in 500 parts of cold, or 960 of hot water; before ignition it is soluble in many acids.

The Sulphide is produced by saturating a solution of an alkaline molybdate with hydrosulphuric acid gas, whereby an alkaline sulphomolybdate is first formed ($KMoO_2+2H_2S=KMoS_2+2H_2O$); the sulphomolybdate is then decomposed by the addition of hydrochloric acid ($2KMoS_2+2HCl=Mo_2S_3+H_2S+2KCl$). It is a brown precipitate. Acid solutions of molybdic anhydride (Mo_2O_3) are coloured blue when hydrosulphuric acid is first passed through them: after a time, a brown precipitate of the ter-sulphide containing free sulphur occurs; but the molybdenum is never wholly precipitated. The formula of the brown sulphide is Mo_2S_3. It dissolves in the hydrates and sulphides of the first subdivision, forming the sulphomolybdates.

THE SULPHATE, obtained by acting on molybdate of barium with sulphuric acid, is soluble.

THE CARBONATE does not exist.

THE OXALATE is soluble.

THE FERROCYANIDE is produced by adding ferrocyanide of potassium to an acid solution of molybdic anhydride (Mo_2O_3), and appears as a reddish precipitate, which dissolves in excess of its precipitant, and also (with decomposition) in hydrate of ammonium.

THE FERRICYANIDE is produced by ferricyanide of potassium as a pale reddish brown precipitate, which is soluble in hydrate of ammonium.

THE PHOSPHATE is scarcely known.

The other special reagents of the present and three preceding subdivisions are not known to give any decisive results with solutions of ter-molybdic salts, or of the molybdates.

The most characteristic salts of this series are the oxide and the sulphide, together with the derivatives of the oxide known as the "molybdates."

SALTS OF VANADIUM.

This metal resembles molybdenum in forming a considerable number of different combinations with oxygen and other salt-radicals. The first series, that of vanadious salts, is represented only by the oxide V_2O, which is dissolved by nitric acid alone, and which, if exposed to the air, passes into vanadic oxide. The second series, that of vanadic salts, is represented by the oxide V_2O_2, and the chloride VCl_2,—whilst the third series, that of the ter-salts of vanadium, is typified by the oxide V_2O_3 (the anhydrous vanadic acid) and the chloride VCl_3. Between the oxides of the two latter series there are certain other oxides of a blue or green colour.

The metal zinc precipitates metallic vanadium from its solutions.

VANADIC SALTS, OR BI-SALTS OF VANADIUM.

The anhydrous salts of this series are green or brown, while their solutions are of a blue colour, which varies in intensity with different salts, and which often changes to a green by oxidation. The oxide is prepared by the ignition of vanadite of ammonium; it dissolves slowly in acids.

The principal insoluble salts are the cyanide, the hydrate, the ferrocyanide, and the ferricyanide.

THE CYANIDE is formed by digesting the hydrate in a solution of hydrocyanic acid, as a dark-brown gelatinous mass, which is soluble in cyanide of potassium.

THE CHLORIDE, THE IODIDE, and THE CHROMATE are soluble.

The Hydrate is best produced by precipitating a vanadic salt (through the solution of which hydrosulphuric acid gas has been passed, in order to reduce the vanadic oxide) by slight excess of carbonate of sodium. The precipitate is greyish white: and the liquid should be left perfectly colourless; for if blue, carbonate of sodium enough has not been added, while, if green, vanadic oxide is present. The grey precipitate, if exposed to the air, speedily becomes brown. Its composition has not been ascertained. It dissolves in excess of alkaline hydrates, forming brown solutions containing *vanadites*; from these solutions it is reprecipitated by more alkaline hydrate. In neutral or acid alkaline carbonates it dissolves, forming pale blue solutions.

Solutions of vanadic salts (also the insoluble hydrate), when mixed with excess of hydrate of ammonium, yield a brown precipitate of *vanadite* of ammonium, in which the vanadium enters as a constituent of the acid-radical. Vanadite of ammonium is insoluble in hydrate of ammonium, but dissolves in water, with a brown colour.

The Sulphide is not produced by hydrosulphuric acid gas; but by the addition of alkaline sulphydrates (*e. g.* NH_4HS) to solutions of vanadic salts, a brownish black precipitate is obtained. Its composition is V_2S_2. It dissolves in excess of its precipitants, forming solutions of a beautiful purplish colour; it dissolves also in a boiling solution of carbonate of sodium, with a brownish yellow colour. It is not affected by hydrochloric or sulphuric acid; but by nitric acid it is converted into vanadic sulphate, which is a soluble salt.

The Carbonate and the Oxalate seem to be soluble.

The Ferrocyanide is produced by the action of ferrocyanide of potassium: it is a bulky, lemon-yellow precipitate, which becomes green by exposure to the air.

The Ferricyanide is produced by ferricyanide of potassium, as a gelatinous yellow-green precipitate.

The Phosphate is soluble.

In most instances the other special reagents of the present and three preceding subdivisions have been found to give no characteristic reactions with vanadic salts; the action of others has not been ascertained.

The insoluble hydrate, sulphide, and ferrocyanide are the most characteristic vanadic salts.

TER-SALTS OF VANADIUM.

The oxide of this series (V_2O_3) plays the same part as the corresponding oxide of molybdenum; and this metal occurs in nature in the form of a vanadiate, just as molybdenum occurs as a molybdate. Several salts, however, containing other salt-radicals than oxygen, belong to the ter- or pervanadic series. The vanadiates are colourless, yellow, or occasionally red,—while the ter-salts are also generally red or yellow, and give solutions of the same colour: by the action of reducing agents (*e.g.* H_2S *or* $H_2\bar{O}$) they become blue.

The Chloride (VCl_3) is a liquid which dissolves in large excess of water, forming a pale yellow solution, which decomposes in a few days, becoming green or blue, and evolving chlorine, and forming the bichloride VCl_2.

The Iodide and the Chromate are unknown.

The Oxide is produced by the action of nitric acid on the lower oxides, or directly from the ores; it may also be obtained by the action of the hydrates of potassium or ammonium on vanadic salts. It is a reddish yellow or brick-red precipitate. Its formula is V_2O_3. It dissolves in the hydrates of potassium and ammonium, forming vanadiates, the solutions of which are yellow or brown (most metallic vanadiates are soluble). 1 part of ter-oxide requires 1000 parts of boiling water for solution. It dissolves readily in acids.

The Sulphide is not produced by hydrosulphuric acid gas; but by the addition of sulphydrate of ammonium a brown precipitate falls. Its formula is V_2S_3. It dissolves in the hydrates, sulphides, and carbonates of the first subdivision, forming sulphovanadiates. It is not decomposed by sulphuric acid.

The Sulphate is soluble.

The Carbonate does not exist.

The Oxalate is soluble.

The Ferrocyanide is produced by ferrocyanide of potassium, as a beautiful green precipitate, which is insoluble in acids.

THE FERRICYANIDE is unknown.

THE PHOSPHATE is yellow, and comparatively soluble in water.

The other special reagents of the present and three preceding subdivisions have generally been found to give no characteristic reactions with ter-salts of vanadium.

Ter-salts of vanadium may be recognized best by the formation and reactions of the oxide, and also of the sulphide.

SALTS OF SELENIUM AND TELLURIUM.

These two bodies, which will be fully treated of in the next Chapter, are mentioned here because they are precipitated as sulphides from their acid solutions, in conjunction with the members of the fourth subdivision, by the passage of hydrosulphuric acid gas.

The Sulphide of selenium is yellow. Its formula is SeS_2. It dissolves in excess of sulphydrate of ammonium.

If the sulphide be dissolved in nitrohydrochloric acid and evaporated to dryness, selenious anhydride (SeO_2) will be obtained, which may be recognized by the following reactions:—

a. If a portion be dissolved in water, with which it combines to form selenious acid ($H_2 SeO_3$), and some hydrochloric acid and a strip of zinc be then introduced into the solution, the zinc will become coated with *a copper-coloured film*, and subsequently *red or red-brown flocks of selenium* are deposited.

β. If another portion of the selenious anhydride, or some of the precipitated selenium of experiment *a.* be dried at a gentle heat, and then volatilized before the blowpipe flame, *a peculiar odour, resembling that of horse-radish*, is perceived.

The Sulphide of tellurium is a dark brown precipitate. Its formula is TeS_2. It is soluble in excess of sulphydrate of ammonium, and in boiling solutions of the hydrates of potassium and sodium, yielding salts known as sulphotellurites.

We now subjoin a method for the analysis of the 2nd Section of this subdivision, supposing that we have one only of its important members present. The Table for the 1st Section has been already given (p. 190).

On pp. 246 and 247, the synopsis of reactions will be found.

Analysis of Subdivision IV.

Section II.—Salts of metals which form Sulphides soluble in Sulphide of Ammonium.

The salt may be one of TIN, ANTIMONY, ARSENIC, PLATINUM, or GOLD.

<table>
<tr><td colspan="5">If, as is probable, it is a sulphide, wash thoroughly; add hydrochloric acid; boil, and add, while boiling, a few drops of nitric acid, drop by drop, until the precipitate is dissolved. Pour the solution down the funnel-tube of a hydrogen apparatus fitted with an "arsenic-tube" (see p. 213). Apply the heat of a spirit-lamp, urged by a blowpipe, to the arsenic-tube. The formation of a mirror after the lapse of a few minutes indicates</td></tr>
<tr><td rowspan="3">the presence of Arsenic or Antimony.
Dissolve the mirror out of the tube by a drop of hot nitric acid; evaporate in a porcelain dish to dryness at 100° C.; redissolve in a drop of water, and add nitrate of silver.
A yellow or red precipitate indicates Arsenic; no change indicates Antimony.</td><td colspan="4">If no mirror is obtained when the action in the hydrogen apparatus has ceased, brush the black powder which is found, carefully from the surface of the zinc; it may contain Tin, Antimony, Platinum, or Gold.
Wash it by decantation, boil it with hydrochloric acid, and filter.</td></tr>
<tr><td colspan="2">Any residue indicates the presence of Platinum or Gold.
Boil in hydrochloric acid, and add a drop or two of nitric acid, just to dissolve; boil to decompose any nitric acid remaining, then add some concentrated solution of oxalic acid, and keep warm for some time.</td><td colspan="2">Perfect solution indicates the presence of Tin or Antimony.
Boil the hydrochloric solution, add a drop or two of nitric acid, or a crystal of chlorate of potassium; cool, and add excess of solution of sesquicarbonate of ammonium: the formation of a precipitate insoluble in excess indicates</td></tr>
<tr><td>A brown precipitate, or yellow metallic spangles, indicates the presence of Gold.</td><td>If no precipitate occurs, the solution should be neutralized with ammonia; a yellow precipitate will indicate the presence of Platinum.</td><td>the presence of Tin.
This should be verified by reducing this precipitate by fusion with cyanide of potassium, dissolving the washed metal in hydrochloric acid, and testing it with protochloride of mercury: a white or grey precipitate indicates Tin.</td><td>The solution may contain Antimony.
Pass hydrosulphuric acid gas into it, and then acidify with hydrochloric acid: a reddish-orange precipitate indicates the presence of Antimony.</td></tr>
</table>

TABLE OF

REACTIONS.	Sn. (Stannous salts.) (see page 192)	Sn. (Stannic salts.) (see page 196)	Sb. (Antimonious salts.) (see page 204)	Sb. (Antimonic salts) (see page 207)
Chloride	—	—	—	—
Iodide	yellowish white	orange	—	—
Cyanide.........	*	*	—	—
Chromate	yellowish white	yellow	brownish yellow	—
Hydrate.........	white	white	⸸	white
Oxide...........	olive	white	white	white
Oxychloride ...	white	—	white	—
Sulphide	brownish black	yellow	orange-red	orange-yellow
Sulphate	—	—	white	—
Carbonate	*	*	*	*
Oxalate	white crystalline	—	white	—
Ferrocyanide...	white	brownish yellow	white	—
Ferricyanide...	white	—	—	—
Phosphate......	white	white	white	—
BLOWPIPE REACTIONS.	With carbonate of sodium in the reducing flame (on charcoal), stannous and stannic salts yield a malleable globule of tin. The incrustation on the charcoal is white.		With carbonate of sodium in the reducing flame (on charcoal), antimonious and antimonic salts yield a brittle globule of antimony, and a bluish white incrustation.	

* Signifies that a precipitation occurs, but not

⸸ Signifies that the precipitate which is formed consists of

REACTIONS.

As. (Arsenious salts.) (see page 215)	**As.** (Arsenic salts.) (see page 218)	**Pt.** (Platinic salts.) (see page 222)	**Au.** (Auric salts.) (see page 234)
—	—	—	—
—	—	brown	green
—	—	?	yellow
—	—	deep red	—
—	—	black	reddish yellow
white	white	—	brown
—	—	—	—
yellow	yellow	brownish black	black
—	—	—	—
—	—	*	*
—	—	—	—
?	—	—	—
—	—	—	—
—	—	—	—
Arsenious and arsenic salts, when heated to redness on charcoal, in the reducing flame, emit a characteristic garlic odour, and, when heated in a tube (closed at one end) with a mixture of carbonate of sodium and charcoal, give a black lustrous mirror. (See page 210.)		The metal is reduced, and appears as a black or grey powder, when platinum salts are heated with carbonate of sodium (or alone) in either flame.	The metal is reduced, and appears as a malleable globule, if a sufficient temperature has been attained.

of the salt indicated in the horizontal column.

the salt indicated in the horizontal column next below.

CHAPTER VII.

DETECTION OF THE ACID-RADICALS IN THEIR COMPOUNDS.

THE reactions of the basic radicals having been fully described in the preceding Chapter, the student may now acquaint himself with the tests by the application of which the presence or absence of the acid-radicals is determined.

The slightest consideration will show that, to a great extent, the same means which serve for the detection of the basic constituents of salts will also be available for the recognition of their acid-radical; for it is obvious that, if a soluble chloride produces a white, curdy, insoluble precipitate in solutions of silver salts, a solution of a silver salt will prove an equally certain test for the presence of a soluble chloride. Still, owing to the numerous broad distinctions, physical and chemical, which exist between the two classes of radicals themselves, other means of no less decisive nature are at hand in abundance, by the employment of which, the class and also the individual characteristics of the acid constituent present in any given salt can be determined.

A few remarks upon each of these methods of testing may not be out of place as an introduction to the present Chapter. And, firstly,—*of the detection of the acid-radical by the formation of certain saline compounds of well-defined chemical or physical properties.* As just now stated, a very large number of salts (easily recognizable by such characteristics as the following,—solubility in certain menstrua and insolubility in others, or insolubility in all, or again, the possession of some remarkable features of form or colour) are employed in common, as the products by the formation of which the presence either of the basic or of the acid-radical contained in them can be safely predicated.

Thus chloroplatinic acid ($HPtCl_3$), usually employed as the test for the presence of potassium, may itself be recognized by the employment, as a reagent, of a soluble salt of potassium. Sulphuric acid, often employed to detect the presence of barium, may itself be recognized infallibly by a soluble barium salt. The presence of mercury in a solution may be evidenced by the action of a soluble chromate, which, in its turn, may be recognized by a mercury salt. Lead may be detected by hydrosulphuric acid, and hydrosulphuric acid by lead. By these instances it may therefore be seen, that the same reaction differently applied may be used to indicate both a basic and an acid-radical. Nor, be it observed, is it necessary that the hydrogen salt of the acid-radical be employed; in almost every instance (as in the third of the examples just given), any salt will be as efficient as the acid itself or salt of hydrogen, provided only it be soluble: thus, in the cases cited above, chloroplatinate of sodium is as good a precipitant as chloroplatinate of hydrogen, *i.e.* chloroplatinic acid; the sulphides and sulphates of potassium, sodium, and ammonium act equally well with the acids themselves, *i.e.* the corresponding salts of hydrogen, the hydrosulphuric and sulphuric acids. And indeed it frequently happens that the desired reaction does not take place when the acid is employed, but only upon the addition of some other than the hydrogen salt; the reason of this may be stated to consist in this,—that the hydrogen compound or acid liberated at the time of the formation of the new compound, either keeps that compound completely in solution, or prevents its entire precipitation. Thus, if hydrosulphuric acid (H_2S) be added to ferrous chloride ($FeCl$), no sulphide of iron (Fe_2S) falls, since this ferrous sulphide is soluble in hydrochloric acid, the necessary complementary product of the reaction. But if, on the other hand, a soluble sulphide, such as the sulphide of potassium, sodium, ammonium, barium, strontium, or calcium, be added to ferrous chloride, an immediate precipitation of ferrous sulphide occurs; for it is no longer the chloride of *hydrogen*, *i.e.* hydrochloric acid, which forms the secondary product of the reaction, but the chloride of a far more powerfully basic radical, a chloride therefore which exerts no decomposing or solvent action on the ferrous sulphide: in this case the reaction is as follows:—

$$K_2S + 2FeCl = \underset{\text{precip.}}{Fe_2S} + 2KCl.$$

Occasionally, as the student will have already observed in the reactions employed to detect the basic radicals, the recognition of substances does not depend upon the formation of a salt of extreme insolubility, or of remarkable physical features of form or colour, but upon *the production of a body which is readily volatilizable, and possessed of an easily recognized odour.*

The detection of the basic radical ammonium depends upon a decomposition of this kind, which the following equation will recall:—

$$NH_4Cl + KHO = NH_4HO + KCl.$$

In this case the hydrate of ammonium is resolved immediately into the gas ammonia (NH_3) and water (H_2O); and ammonia is remarkable for a peculiar and pungent odour. Upon a similar formation of an odorous and volatile body depends, in great measure, the recognition of the presence of the acetic acid-radical. To the substance supposed to be or contain an acetate, sulphuric acid and alcohol (C_2H_5HO) are added, and the mixture heated. The former reagent will produce, with an acetate, acetic acid (*i.e.* acetate of hydrogen) ($HC_2H_3O_2$ *or* $H\bar{A}$); and this, acting in the *nascent* state on the alcohol or hydrate of ethyle (C_2H_5HO, *or* EHO), yields a fragrant body, the acetate of ethyle, thus—

$$H\bar{A}+EHO=H_2O+\underset{\substack{\text{acetate of}\\\text{ethyle.}}}{E\bar{A}.}$$

The acetate of ethyle, or acetic ether, is volatilized at the temperature employed, and, possessing a most peculiar and agreeable fruity odour, is easily identified.

We will now consider briefly the second method of detecting acid-radicals, by *the actual elimination of the acid-radical itself, and the subsequent identification of its peculiar properties.* And here it must be borne in mind, that a great distinction must necessarily exist between the behaviour of the acid- and basic radicals, simply on account of their inherent nature. The basic radicals with which the student has been made acquainted, and which occur in great abundance, are (with a few exceptions) elements, and, moreover, they are all (ammonium, mercury, and hydrogen only excepted) solid at the ordinary temperature. On the other hand, however, more than half of the acid-radicals of common occurrence, and almost all the rarer ones, are compound bodies, which are characterized by great diversity of physical condition, several being gaseous, some liquid, and others solid. The fact of a body being compound frequently adds to our facilities of recognizing it; for, in addition to any peculiarities which it may exhibit as a compound, we have other clues to its presence in the characteristic properties which its constituents may individually manifest when, by its decomposition, they have been set free. In fact, those acid-radicals which are complex cannot, with but few exceptions, be obtained in the isolated condition, but are resolved either into other and generally simpler compounds, or into their elementary constituents. Whilst, therefore, we indubitably prove the presence of an elementary acid-radical by obtaining it in the free state and examining its properties, we no less distinctly show the existence of a compound acid-radical when we observe some of the well-ascertained features of the decomposition which it undergoes when liberated.

To illustrate the foregoing cases, we will take two examples. When chlorine acts upon a bromide, decomposition ensues, with separation of the element bromine, the peculiar features of which, such as the yellow colour which it imparts to a solvent, or the orange tint which starch-paper exposed to its vapour assumes, or its peculiar suffocating odour, may be immediately recognized—

$$MBr+Cl=MCl+Br.$$

But if, on the other hand, we deal not with an elementary, but with a compound acid-radical, such as that existing in the oxalates, by treating the salt in such a manner as to decompose it into new and characteristic products, the latter frequently furnish us with good proof of the previous existence of the compound acid-radical. These products, in the case of the oxalates, are the two gases carbonic anhydride (CO_2) and carbonic oxide (CO); and they are obtained by the action of sulphuric acid upon oxalates, the decomposition being aided by heat, thus—

$$M_2C_2O_4+2H_2SO_4=M_2SO_4+\underbrace{H_2SO_4, H_2O}_{\text{hydrate of sulphuric acid.}}+CO_2+CO.$$

The more easily recognizable gaseous product, or at least the more characteristic, is carbonic oxide (CO), which, when the carbonic anhydride (CO_2) has been removed by an appropriate agent, may be readily kindled on the application of a light, burning with a blue flame.

The preceding hints will perhaps suffice to show the general principles upon which the detection of acid-radicals is based, and to exhibit the chief points in which their reactions resemble, and also those in which they differ from the reactions of the basic radicals. We now proceed to detail these reactions, adopting the subdivisions which have already been chosen in the description of the acid elements. The classification of the acid-radicals is thus entirely founded upon the chemical characters of each group, and not upon their similarity in an analytical point of view.

1. Salts containing the acid-radicals of Subdivision I. (page 17).

SALTS OF CHLORINE, BROMINE, IODINE, AND FLUORINE, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

2. Salts containing the acid-radicals of Subdivision II. (p. 18).

SALTS OF OXYGEN, SULPHUR, SELENIUM, AND TELLURIUM, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

3. Salts containing the acid-radicals of Subdivision III. (p. 18).

SALTS OF CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

4. Salts containing the acid-radicals of Subdivision IV. (p. 18).

SALTS OF NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY, AND OF THE COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

SUBDIVISION I.

SALTS OF CHLORINE, BROMINE, IODINE, AND FLUORINE, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

The three first-named members of this Subdivision present the most striking resemblance to each other, both in the salts which they form by simple union with the basic radicals, and also in those in which they exist as a part only of a compound acid-radical. Fluorine differs in many respects, and in none more decisively than in not forming compound acid-radicals similar to those which the other members of the group are known to yield.

In the further arrangement of the present Subdivision, as also in the arrangement of those which follow, we take advantage of the differing chemical constitution of the members, and not of any analytical characteristics which they may present. In accordance with this plan, we now proceed to divide the present group into three Sections, as follows:—

SECTION I.—SALTS OF CHLORINE, BROMINE, IODINE, AND FLUORINE.

The chlorides, bromides, iodides, and fluorides.

SECTION II.—SALTS OF THE ACID-RADICALS WHICH CONTAIN CHLORINE, BROMINE, AND IODINE COMBINED WITH OXYGEN.

The hypochlorites, chlorites, chlorates, perchlorates, hypobromites, bromates, iodites, iodates, and periodates.

SECTION III.—SALTS OF THE ACID-RADICALS WHICH CONTAIN CHLORINE, BROMINE, AND IODINE COMBINED WITH METALS.

The chloropalladiates, chloroplatinates, chlororhodiates, chlororutheniates, chloriridiates, and chloraurates.

SECTION I.—*The chlorides, bromides, iodides, and fluorides.*

SALTS OF CHLORINE, BROMINE, IODINE, AND FLUORINE.

The radicals of this Section are monobasic, and when combining with monatomic basic radicals yield compounds having the general formula MR. They are detected by both the methods described in the preliminary observations to the present Chapter, *i. e.* both by presenting to a soluble chloride, bromide, iodide, or fluoride a soluble salt of some basic radical known to form, with the acid element sought for, an insoluble salt of easily recognizable properties,—and also by submitting the chloride, bromide, or iodide to such decomposing influences as are calculated to eliminate their acid-radical.

SALTS OF CHLORINE, OR CHLORIDES.

These salts are for the most part soluble in water, sparingly soluble in alcohol, and nearly insoluble in ether. Their formulæ vary according to the atomic nature of the combined basic constituent; but the following are the most usual:—

$$M_2Cl,\ MCl,\ M_2Cl_3,\ MCl_2, \text{ and } MCl_3.$$

When heated before the blowpipe on charcoal, the deportment of chlorides differs according to the nature of the combined basic radical: if the metal belongs to Subdivision I., the compound fuses, and sinks into the charcoal; if to Subdivision II., it fuses and generally remains as a molten mass upon the charcoal: the chloride of magnesium is the exception here; for, as it cannot exist in the presence of aqueous vapour, it suffers decomposition, and leaves a white residue of oxide. Some of the remaining chlorides, such as those of silver and lead, fuse without change; others again, as those of tin, antimony, and arsenic, volatilize, whilst others, such as those of platinum and gold, decompose into chlorine and the metal.

If a bead of microcosmic salt be fused upon a platinum wire, and cupric oxide (Cu_2O) added to it until the bead is saturated, if a chloride be then introduced, and the bead submitted to the heat of the blowpipe jet, *a blue colour will be imparted to the flame.*

THE HYDROGEN SALT (HCl), or hydrochloric acid, is a transparent colourless gas at ordinary temperatures, which, at 45°·3 C., and under the pressure of 40 atmospheres, becomes a colourless liquid, highly dispersive of light. 1 volume of water dissolves 480 volumes of the gas.

The principal insoluble salts of this acid-radical are—as the student will readily recollect—the cuprous, argentic, plumbic, mercurous, and platinous chlorides.

THE CUPROUS SALT is produced by the action of a soluble cupric salt on a solution of stannous chloride. Its formula is Cu_2Cl. It is insoluble in water, but soluble in most acids.

The Argentic or Silver Salt is produced by the action of a soluble silver salt on hydrochloric acid or any other soluble chloride: it is a white curdy precipitate, which assumes a grey tinge on exposure to light.

Its formula is $AgCl$.

It is insoluble in water, soluble to a slight extent in solutions of certain chlorides and in concentrated acids, and easily dissolves in hydrate of ammonium, in cyanide of potassium, and in hyposulphite of sodium.

THE MERCUROUS SALT is produced by the action of a soluble mercurous salt (*e. g.* mercurous nitrate [Hg_2NO_3]) on hydrochloric acid, or a soluble chloride. It is a dense white precipitate. Its formula is Hg_2Cl. It is but slightly soluble in water.

THE LEAD SALT is produced by the action of a soluble lead salt on hydrochloric acid or any soluble chloride. It is a white crystalline precipitate. Its formula is PbCl. It is dissolved by a large quantity of cold water, but is soluble in a much smaller amount of boiling water.

The platinous and other insoluble chlorides are not employed in testing for chlorine.

Many of the remaining chlorides are soluble either in water or in dilute hydrochloric acid.

The other methods by which this acid-radical is identified are the following:—

a. Concentrated sulphuric acid and peroxide of manganese (Mn_2O_2) are added to a chloride, and the mixture warmed: the sulphuric acid liberates hydrochloric acid—

$$2MnCl + H_2SO_4 = 2HCl + Mn_2SO_4;$$

the peroxide then acts upon the hydrochloric acid—

$$4HCl + Mn_2O_2 = 2MnCl + 2H_2O + 2Cl.$$

It is believed that bichloride of manganese ($MnCl_2$) is first formed, and then decomposed into the protochloride (MnCl) and free chlorine.

The free chlorine thus produced is recognized by its odour and bleaching properties, while it is distinguished from bromine and iodine by the absence of any coloured reaction with starch.

β. When 1 part of chromate of potassium and 3 parts of oil vitriol are mixed with 1 part of the supposed chloride, and the resulting pasty liquid heated in a test-tube, to which a dry cork and bent tube have been fitted, the other end of the bent tube dipping into a test-tube free from any trace of water, and kept cool, *a blood-red liquid* distils over, to which the name *chlorochromic acid*, and the formula $CrCl_3, Cr_2O_3$, have been given:—

$$^{*}3KCrO_2 + 3NaCl + 3H_2SO_4 = CrCl_3, Cr_2O_3 + 3KNaSO_4 + 3H_2O.$$

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* Possibly this reaction is more simple,—

$$KCrO_2 + NaCl + H_2SO_4 = CrO\,Cl + KNaSO_4 + H_2O.$$

In this case the product usually termed chlorochromic acid might be con-

If to this red distillate a few drops of ammonia-water are added, a yellow liquid is obtained, which is a solution of chromate and chloride of ammonium,—

$$CrCl_3, Cr_2O_3 + 6NH_4HO = 3NH_4Cl + 3NH_4CrO_2 + 3H_2O;$$

and if into this solution, after the addition of a slight excess of acetic acid, a few drops of nitrate of silver be introduced, a beautiful crimson precipitate will be obtained, thus—

$$NH_4CrO_2 + AgNO_3 = NH_4NO_3 + \underset{\text{crimson ppt.}}{AgCrO_2}.$$

SALTS OF BROMINE, OR BROMIDES.

The bromides bear the closest resemblance to the chlorides; they are isomorphous with them. They are for the most part soluble in water, but sparingly soluble in alcohol, and nearly insoluble in ether. Bromine is monobasic; but when combined with biatomic acid-radicals, it yields salts having the formulæ already given as those of the various chlorides.

Heated before the blowpipe on charcoal, the bromides exhibit the same deportment as the corresponding chlorides. They colour the flame green when fused with a bead of microcosmic salt saturated with cupric oxide.

The Hydrogen Salt (HBr), or hydrobromic acid, is a transparent colourless gas at ordinary temperatures, which, however, liquefies at 33°·3 C., and solidifies at —37°·7. Hydrobromic acid is very soluble in water, the solution possessing the property of dissolving a large quantity of bromine, forming a red liquid.

The insoluble bromides are those which contain the same basic radicals as the insoluble chlorides, viz. the cuprous, argentic, mercurous, and plumbic bromides. The platinous bromide is unknown.

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sidered the chloride of a compound basic radical *chromyle* (CrO), thus CrO, Cl. The reaction of this body with hydrate of ammonium will be thus expressed in an equation:—

$$CrO, Cl + 2NH_4HO = NH_4Cl + NH_4CrO_2 + H_2O.$$

$3(CrO,Cl) = CrCl_3, Cr_2O_3$.

The Cuprous Salt is obtained by the action of a solution of a cuprous salt on a soluble bromide. It is a white precipitate. Its formula is Cu_2Br. It is insoluble in water, but soluble in hydrate of ammonium, and in hydrochloric and hydrobromic acids. In nitric acid it dissolves with decomposition; but boiling sulphuric acid does not decompose it.

The Argentic or Silver Salt is produced by the action of a soluble silver salt on hydrobromic acid or other soluble bromides. It may also be obtained by adding the silver solution very cautiously to a mixture of hydrochloric and hydrobromic acids, when the bromide is first removed from the solution. It is a yellowish white curdy precipitate.

Its formula is $AgBr$.

It is slowly dissolved (but in considerable proportion) by a concentrated solution of ammonia; it is but very slightly soluble in other ammonium salts; it dissolves, however, to some extent in a boiling solution of chloride of ammonium. It is slightly soluble in a concentrated solution of an alkaline bromide; and when boiled with an alkaline iodide, it is wholly converted into iodide of silver (AgI). Bromide of silver dissolves slightly in concentrated hydrochloric or hydrobromic acid; boiling nitric acid has no decomposing action on it, but boiling sulphuric acid alters it slightly.

The Mercurous Salt is obtained by the action of a soluble mercurous salt (*e.g.* Hg_2NO_3) on a soluble bromide: it is a yellowish white precipitate. Its formula is Hg_2Br. It is insoluble in ammonium salts, but, on ebullition with some of them, undergoes decomposition into mercuric bromide and mercury.

The Lead Salt is obtained by adding a soluble lead salt to hydrobromic acid or other soluble bromide. Its formula is $PbBr$. It is soluble in solutions of some ammonium salts, especially on warming; it is almost insoluble in cold water, and but sparingly soluble in hot. It is somewhat more soluble in dilute acids.

The other insoluble bromides are not employed in testing for bromine.

Many of the remaining bromides are soluble either in water or in hydrobromic acid.

The other methods by means of which this acid-radical is identified are the following:—

a. Bromine is readily distinguished by the properties which it possesses: it is eliminated from the bromides just as chlorine from the chlorides, by the joint action of sulphuric acid and binoxide of manganese. A remarkable peculiarity, however, belongs to the combinations of this substance with salt-radicals when they are treated with sulphuric acid, which, whether dilute or concentrated, when acting upon chlorides, liberates hydrochloric acid only; but with the bromides the reaction varies with the strength of the acid employed: if the acid be weak, hydrobromic acid is set free, just as in the case of the chlorides—

$$2MBr + H_2SO_4 = 2HBr + M_2SO_4;$$

but if the acid be concentrated, the hydrobromic acid, which we may suppose to be first produced, is decomposed by a portion of the sulphuric acid, with formation of sulphurous acid and separation of *bromine*, thus—

$$2MBr + 2H_2SO_4 = 2Br + H_2O + H_2SO_3 + M_2SO_4.$$

This is by no means the only method of liberating bromine; for this element is set free equally well when chlorine gas is passed (not in excess) into the solution of a bromide, or when to the latter a few drops of concentrated nitric acid are added: in the first case the bromine is set free by its place being occupied by the chlorine; in the second process by a reaction similar to that exercised by sulphuric acid, given above in the form of an equation. The tests for the detection of bromine have been already given (p. 21), but may be here advantageously recapitulated.

Besides its peculiar odour (which is very suffocating and offensive) and its bleaching properties, the colour of liquid and of gaseous bromine (a colour which it imparts to solvents) may be applied for its recognition, in the following manner:—

1. Some chlorine water is added to the solution of the bromide; the bromine is liberated, and dissolves in the water present, imparting to it a yellow colour. To the coloured solution enough ether is now added to form a distinct stratum upon the

surface of the liquid, and the whole shaken in a narrow vessel, and then allowed to rest in order to admit of the ether rising to the surface and forming a layer there. This will contain all the free bromine of the solution, dissolved in it in virtue of the greater solubility of bromine in ether than in water; and its colour will vary from a *pale yellow* to a *deep orange*, according to the proportion of bromine present. The chlorine water in this experiment must be added cautiously; but if, after one treatment as above described, and separation of the etherial layer, the solution should still give a yellow colour with chlorine, the shaking with ether, &c. may be again repeated if it is desired to effect a perfect separation of the bromine. The etherial solution is shaken with a few drops of hydrate of potassium solution; evaporated to dryness; and then the ignition of the residue will give rise to the formation of bromide of potassium. Previously to the ignition, bromate of potassium would be present in addition:

$$6Br + 6KHO = \underset{\substack{\text{bromide}\\ \text{of potas.}}}{5KBr} + \underset{\substack{\text{bromate}\\ \text{of potas.}}}{KBrO_3} + 3H_2O.$$

2. The starch-test is a good method of distinguishing bromine, as well as iodine, from chlorine. When bromine-vapour is allowed to come into contact with starch paste (as by introducing a glass rod smeared with this substance into a test-tube in which bromine vapour is being disengaged), a yellow colour is produced if that acid-radical be present in minute quantity, or, if in larger proportion, a rich orange tint. Or the test may be applied by mixing the bromide with some starch paste in a porcelain dish, warming the mixture over the lamp, and dropping into its centre one drop of concentrated nitric acid: the liberated bromine immediately colours the starch.

β. When a bromide is distilled with chromate or bichromate of potassium and sulphuric acid, a brown distillate passes over (p. 255), which dissolves in hydrate of ammonium, forming a colourless solution, which is precipitated white by nitrate of silver: this distillate is only bromine set free by the action of the sulphuric acid on the bromide; for there is no bromochromic acid known.

SALTS OF IODINE, OR IODIDES.

The iodides present the closest analogy with the bromides and chlorides, with which they are, for the most part, isomorphous. A large number of them are soluble in water; a few, chiefly those of Subdivisions I. and II., somewhat soluble in alcohol; but nearly all are insoluble in ether.

Heated before the blowpipe on charcoal, the iodides behave in a similar manner to the corresponding bromides. They colour the flame of a fine *green* colour when fused with a bead of microcosmic salt saturated with cupric oxide.

THE HYDROGEN SALT (HI), or hydriodic acid, is a transparent colourless gas at ordinary temperatures, which, however, liquefies with cold, and solidifies at about —51° C. It is very soluble in water, the solution possessing the property of dissolving some quantity of iodine, forming a brown solution.

The chief iodides possessing remarkable features are the cuprous, argentic, plumbic, mercurous, mercuric, bismuthic, and palladious salts. The platinous iodide is also insoluble.

THE CUPROUS SALT is produced by the action of a soluble cuprous salt on a solution of an iodide. The cuprous salt employed is often prepared extemporaneously, by adding to a solution of the cupric salt sulphurous acid or ferrous sulphate, before mixing it with the iodide: the ferrous sulphate is most frequently employed for this purpose, and acts as follows:—

$$2Cu_2\,SO_4 + 2Fe_2\,SO_4 = (Cu_2)_2\,SO_4 + (Fe_2)_2\,(SO_4)_3.$$

The cuprous iodide is a white precipitate, with a tinge of brown. Its formula is $Cu_2\,I$. It is slightly soluble in hydrochloric acid; but when heated with nitric or sulphuric acid, it is completely decomposed, with evolution of iodine.

The Argentic or Silver Salt is produced by the action of a soluble silver salt on the solution of hydriodic acid or of a soluble iodide. It is a pale yellow precipitate.

Its formula is AgI.

It is soluble to a considerable extent in concentrated solutions of chloride of potassium or ammonium, also in concentrated solutions of mercuric nitrate. It is scarcely soluble in concentrated hydrate of ammonium solution, 1 part requiring 2510 parts of the strongest ammonia-water to dissolve it. Dilute acids are without action on it; but concentrated nitric and sulphuric acids dissolve it with separation of a small proportion of iodine.

THE MERCUROUS SALT is produced by the action of a soluble mercurous salt on hydriodic acid or a soluble iodide; but the salts should be mixed in equivalent proportions, to obtain a precipitate free from metallic mercury or a mercuric salt. Mercurous iodide is a green precipitate. Its formula is $Hg_2 I$. It dissolves partially in concentrated solutions of most soluble iodides, and in hydriodic acid; but it is decomposed into mercuric iodide and mercury by the action of the reagents just mentioned, —by certain chlorides and by hydrochloric acid. It dissolves in about 2375 parts of water, but is insoluble in alcohol.

The Mercuric Salt is produced by the action of a soluble mercuric salt on hydriodic acid or a soluble iodide; the addition of equivalents of the iodide and of the mercuric salt causes a perfect precipitation. It is a magnificent scarlet crystalline precipitate, which, when it begins to form, has a bright yellow tint.

Its formula is HgI.

It is very soluble in the alkaline iodides and chlorides, also in many ammonium salts; in most mercuric salts it is also very soluble. In water and ether it dissolves sparingly, but more abundantly in hot alcohol. It is soluble in hydriodic and hydrochloric acids.

The Lead Salt is obtained by the action of a soluble lead salt upon hydriodic acid or a soluble iodide. It is an orange-yellow crystalline precipitate.

Its formula is PbI.

It dissolves in concentrated solutions of most soluble iodides, also in chloride of ammonium, but not in other ammonium salts. 1 part dissolves in 1235 parts of cold, and in 194 parts of boiling water, and may thus be purified from the oxyiodide, which is insoluble in water; it is slightly soluble in alcohol. Acids exert a slight decomposing influence upon it.

THE BISMUTH SALT is produced by the action of a soluble salt of bismuth on a solution of a soluble iodide. It is a brown crystalline precipitate. Its formula is BiI_3.

The Palladious Salt is obtained by the action of palladious chloride on hydriodic acid or a soluble iodide.

Its formula is PdI.

It is insoluble in water, alcohol, ether, and hydriodic acid.

The other insoluble iodides are not employed in testing for iodine.

Many of the remaining iodides are soluble in water or in hydriodic acid.

The recognition of iodides by the separation of their acid-radical, is even more easy and certain than the detection of bromides by similar means. Iodine is liberated just as chlorine and bromine by the conjoint action of sulphuric acid and binoxide of manganese; but iodides differ from chlorides, and resemble bromides, in the elimination of their acid constituents by the action of concentrated sulphuric acid employed without the addition of binoxide of manganese.

a. Iodine, by whatever method liberated, may be recognized by the properties which have been already stated as belonging to this acid-radical (p. 22).

1. Not only by its characteristic odour may this element be detected, but, if it be present in some quantity in the substance under examination, it may be recognized by its separation in minute bluish black crystals when strong sulphuric acid is added to the aqueous solution of an iodide. If this solution become very hot on the addition of the acid, or if it be afterwards heated over the lamp, the beautiful rich violet-coloured vapour of iodine will float over the surface of the liquid, and gradually condense upon cooler parts of the test-tube in glistening crystals of a bluish black. If chlorine (not in excess) be passed into the aqueous solution of an iodide, and a little ether (or, better, benzole) be shaken up with the mixture, the ether or benzole will carry up the whole of the free iodine present to the surface of the

liquid, and appear there, after standing, as a red or beautiful violet-coloured stratum. The iodine may then be converted into iodide of potassium, and tested with nitrate of silver in the usual manner.

2. The starch-test is as good a test for iodine as for bromine, and perhaps more delicate. If a glass rod which has been dipped in starch paste be immersed into a tube containing the violet vapour of iodine, a *blue* colour will be produced, which passes into a black if much iodine be present. The same effect is arrived at by dissolving a small quantity of an iodide in water, adding a little starch paste, then a drop or two of pure sulphuric acid, and lastly a very minute trace of nitrous acid, or of a soluble nitrite (*e.g.* nitrite of potassium KNO_2), or else a very small quantity of chlorine water.

β. When an iodide is distilled with bichromate of potassium and sulphuric acid, no iodochromic acid is obtained, vapours of iodine only being evolved.

SALTS OF FLUORINE, OR FLUORIDES.

This acid-radical never having been isolated, the precise analogies which it may present to the three preceding elements are unknown; its salts have, however, some features in common with the chlorides, bromides, and iodides, although presenting also many points of difference. The salts of fluorine are often isomorphous with these last-named salts, crystallizing generally in the regular system.

Heated upon charcoal, many of the fluorides fuse, but without suffering decomposition. They impart no colour to the blowpipe flame when added to a bead of microcosmic salt saturated with cupric oxide.

The perfectly dry HYDROGEN SALT of fluorine (HF), or hydrofluoric acid, is believed to be a transparent colourless gas under ordinary conditions, and to have no action on glass, &c.; but, as usually obtained in the form of an aqueous solution, hydrofluoric acid is remarkable as one of the most powerful solvents known, dissolving such bodies as the silicic, titanic, molybdic, and tungstic anhydrides, which are quite unattacked by all other acids.

Fluorides vary considerably as to their solubility in water. The fluorides of the first subdivision are soluble; those of the second subdivision insoluble, thus exhibiting a remarkable contrast with the chlorides, bromides, and iodides of the same group of metals. Most of the other *protofluorides* (MF) are insoluble, or but sparingly soluble in water, though slightly more soluble in aqueous hydrofluoric acid; they are often resolved by excess of water, or on the application of heat, into oxyfluorides. The sesqui-, bi-, and terfluorides are very soluble: the terfluoride of antimony, unlike the corresponding chloride, bromide, and iodide, is not decomposed by water with formation of the oxyfluoride.

Since the fluorides of the second subdivision of the basic radicals are insoluble, fluorine may be recognized by the formation of these salts, as also by that of the cuprous and plumbic fluorides.

The Barium Salt is produced by the action of a soluble barium salt upon hydrofluoric acid or a soluble fluoride: it is a white precipitate.

Its composition is BaF.

It is insoluble in water, but readily dissolves in hydrochloric, hydrofluoric, or nitric acid.

THE STRONTIUM SALT is produced by the action of a soluble strontium salt upon a solution of a fluoride: it is a white precipitate, insoluble in water and most acids.

The Calcium Salt is produced by adding a soluble calcium salt to hydrofluoric acid or a soluble fluoride: it is generally a mere gelatinous precipitate, hardly perceptible; but on the addition of a little hydrate of ammonium, it becomes more visible.

Its composition is CaF.

This precipitate is somewhat soluble in solutions of ammonium salts; it is almost insoluble in water or in hydrofluoric acid, sparingly soluble in cold hydrochloric or nitric acid, but more soluble in these acids when hot.

The Magnesium Salt is produced by the action of a soluble magnesium salt on solutions of fluorides: it is a white precipitate, nearly insoluble in water and acids.

The Cuprous Salt appears to be insoluble both in water and in hydrofluoric acid, but soluble in strong hydrochloric acid.

The Silver Salt is soluble.

The Lead Salt is produced by the action of soluble lead salts upon hydrofluoric acid or a soluble fluoride: it is a white precipitate, which easily fuses into a thick yellow liquid. Its formula is PbF. It is but slightly soluble in water or hydrofluoric acid, more abundantly in hydrochloric or nitric acid.

The Mercurous Salt is not produced by the action of soluble mercurous salts upon solutions of fluorides, but only by sublimation.

The Mercuric Salt is soluble.

The Bismuth Salt appears to be soluble.

The Platinous and Palladious Salts are not known.

The other insoluble salts are not employed in testing for fluorine.
Many of the remaining fluorine salts are soluble in water.

Although the isolation of fluorine cannot be accomplished, we are at no loss for a method of recognizing this elementary salt-radical, on account of the very remarkable affinity which it possesses for silicon; this fact is taken advantage of in two ways:—

1. In the etching test. A soluble or insoluble fluoride is placed in the dry state in a platinum capsule. A watch-glass is then taken to serve as a cover; a little wax is melted in it, and allowed to run over every part, and through this coating a device is scratched with a wooden point, so as to expose the glass beneath. Several drops of strong sulphuric acid are then poured into the capsule, which is closed immediately afterwards with the coated glass, and then gently warmed, taking care not to melt the wax. The design traced on the cover will be found distinctly etched after the removal of the wax from the glass by means of turpentine or other solvent. The change described may be thus expressed, in the form of two equations:—

$$2MF + H_2SO_4 = 2HF + M_2SO_4;$$

$$Si_2O_3 + 6HF = 2SiF_3 + 3H_2O.$$

Thus the hydrofluoric acid first formed acts upon the silicon contained in the glass, yielding water and the gaseous fluoride of silicon, the formation of which is itself an excellent test for fluorine.

2. The terfluoride of silicon test. A fluoride mixed with some quantity of sand (Si_2O_3) and of sulphuric acid, when heated, evolves, as has been already shown, gaseous terfluoride of silicon. The above mixture may be made in a test-tube (perfectly dry), fitted with a cork and bent tube dipping under water in another glass vessel. When heat is applied, the terfluoride is immediately evolved, and, passing through the water, suffers the following decomposition:—

$$3SiF_3 + 2H_2O = \underset{\text{gelat. ppt.}}{HSiO_2} + H_3Si_2F_9.$$

So rapid is the decomposition when the gas meets the water, that the aperture of the delivery tube soon becomes blocked with the silica deposited; to avoid this, the point of the delivery-tube dips beneath a layer of mercury (fig. 7, p. 65). The formation of hydrofluosilicic acid ($H_3Si_2F_9$), in the experiment just described, furnishes another proof of the presence of fluorine in the substance examined; this acid may be recognized by adding to the filtrate from the gelatinous precipitate of silica, a few drops of chloride of barium solution, when, after agitation, we obtain a gelatinous precipitate of silicofluoride of barium ($Ba_3Si_2F_9$), a salt with which the student has already become familiar.

SECTION II.—*The hypochlorites, chlorites, chlorates, perchlorates, hypobromites, bromates, iodites, iodates, and periodates.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN CHLORINE, BROMINE, AND IODINE COMBINED WITH OXYGEN.

Of the acid-radicals containing chlorine combined with oxygen, those existing in the acids or hydrogen salts, termed hypochlorous, chloric, and perchloric, are the most important in an analytical point of view.

SALTS OF THE HYPOCHLOROUS RADICAL, OR HYPOCHLORITES.

A few only of these salts are known; they are extremely unstable. The mode in which they are commonly produced is by passing chlorine either into a solution of hydrate of potassium or over solid hydrate of calcium; the temperature of the materials must not be allowed to be more than lukewarm.

$$2CaHO+2Cl=CaClO+CaCl+H_2O.$$

The hypochlorites are decomposed on a slight increase of temperature, and give no characteristic blowpipe reactions.

The anhydrous hypochlorous acid (Cl_2O) is a yellow gas, very soluble in water, and possessing a peculiar odour distinct from, and yet recalling, that of chlorine. Water dissolves more than 100 times its volume of the gas, and yields the hydrogen salt, or hypochlorous acid ($HClO$). The gas (Cl_2O) is a powerful bleaching agent, yielding up both oxygen and chlorine, and indeed, from its great instability, decomposing readily, with explosion, when gently heated.

No insoluble hypochlorites are known; the aqueous solutions of the hypochlorites acquire a most sickly and disagreeable odour by contact with organic matter; and in sunlight, or when heated, decompose into chloride and chlorate, with evolution of oxygen and chlorine.

α. Hypochlorous acid, or a hypochlorite, may be immediately detected by warming the solution of the former, or by adding an acid to that of the latter, when, in either instance, their own peculiar odour is converted into the characteristic odour of chlorine. The following equations represent the metamorphoses of a hypochlorite:—

$$MClO+HCl=HClO+MCl;$$

$$2HClO=H_2O+\overset{\nearrow}{2Cl}+\overset{\nearrow}{O}.$$

β. If a solution of a hypochlorite be mixed with a solution of a manganese salt, a brownish black precipitate of the bihydrate (MnH_2O_2) falls, thus—

$$CaClO+2MnCl+3H_2O=CaCl+\underset{\text{brown-black ppt.}}{2MnH_2O_2}+2HCl.$$

γ. If a solution of a hypochlorite be mixed with a solution of a lead salt, at first a white precipitate of plumbous chloride (PbCl) is produced (it must be remembered that hypochlorites are almost invariably accompanied by chlorides); this white precipitate, however, speedily becomes brown, being converted, with evolution of chlorine, into the binoxide of lead (Pb_2O_2):

$$2PbCl+2CaClO=\underset{\text{brown ppt.}}{Pb_2O_2}+2CaCl+2Cl.$$

δ. If a solution of a hypochlorite be mixed with oxide of silver (Ag_2O), the latter is rapidly converted into the chloride (AgCl) with violent evolution of oxygen, derived partly from the oxide of silver, and partly from the hypochlorite employed. If the same experiment be performed, only substituting the nitrate for the oxide of silver before used, a black precipitate, formerly believed to be peroxide of silver (Ag_2O_2), is deposited.

ϵ. The hypochlorites oxidize hydrosulphuric with formation of sulphuric acid and separation of sulphur; by the addition of more hypochlorite, the sulphur is itself oxidized.

The hypochlorites are recognized by the tests α, β, γ, and δ, just described, and by their powerful bleaching action on indigo, litmus, and other vegetable colouring matters.

SALTS OF THE CHLOROUS RADICAL, OR CHLORITES.

The chlorites do not occur in the course of analysis. The formula of the anhydrous acid is Cl_2O_3, and that of the salts $MClO_2$. Most of the known chlorites are readily soluble in water; the argentic and plumbic chlorites are, however, nearly insoluble: the latter is a beautiful pale yellow precipitate, crystallizing in scales. The chlorites differ from the hypochlorites in the fact that their bleaching power is not destroyed by a solution of arsenious oxide in nitric acid.

SALTS OF THE CHLORIC RADICAL, OR CHLORATES.

These salts are far more stable under ordinary circumstances than the hypochlorites; the most common salt is that of potassium, which is generally prepared by passing chlorine into a solution of hydrate of potassium, and not preventing the consequent rise of temperature:

$$6KHO+6Cl=KClO_3+3H_2O+5KCl.$$

The chlorates, when heated on charcoal before the blowpipe, deflagrate with great brilliancy, the charcoal being consumed and converted into carbonic anhydride, and a residue of chloride, oxide, or metal left, according to the nature of the basic radical present, unless indeed complete volatilization occur. The chlorate of barium imparts a green, that of strontium a crimson colour to the blowpipe flame.

When heated alone in the solid state, the chlorates are decomposed, any residue being either a chloride or an oxide, an evolution of oxygen also occurring.

THE HYDROGEN SALT ($HClO_3$), or chloric acid, is only known dissolved in water; in this state it is decomposed when heated above 40°.

No insoluble chlorates are known; some of the important reactions of acids, &c. upon these salts are given in subsequent paragraphs.

a. The chlorates are easily recognized by the peculiar decompositions which their acid-radical suffers. When a chlorate is mixed with concentrated sulphuric acid, chloric acid ($HClO_3$) is evolved, thus—

$$2MClO_3 + H_2SO_4 = 2HClO_3 + M_2SO_4;$$

as the temperature rises, the chloric acid decomposes, thus—

$$3HClO_3 = HClO_4 + H_2O + \overset{\nearrow}{Cl_2O_4}.$$

This decomposition is accompanied by a peculiar crackling noise, and the evolution of the greenish yellow gas, hypochloric anhydride (Cl_2O_4), which, if the temperature rises too high, explodes with great violence. This gas has a most peculiar, almost aromatic odour, quite unlike that of chlorine; but no sooner has the explosion and decomposition of the gas into oxygen and chlorine taken place, than the suffocating smell of the latter gas may be directly perceived. Sulphuric acid acts much more readily upon chlorate of potassium when chloride of potassium is also present.

β. When a minute quantity of a chlorate is produced, and then rubbed gently in a mortar with a very small particle of sulphur, frequent and sharp detonations occur.

γ. If a chlorate be mixed with an organic substance, such as sugar, the mass placed in a dish, and then a single drop of concentrated sulphuric acid allowed to fall from a glass rod upon the mixture, vivid combustion takes place, due, of course, to the liberation of chloric acid and its oxidizing effect upon the carbon and hydrogen of the sugar.

δ. A solution of a chlorate, even if somewhat dilute, when mixed cold with tincture of litmus, and then a few drops of strong sulphuric acid added, bleaches the litmus. This test forms one of the best characteristics by means of which we can distinguish between the chlorates and nitrates.

ε. A solution of a chlorate mixed with a solution of indigo in sulphuric acid bleaches the indigo on the application of heat, just as a nitrate would do.

ζ. Hydrosulphuric acid does not decompose a solution of chlorate of potassium.

The tests α. and δ. are among those most usually employed for the recognition of the chlorates.

SALTS OF THE PERCHLORIC RADICAL, OR PERCHLORATES.

The perchlorates are remarkably stable salts; the perchlorate of potassium withstands a higher temperature than the chlorate without decomposition, and is among the first products formed when chlorate of potassium is heated, since it is not itself resolved into chloride of potassium and oxygen, except at a more elevated temperature.

Perchlorates, when fused upon charcoal, explode with violence; but with combustible bodies in general they do not detonate so violently as the chlorates.

THE HYDROGEN SALT ($HClO_4$), or perchloric acid, is a white crystalline solid, which melts at 45° C., and is very soluble in water.

The potassic perchlorate is the only salt of the series which may be considered comparatively insoluble.

The Potassium Salt is obtained by the addition of certain soluble potassium salts (*e.g.* the carbonate [K_2CO_3]) to an aqueous solution of perchloric acid, or by fusing chlorate of potassium at a gentle heat and for some time, and, after cooling, separating the chloride of potassium formed, from the perchlorate by water. It is a white crystalline powder.

Its formula is $KClO_4$.

It dissolves in 65 parts of water at 15° C., and in a smaller quantity of boiling water: it is quite insoluble in alcohol.

The Ammonium Salt is produced by the addition of hydrate or carbonate of ammonium to aqueous perchloric acid: it is a white crystalline precipitate, very slightly soluble in alcohol, but requiring only 5 parts of cold water for solution.

The barium and all the other known salts of the perchloric radical are soluble in water.

The perchlorates are detected by the precipitation of the insoluble potassium salt, while they are distinguished from the chlorates by not becoming yellow on treatment with sulphuric acid (concentrated) in the cold.

Of the acid-radicals containing bromine combined with oxygen, that existing in the acid (or hydrogen salt) termed bromic acid is the only important one in an analytical point of view.

SALTS OF THE HYPOBROMOUS RADICAL, OR HYPOBROMITES.

From the similarity of bromine to chlorine, and from the peculiar properties of the solution formed when bromine is added to the carbonates or hydrates of potassium or sodium, the alkali being in excess, it is extremely probable that a series of hypobromites exist of the formula MBrO, possessed of bleaching powers like the hypochlorites, and decomposing, when ignited, into bromide of the metal and oxygen. They are of no analytical importance.

SALTS OF THE BROMIC RADICAL, OR BROMATES.

These salts resemble the chlorates in their general characters, and are produced generally by the action of bromine in excess on the hydrates and carbonates of the alkaline metals, with simultaneous formation of bromides.

The bromates, when heated with charcoal or other combustibles, deflagrate or detonate just as the chlorates. They are also decomposed when heated alone.

The Hydrogen Salt ($HBrO_3$), or bromic acid, is known as dissolved in water; but it is readily decomposed upon the application of heat.

The insoluble salts of this series which are most important are the argentic, mercurous, mercuric, and plumbic bromates.

The Potassium and Ammonium Salts are soluble.

The Barium Salt is produced by the action of a soluble barium salt on a moderately concentrated solution of bromate of potassium: it is a white crystalline precipitate, which requires 130 parts of cold, and 24 parts of boiling water for its solution.

The Strontium, Calcium, and Magnesium Salts are soluble.

The Cuprous Salt does not exist; the Cupric Salt is soluble.

The Argentic or Silver Salt is produced by the action of a soluble silver salt on a solution of bromic acid or other soluble bromate. It is a white precipitate.

Its formula is $AgBrO_3$,

This salt is insoluble, or nearly so, in water and in nitric acid, but dissolves in hydrate of ammonium.

THE MERCUROUS SALT is produced by the action of a soluble mercurous salt on solutions of bromates or of bromic acid: it is a yellowish white precipitate.

Its formula is Hg_2BrO_3.

It is decomposed by washing with water, into bromic acid and a basic salt (Hg_2O, Hg_2BrO_3); in hydrochloric acid it dissolves, with formation of mercuric chloride; it is dissolved less easily by nitric acid.

THE MERCURIC SALT is produced by the action of soluble mercuric salts upon solutions of bromic acid or of other bromates: it is a white precipitate.

Its formula is $HgBrO_3+aq$.

It is soluble in 650 parts of cold, and in 64 parts of boiling water; it is dissolved by hydrochloric and by nitric acid.

THE LEAD SALT is produced by the action of concentrated solutions only of lead salts on soluble bromates. It is a white precipitate, soluble in 75 parts of cold water; and to it the formula $PbBrO_3+\frac{1}{2}aq$ has been assigned.

Nearly all the remaining bromates that are known are insoluble in water.

α. The bromates may be recognized, as easily as the chlorates, by the decomposition of their acid constituent; but in their case, bromine, and not an oxide, is liberated. Thus, when sulphuric acid (concentrated), or even a dilute mineral or organic acid (such as acetic), is added to a solution of a bromate, oxygen and bromine are set free, and then the latter may be at once identified by its action on starch.

β. A fragment of a bromate in powder, when rubbed in a mortar with such bodies as carbon, sulphur, or antimony, explodes or detonates. A similar result is obtained on heating the powdered mixture.

γ. Bromates mixed with sugar frequently cause the inflammation of the latter when the mixture is moistened with sulphuric acid.

δ. Bromates are decomposed by hydrosulphuric acid,—a white precipitate of sulphur being formed, and sulphuric and hydrobromic acids remaining in the solution.

The bromates are recognized by the precipitation of the silver, mercury, and lead salts, and by the tests *α.* and *β.*

Of the acid-radicals containing iodine combined with oxygen, those existing in the acids or hydrogen salts, termed iodic and periodic acids are the most important in an analytical point of view.

It is probable that the hypo-iodous (HIO) and iodous (HIO_2) acids exist; but nothing definite has as yet been ascertained concerning them.

SALTS OF THE IODIC RADICAL, OR IODATES.

These salts are quite analogous to the bromates, and may be prepared similarly, by the action of iodine on the alkaline hydrates and carbonates. They exist, however, in several closely-related modifications; for, while to the ordinary iodates the formula MIO_3 is assigned, there are also other salts represented by the formulæ $M_2I_4O_{11}$ and MI_3O_8, all derivable from the action of iodic acid on metallic oxides. A very remarkable series of salts will be found described in the observations upon the phosphates; and we have already had peculiar instances among the sulpharseniates.

Iodates, when heated, are converted either into iodides, with evolution of 3 equivalents of oxygen, or into oxides, with evolution of iodine and of a less proportion of oxygen or formation of periodates; the former decomposition is that which the iodates of the first subdivision of basic radicals suffer, while the latter change is that experienced by the iodates of the second subdivision.

THE HYDROGEN SALT, or iodic acid, may be made directly by heating iodine with nitric acid, or with nitric acid and chlorate of potassium. It is exceedingly soluble in water; and the solution, which is syrupy, is extremely corrosive. Iodic acid, HIO_3, when heated to 170° C., yields the iodic anhydride (I_2O_5), which decomposes at a higher temperature into its constituents.

The most important insoluble salts of this series are the argentic, mercurous, and plumbic iodates.

THE POTASSIUM and AMMONIUM SALTS are soluble.

The Barium Salt is produced by the action of a concentrated solution of a barium salt on a soluble iodate: it is a white granular precipitate.

Its formula is $BaIO_3+\frac{1}{2}aq$.

It requires 1746 parts of water at 15°, and 600 parts of boiling water, to effect its solution; it dissolves with difficulty in warm nitric acid.

THE STRONTIUM SALT is soluble.

THE CALCIUM SALT is produced in the same manner as the barium salt: it is a white crystalline precipitate, soluble in 260 parts of cold water, and in 75 of boiling water, but much more easily dissolved by nitric acid.

THE MAGNESIUM SALT is soluble.

THE CUPROUS SALT does not exist.

THE CUPRIC SALT is produced by the action of cupric sulphates on iodate of sodium or iodic acid, and allowing the mixture to stand. If the precipitant were concentrated, the precipitate is bluish green; if dilute, white. It dissolves in 302 parts of water at 15°, or in 145 parts of boiling water, and is readily soluble in hydrate of ammonium.

The Argentic or Silver Salt is obtained by the action of a soluble silver salt on a solution of a soluble iodate: it is a white precipitate.

Its formula is $AgIO_3$.

It dissolves in hydrate of ammonium, and sparingly in nitric acid; by hydrochloric acid it is decomposed.

The Mercurous Salt is obtained by the action of a soluble mercurous salt on solutions of iodic acid or iodates: it is a white precipitate, having a pearly lustre.

It is slightly soluble in water, and is dissolved by most acids.

The Mercuric Salt is soluble.

The Lead Salt is produced by the addition of a soluble lead salt to a solution of an iodate or of iodic acid: it is a white precipitate, which dissolves sparingly in water, and with difficulty in nitric acid.

Most, if not all, of the remaining iodates that are known are comparatively soluble in water.

α. Iodates may be identified, with the same ease as bromates, by the decomposition of their acid constituent. This change is, however, generally effected by the action of a reducing agent, such as sulphurous acid gas (SO_2), which separates iodine, this element being subsequently recognized by the usual tests. The strong acids generally liberate iodic acid from the iodates in solution.

β. Iodates detonate when heated with combustible bodies, or when the mixtures containing these bodies are struck; the detonation is not nearly equal in violence to that of the chlorates, bromates, and nitrates when similarly treated.

γ. If to a solution of an iodate a soluble iodide be added, and then a strong acid, the hydriodic and iodic acids, at the moment of liberation, act upon one another in the following manner:—

$$7HI + HIO_4 = 4H_2O + 8I.$$

The black precipitate, or brown colouration produced in the solution, is an excellent indication of the presence of iodine.

δ. Iodates are decomposed by hydrosulphuric acid, a white precipitate of sulphur being formed, and sulphuric and hydriodic acids remaining in the solution.

The iodates are recognized by the precipitation of the barium, silver, and lead salts, and by the tests *α*, *γ*, and *δ*.

SALTS OF THE PERIODIC RADICAL, OR PERIODATES.

The periodates are, in some respects, similar to the perchlorates. They resemble the iodates in the facility with which they pass into new modifications possessing a different proportion of the basic constituent. The formula of the normal periodates would be MIO_4; but others are known, to which the formulæ $M_4I_2O_9$, M_5IO_6, $M_5H_5I_2O_{12}$, &c., have been assigned. Most of the insoluble periodates belong either to the second or third of these classes.

Heated on charcoal or with other combustibles, periodates detonate, but not violently; when heated alone, they behave in a similar manner to the iodates.

The Hydrogen Salt, or periodic acid, may be obtained in colourless crystals (HIO_4+2aq), which dissolve readily in water; the solution may be boiled without decomposition.

Among the insoluble periodates the sodium, barium, silver, mercurous, mercuric, and lead salts are the most important.

The Sodium Salt is obtained by passing chlorine through an aqueous solution of carbonate of sodium, and adding iodine; also in other ways. It is a pearly, white, crystalline precipitate.

Its formula is $Na_4I_2O_9+3aq$.

It is insoluble in cold, but sparingly soluble in hot water; it is easily soluble in acids. The normal salt ($NaIO_4$) is very soluble in water.

THE POTASSIUM SALTS (KIO_4 and $K_4I_2O_9$) are soluble.

THE BARIUM SALTS (Ba_5IO_6 and $Ba_5H_5I_2O_{12}$) are produced in several decompositions, generally by the action of the soluble periodates of sodium. They are insoluble in water, but dissolve in dilute nitric acid.

THE STRONTIUM and CALCIUM SALTS are not well known, but are believed to be insoluble.

THE MAGNESIUM and CUPROUS SALTS are unknown.

THE CUPRIC SALT is a light green precipitate, soluble in dilute nitric acid.

The Argentic or Silver Salt is produced by the addition of nitrate of silver to the solution of periodate of sodium in dilute nitric acid, and falls as a light yellow crystalline powder, to which the formula $Ag_4I_2O_9$ has been given. It is insoluble in water, sparingly soluble in nitric acid.

THE MERCUROUS SALT is said to be produced by the action of mercurous nitrate on the soluble periodate of sodium ($NaIO_4$). It is a yellow precipitate, which when warmed becomes reddish brown; it is easily soluble in dilute acids.

THE MERCURIC SALT is said to be produced by the action of mercuric nitrate on the soluble variety of periodate of sodium. It is a white precipitate, which when heated becomes yellow; it is soluble in dilute nitric acid.

THE LEAD SALT is produced by the addition of a solution of plumbic nitrate ($PbNO_3$) to an aqueous solution of the normal periodate of sodium, as a white precipitate, nearly insoluble in water, but soluble in dilute nitric acid.

The PALLADIOUS and PLATINOUS, and several other salts are unknown.

Some of the remaining periodates that are known are soluble; a few, chiefly belonging the class $M_4I_2O_9$, are insoluble.

The periodate of sodium ($Na_4I_2O_9$) is the most characteristic salt of the present series.

Section III.—*The chlorocadmiates, chloropalladiates, chloroplatinates, chlororhodiates, chlororutheniates, chloriridiates, and chloraurates, &c.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN CHLORINE, BROMINE, AND IODINE COMBINED WITH METALS.

The radicals contained in the salts of this section are monobasic; and consequently the general formula of these salts will be MR. The chlorocadmiates are represented by the expression $MCdCl_2$, the chloropalladiates by $MPdCl_3$, the chloroplatinates by $MPtCl_3$, and the chloraurates by $MAuCl_4$. The other acid-radicals containing a metal and chlorine have 3 equivalents of the latter element. Many corresponding compounds containing bromine and iodine combined with metals are also formed, but they are as yet but imperfectly known.

TABLE OF

SALTS.	Cl (see page 254)	Br (see page 256)	I (see page 260)	F (see page 263)
Potassium ...	—	—	—	—
Barium	—	—	—	white
Strontium ...	—	—	—	white
Calcium	—	—	—	white
Magnesium ..	—	—	—	white
Cuprous	white	white	brownish white	red
Cupric	—	—	—	—
Silver	white	white	yellow	white
Mercurous ...	white	white	green	white
Mercuric ...	—	—	scarlet	yellow
Lead	white	white crystalline	orange-yellow crystalline	white

These radicals may be recognized best by the insoluble salts which they yield with certain basic radicals, chiefly potassium, ammonium, and the *organic* compound ammoniums. These insoluble salts are almost all of a yellow, orange, brown, or red colour; and as they have been named or described under their respective metals, they need not be again noticed here.

These radicals may also be identified by their decomposition into new products, &c. When, for instance, a stream of hydrosulphuric acid gas is passed through a neutral or acid solution of chloroplatinate of sodium, one of the products of the reaction is sulphide of platinum. This reaction, described in the appended equation, takes place with all the salts of the acid-radicals contained in this section:—

$$2KPtCl_3+2H_2S=2KCl+4HCl+Pt_2S_2.$$

REACTIONS.

ClO (see page 267)	ClO_3 (see page 269)	BrO_3 (see page 271)	IO_3 (see page 273)	$PtCl_3$ (see page 220)
—	—	—	—	orange-yellow crystalline
—	—	white crystalline	white	—
—	—	—	—	—
—	—	—	white crystalline	—
—	—	—	—	—
—	—	—	—	—
—	—	—	bluish green	—
—	—	white	white	—
—	—	yellowish white	white pearly	—
—	—	white	—	—
—	—	white	white	—

Analysis of Subdivision I.

The acid-radicals of more common occurrence only being included, the salt may be a CHLORIDE, BROMIDE, IODIDE, FLUORIDE, HYPOCHLORITE, CHLORATE, BROMATE, IODATE, or a CHLOROPLATINATE.

Evidence of the presence of any one of these salt-radicals may be obtained by adding to the solid salt, or its strong solution, some concentrated sulphuric acid. The following effects will be produced, either immediately or on warming the mixture:—

Pungent *colourless* vapours (of HCl) indicate a chloride.
" *red-brown* " (of Br) indicate a bromide or bromate.
" *violet* " (of I) indicate an iodide or iodate.
" *colourless* " (of HF), etching glass, indicate a fluoride.
" *yellow* " (of Cl_2O), having the odour of bleaching-powder, indicate a hypochlorite.
" *orange yellow* " (of Cl_2O_4), explosive, indicate a chlorate.

Further Analysis.

Through the solution of the salt, pass hydrosulphuric acid gas.

<table>
<tr>
<td rowspan="2">A black precipitate of Pt_2S_2 would indicate the presence of $PtCl_3$.</td>
<td colspan="2">If no precipitate, the solution may contain Cl, Br, or I;
any ClO, BrO_3, or IO_3, would have been decomposed by the passage of the hydrosulphuric acid. Boil to expel H_2S; add nitrate of silver. A white or yellow precipitate falls, of
AgCl, AgBr, or AgI.
Add ammonia, and warm.</td>
</tr>
<tr>
<td>Yellow residue of AgI indicates I.</td>
<td>If wholly dissolved, test a portion of the original solution by means of Mn_2O_2 and H_2SO_4 for Cl or Br.</td>
</tr>
</table>

SUBDIVISION II.

SALTS OF OXYGEN, SULPHUR, SELENIUM, AND TELLURIUM, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

The members of this subdivision present many analogies with those of the preceding; three of them, sulphur, selenium, and tellurium, bear the closest relation to each other, exhibiting a curious progression towards the basic character, whilst a fourth, oxygen, has a more distant resemblance. In addition to the salts which these form by direct combination with basic radicals, there are many others in which sulphur, selenium, and tellurium exist in the form of a compound acid-radical containing oxygen or a metal. The majority of the salts of this subdivision are bibasic; some, however, are tribasic.

Section I.—SALTS OF OXYGEN, SULPHUR, SELENIUM, AND TELLURIUM.

The oxides, sulphides, selenides, and tellurides.

Section II.—SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN SULPHUR, SELENIUM, AND TELLURIUM COMBINED WITH OXYGEN OR AMONG THEMSELVES,

The hyposulphites, sulphites, hyposulphates, trithionates, tetrathionates, pentathionates, and sulphates; the selenites, seleniates, tellurites, and telluriates.

Section III.—SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN OXYGEN AND SULPHUR COMBINED WITH METALS.

The aluminates, chromites, chromates, perchromates, ferrites, ferrates, manganates, permanganates, bismuthates, stannates, metastannates, platinates, rhodiates, rutheniates, iridiates, osmites, osmiates, aurates, tungstites, tungstates, molybdates, vanadites, and vanadiates; the sulphostannates, sulphoplatinates, sulphorhodiates, sulphorutheniates, sulphiridiates, sulphosmiates, sulphaurates, sulphotungstates, sulphomolybdates, and sulphovanadiates.

SECTION I.—*The oxides, sulphides, selenides, and tellurides.*

SALTS OF OXYGEN, SULPHUR, SELENIUM, AND TELLURIUM.

We have already seen that these four acid-radicals are bibasic, and that the following formulæ are some of those which belong to the various combinations of metals with oxygen—$(M_2)_2O$, M_2O, $(M_2)_2O_3$, M_2O_2, M_2O_3, M_2O_5,—while, besides these common oxides, which can exist in the isolated condition, there are many others which play the part of acid-radicals, and are only known to us in combination with a basic constituent: such compounds are represented by the following formulæ among others:—MO, MO_2, MO_3, MO_4, M_2O_4, M_2O_7, &c. And in addition to these hypothetical compounds of metals with oxygen, there are numerous existing combinations of oxygen with other acid-radicals. What has been here said concerning oxygen, is true also as regards sulphur, and to a great extent with reference to selenium and tellurium.

In common with other polybasic radicals, the members of the present subdivision possess the power of combining with, and uniting in one salt, separate single equivalents of two different basic radicals; and although, in the class before us, one of these basic bodies is invariably hydrogen, yet, in salts containing more complex acid-radicals, two different metals are frequently combined with one and the same equivalent of acid-radical. The hydrates and sulphydrates already mentioned are salts in which this peculiarity occurs (1 eq. of hydrogen and 1 eq. of metal are united with a single equivalent of the biatomic radical oxygen); and they are comparable with the oxides and sulphides, in which 2 eqs. of metal are united with a single equivalent of the biatomic radical:—

Oxides.	Hydrates.	Sulphides.	Sulphydrates.
MMO.	MHO.	MMS.	MHS.

The salts of the present subdivision may be recognized by the employment of the same means that are used for the detection of the members of the preceding subdivision: *i. e.*, 1st, by the formation of insoluble compounds; 2nd, by their decomposition, and the subsequent recognition of their acid-element.

SALTS OF OXYGEN, OR OXIDES.

There are very many oxides known; as a general rule they may be regarded as very stable salts. Many oxides are of brilliant colours; some are white. Several of the oxides which occur in nature, and also of those which have been fused or crystallized, possess a metallic lustre.

Oxides, when heated upon charcoal, are frequently reduced to the metallic state; some, indeed, are thus decomposed by heat alone, others by the joint action of heat and of the affinity, for the oxygen of the salt, which the carbon exerts. There are oxides, however, which can be decomposed only by the most powerful chemical agencies. The various blowpipe reactions of the metallic oxides have been already described under their respective metals.

THE HYDRATE OF HYDROGEN (HHO), hydric acid, or water, is a body too well known to need description: it plays the part of an acid, exchanging 1 eq. of hydrogen, under suitable conditions, for an equivalent of a different basic radical; but so nicely are the opposing properties of its constituents balanced, that it is a very stable body, and is quite neutral with reference to a great many salts. This neutrality, combined with its vast solvent power on solids, liquids, and gases, renders water of the utmost service in chemical operations; and in this capacity of a solvent it cannot be replaced by any known substance. The presence of water in certain salts as water of crystallization or of hydration is little understood; but perhaps it is connected in some way with this neutrality of which we have been speaking.

There is no oxide known which is soluble in water without decomposition; for all the oxides upon which water seems to exert a solvent action are in fact decomposed by it. When water is viewed as hydric acid, this change becomes intelligible; with oxide of potassium it may be represented thus—

$$KKO + HHO = KHO + KHO.$$

Water, indeed, may be regarded as the normal oxide of hydrogen, but, being itself the universal solvent, cannot be regarded as soluble.

The presence of oxygen cannot be well ascertained by double decompositions in which oxides and hydrates are precipitated; it is always preferable to employ other means. Those methods which are admissible are of two kinds: in one we prove the absence of all other salt-radicals except oxygen; and in the other we detect the oxygen by the decomposition of the salt under examination.

For the sake of comparison with the salts of other acid-radicals, we give a few of the more important insoluble oxides and hydrates, produced by the action of a solution of hydrate of potassium on the different metallic solutions, neither reagent being in excess.

THE POTASSIUM, SODIUM, and AMMONIUM SALTS (hydrates) are very soluble in water.

THE BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS (hydrates) are somewhat sparingly soluble.

THE CUPROUS SALT ($[Cu_2]_2O$) is orange-yellow. It is soluble in most acids.

THE CUPRIC SALT ($CuHO$) is blue. It is soluble in hydrate of ammonium, and in most acids.

THE SILVER SALT (Ag_2O) is brown. It is soluble in hydrate of ammonium, and in most acids.

THE MERCUROUS SALT ($[Hg_2]_2O$) is brownish black. It is soluble in most acids.

THE MERCURIC SALT ($HgHO, H_2O$) is yellow. It is soluble in most acids.

THE LEAD SALT (Pb_3HO_2) is white. It is soluble in most acids.

The other oxides and hydrates have been already described under their respective metals in Chapter VI.

a. The negative evidence mentioned above as being employed in the identification of the compounds of oxygen, will not need further description; but the method of recognizing the salts of the radical now under consideration, by its elimination, may be here noticed.

β. The oxides which can be decomposed into metal and oxygen by the mere action of heat are few in number. Of these the oxygen salts of silver, mercury, and gold are the most important. Lead also, under certain circumstances, may be obtained by heating its oxide. If a small quantity of oxide of silver (Ag_2O) be heated in a dry test-tube, it will readily split into metallic silver and oxygen gas, the latter being easily recognizable by the usual test,—the insertion, into the vessel used for the experiment, of the glowing end of a wooden match which has been previously lighted, allowed to burn for a minute, and then blown out. If there has been only a small quantity of oxygen liberated, the red-hot end of the match will only glow more brightly; but if a considerable amount, it will be rekindled.

SALTS OF SULPHUR, OR SULPHIDES.

A great resemblance exists between these salts and the oxides, some of them possessing remarkably brilliant colours, others again being of an intense brown colour, or even black. When fused, or naturally occurring in crystals, many sulphides have a peculiar metallic lustre. To these salts belong the same formulæ as those given under the salts of oxygen.

When heated before the blowpipe, sulphides are generally decomposed, the sulphur they contain being oxidized into the sulphurous or sulphuric radical, which remains combined with the metal; but, on the other hand, when the sulphites and sulphates thus produced are heated on charcoal, they are for the most part reduced to the state of sulphide. Sulphides, when heated alone in the air, often yield the oxide, and sometimes even the metal.

The Hydrogen Salt (H_2S), hydrosulphuric or sulphydric acid or sulphuretted hydrogen, is a gas at ordinary temperatures and pressures, possessing a peculiarly disagreeable and sickly smell, and being very poisonous and narcotic. It may be condensed, by combined cold and pressure, into a colourless transparent liquid, more mobile and less adhesive even than ether, while by further cold it may be made to assume the solid form, and then appears as a white crystalline mass. The gas has a density of 1·191. Water dissolves about its own volume of sulphuretted hydrogen at the common temperature, forming a solution which, by exposure to the air, oxidizes, a deposit of sulphur taking place. The gas is combustible, burning with a blue flame, and may be ignited at a comparatively low temperature, as by a red-hot coal; the products of its combustion are sulphurous anhydride (SO_2) and water:

$$H_2S+3O=H_2O+SO_2.$$

Most sulphides are insoluble in water, although many are soluble in acids. The sulphides of the first and second subdivisions are, however, soluble in water, though it may be presumed that they really undergo a decomposition during solution, becoming partially converted into sulphydrates, just as certain oxides yield hydrates under similar circumstances:

$$KKS+HHO=KHS+KHO.$$

With hydrosulphuric acid solution instead of water only, 2 eqs. of the sulphydrate are formed:

$$KKS+HHS=KHS+KHS.$$

The chief insoluble sulphides have been already described under their respective basic radicals; for the sake of comparison, however, with the salts of other acid-radicals, we give a list of the more important, premising that, of the insoluble sulphides given, all but the six first are precipitable from their neutral solutions by sulphuretted hydrogen.

THE POTASSIUM, SODIUM, AMMONIUM, BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE FERROUS (Fe_2S) and FERRIC ($[Fe_2]_2S_3$) SALTS are black.

THE MANGANOUS SALT (Mn_2S) is buff or flesh coloured, and soluble in dilute acids.

THE COBALT (Co_2S) and NICKEL (Ni_2S) SALTS are black, and soluble in dilute acids.

THE ZINC SALT ($Zn_2 S$) is white, insoluble in water, but soluble in dilute acids.

THE CADMIUM SALT ($Cd_2 S$) is bright yellow.

THE CUPROUS ($[Cu_2]_2 S$), CUPRIC ($Cu_2 S$), SILVER ($Ag_2 S$), MERCUROUS ($[Hg_2]_2 S$), MERCURIC ($Hg_2 S$), LEAD ($Pb_2 S$), and PALLADIOUS ($Pd_2 S$) SALTS are black or brownish black, and insoluble or nearly so in cold water and in dilute acids. The cupric sulphate is easily oxidized by atmospheric oxygen into the sulphate.

THE STANNOUS SALT ($Sn_2 S$) is brownish black.

THE STANNIC SALT ($Sn_2 S_2)$) is white, inclining to yellow.

THE ANTIMONIOUS ($Sb_2 S_3$), ANTIMONIC ($Sb_2 S_5$), ARSENIOUS ($As_2 S_3$), and ARSENIC ($As_2 S_5$) SALTS are of a fine orange yellow colour, inclining to red.

The presence of sulphur in its compounds may be recognized also by processes of decomposition:—

α. Most sulphides, when warmed with strong hydrochloric or sulphuric acid, decompose with evolution of hydrosulphuric acid gas (the odour of which is so characteristic), and occasionally also with separation of sulphur:

$$M_2 S + H_2 SO_4 = H_2 S + M_2 SO_4.$$

When nitric acid is employed, the sulphide is generally oxidized and converted into the corresponding sulphate or nitrate (see δ.).

β. When an *insoluble* sulphide is fused with carbonate of sodium on charcoal, sulphide of sodium ($Na_2 S$) is formed; and if the mass be then scooped out, laid on a silver coin and moistened with water, a black stain ($Ag_2 S$) is immediately produced.

γ. When hydrosulphuric and sulphurous acids meet in the presence of water, a white or very pale yellow precipitate of sulphur is produced, while the solution will be found to contain an acid known as pentathionic ($H_2 S_5 O_6$):

$$5H_2 S + 5H_2 SO_3 = H_2 S_5 O_6 + 9H_2 O + \underset{\text{white ppt.}}{5S}.$$

δ. Very generally, when sulphides are boiled with nitric acid, a separation of sulphur takes place, and the latter substance often fuses and floats as an oily globule upon the surface of the liquid, solidifying, on cooling, in the form of a little circular cake.

This action of nitric acid also gives rise to the simultaneous formation of sulphuric acid, and to the most highly oxygenated combination which the metal of the sulphide employed is capable of forming: thus with ferrous sulphide—

$$\underset{\substack{\text{ferrous}\\\text{sulphide.}}}{2Fe_2S} + 10HNO_3 = \underset{\text{ferric nitrate.}}{2Fe_2(NO_3)_3} + \underset{\substack{\text{sulphuric}\\\text{acid.}}}{H_2SO_4} + 4H_2O + \underset{\text{ppt.}}{S} + 2N_2O_2.$$

ϵ. A very excellent test for the presence of sulphur in the form of a soluble sulphide (and by process β. all insoluble sulphides may be made to yield the soluble sulphide of sodium) is found in a solution of nitroprusside of sodium. The most minute trace of sulphur is discoverable by the magnificent violet or purple colour which a drop of a dilute solution of this reagent immediately produces.

Hydrosulphuric acid and other soluble salts of sulphur are usually detected by the formation of coloured metallic sulphides, and particularly by their action on lead salts (which, for this purpose, may be applied in the form of aqueous solution to strips of white paper), and also by the tests α, β, γ, ϵ.

SALTS OF SELENIUM, OR SELENIDES.

A most marked resemblance exists between the selenides and sulphides; they do not, however, possess the same variety of brilliant colours, most of them, when freshly precipitated by hydroselenic acid (H_2Se) being brownish black or flesh-coloured. Natural selenides often possess a metallic lustre.

When heated on charcoal in the air, the selenium of these salts burns slowly with a reddish blue flame, with evolution of a most powerful odour of horse-radish, due to the formation of a gaseous oxide of selenium, probably SeO. Selenium is more slowly expelled from selenides, by this process of "roasting," than sulphur from sulphides.

The Hydrogen Salt (H_2Se), hydroselenic acid or seleniuretted hydrogen, is a gas under ordinary circumstances, of specific gravity 2·795. At first, its smell seems to resemble that of the corresponding sulphur acid; but it subsequently painfully affects the mucous membrane of the nose, and destroys the sense of smell. It is intensely poisonous. It burns with a bluish flame. It is more soluble in water than hydrosulphuric acid; the aqueous solution decomposes by exposure to the air, depositing selenium in red flakes.

Most selenides are insoluble in water; but they have not been much studied.

The Potassium and Sodium Salts are the best known soluble selenides.

The Barium and Strontium Salts are soluble, the Calcium and Magnesium Salts nearly insoluble in water.

The Manganese Salt is pale red, the Zinc Salt yellow; they are both insoluble in water.

The Cupric, Silver, Mercuric, and Lead Salts are black, becoming grey on drying; they are insoluble in water or neutral solutions.

The presence of selenium in its compounds may be readily recognized by several processes of decomposition:—

a. Upon treatment of a selenide with hydrochloric or sulphuric acid, hydroselenic acid is evolved, which may be recognized by its peculiar odour. Nitric acid generally converts selenides into selenites, with occasional separation of selenium.

β. A selenide fused with carbonate of sodium on charcoal, transferred to a silver surface, and moistened with hydrochloric acid, will produce a black stain.

γ. Sulphurous acid produces, in an aqueous solution of hydroselenic acid, a bright reddish precipitate of selenium.

δ. Selenides heated on charcoal with carbonate of sodium or microcosmic salt, give the characteristic odour of horse-radish.

ε. To detect traces of selenium, it is recommended to fuse the substance under examination with hydrate of potassium, to dissolve in water, filter, and expose the solution to the air; if selenium be present it will slowly appear, causing a reddish turbidity, or it will separate in reddish flakes.

Selenium may be conveniently recognized by the tests *δ.* and *ε.*

SALTS OF TELLURIUM, OR TELLURIDES.

These salts greatly resemble the selenides; they, however, partake more of the character of alloys (or combinations of metals with one another) than of that of saline compounds. In tellurides the metallic appearance of the basic radical is scarcely masked by the tellurium; even the potassium salt has a metallic lustre. The tellurides of the heavy metals, obtained by passing telluretted hydrogen through their aqueous solutions, are generally brown or black, and insoluble in water.

When tellurides are heated on charcoal before the blowpipe, the tellurium burns with a blue flame edged with green, and emits a peculiar odour, different from that of selenium.

The Hydrogen Salt (H_2Te), hydrotelluric acid or telluretted hydrogen, is a gas of specific gravity 4·489, its odour somewhat resembling that of the corresponding sulphur compound. It is poisonous. It is absorbed by water, imparting to that solvent a pale red colour; the aqueous solution, by exposure to the air, becomes brown, from separation of tellurium.

Most tellurides are insoluble in water; but they have not been much studied.

The Potassium and Sodium Salts are soluble in water.

The Cupric, Silver, Mercuric, and Lead Salts are brown or black precipitates, insoluble in water.

The presence of tellurium in its compounds may be readily recognized by several processes of decomposition:—

α. A telluride treated with hydrochloric acid evolves telluretted hydrogen, the odour of which is characteristic. Nitric acid converts tellurides into tellurites.

β. A telluride fused with carbonate of sodium on charcoal, transferred to a silver surface, and then moistened with hydrochloric acid, imparts a brown stain to the metal.

γ. Sulphurous acid and several other similar reagents produce, in aqueous solutions of hydrotelluric acid, a dark brown precipitate of tellurium.

δ. If a telluride be fused with hydrate of potassium, the fused mass dissolved in water, and the solution exposed to the air, tellurium will be precipitated.

SECTION II.—*The hyposulphites, sulphites, hyposulphates, trithionates, tetrathionates, pentathionates, and sulphates; the selenites, seleniates; tellurites, and telluriates.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN SULPHUR, SELENIUM, AND TELLURIUM COMBINED WITH OXYGEN OR AMONG THEMSELVES.

The acid-radicals which contain oxygen, sulphur, selenium, and tellurium are bibasic, like these elements themselves. A sulphate, just like a sulphide, may contain two different basic radicals—1 eq. of a metal, for instance, together with 1 eq. of hydrogen. With the sulphurous and several other acid-radicals of the present section, such compound or *double* combinations are known to occur; and the remainder have not as yet been sufficiently investigated.

Of the acid-radicals containing sulphur combined with oxygen, those existing in the acids or hydrogen salts termed hyposulphurous, sulphurous, and sulphuric are the most important in an analytical point of view.

SALTS OF THE HYPOSULPHUROUS RADICAL, OR HYPOSULPHITES.

The hyposulphites of the first and second subdivisions of the basic radicals are best known; and from them most of the other hyposulphites may be prepared. They may be formed in various ways: when, for instance, an alkaline sulphite is boiled with sulphur, the sulphur is dissolved in considerable quantity, the following reaction taking place:—

$$K_2SO_3+S=K_2S_2O_3.$$

The sodium salt is largely prepared, and may be made by boiling a strong solution of the hydrate with excess of sulphur, and then passing sulphurous acid gas (SO_2), evaporating and crystallizing the solution.

Many hyposulphites, when heated on charcoal, yield a large quantity of the corresponding sulphides. When heated alone with access of air, they yield water, sulphurous acid, and sulphates; out of contact of air they are resolved into water, hydrosulphuric acid, and sulphur, which volatilize, while a mixture of alkaline sulphides, sulphites, and sulphates remains.

The hyposulphites of the first and second subdivisions of the basic elements are tolerably stable if kept out of contact of air; but the remainder are exceedingly unstable, and can scarcely be said to exist. Hyposulphurous anhydride (S_2O_2) is itself a very unstable substance; but its elements being capable of uniting in other proportions to form compounds of extreme stability, readily yield such products: any excess of sulphur left uncombined with oxygen is either precipitated or, by entering into combination with a portion of the metal present, produces a sulphide. Thus hyposulphite of silver ($Ag_2S_2O_3$) undergoes the following changes on heating, or by standing:—

$$\underset{\substack{\text{white}\\\text{hyposulphite}\\\text{of silver.}}}{Ag_2S_2O_3} + H_2O = \underset{\substack{\text{black}\\\text{sulphide}\\\text{of silver.}}}{Ag_2S} + H_2SO_4.$$

THE HYDROGEN SALT ($H_2S_2O_3$), or hyposulphurous acid, is believed to be produced when hyposulphites are decomposed by stronger acids, as when hyposulphite of lead is diffused in water at 0° C., and a stream of hydrosulphuric acid gas allowed to act upon it,—sulphide of lead being precipitated, and hyposulphurous acid obtained in solution. This acid, however, speedily decomposes, thus—

$$\underset{\substack{\text{hypo-}\\\text{sulphurous}\\\text{acid.}}}{H_2S_2O_3} = \underset{\substack{\text{sulphurous}\\\text{acid.}}}{H_2SO_3} + S.$$

The hyposulphites may be recognized by the formation of certain insoluble salts, and by the decomposition of their acid-radical.

The hyposulphites of the first and second subdivisions of basic radicals are soluble, with the exception of the barium salt. Nearly all the remaining salts are, as far as known, insoluble in water.

THE POTASSIUM and SODIUM SALTS are soluble. The latter is much employed in photographic processes, for dissolving iodide, bromide, and chloride of silver.

THE BARIUM SALT is produced by the action of a soluble barium salt on a tolerably concentrated solution of hyposulphite of sodium ($Na_2S_2O_3$). Its formula is $Ba_2S_2O_3$ + aq. It is somewhat soluble in water, soluble in hydrochloric acid, while with nitric acid it is converted into the sulphate.

THE STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE FERROUS, CUPROUS, and CUPRIC SALTS, also many other salts of the metals contained in the third and fourth subdivisions of the basic radicals, are soluble in water.

The Silver Salt is a white precipitate, which becomes yellow, red-brown, and finally black, sulphide of silver being produced. Its formula is $Ag_2 S_2 O_3$. It is slightly soluble in water, and very soluble in alkaline hyposulphites; if to this solution a soluble chloride be added, it gives no precipitate when excess of alkaline hyposulphite is also present.

The Mercurous Salt does not appear to exist, a black precipitate of sulphide being produced. The Mercuric Salt is white or yellow, becoming brown or black on boiling, from formation of mercuric sulphide.

The Lead Salt is a white precipitate, which becomes black below 100°. Its formula is $Pb_2 S_2 O_3$. It is soluble in 3266 parts of water, and easily dissolves in alkaline hyposulphites. By nitric acid it is converted into the sulphate, which is very insoluble.

The hyposulphites may also be recognized by the following processes of decomposition:—

α. When an acid is added to a soluble hyposulphite, an immediate precipitation of sulphur occurs, the hyposulphurous acid set free being at once resolved into sulphurous acid and sulphur:

$$Na_2 S_2 O_3 + 2HCl = 2NaCl + H_2 O + SO_2 + \underset{\text{ppt.}}{S}.$$

The sulphurous acid ($H_2 SO_3$) decomposes instantly into water and sulphurous anhydride, the latter being readily recognizable by its odour.

β. When a hyposulphite is fused with carbonate of sodium on charcoal, a sulphide is obtained which, when treated with an acid upon a silver surface, gives a black stain of sulphide of silver, while hyposulphites previous to fusion give no such result.

γ. When a soluble hyposulphite is brought in contact with a hydrochloric solution of stannous chloride, a brown precipitate of stannous sulphide is produced.

This radical is generally recognized by the decompositions which its various combinations so easily undergo. The changes which the hyposulphite of silver suffers, and the tests *α*, *β*, and *γ*. are perhaps the most characteristic examples of these methods of identification.

SALTS OF THE SULPHUROUS RADICAL, OR SULPHITES.

These salts are bibasic. They are of much easier production than the hyposulphites, and are much more stable. Sulphurous anhydride (SO_2) is produced whenever sulphur is burnt in the air; and from it the sulphites may in general be obtained. Sulphites have a tendency to absorb oxygen from the air, especially when kept moist or in solution, and by so doing pass into sulphates:

$$M_2SO_3+O=M_2SO_4.$$

On account of this property, sulphurous acid and other sulphites are employed as reducing agents.

Heated on charcoal, many sulphites yield the corresponding sulphides, while others are reduced to the metallic state.

THE HYDROGEN SALT (H_2SO_3), sulphurous acid, is known to exist only in combination with water, the compound having the formula H_2SO_3+8aq, and occurring in white crystals. It is decomposed with great readiness into the substance known as sulphurous anhydride, or sulphurous acid gas (SO_2), and water. This gas has a density of 2·222; its odour is most unpleasant, and produces a painful choking sensation. By a cold of $-12°$ it may be liquefied, and at a lower temperature it may even be solidified; it may also be rendered liquid by the pressure of from three to five atmospheres at the ordinary temperature.

The sulphites may be recognized not only by the formation of insoluble salts, but also by the transformation and decomposition of their acid-radical.

The majority of the sulphites are insoluble in water and in saline solutions. The sulphites of the alkaline metals and the acid sulphites ($MHSO_3$) are, however, soluble. All sulphites are readily soluble in weak acids, the sulphurous acid being easily displaced. Of the insoluble sulphites the most interesting and characteristic are the barium, cuprous, argentic, and plumbic salts.

THE POTASSIUM and SODIUM SALTS are soluble.

The Barium Salt is produced by the action of soluble barium salts on solutions of the alkaline sulphites. It is a white precipitate, having the formula Ba_2SO_3. It is scarcely soluble in water, but soluble in sulphurous, hydrochloric, and dilute nitric acid, if the sulphite were quite free from sulphate. Upon slightly heating the nitric acid solution, the sulphite of barium it contains is converted into sulphate, which, being very insoluble, is immediately precipitated.

THE CUPROUS SALT is obtained when a cupric salt is mixed with an alkaline sulphite, the cupr*ic* sulphite first formed splitting into cuprous sulphite, cupric sulphate, and sulphurous anhydride:

$$3Cu_2SO_3 = \underset{\text{cuprous sulphite.}}{(Cu_2)_2SO_3} + Cu_2SO_4 + SO_2.$$

It is a light brown precipitate, scarcely soluble in water, soluble in ammonia water and dilute sulphuric acid, but decomposed by most acids.

The Argentic or Silver Salt is precipitated from silver salts by a soluble sulphite, as a white granular precipitate, which, when boiled in the solution from which it has been deposited, decomposes into metallic silver, and sulphuric acid which remains in solution. The formula of the argentic sulphite is Ag_2SO_3.

It dissolves in alkaline sulphites, and in ammonia water, but scarcely in sulphurous acid or water.

THE MERCURY SALTS do not appear to exist.

THE LEAD SALT is a white precipitate, which has the formula Pb_2SO_3, and which is insoluble in water, decomposed by strong acids, and by nitric acid especially; with the aid of heat it is converted into sulphate.

Sulphites may also be recognized by the decomposition of their acid-radical:—

a. Sulphurous acid, when produced by the action of strong acids (such as hydrochloric acid) upon sulphites, decomposes instantly into sulphurous anhydride (SO_2) and water, *no sulphur being precipitated.*

β. Sulphites fused with carbonate of sodium on charcoal yield sulphide of sodium, which may be recognized by its action on metallic silver.

γ. A hydrochloric solution of stannous chloride added to a soluble sulphite produces a gradually increasing precipitate of brown sulphide of tin. But if to the solution of a soluble sulphite some quantity of hydrochloric acid be first added, and subsequently some stannous chloride,—and if, under the glass plate which covers the containing vessel, a slip of lead paper be suspended, this latter will speedily be blackened by the sulphuretted hydrogen given off. The formation of the brown or brownish yellow precipitate of sulphide of tin, and the evolution of hydrosulphuric acid, are due to the tendency which sulphites possess to pass into sulphates, by a change in which a portion of sulphur already combined with oxygen parts with that element, in order to increase the proportion of oxygen in the remaining compound. The sulphur thus liberated unites either with tin or hydrogen, according to the conditions of the experiment.

δ. The action of sulphuretted hydrogen (H_2S) upon sulphurous anhydride (SO_2) has been already described (p. 285, γ).

ϵ. Soluble sulphites treated with zinc and hydrochloric acid evolve sulphuretted hydrogen, which may be tested in the usual way with lead paper.

ζ. A soluble sulphite acidified with hydrochloric acid, decolourizes permanganate of potassium (KMn_2O_4), reduces ferric to ferrous salts, and in general exerts a powerful reducing action.

The methods chiefly employed for the recognition of the sulphites are these:—the precipitation and metamorphoses of the barium and silver salts, and the tests $\alpha, \beta, \gamma, \delta, \epsilon, \zeta$; they are more particularly distinguished from the hyposulphites by the test α, in the case of the sulphites no precipitate occurring, while with the hyposulphites a deposit of sulphur takes place.

SALTS OF THE HYPOSULPHURIC RADICAL, OR HYPOSULPHATES.

The manganese salt of this radical is generally prepared; and from it the other compounds may be obtained. Binoxide of manganese suspended in water, and sulphurous acid gas (SO_2) passed through it, yields hyposulphate of manganese tolerably free from sulphate if the temperature of the solution be low:

$$Mn_2O_2+2SO_2=Mn_2S_2O_6.$$

When heated, in some cases only to 100°, these salts evolve 1 eq. of sulphurous acid gas, and leave a neutral sulphate:

$$Mn_2S_2O_6=Mn_2SO_4+SO_2.$$

The Hydrogen Salt ($H_2S_2O_6$), or hyposulphuric acid, is a strongly acid liquid, which by exposure to the air is converted into sulphuric acid; by ebullition it also decomposes, just as the other salts decompose, viz.—

$$H_2S_2O_6=H_2SO_4+SO_2.$$

There are no known hyposulphates insoluble in water.

The hyposulphates may be identified by the decomposition of their acid-radical:—

α. The addition of a strong acid to a hyposulphate liberates hyposulphuric acid; and if the solution be then boiled, sulphurous acid gas escapes, sulphuric acid remaining in solution, which may be tested in the usual manner: no deposit of sulphur takes place.

β. Fused with carbonate of sodium on charcoal, hyposulphates yield sulphide of sodium.

γ. Dilute hyposulphuric acid, or a soluble hyposulphate acidified with hydrochloric acid, dissolves zinc without forming hydrosulphuric acid; but after ebullition it behaves as a solution of sulphurous acid would.

δ. Hyposulphuric acid does not decolourize permanganate of potassium, nor reduce ferric sulphate, nor precipitate sulphur from hydrosulphuric acid; but after boiling it behaves as sulphurous acid.

For the detection of this radical the tests just described may be used, while, for distinguishing it from the hyposulphurous and sulphurous radicals, the reactions described under *γ*. and *δ*. may be employed.

SALTS OF THE TRITHIONIC RADICAL, OR TRITHIONATES.

Of these salts, which are prepared with difficulty, that of potassium is the only one well known. The general formula of the salts is $M_2S_3O_6$; they are all soluble in water, and are easily destroyed.

SALTS OF THE TETRATHIONIC RADICAL, OR TETRATHIONATES.

Several tetrathionates are known, which are not very soluble in water, and much more stable than the trithionates. THE HYDROGEN COMPOUND ($H_2S_4O_6$) may be boiled without decomposition, thus differing from trithionic acid.

SALTS OF THE PENTATHIONIC RADICAL, OR PENTATHIONATES.

The pentathionates are very prone to decomposition. Their general formula is $M_2S_5O_6$; but one or two acid salts (MHS_5O_6) are known. THE HYDROGEN COMPOUND is very soluble in water, has an intensely acid taste, and gives precipitates with copper, silver, mercury, and lead salts, of various colours at first, but which speedily become dark brown or black, the sulphide being formed.

SALTS OF THE SULPHURIC RADICAL, OR SULPHATES.

The salts of the sulphuric radical are more stable than those of any other acid-radical containing sulphur and oxygen; and it is indeed remarkable in this respect among compound acid-radicals in general. It is in the form of combination which we are now considering that sulphur exists, to a considerable extent, in nature, and supplies the necessary quantity of this element to the animal and vegetable economy. The sulphates are, with few exceptions, soluble salts, and are met with in all, or almost all, the different varieties of water found in the earth.

Many sulphates, when heated alone on charcoal, yield the metal; others, such as those of magnesium and zinc, are resolved into metallic oxides,—while some few give a residue of sulphide. In all cases, however, a mixture of sulphurous (SO_2) and carbonic (CO_2) anhydrides is evolved.

THE HYDROGEN SALT (H_2SO_4), or sulphuric acid, is a dense liquid, to which the common term "oil of vitriol" is by no means inappropriate. The density of the acid H_2SO_4 is 1·848; it evolves great heat when mixing with water, and combines with it to form a hydrated sulphuric acid, which is strictly analogous to a sulphate with 1 equivalent of water of crystallization, has the formula H_2SO_4+aq, and crystallizes at 9° C. Other such hydrates are known, such as H_2SO_4+2aq. There is an acid obtained by distilling ignited and oxidized ferrous sulphate and receiving the products in ordinary oil of vitriol, which is termed Nordhausen sulphuric acid, or fuming oil of vitriol: this liquid has a specific gravity of 1·896, and contains dissolved in it a substance which is known as anhydrous sulphuric acid, or sulphuric anhydride (SO_3), and which may be separated from the fuming acid by distillation. Thus obtained, it occurs in long silky needles; it bears the same relation to sulphuric acid (H_2SO_4) as sulphurous anhydride (SO_2) does to sulphurous acid (H_2SO_3).

The great majority of the normal sulphates (M_2SO_4), all the acid sulphates ($MHSO_4$), and all the so-called tersulphates are soluble in water. The few sulphates that are insoluble or sparingly soluble in water are dissolved to some extent by strong sulphuric acid.

Sulphates may be recognized by the formation of insoluble salts, and by the decomposition of their acid-radical.

The barium, mercuric, and lead salts are among the more important insoluble sulphates.

THE POTASSIUM and SODIUM SALTS are soluble.

The Barium Salt is produced by the addition of a soluble barium salt to sulphuric acid, or to a neutral or acid solution of any sulphate: it is a heavy white precipitate.

Its formula is $Ba_2\,SO_4$.

It requires 43,000 parts of cold water for its solution, and is but slightly more soluble in hot water, acids, or saline solutions, although there are circumstances in which certain organic salts, those of citric acid especially, prevent the precipitation of sulphate of barium. It dissolves sparingly in concentrated sulphuric acid.

THE STRONTIUM SALT is produced by the addition of a soluble strontium salt to sulphuric acid or to solutions of soluble sulphates (even of sulphate of calcium): it is a white precipitate. Its formula is $Sr_2\,SO_4$. It is soluble in 6895 parts of water at 14°, and in 9638 parts of boiling water.

THE CALCIUM SALT is produced by the addition of a soluble calcium salt to sulphuric acid or to solutions of soluble sulphates. It is a white precipitate, to which the formula $Ca_2\,SO_4+2aq$ has been assigned. It is far more soluble than the corresponding strontium salt, 1 part requiring only 460 parts of boiling or cold water for its solution.

THE MAGNESIUM, FERROUS, FERRIC, MANGANOUS, COBALT, NICKEL, ZINC, CADMIUM, CUPROUS, and CUPRIC SALTS are soluble.

THE SILVER SALT ($Ag_2\,SO_4$) is sparingly soluble, 1 part requiring 87 of water for solution; it is more soluble in nitric acid, and very much more soluble in sulphuric acid.

THE MERCUROUS SALT is produced by the addition of a soluble mercurous salt to sulphuric acid or a soluble sulphate. Its formula is $(Hg_2)_2\,SO_4$. It is somewhat soluble in water; but a basic salt is thereby produced. It dissolves in dilute nitric acid, but is reprecipitated on the addition of dilute sulphuric acid. It dissolves abundantly in strong sulphuric acid.

THE MERCURIC SALT is obtained by precipitating a mercuric salt with a soluble sulphate at a high temperature. It is a basic salt ($Hg_2SO_4, 2Hg_2O$). It dissolves in 2000 parts of cold, or 600 of boiling water.

THE LEAD SALT is obtained by the addition of a soluble lead salt to sulphuric acid or a solution of a soluble sulphate. It is a dense white precipitate. Its formula is Pb_2SO_4. It dissolves in 22,816 parts of water at 10°, and in 36,505 of dilute sulphuric acid; it is more soluble in concentrated sulphuric acid, and also in nitric acid. Certain ammonium salts also dissolve it sparingly.

The sulphates may also be recognized by the following tests :—

α. When sulphates are acted on by strong mineral acids, no apparent liberation of the acid (H_2SO_4) takes place, nor is any characteristic reaction produced.

β. Sulphates, when fused on charcoal with carbonate of sodium, are reduced, in common with other salts of radicals containing sulphur and oxygen, to sulphides.

γ. Sulphuric acid and sulphates do not yield any trace of hydrosulphuric acid on the addition of hydrochloric acid and stannous chloride.

δ. Sulphuric acid and sulphates give no characteristic reaction with sulphuretted hydrogen.

ϵ. Sulphuric acid and sulphates are not reduced to a lower stage of oxidation by hydrochloric acid and zinc.

ζ. Sulphuric acid and sulphates exert no reducing action upon ferric salts, &c.; nor do they decolourize permanganate of potassium.

This radical is generally recognized by the formation of the insoluble barium salt, and by the test β,—while it is distinguished from the other radicals containing sulphur and oxygen, by the absence of reaction on the application of the tests $\alpha, \gamma, \delta, \epsilon, \zeta$.

Of the acid-radicals containing selenium combined with oxygen, only two are known—the selenious and selenic; for the combination of selenium with oxygen, the gas (SeO), to which is attributed the odour of horseradish produced whenever selenium or a selenium compound is heated strongly in the air, appears itself to possess no acid characters.

SALTS OF THE SELENIOUS RADICAL, OR SELENITES.

When selenium is burnt in air, or treated with nitric or nitrohydrochloric acid, the compound SeO_2 is produced, analogous to the gas SO_2; the former compound is, however, a crystalline solid, which vapourizes at about 300° C., yielding a gas of the colour of chlorine. This body yields the salts termed selenites when brought into contact with basic oxides. Selenites easily decompose with reducing agents, giving a deposit of selenium, but are not readily oxidized; nitric acid does not convert them into seleniates.

When heated alone on charcoal, selenites leave a residue of selenide, or, parting with the whole of their selenium, of metallic oxide.

The Hydrogen Salt (H_2SeO_3), or selenious acid, may be obtained from the aqueous solution of the anhydride (SeO_2) in crystals resembling those of nitre, and soluble in alcohol: when heated, selenious acid decomposes into water and selenious anhydride (SeO_2), which sublimes.

The majority of the normal selenites are insoluble in water; the selenites of the alkaline metals and the acid selenites are, however, soluble. They may thus be recognized not only by products of decomposition, but also by the formation of insoluble salts.

Of the insoluble selenites, the barium, cupric, silver, mercuric, and lead salts are the most remarkable.

The Potassium and Sodium Salts are soluble.

The Barium Salt is produced by the action of a soluble barium salt on a soluble selenite: it is a white precipitate. Its formula is Ba_2SeO_3. It is insoluble in water, but soluble in selenious, hydrochloric, or nitric acid. It is not converted into seleniate by nitric acid, thus differing from the sulphite.

The Strontium, Calcium, and Magnesium Salts are white precipitates, insoluble, or sparingly soluble, in water.

The Ferrous, Ferric, Zinc, Cuprous, and many other Salts containing metals of the third and fourth subdivisions are white precipitates, insoluble in water.

The Cupric Salt is a crystalline greenish blue precipitate, insoluble in water and selenious acid, but soluble in ammonia water.

The Silver Salt is a white crystalline precipitate (Ag_2SeO_3) sparingly soluble in cold, more so in hot water: it easily dissolves in nitric acid; and from this solution water precipitates it.

The Mercurous Salt is produced by the action of soluble mercurous salts upon solutions of selenites or selenious acid. It is a white precipitate, insoluble in water and selenious acid.

The Mercuric Salt is a white precipitate, insoluble in water.

The Lead Salt is precipitated by a soluble lead salt from solutions of selenites or selenious acid: it is a dense white precipitate. Its formula is Pb_2SeO_3. It is almost insoluble in water or in selenious acid, and but sparingly soluble in hydrochloric or nitric acid; it dissolves in hot nitric acid without decomposition.

But selenites may also be readily recognized by the decomposition of their acid-radical:—

α. Selenites heated on charcoal in the reducing flame give a most powerful odour of horseradish, and often a white incrustation of selenious anhydride.

β. Selenites do not give any characteristic reactions on the addition of strong acids.

γ. Selenites fused with carbonate of sodium on charcoal, and the resulting mass placed on a silver coin and moistened with water, give a brown stain of selenide of silver.

δ. Selenites are reduced, giving a red deposit of selenium, by a hydrochloric solution of stannous chloride, by ferrous salts, and some other reducing agents.

ε. Hydrosulphuric acid passed through the aqueous or acid solution of a selenite of the first and second subdivisions, gives a reddish yellow precipitate of selenious sulphide (SeS_2), which is soluble in sulphide of ammonium.

ζ. If a solution of a selenite containing a metal of the first or second subdivision be acidified with hydrochloric acid, and a plate of iron or zinc immersed in it, the selenium is deposited either as a copper-coloured film, or in red-brown or greyish-black flakes.

η. If sulphurous acid gas be passed through a neutral or acidified solution of a selenite, a red precipitate of selenium is produced in the cold, a grey one if the solution be heated.

θ. Selenites ignited in a hard glass tube with chloride of ammonium give a sublimate of selenium. The selenite of ammonium formed in the reaction decomposes in the following manner:—

$$3(NH_4)_2SeO_3 = 3Se + 4N + 2NH_3 + 9H_2O.$$

Selenites may be recognized by the formation of the insoluble barium and and lead salts, and by the tests α, ϵ, ζ, η, and θ, while they are more particularly discriminated from the sulphites by the tests β, ζ, and θ.

SALTS OF THE SELENIC RADICAL, OR SELENIATES.

By the action of fusing nitrate of potassium upon selenium, selenides, or selenites, seleniates are formed; the action of chlorine on solutions of alkaline selenites also yields the same products. Seleniates greatly resemble the sulphates.

Seleniates thrown on glowing charcoal detonate and evolve the characteristic odour of horseradish, generally leaving a residue of selenide.

The Hydrogen Salt (H_2SeO_4), selenic acid, has never yet been obtained in the pure state; for, as its aqueous solution evaporates, it exhibits a great tendency to decompose into selenious acid and oxygen. From this proneness to change, it has not yet been found possible to obtain the selenic anhydride (SeO_3), corresponding to sulphuric anhydride (SO_3), since the solution of selenic acid (which has nearly the formula H_2SeO_4), when heated above 285°, decomposes rapidly into selenious anhydride, water, and oxygen. The concentrated acid evolves nearly as much heat when mixed with water as sulphuric acid; it also absorbs water from the air.

The great majority of the seleniates are soluble in water. This radical may, however, be recognized not only by its decompositions, but by those few characteristic insoluble salts which it forms.

Of the insoluble seleniates those of barium, strontium, and lead are the most characteristic.

THE POTASSIUM and SODIUM SALTS are insoluble.

The Barium Salt is produced by the action of soluble barium salts upon solutions of selenic acid or of seleniates. Its formula is Ba_2SeO_4. It is insoluble in water, and in hydrochloric or nitric acids; by long boiling, however, with hydrochloric acid, it is gradually decomposed and dissolved, being converted into selenite, thus—

$$Ba_2SeO_4+2HCl=Ba_2SeO_3+H_2O+2Cl.$$

THE STRONTIUM SALT is a white powder, nearly insoluble.

THE CALCIUM SALT is unknown; THE MAGNESIUM SALT is soluble.

THE FERROUS, ZINC, CUPRIC, SILVER, and MANY OTHER SALTS containing metals of the third and fourth subdivisions are soluble.

THE LEAD SALT is a white precipitate, insoluble in water.

Seleniates may be recognized by the following processes of decomposition:—

a. Seleniates heated before the blowpipe on charcoal detonate, emitting an odour of horseradish. The same odour is perceived when these salts are heated with borax or microcosmic salt. Heated with carbonate of sodium, they give the same results as selenites.

β. The strong acids in general exert no apparent decomposing influence upon selenites; hydrochloric acid, however, long heated with selenic acid or seleniates, gradually reduces the acid to selenious acid, and the salts to selenites.

γ. A hydrochloric solution of stannous chloride exerts no decomposing action upon seleniates.

δ. Sulphurous acid gas (SO_2) or zinc with hydrochloric acid exert no decomposing action upon the selenic radical; but both selenic acid and the seleniates give reactions of selenites, after their solutions have been boiled for some time with hydrochloric acid.

Seleniates are most readily identified by the formation of the insoluble barium and lead salts, and by the action of boiling hydrochloric acid upon them (*β.*).

Of the acid-radicals containing tellurium combined with oxygen, only two are known. These bear the closest analogy in composition to the compounds of selenium; their hydrogen compounds are known as tellurious (H_2TeO_3) and telluric (H_2TeO_4) acids.

SALTS OF THE TELLURIOUS RADICAL, OR TELLURITES.

Tellurium heated in the air or boiled with nitric or sulphuric acid yields a body, tellurious anhydride (TeO_2), the analogue of SO_2 and SeO_2. It is a white crystalline body, volatile at a high temperature, and fusible at a low red heat to a yellow liquid. When brought in contact with water or metallic oxides, saline combinations are formed, many of which are easily decomposed, even by the carbonic acid of the air.

Tellurites, heated with charcoal, generally yield tellurium, and a white incrustation of tellurious anhydride; they also impart a green colour to the flame.

THE HYDROGEN SALT (H_2TeO_3), or tellurious acid, occurs in white voluminous flakes, which are earthy when dry, redden litmus paper, and have a sharp metallic taste. This acid, when mixed with water, is resolved at 40° into water and the anhydride. The body TeO_2 partakes much of the character of a metallic oxide; and the corresponding sulphate and nitrate are also known.

The tellurites, with the exception of those of the first subdivision, are insoluble, or very sparingly soluble in water. The insoluble salts are in general dissolved by concentrated hydrochloric acid.

THE POTASSIUM and SODIUM SALTS are soluble.

The Barium Salt is a white voluminous precipitate, very slightly soluble in water, but soluble in strong acids. It is produced by adding together solutions of chloride of barium and normal tellurite of potassium (K_2TeO_3).

THE STRONTIUM and CALCIUM SALTS are sparingly soluble; THE MAGNESIUM SALT much more so.

THE FERROUS, FERRIC, ZINC, and MANY OTHER SALTS containing the metals of the third and fourth subdivisions are yellow or white insoluble precipitates.

THE CUPRIC SALT is a green precipitate, insoluble in water.

THE SILVER SALT is a yellowish white precipitate, insoluble in water, but soluble in hydrate of ammonium.

THE MERCUROUS SALT is yellow when freshly deposited, but rapidly becomes brown.

THE MERCURIC SALT is a milk-white precipitate.

THE LEAD SALT is white, and, though nearly insoluble in water, dissolves readily in acids.

Tellurites may be recognized by the following processes of decomposition:—

α. When heated before the blowpipe on charcoal in the reducing flame, they impart a green colour to the light.

β. The addition of a few drops of acid, even of the weakest, to a soluble tellurite, decomposes it, liberating and precipitating the acid in white flakes.

γ. Most tellurites (the zinc, silver, and some other salts excepted), when fused with carbonate of sodium on charcoal, give a saline mass, which, when dissolved in water, forms a wine-red solution of telluride of sodium.

δ. A solution of stannous chloride, added to solutions of tellurites, especially on the addition of hydrochloric acid, produces a brown-black precipitate of tellurium, which, when pressed and rubbed, exhibits a metallic lustre.

ϵ. Hydrosulphuric acid precipitates, from solutions of tellurites, a black powder of sulphide of tellurium (TeS_2), soluble in sulphide of ammonium.

ζ. The metals zinc, iron, copper, &c. precipitate tellurium from tellurites as a black powder; lead precipitates it in dendritic masses.

η. Sulphurous acid produces a precipitate of tellurium.

θ. Tellurite of ammonium does not decompose in the same way as the selenite.

Tellurites may best be recognized by the formation of the barium salt, and by the tests β, γ, δ, ϵ, ζ, η,—while they may be distinguished from the sulphites by the same experiments, and from the selenites by the test θ.

SALTS OF THE TELLURIC RADICAL, OR TELLURIATES.

The most common telluriate, that of potassium, is made in the same way as the seleniate, by fusing tellurious anhydride, (TeO_2) with nitrate of potassium, or by the action of chlorine on tellurite of potassium.

Heated on charcoal before the blowpipe, many telluriates yield tellurium, the reduction being frequently attended with slight detonation. When heated strongly alone, many telluriates fuse, become yellow or brown, and evolve oxygen, yielding tellurites.

The Hydrogen Salt (H_2TeO_4), or telluric acid, is prepared from the barium salt. It may be crystallized as the hydrated acid ($H_2TeO_4+H_2O$). This, heated to 160°, gives the acid H_2TeO_4; and this, if more strongly heated, yields the anhydride TeO_3, an orange-yellow crystalline mass (the analogue of SO_3 and SeO_3). The crystallized acid is very soluble in water, but insoluble in alcohol.

The telluriates of the first subdivision are soluble; the rest are insoluble, or nearly so.

The Potassium and Sodium Salts are soluble.

The Barium Salt is at first a bulky white precipitate, which gradually becomes denser. Its formula is Ba_2TeO_4. It is slightly soluble in cold water, more so in hot, and easily dissolves, without decomposition, in nitric acid.

The Strontium, Calcium, and Magnesium Salts are somewhat more soluble in water than the barium salt.

The Ferrous, Ferric, and most other Salts containing metals of the third and fourth subdivisions are insoluble, or nearly so, in water.

The Cupric Salt is pale green.

The Silver Salt is deep yellow. It is soluble in hydrate of ammonium.

The Mercurous Salt is yellowish brown.

The Mercuric Salt is a bulky white precipitate.

The Lead Salt is a white, heavy, somewhat soluble precipitate.

Telluriates may also be recognized by the following processes of decomposition:—

α. Telluriates, when heated on charcoal before the blowpipe in the reducing flame, impart to it a green colour, often detonating slightly and yielding tellurium and a white sublimate of tellurious anhydride (TeO_2).

β. By the action of boiling hydrochloric acid, telluriates are reduced to tellurites.

γ. With carbonate of sodium on charcoal, telluriates (like tellurites) give a mass containing telluride of sodium.

δ. Sulphurous acid gas (SO_2), passed into a hot hydrochloric solution of a telluriate, precipitates the tellurium.

Telluriates may be recognized by the formation of several insoluble compounds, such as that of barium, and by the tests *α*. and *β*.

Of the acid-radicals containing tellurium combined with sulphur, only two are known. Their salts are termed sulphotellurites and sulphotelluriates. The sulphotellurites containing the metals of the first and second subdivisions are yellow crystalline salts, soluble in water: the insoluble salts of the third subdivision are white or yellow; of the fourth, brown or black. The sulphotelluriates have scarcely been examined.

SECTION III.—*The aluminates, chromites, chromates, perchromates, ferrites, ferrates, manganates, permanganates, bismuthates, stannates, metastannates, platinates, rhodiates, rutheniates, iridiates, osmites, osmiates, aurates, tungstites, tungstates, molybdates, vanadites and vanadiates; the sulphostannates, sulphoplatinates, sulphorhodiates, sulphorutheniates, sulphiridiates, sulphosmiates, sulphaurates, sulphomolybdates, and sulphovanadiates.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN OXYGEN AND SULPHUR COMBINED WITH METALS.

A very large class of compound acid-radicals, some of which are extremely powerful, are produced by the union of monatomic and biatomic molecules of certain basic radicals with a preponderating proportion of an acid element. Many of these bodies form salts of great stability—witness the chromates, stannates, tungstates, and molybdates; but their hydrogen compounds, or acids, are usually unstable. Some of these compound acid-radicals are monobasic, some bibasic, and others tribasic; the latter are known, in many instances, to yield acid salts containing 1 or 2 eqs. of basic hydrogen unreplaced by a metal.

Most of these acid-radicals are very easy of detection. They form numerous insoluble compounds, some of which are of extremely brilliant colours; in addition to this, the comparative readiness with which they may be caused to decompose, greatly facilitates their recognition.

One compound acid-radical containing aluminium and oxygen is known; or at least the compound called hydrate of aluminium is considered to be an acid (aluminic acid); and when this body is acted upon by hydrate of potassium, the potassium salt is formed. Viewed in this light, the formula $H_3Al_2O_3$ may be assigned to the acid, and $KH_2Al_2O_3$ to the potassium salt. Other modes of representing these compounds may be seen on referring to pp. 109, 110. Several aluminates have been obtained.

Of the acid-radicals containing chromium and oxygen, one only is of any analytical importance—that, namely, which is contained in chromic acid ($HCrO_2$); the salts of the other acid-radicals, which are known as chromites and perchromates, are of rare occurrence. The chromites have the general formula MCr_2O_2; the potassium, magnesium, and iron salts are tolerably well known.

SALTS OF THE CHROMIC RADICAL, OR CHROMATES.

These salts are usually made from the potassium salt, which is easily prepared by fusing chromic oxide ($[Cr_2]_2O_3$) with nitrate of potassium in a crucible. The chromates are often of a red or yellow colour.

Many chromates, when strongly heated, yield chromic oxide and oxygen, while others (*e.g.* chromate of magnesium) yield chromites; other blowpipe reactions of the compounds of chromium will be found on p. 111.

The Hydrogen Salt ($HCrO_2$), or chromic acid, has not yet been isolated; when its aqueous solution is concentrated, fine crimson acicular crystals separate, which consist of the compound Cr_2O_3, *i. e.* chromic anhydride*. This body possesses the property of uniting with 2 eqs. of certain neutral chromates to form new salts, which require no additional equivalent of basic radical. These salts have been called bichromates; terchromates are also known, and some compounds even which may be termed quadri-

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* Just as chlorochromic acid may be viewed as chloride of chromyle (CrO, Cl), so anhydrous chromic acid may be considered as the oxide of that radical ($[CrO]_2O$); there is, however, some ground for doubling the formulæ here assigned to chromyle and the neutral chromates.

chromates. All such salts are usually of a darker colour than the simple chromates, which are generally yellow.

The bichromates, &c. are thus formed:—

$$2KCrO_2 + Cr_2O_3 = \underset{\text{of potassium.}}{\underset{\text{bichromate}}{K_2Cr_4O_7}}.$$

The chromates of the first and second divisions of the basic elements are soluble, the barium salt excepted; most of the other chromates are insoluble in water, but easily soluble in acids.

The chromates may be recognized, not only by the formation of insoluble salts, but by several processes of decomposition.

The most remarkable insoluble salts of this series are those of barium, silver, mercury, and lead.

THE POTASSIUM and SODIUM SALTS are soluble.

The Barium Salt is produced by the action of a soluble barium salt on solutions of neutral chromates or of bichromates.

Its formula is $BaCrO_2$.

It is a pale yellow precipitate, nearly as insoluble in water as the sulphate, but soluble in hydrochloric, nitric, or chromic acid, and in solutions of bichromates.

THE STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE FERRIC, MANGANOUS, and MANY OTHER SALTS of the third subdivision are brown or yellow precipitates, nearly insoluble in water.

THE CUPROUS SALT is unknown. THE CUPRIC SALT is produced by adding a cupric salt to a soluble chromate. With bichromates no precipitate is produced. It is a yellowish brown precipitate. It is soluble in nitric acid, and in hydrate of ammonium.

The Silver Salt is produced by the action of a soluble silver salt on a chromate. It is a crimson crystalline precipitate.

Its formula is $AgCrO_2$.

It is soluble in alkaline chromates, in hydrate of ammonium, and in acids. When formed in acid solutions, this precipitate is the bichromate ($Ag_2Cr_4O_7$), and has a more brilliant colour.

THE MERCUROUS SALT is produced by a soluble mercurous salt when added to a solution of a chromate: it is a red precipitate.

Its formula is Hg_2CrO_2; but frequently the salt $3Hg_2CrO_2, (Hg_2)_2O$ is precipitated. It is slightly soluble in solutions of ammonium salts, in water, and in nitric acid.

THE MERCURIC SALT resembles the mercurous salt very closely. It is soluble in excess of many soluble mercuric salts.

The Lead Salt is produced by the action of a soluble lead salt on chromate or bichromate of potassium. It is a yellow precipitate.

Its formula is $PbCrO_2$.

It is slightly soluble in excess of the chromate or bichromate of potassium, and in hydrate of potassium; it is insoluble in chloride of ammonium and in water, but soluble in nitric acid.

This acid-radical may also be recognized by the following experiments:—

α. Chromates, when heated before the blowpipe with a borax bead, give evidence of chromium in the green tint produced; care must, however, be taken that other interfering bases are absent.

β. When boiled for some time with hydrochloric acid, chromates are reduced, yielding the sesquichloride (Cr_2Cl_3), with evolution of chlorine. If sulphuric acid be employed instead, oxygen is set free.

γ. The passage of hydrosulphuric acid through the aqueous solution of a chromate also effects its reduction,—a chromic salt with separation of sulphur being the results:

$$4KCrO_2 + 5H_2S = \underset{\substack{\text{chromic hydrate,}\\ \text{green ppt.}}}{2Cr_2H_3O_3} + 2K_2S + 2H_2O + \underset{\text{ppt.}}{3S}.$$

Sulphurous anhydride (SO_2) produces a similar effect, sulphuric and hyposulphuric acids being formed. Nascent hydrogen and many other reducing agents also give the same results.

Numerous organic bodies are capable of rapidly reducing the chromates—such substances as alcohol, sugar, oxalic and tartaric acids. When warmed with alcohol and hydrochloric acid, a chromate decomposes thus:—

$$4KCrO_2 + 10HCl + \underset{\text{alcohol.}}{3C_2H_6O} = \underset{\substack{\text{green}\\ \text{chromic}\\ \text{chloride.}}}{2Cr_2Cl_3} + 4KCl + 8H_2O + \underset{\text{aldehyde.}}{3C_2H_4O}.$$

The hydrochloric acid acts partly as a solvent for the chromic hydrate, which we may suppose to be formed at first.

δ. Fused with carbonate of sodium many insoluble chromates yield the soluble chromate of sodium (see p. 112).

The chromic radical is generally recognized by the formation of the insoluble silver and lead salts, and by the tests α. and β.

SALTS OF THE PERCHROMIC RADICAL, OR PERCHROMATES.

The hydrogen compound of this radical is known, but only as dissolved in ether: it is obtained by the action of a hydrochloric solution of peroxide of barium on bichromate of potassium; the perchromic acid thus liberated is taken up by ether, which becomes of a beautiful blue colour. It is immediately decomposed by hydrate of potassium, but may be made to unite with ammonium and certain organic bases, forming comparatively stable salts, from which acids separate the blue perchromic acid, which then speedily decomposes into chromic acid and oxygen.

Of compound acid-radicals containing iron and oxygen, two are known, but they are of very slight importance. When carbonate of sodium and ferric oxide are strongly ignited, a compound termed *ferrite* of sodium is said to be obtained in very small proportion. Similar salts are believed to be formed when a solution containing ferric chloride and the chloride of an alkaline earth is precipitated (under certain conditions) by a hydrate of the first subdivision. But the only definite acid-radical of iron and oxygen is that contained in the ferrates ($MFeO_2$). The ferrate of potassium is obtained by igniting iron or ferric oxide with hydrate or nitrate of potassium, by the action of chlorine on ferric oxide suspended in hydrate of potassium solution, or by the electrolytic evolution of oxygen gas from an iron plate immersed in a concentrated solution of hydrate of potassium. By all these methods the potassium salt is obtained, sometimes in the crystalline form; it dissolves in water, forming a red-violet solution, which is instantly decomposed and decolourized by ammoniacal salts and the weakest reducing agents, and even by a heat of less than 100°: the products of this decomposition are ferric oxide and oxygen. The hydrogen compound, or ferric acid, cannot be obtained, as any attempt at its liberation results in its instant decomposition.

Of the acid-radicals containing manganese and oxygen, two are well known and easily produced. These are the manganic (MnO_2) and permanganic (Mn_2O_4) radicals. They are both monobasic. The potassium salt of the former is obtained by igniting manganese, or one of its oxides, with hydrate of potassium in contact with air, or with hydrate of potassium mixed with nitrate or chlorate of potassium. The manganates of the first and second subdivisions are known; they are dark bluish green compounds, those of the alkaline metals dissolving in water to form green solutions. The hydrogen compound is not known.

Permanganic acid (HMn_2O_4) is produced by the action of dilute nitric acid on the aqueous solution of a manganate. Its colour is a beautiful violet; the solutions of the alkaline permanganates have the same tint. The permanganates, as far as known, are all soluble, no precipitates being formed with saline solutions except in cases where the latter act as reducing agents, and precipitate the peroxide of manganese (Mn_2O_2).

Of acid-radicals containing bismuth and oxygen, one only is known. When bismuthic oxide (Bi_2O_3) is fused with hydrate of potassium, or when it is suspended in a concentrated solution of hydrate of potassium through which a current of chlorine is passing, a double salt of bismuthate of potassium and bismuth is formed, which contains the radical BiO_3. One or two salts are known, and the hydrogen compound ($HBiO_3$).

Of acid-radicals containing tin and oxygen, two are known. Their hydrogen compounds are stannic acid ($H_2Sn_2O_3$) and metastannic acid ($H_2H_8Sn_{10}O_{15}$). The acids themselves being very insoluble bodies, no characteristic reactions can be obtained from them, except such as, by destroying the radical, prove the presence of its metallic constituent.

Of the acid-radicals containing the rare metals of the fourth subdivision combined with oxygen, none are of analytical importance. The higher oxides of platinum, rhodium, ruthenium, iridium, osmium, and gold have the property of uniting with the elements of water to form acid compounds, and with the oxides of some few basic radicals, as those of the first subdivision, to form salts. These salts, with the exception of the gold compounds, have not been thoroughly examined. The existence of a definite auric acid ($HAuO_2$) is doubtful; but the anhydride (Au_2O_3) is known: the aurate of potassium too has been obtained, crystallized, in small needles of a yellow colour, and having the formula $KAuO_2+3aq$; a solution of this salt in water produces precipitates in many metallic solutions, proving that there are many insoluble aurates;—insoluble, that is, in water, for they frequently dissolve in excess of of their precipitants to form double salts. It will be at once seen that these acid-radicals correspond closely to those mentioned under Section III. of the first subdivision of the acid-radicals (p. 276).

Of the acid-radicals which contain tungsten combined with oxygen, one only is of any analytical importance, although another is known to exist in a few compounds. The tungstic radical (WO_2) is a very powerful one, and forms stable salts termed tungstates, which impart to water a bitter metallic taste.

SALTS OF THE TUNGSTIC RADICAL, OR TUNGSTATES.

These salts are not decomposed by heat alone, unless their basic constituent is volatile or compound, and when heated on charcoal sometimes yield the brown oxide, although they are reduced or decomposed in different ways according to the base present. The other blowpipe reactions of tungstic acid and tungstates will be found among the processes of decomposition employed for detecting the tungstic radical (see p. 236).

The Hydrogen Salt (HWO_2) does not appear to be known; for when the acid is liberated by the action of other acids upon solutions of tungstates in the cold, the white precipitate which occurs, though thought by some to be the acid, rapidly becomes yellow when the solutions are heated, or when the precipitate is allowed to stand. This yellow body has the formula W_2O_3, and so bears the same relation to the acid (HWO_2) as auric anhydride (Au_2O_3) does to auric acid ($HAuO_2$), or hypochlorous anhydride (Cl_2O) to to the acid ($HClO$). Tungstic anhydride is lemon-yellow and crystalline. Recent researches have shown that there are many modifications of tungstates, in which varying quantities of oxygen and tungsten are united to form acid-radicals; yet they will all group in a singular manner around the anhydride (W_2O_3), which may be produced by the decomposition of all. The union of the anhydride with normal tungstates gives, on the other hand, compound salts resembling the bichromates, &c.

Tungstates may be recognized by the formation of some of the most characteristic insoluble salts, but are more usually identified by processes of decomposition.

The tungstates of the first subdivision are soluble; all the other salts, excepting that of magnesium, are insoluble in water.

The Barium Salt is produced by the action of soluble barium salts on the neutral tungstate of potassium: it is a white precipitate. Its formula is $BaWO_2$. It is insoluble in water and in phosphoric acid, but is decomposed by stronger acids; it is dissolved by a boiling solution of oxalic acid.

The Strontium and Calcium Salts are white precipitates, sparingly soluble in water.

The Magnesium Salt is soluble.

The Ferrous and many other Salts containing metals of the third and fourth subdivisions are insoluble, or nearly so, in water.

The Cupric Salt is obtained by the action of a soluble cupric salt on tungstate of sodium: it is a grass-green precipitate. Its formula is $CuWO_2$. It is insoluble in water and oxalic acid, soluble in acetic and phosphoric acids.

The Silver Salt is a white insoluble powder, produced when a silver salt is added to a solution of bitungstate of sodium. Its formula is $Ag_2W_4O_7$.

The Mercurous Salt is produced by the action of a soluble mercurous salt upon tungstate of potassium: it is a yellow precipitate, so insoluble in water as to be *used for the quantitative estimation of tungstic acid.*

THE MERCURIC SALT is white if the mercury solution be in excess; otherwise it is yellow, red, or brown. It is insoluble in water.

THE LEAD SALT is a white precipitate, insoluble in cold water or cold nitric acid, soluble in hydrate of potassium.

Tungstates are, however, most readily recognized by the decomposition of their acid constituent; the following tests may be employed:—

α. Tungstic anhydride (W_2O_3) does not volatilize when heated on charcoal, but yields a brown oxide of tungsten; before the blowpipe, with microcosmic salt, *this body* ([W_2O_3] which, as we have seen, may be easily produced from tungstates) *gives in the reducing flame a fine blue colour*, which disappears in the oxidizing flame; if iron be present, a blood-red colour will be produced.

β. Solutions of the tungstates containing the alkaline metals are precipitated by hydrochloric, nitric, acetic, sulphuric, and phosphoric acids; and the precipitate is insoluble in all the above acids, excepting the last-named, which dissolves it readily. Oxalic, tartaric, and citric acids do not separate the anhydride (W_2O_3).

γ. When the body, W_2O_3, is precipitated from a soluble tungstate by the addition of a mineral acid, a small quantity of tungstic acid remains in solution; and if then a strip of zinc be introduced into the acid solution, the liquid will be coloured blue from the formation of the blue oxide of tungsten.

This radical is usually recognized by the formation of the insoluble barium and mercurous salts; but more especially by the tests α. and γ. (See also p. 237.)

SALTS OF THE MOLYBDIC RADICAL, OR MOLYBDATES.

The radical MoO_2 bears considerable resemblance to the radical WO_2: the soluble molybdates have a faint metallic taste; several of the insoluble salts have a yellow colour.

Heated alone, they are fixed, unless their base is volatile or decomposable; on charcoal, before the blowpipe, several molybdates are partially reduced, particularly in the presence of carbonate of sodium.

THE HYDROGEN SALT ($HMoO_2$) is not known; when an attempt is made to liberate it by the action of acids on molybdates, the anhydride (Mo_2O_3) separates as a white curdy precipitate. This body unites with molybdates to form bimolybdates, &c., analogous to the bichromates, bitungstates, &c.

Molybdates are recognized by the formation of certain insoluble salts, and also by several processes of decomposition.

The molybdates of the first subdivision are soluble in water; the others insoluble, or sparingly soluble.

THE POTASSIUM and SODIUM SALTS are soluble.

The Barium Salt is produced by the action of soluble barium salts on molybdate of potassium: it is a white precipitate, probably having the formula $BaMoO_2$. It is insoluble in water, but soluble in dilute nitric or hydrochloric acid.

THE STRONTIUM and CALCIUM SALTS are white, insoluble in water.

THE MAGNESIUM SALT is comparatively soluble, particularly in hot water.

THE FERROUS and MANY OTHER SALTS of the third and fourth subdivisions are yellow or brown precipitates, insoluble in water, soluble in hydrochloric or nitric acid.

THE CUPRIC SALT is yellowish green, insoluble (or nearly so) in water, decomposed by acids and alkalies.

THE SILVER SALT is greenish white, slightly soluble in water and in dilute nitric acid.

THE MERCUROUS SALT is white, soluble in 500 or 600 parts of water, decomposed by nitric acid.

The Lead Salt is produced by precipitating plumbic nitrate with normal molybdate of ammonium: it is a white insoluble precipitate. The native variety is the chief ore of molybdenum.

Molybdates may also be detected by several processes of decomposition:—

α. Molybdic anhydride, when heated in the reducing flame on platinum wire, imparts a yellowish green tinge to the light; it also gives with microcosmic salt a fine green colour, and with borax a brown bead, when heated in the inner blowpipe flame.

β. When to a neutral concentrated solution of a soluble molybdate, a few drops of hydrochloric or nitric acid are added, the anhydride (Mo_2O_3) separates; it dissolves, however, on the addition of more acid, or even upon dilution with much water. Oxalic and phosphoric acids do not produce this effect.

γ. By immersing a strip of zinc in a hydrochloric solution of a molybdate, a blue colour is produced, from separation of the blue oxide of molybdenum; the colour gradually changes to green, and then becomes nearly black.

δ. By evaporating nearly to dryness a nitric solution of an alkaline phosphate or of phosphoric acid, and adding a drop of molybdate of ammonium, a yellow precipitate is obtained, which is insoluble in hot nitric acid.

ε. A trace of hydrosulphuric acid produces in solutions of molybdates a blue colouration; larger quantities of the gas give a brown precipitate of molybdous sulphide (Mo_2S_2).

Molybdenum is usually recognized, when existing as the molybdic radical, by the precipitation of the barium and lead salts, and by the tests *β*. and *δ*. (See also p. 241.)

Of acid-radicals containing vanadium and oxygen, two are known; of these the vanadic only is of any importance; the vanadites are derived from the binoxide (V_2O_2).

SALTS OF THE VANADIC RADICAL, OR VANADIATES.

The acid-radical VO_2 resembles the tungstic and molybdic radicals in many points: many of its salts are yellow or orange; they have no characteristic taste. Generally speaking, they are comparatively soluble in water.

A red heat produces no change in the vanadiates, unless the basic constituent is volatile or decomposable. Vanadic anhydride (V_2O_3) heated on charcoal is partially reduced to a lower oxide, and partly to vanadium itself; vanadiates of the heavy metals yield alloys of vanadium.

THE HYDROGEN SALT (HVO_2) is unknown, the addition of an acid to a soluble vanadiate precipitating the anhydride (V_2O_3) in an impure state, as a yellow substance, soluble in acids, yielding yellow solutions. From the anhydride, vanadiates and bivanadiates are prepared.

This radical may be recognized both by the formation of insoluble salts and by certain processes of decomposition.

Many vanadiates are soluble in water.

THE POTASSIUM and SODIUM SALTS are soluble.

The Ammonium Salt (NH_4VO_2) is remarkable for being quite insoluble in a saturated solution of chloride of ammonium.

The Barium Salt is produced by the action of a soluble barium salt on an aqueous solution of vanadiate of ammonium: it is a yellow gelatinous precipitate, which becomes white and dense after standing. Its formula is $BaVO_2$. It is slightly soluble in water, and dissolves with a red colour in suphuric acid.

THE STRONTIUM SALT is a white crystalline granular precipitate, more soluble than the barium salt.

THE CALCIUM SALT is soluble, and THE MAGNESIUM SALT exceedingly soluble in water.

THE FERRIC, NICKEL, and MANY SALTS containing metals of the third and fourth subdivisions are yellow and soluble in water.

THE CUPRIC SALT is soluble.

THE SILVER SALT is obtained by the action of nitrate of silver on vanadiate of ammonium, and is a pale yellow or white precipitate, soluble in nitric acid and in hydrate of ammonium.

THE MERCUROUS, MERCURIC, and LEAD SALTS are yellow and more or less soluble in water.

The vanadic radical may also be recognized by processes of decomposition, &c.:—

α. Vanadiates generally fuse when heated; the anhydride (V_2O_3) does not volatilize. With borax or microcosmic salt, the anhydride gives a green glass in the reducing, and a yellow in the oxidizing flame.

β. Vanadic anhydride dissolves in the stronger acids, forming yellow or red solutions, which often become colourless on ebullition, and yield red or yellow crystallized compounds or salts of vanadic acid. The sulphate of vanadic acid is said to have the formula $V_2(SO_4)_3$.

γ. Hydrosulphuric acid precipitates a mixture of binoxide of vanadium and sulphur from an acid solution of vanadic oxide.

δ. Ferrocyanide of potassium produces a beautiful green precipitate with soluble vanadiates.

ε. Solutions of vanadiates with tincture of galls yield a blackish blue or black mixture.

Vanadiates are usually detected by the tests β, δ, and ε.

Of the acid-radicals which contain metals and sulphur, none are of sufficient importance to justify description here. They generally form yellow, reddish brown, brown, or brownish black salts, which correspond closely to the analogous salts containing the same metals combined with chlorine or oxygen. They are generally formed by the solution of the metallic sulphide in sulphide of potassium, sodium, &c. The salts formed by these radicals are termed sulphostannates ($M_2Sn_2S_3$), sulphoplatinates ($M_2Pt_2S_3$), sulphorhodiates (MRS_2), sulphorutheniates ($M_2Ru_2S_3$), sulphiridiates ($M_2Ir_2S_3$), sulphosmiates ($MOsS_2$), sulphaurates ($MAuS_2$), sulphotungstates (MWS_2), sulphomolybdates ($MMoS_2$), and sulphovanadiates (MVS_2).

TABLE OF REACTIONS.

SALTS.	O (see page 281)	S (p. 283)	SO_3 (p. 290)	SO_4 (p. 295)	CrO_2 (p. 305)
Barium......	white	—	white	white	pale yellow
Strontium...	white	—	white	white	—
Calcium ...	white	—	white	white	—
Magnesium	white	—	—	—	—
Ferrous	greenish white	black	—	—	yellowish brown
Ferric	red	black	—	—	brown
Zinc	white	white	—	—	yellow
Cuprous ...	orange yellow	black	brownish red	—	?
Cupric	black	black	—	—	yellowish brown
Silver	brown	black	white	—	crimson
Mercurous ..	brownish black	black	white	white	red
Mercuric ...	orange red	black	white	white	yellow
Lead.........	white	black	white	white	yellow

Analysis of Subdivision II.

The acid-radicals of more common occurrence only being included, the salt may be an OXIDE, SULPHIDE, SULPHITE, SULPHATE, CHROMATE, or TUNGSTATE.

<table>
<tr><td colspan="4">The addition of strong sulphuric acid to the solid salt or its concentrated solution may produce an effervescence; if so, the evidence sought will probably be better obtained with a weaker acid, aided by heat.
A gas having <i>an odour of rotten eggs</i> (H_2S) indicates a sulphide.
,, ,, ,, <i>burning sulphur</i> (SO_2) indicates a sulphite.</td></tr>
<tr><td colspan="4"><i>Further Analysis.</i>
Acidify the solution with hydrochloric acid, and warm for some time.</td></tr>
<tr><td rowspan="3">A lemon-yellow precipitate of W_2O_3 would indicate the original presence of WO_2.</td><td colspan="3">If no precipitate occurs, the solution may contain a chromate, sulphate, or oxide. Add a few drops of alcohol, and boil for some minutes; if the liquid changes from a reddish yellow to an emerald-green colour, the previous existence of CrO_2 may be inferred. Add excess of ammonia.</td></tr>
<tr><td rowspan="2">A green precipitate of $Cr_2H_3O_3$ would indicate the original presence of CrO_2.</td><td colspan="2">If no green colour or precipitate occurs, add a few drops of chloride of barium.</td></tr>
<tr><td>A white precipitate of Ba_2SO_4 would indicate the presence of SO_4.</td><td>If no precipitate occurs, and the substance under examination is obviously not a basic radical, <i>i. e.</i> a metal, we infer the presence of O as the acid-radical.</td></tr>
</table>

SUBDIVISION III.

SALTS OF CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

This group, with the exception of its four latter and rarer members, presents but little analogy with either of the preceding subdivisions. One distinctive feature is, that no member of this subdivision combines directly with hydrogen to form a compound of acid properties, although they combine with almost all metals to form salts. All these acid-radicals, however, form, by union with oxygen, compound acid-radicals, which yield extremely stable salts with hydrogen and metals. Another great peculiarity of this group is the property possessed by carbon of uniting with hydrogen and oxygen, with hydrogen, oxygen, and nitrogen, and with other basic radicals, such as with iron and nitrogen, to form acid-radicals, many of which combine with basic radicals to form salts of great stability: most of such compounds are generally termed "organic," from their frequent occurrence in the animal and vegetable kingdoms, or from being obtained among the products of their decomposition. Examples of such compounds are—

$H_2C_4H_4O_4$,	$H_3C_5H_3N_4O_4$,	$H_3Co_2C_6N_6$.
succinic acid.	uric acid.	hydrocobalticyanic acid.

Among these bodies many are monobasic, many bibasic, and some tribasic.

SECTION I.—SALTS OF CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM.

The carbides, borides, silicides, tantalides, niobides, pelopides, and titanides.

SECTION II.—SALTS OF THE ACID-RADICALS WHICH CONTAIN CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM COMBINED WITH FLUORINE, OXYGEN, OR SULPHUR.

The borofluorides, silicofluorides, carbonates, oxalates, borates, silicates, tantalates, niobiates, pelopiates, titanates, and sulphocarbonates.

SECTION III.—SALTS OF THE ACID-RADICALS WHICH CONTAIN CARBON COMBINED WITH NITROGEN, WITH NITROGEN AND OXYGEN, WITH NITROGEN AND SULPHUR, WITH NITROGEN AND METALS, WITH OXYGEN AND HYDROGEN, AND WITH OXYGEN, HYDROGEN, AND NITROGEN.

The cyanides, cyanates, and sulphocyanides; the ferrocyanides, ferricyanides, and cobalticyanides; the formiates, acetates, benzoates, succinates, tartrates, lactates, citrates, gallates, tannates, and urates.

SECTION I.—*The carbides, borides, silicides, tantalides, niobides, pelopides, and titanides.*

SALTS OF CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM.

The radicals of this third subdivision, although they combine with metals, can scarcely be said to yield saline compounds, since it is with the greatest difficulty that the bodies are made to unite in definite proportions, and then the products of the union partake more of the character of alloys. It is probable that their combinations, especially those of carbon and silicon (or of phosphorus), with the metal, exist diffused through the mass of metal, which presents, in different specimens, different properties. Thus the varieties of commercial iron known as cast-iron and steel are entirely due to the presence of a small difference in the proportion of carbon present, which, after all, never rises above 2 per cent. It is thought that the known carbide of iron (Fe_8C) exists diffused in the mass, which also contains carbon in the form of graphite.

Silicon and phosphorus again are known to exert a very deleterious influence upon the quality of iron and of other metals, even when they are present in very small proportion. Numerous compounds of carbon with hydrogen are known; they are termed hydrocarbons. A compound of silicon with hydrogen has been discovered recently; but neither it nor the hydrocarbons possess acid properties or reactions.

SECTION II.—*The borofluorides, silicofluorides, carbonates, oxalates, borates, silicates, tantalates, niobiates, pelopiates, titanates, and sulphocarbonates.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN CARBON, BORON, SILICON, TANTALUM, NIOBIUM, PELOPIUM, AND TITANIUM COMBINED WITH FLUORINE, OXYGEN, OR SULPHUR.

The acid-radicals of the present section are for the most part powerful; they possess different degrees of basicity. Those most important to the student will be found to be the compounds the acids of which are termed hydrofluosilicic, carbonic, oxalic, boracic, and silicic. With the reactions of the five acids just named, the analyst should early make himself acquainted.

Of acid-radicals formed by the union of boron with fluorine, one only is known: it is the radical contained in the borofluorides, and is produced when the gas known as terfluoride of boron (BoF_3) or its aqueous solution is mixed with a large quantity of water. The water effects a decomposition of the compound BoF_3, boric anhydride (Bo_2O_3) being precipitated, and the compound $HBoF_4$ remaining in solution: this compound is hydrofluoboric acid; and the decomposition which gives rise to its formation is as follows:—

$$8BoF_3+3H_2O=Bo_2O_3+\underset{\substack{\text{hydrofluoboric}\\\text{acid.}}}{6HBoF_4}.$$

THE HYDROGEN SALT ($HBoF_4$) is not known in an isolated state, but only in aqueous solution.

The fluoborides are all soluble in water, as far as has been ascertained.

The radical must be recognized in its salts by processes of decomposition.

SALTS OF SILICOFLUORINE, OR SILICOFLUORIDES.

This radical (that contained in the silicofluorides) is of much greater importance than the preceding one, but is prepared in precisely the same manner. The method for its preparation has been already given (p. 65). When the gaseous body terfluoride of silicon (SiF_3) is passed into water, the hydrogen compound of the radical in question is obtained in solution, gelatinous silicic acid ($HSiO_2$) being precipitated:

$$3SiF_3 + 2H_2O = HSiO_2 + H_3Si_2F_9.$$

Heated on charcoal, silicofluorides suffer various changes, according to the nature of the basic radical present.

THE HYDROGEN SALT ($H_3Si_2F_9$) is known only in aqueous solution.

This radical may be recognized both by the formation of insoluble salts and by processes of decomposition.

The majority of the silicofluorides are soluble with greater or less facility in water; it is remarkable, however, that those of the first and second subdivisions of the basic radicals are the least soluble.

THE POTASSIUM SALT is produced by the action of a soluble potassium salt on hydrofluosilicic acid: it is a white gelatinous precipitate. Its formula is $K_3Si_2F_9$. It is very slightly soluble in cold water, but dissolves somewhat more freely in hot.

The Barium Salt is produced by the action of a soluble barium salt upon hydrofluosilicic acid: it is a gelatinous precipitate, but appears crystalline under the microscope. It is precipitated more speedily on stirring the solution.

Its formula is $Ba_3Si_2F_9$.

It is but slightly soluble in cold water, 1 part requiring 3802 parts of pure water for its solution, and 733 parts of water acidulated with hydrochloric acid. In alcohol it is insoluble.

THE STRONTIUM and CALCIUM SALTS are comparatively soluble.

THE MAGNESIUM SALT is exceedingly soluble.

THE FERROUS, FERRIC, CUPROUS, ARGENTIC, and MANY OTHER SALTS containing metals of the third and fourth subdivisions are soluble in water.

THE MERCUROUS SALT ($[Hg_2]_3Si_2F_9$) is sparingly soluble.

THE MERCURIC and LEAD SALTS are soluble.

The salts of this acid-radical may be detected by the following processes of decomposition:—

a. Hydrofluosilicic acid gradually decomposes when exposed to the air in a glass vessel, terfluoride of silicon being given off, and the hydrofluoric acid thereby left attacking the glass and yielding another portion of the volatile terfluoride. In a glass bottle from which the air is always carefully excluded, and the volatilization of any part of the gas SiF_3 thus prevented, no decomposition ensues.

β. Alkalies decompose hydrofluosilicic acid, yielding fluorides and silicates.

γ. Strong sulphuric acid liberates gaseous terfluoride of silicon from hydrofluosilicic acid. From silicofluorides, acids separate a portion of silicic acid, chiefly on ebullition.

Of the acid-radicals which contain carbon and oxygen, two merit the attention of the student—the carbonic and the oxalic; both are bibasic. The salts of the former radical are of very common occurrence in nature, forming (in addition to their general distribution through the earth's crust) extensive deposits, as the strata of limestones, of which they are practically the sole constituents. The salts of the latter radical, the oxalic, are of less frequent occurrence, although they also are found in nature, existing in several members of the vegetable kingdom; nevertheless they are important as standing on what may be termed the neutral ground between the organic and inorganic domains of chemistry. The oxalates are also interesting, since they exhibit the simplification which complex organic molecules undergo in their gradual conversion into simpler forms. The oxalate is frequently the last stage of combination into which the carbon and oxygen of a complex body enter previously to their appearance as a carbonate, a salt which is very generally assumed to belong to inorganic nature.

SALTS OF THE CARBONIC RADICAL, OR CARBONATES.

These salts are not very numerous; for the radical is one of such weak combining power that it is only when in union with the most powerful basic constituents (those of the first or second subdivisions), or where the salt is insoluble, that stable compounds are formed by it. For this reason, and on account of the facility with which carbonates, especially on the application of heat, divide into metallic oxides or hydrates and carbonic anhydride (CO_2), it is found that many of the precipitates which in double decompositions should be carbonates, are in reality mixed carbonates and hydrates. Take, for example, the precipitate produced by the action on carbonate of sodium of a zinc salt or any of the weaker bases, such as the triatomic molecules Al_2, Cr_2, Fe_2, or Sb, some of which will not combine with this radical at all, or, if they do combine, yield salts which instantly or very rapidly decompose. All these precipitates of mixed hydrate and carbonate, even those which are insoluble in water, dissolve in the aqueous solution of carbonic acid gas; and from the solution of acid carbonate so formed, crystals of neutral carbonate are often deposited: this is the case with the zinc precipitate:

$$\underset{\substack{\text{mixed carbonate}\\ \text{and hydrate.}}}{Zn_2CO_3, 3ZnHO} + 4H_2CO_3 = \underset{\text{acid carbonate.}}{5ZnHCO_3} + 3H_2O;$$

the acid carbonate of zinc thus formed decomposes in the following way:—

$$2ZnHCO_3 = \underset{\substack{\text{crystalline}\\ \text{precipitate.}}}{Zn_2CO_3} + H_2O + \overset{\nearrow}{CO_2}.$$

The alkaline carbonates, and those of barium and strontium, may be fused on charcoal without decomposition; all others are decomposed.

THE HYDROGEN SALT, or carbonic acid (H_2CO_3), is not known in the separate state. It is believed to be formed when the gas CO_2 is passed into water; and the occurrence of acid carbonates leaves little doubt of the existence of the acid, although, from its extreme instability and tendency to be resolved into water and carbonic anhydride, attempts to isolate it have not been successful. The gaseous anhydride has been condensed to a liquid, and even to a solid. The following formulæ represent the composition of carbonic acid and of the two varieties of carbonates:—

$$\underset{\text{carbonic acid.}}{H_2CO_3,} \qquad \underset{\text{acid carbonate.}}{MHCO_3,} \qquad \underset{\substack{\text{neutral (or normal)}\\ \text{carbonate.}}}{M_2CO_3.}$$

The carbonic radical may be recognized both by the formation of insoluble carbonates, and by a process of decomposition.

The carbonates that have been obtained are almost all insoluble, the salts of potassium, sodium, and ammonium being the only exceptions.

The Potassium, Sodium, and Ammonium Salts are soluble.

The Barium Salt is a white precipitate.

Its formula is Ba_2CO_3.

It is soluble in 141,000 parts of a solution of ammonia, or carbonate of ammonium; in 14,130 parts of pure water at 16° to 20°, or in 15,421 parts of boiling water. It is soluble in carbonic and other acids.

The Strontium Salt is a white precipitate, soluble in 18,045 parts of cold water, and readily dissolved by most acids. (See p. 88.)

The Calcium Salt is a white precipitate, soluble in 10,600 parts of cold water, and readily dissolved by most acids. (See p. 91.)

The Magnesium Salt is a white precipitate, which requires 2493 parts of cold water for its solution, and is readily dissolved by nearly all acids. (See p. 94.)

The Ferrous and many other Salts of the third subdivision, if existing at all, decompose soon after formation as already described, or when exposed to the air or to a slight increase of temperature.

The Cupric Salt is produced by the action of cupric sulphate upon soluble carbonates: it is a bluish green precipitate. Its formula is $Cu_2CO_3,2CuHO$. It dissolves in ammonium salts and in acids, but is insoluble in water.

The Silver Salt is produced by the action of nitrate of silver on soluble carbonates: it is a white precipitate. Its formula is Ag_2CO_3. It is soluble in ammonium salts and in acids, but insoluble in water.

The Mercurous Salt is produced by the action of mercurous nitrate on a solution of a carbonate: it is a yellow precipitate. Its formula is $(Hg_2)_2CO_3$.

THE MERCURIC SALT is brownish red. Its formula is Hg_2CO_3, Hg_2O. It is slightly soluble in carbonate of potassium, soluble in chloride of ammonium and in acids; in water it is insoluble.

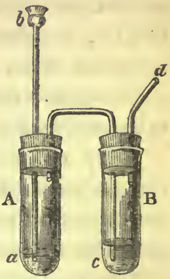
THE LEAD SALT is white. Its formula is $Pb_2CO_3,2PbHO$. It is soluble in 23,450 parts of water containing acetate, hydrate, or carbonate of ammonium, more soluble in water containing nitrate of ammonium; it is readily soluble in many acids. 1 part dissolves in 50,551 parts of pure water at the ordinary temperature.

This acid-radical may be readily recognized by the products of its decomposition.

a. Almost any acid, however weak or dilute, when added to a soluble or insoluble carbonate, causes its decomposition; and the resulting carbonic acid, by its resolution into water and the gaseous anhydride CO_2, gives rise to the phænomenon of effervescence. Effervescence is caused by the escape of several other gases, such as hydrosulphuric acid or sulphurous anhydride, when certain sulphides or sulphites are similarly treated: but a peculiarity attends the formation of carbonic anhydride from carbonates; for all these salts, *whether insoluble or not*, and *whatever basic radicals they may contain*, are decomposed by acids, even the weakest, with evolution of the gas CO_2. Now, although with the sulphides and cyanides of the first and second subdivisions, and with some few others, a somewhat similar evolution of gas takes place, yet it does not occur with all, and in many cases requires the employment of certain powerful acids. Chlorides too, especially alkaline chlorides, effervesce, evolving hydrochloric acid (HCl) when treated with concentrated sulphuric acid; but weak sulphuric acid has no action upon chlorides unless heat also be applied.

β. The carbonic anhydride (CO_2), usually called carbonic acid gas, which is obtained in the reaction of acids upon carbonates, may be recognized by its peculiar smell, but especially by its immediately forming a white precipitate of carbonate of barium when passed into baryta-water—a precipitate which, by the continued passage of the gas, redissolves from formation of the soluble acid carbonate ($BaHCO_3$). The experiment may best be made in the following manner:—Two small test-tubes are taken, fitted with perforated corks and tubes, as in the annexed figure. Into the test-tube A, the suspected carbonate is to be placed, with only just sufficient water to cover the end of the tube at *a*. Sulphuric acid is then to be poured in at *b*, and the gas which issues from the tube *c* will then precipitate, from the baryta-water placed in the tube B, the white carbonate of barium. To assist in the detection of the gas where a small quantity only of material is present, the gas evolved may be drawn into the baryta-water by applying the mouth to the tube *d*, and so removing the original air from the test-tube B.

Fig. 12.



SALTS OF THE OXALIC RADICAL, OR OXALATES.

The oxalates are very numerous, including salts of almost every basic radical, elementary or compound. Under ordinary conditions, oxalic acid and oxalates are very stable bodies. This radical forms an immense number of double salts, and many acid salts. The following formulæ represent some of these compounds:—

$H_2C_2O_4$	MHC_2O_4	$M_2C_2O_4$	$MH_3C_4O_8$.
oxalic acid.	acid oxalate.	normal (or neutral) oxalate.	quadroxalate.

Oxalates, when submitted to a slightly elevated temperature, decompose, leaving a carbonate of the metal and evolving carbonic oxide (CO), or leaving a residue of oxide and evolving both carbonic oxide and carbonic anhydride, thus:—

$$Ca_2C_2O_4 = Ca_2CO_3 + CO\ ;\ \textit{or}\ Zn_2C_2O_4 = Zn_2O + CO + CO_2.$$

This difference in the products depends upon whether the carbonate of a base can withstand the temperature at which the oxalate decomposes. The oxalates of potassium, sodium, and calcium are found in the juices of various plants; and the hydrogen compound of this radical is also a very common product of the action of oxidizing bodies upon complex molecules.

THE HYDROGEN SALT ($H_2C_2O_4$, *or* $H_2\bar{O}$), or oxalic acid, is a white crystalline solid, which sublimes between 100° and 162° without decomposition, and condenses in slender colourless needles: it is poisonous, and its vapour when breathed has a most irritating effect.

The oxalic radical may be detected both by certain insoluble salts, and by its decomposition.

Many oxalates are insoluble in water—in fact, the majority of the neutral salts: many of the acid salts are more soluble; but it is singular to find that, among the oxalates of the first subdivision, the acid salt is generally less soluble than the neutral one.

THE POTASSIUM and SODIUM SALTS are comparatively soluble in water, although the latter ($Na_2C_2O_4$) requires as much as 36·4 parts of cold, or 24·6 of boiling water for its solution.

THE BARIUM SALT is precipitated by adding chloride of barium to solutions of oxalic acid or oxalates: if the acid be employed, crystals of the acid oxalate speedily separate; if a soluble oxalate, an immediate dense white precipitate of neutral oxalate will fall. The complete formula of the former salt is $BaHC_2O_4+2aq$; of the latter, $Ba_2C_2O_4+aq$. They are both sparingly soluble in cold water; the acid salt dissolves more readily in hot water; they both dissolve also in chloride of ammonium solution. (See p. 85.)

THE STRONTIUM SALT is produced by the action of nitrate of strontium on oxalic acid or soluble oxalates. Its formula is $Sr_2C_2O_4$. It is sparingly soluble in cold water, but only requires 19·2 parts of boiling water for solution. (See p. 88.)

The Calcium Salt is produced by the action of soluble calcium salts on oxalic acid or oxalates: it is a white granular precipitate.

Its formula is $Ca_2C_2O_4+aq$.

It is insoluble in chloride of ammonium and in water; it is also insoluble in acetic acid, but dissolves in the stronger acids readily.

THE MAGNESIUM SALT is soluble.

THE FERROUS and SOME OTHER SALTS of the third and fourth subdivisions are soluble; but the majority are sparingly soluble.

The Cuprous Salt is white; it is soluble in hydrate of ammonium.

The Cupric Salt is a greenish blue precipitate. Its formula is $Cu_2C_2O_4+aq$. It is soluble in neutral alkaline oxalates, and in hydrate, carbonate, and succinate of ammonium, but not in other ammonium salts. It is insoluble in water, in oxalic acid, and in warm dilute nitric acid. It dissolves in warm concentrated hydrochloric acid.

The Silver Salt ($Ag_2C_2O_4$) is a white precipitate. It dissolves in hydrate and carbonate of ammonium, and in warm solutions of other ammonium salts. It is scarcely soluble in water, but dissolves in nitric acid.

The Mercurous Salt is precipitated by the action of mercurous nitrate on oxalic acid or soluble oxalates: it is a white precipitate. Its formula is $(Hg_2)_2C_2O_4+aq$. It is but slightly soluble in water or in dilute acids.

The Mercuric Salt is a white precipitate. Its formula is $Hg_2C_2O_4+aq$. It is soluble in solutions of chloride and nitrate of ammonium, insoluble in water and dilute acids, somewhat soluble in sulphuric acid, and dissolved easily by other strong acids.

The Lead Salt is a white precipitate. Its formula is $Pb_2C_2O_4$ (dried at 140°). It is soluble in most ammonium salts, the hydrate and carbonate excepted; it is insoluble in water and in acetic acid, but soluble in nitric acid; it is somewhat soluble in oxalic acid.

The oxalates may be detected by the decomposition of their acid-radical.

a. When to an oxalate some strong sulphuric acid is added, and the mixture warmed, the oxalic acid thus liberated undergoes instant decomposition, partly from the tendency of sulphuric acid to form a hydrate:

$$H_2C_2O_4+H_2SO_4=H_2SO_4,\ H_2O+CO+CO_2.$$

Considerable effervescence ensues from the escape of the carbonic anhydride and carbonic oxide gases; and the latter gas will be found to burn with a blue flame. This action of sulphuric acid, *without any blackening* of the substance under examination, points decisively to the presence of oxalic acid; for though the salts of some of the more complex acid-radicals yield carbonic oxide also, they blacken simultaneously, the ferrocyanides excepted.

β. If, instead of sulphuric acid alone, a mixture of binoxide of manganese (Mn_2O_2) and sulphuric acid be made to act upon oxalic acid, the sole gaseous product of the reaction is carbonic anhydride (CO_2).

SALTS OF THE BORACIC RADICAL, OR BORATES.

These salts are by no means of such frequent distribution in nature as the carbonates; they occur in some few minerals, and in greater abundance in the hot lakes or boracic lagoons of Tuscany, into the waters of which the vapours are conveyed which rise from the volcanic bottom. These vapours, which are charged with boracic anhydride (Bo_2O_3), yield it to the water, with which it combines to form boracic acid. It is generally met with in commerce combined as borax, the biborate of sodium.

Most borates may be heated on charcoal without decomposition. The use of borax as a blowpipe reagent is well known.

THE HYDROGEN SALT crystallizes from a hot aqueous solution; but if these crystals be heated, they evolve water, and yield a fused glassy substance, which is the so-called anhydrous acid (Bo_2O_3). This body bears the same relation to boracic acid as chromic anhydride does to chromic acid. When dissolved to saturation in hot water, it separates on cooling, in the form of hexagonal laminæ having a pearly lustre and the formula $HBoO_2 + aq$. It may be considered as the representative of what are called the monoborates, which have the formula $MBoO_2 + naq$. If these crystals be heated to a temperature considerably above 100°, they part with the elements of water, and another hydrogen compound is obtained ($H_6Bo_4O_9$), which, when written without its 2 eqs. of accidental water, becomes $H_2Bo_4O_7$, and may then be considered as the type of the biborates. The biborates may also be viewed (like the bichromates) as combinations of the anhydride (Bo_2O_3) with the monoborates; thus we have the following equation when we disregard water of crystallization:—

$$2HBoO_2 + Bo_2O_3 = H_2Bo_4O_7.$$

The rationale of the process whereby the biborates are produced may be as follows:—we may suppose that, under the influence of heat, 1 molecule of the anhydride (Bo_2O_3) is formed from 2 equivalents of boracic acid, thus:—

$$2(HBoO_2, H_2O) = Bo_2O_3 + 3H_2O;$$

the body, Bo_2O_3, thus formed, then unites with 2 equivalents of undecomposed acid to form the biborate of hydrogen. Or we may merely express the change as follows:—

$$4(HBoO_2, H_2O) = H_2Bo_4O_7, 2H_2O + 3H_2O.$$

Borates, then, may be of at least two classes, borates and biborates. The latter salts are much more stable than the former—so much so, indeed, that even the potassium salt of the former series, by mere exposure to the air, absorbs carbonic anhydride, and becomes converted into the carbonate and biborate, thus—

$$4KBoO_2 + CO_2 = K_2CO_3 + K_2Bo_4O_7.$$

Nor are these the only classes of borates. Just as boracic anhydride combines with borates to form biborates, so additional proportions of this body yield salts which have been called ter-, quadri-, and sex-borates. The formulæ of the sodium (or potassium) salts of these compounds are—

Borate	$Na\,Bo\,O_2.$
Biborate	$Na_2Bo_4O_7 = 2NaBoO_2 + Bo_2O_3.$
Terborate	$K_2Bo_6O_{10} = 2KBoO_2 + 2Bo_2O_3.$
Quadriborate	$Na_2Bo_8O_{13} = 2NaBoO_2 + 3Bo_2O_3.$
Sexborate	$Na_2Bo_{12}O_{19} = 2NaBoO_2 + 5Bo_2O_3.$

The borates, biborates, and sexborates are pretty well known; but not so the others.

The boracic radical may be recognized both by the formation of sparingly soluble salts, and by processes of decomposition.

The normal borates are more soluble in water than the others. Of the biborates, which are the most common boracic salts, almost all, excepting those of the first subdivision, are insoluble in water.

THE POTASSIUM SALT ($K_2Bo_4O_7+5aq$) is soluble.

THE SODIUM SALT ($Na_2Bo_4O_7+10aq$), or borax, is soluble.

THE BARIUM SALT is produced by the action of soluble barium salts on a solution of borax. It is a white precipitate. Its formula is $Ba_2Bo_4O_7+2aq$. It is soluble in excess of chloride of barium, also in ammonium salts; it dissolves in 100 parts of cold water, and in a smaller quantity of boiling water; it is soluble in acids. Before the blowpipe it fuses to a grey glass.

THE STRONTIUM SALT is produced by the action of a soluble strontium salt on a solution of borax: it is a white precipitate. It dissolves readily in cold solutions of chloride or nitrate of ammonium; 1 part is soluble in 130 parts of boiling water.

The Calcium Salt is produced by the action of a soluble calcium salt on a solution of borax. Its formula is $Ca_2Bo_4O_7+aq$ after having been air-dried. It is scarcely soluble in water, but dissolves in acids. Before the blowpipe it fuses to a glass.

THE FERROUS, FERRIC, and MANY OTHER SALTS of the third and fourth subdivisions are yellowish or white precipitates, insoluble in water.

THE CUPRIC SALT is a pale green precipitate, slightly soluble in water, and dissolved easily by a solution of boracic acid. Before the blowpipe it fuses to a green opaque glass.

THE SILVER SALT is white: its formula, under all circumstances, is $AgBoO_2$. It is sparingly soluble in water.

THE MERCUROUS and MERCURIC SALTS do not appear to exist; the biborates precipitate basic mercury compounds.

The Lead Salt is obtained by the action of soluble lead salts on a solution of borax: it is a white precipitate. Its formula is $Pb_2Bo_4O_7$. It is insoluble in excess of its precipitant, but slightly soluble in pure water.

This acid-radical is also detected by the following experiments.

a. When sulphuric acid is added to the aqueous solution of a borate, boracic acid separates in characteristic crystalline scales ($HBoO_2+aq$). If the boracic acid be then dissolved in alcohol, and the solution kindled, the flame produced will have a *dark green* edge, best seen against a black background. In this experiment, the presence of chlorides and of copper salts should be avoided.

β. The most characteristic reaction of boracic acid is the action of its aqueous solution on turmeric paper. All other acids exert no influence upon ordinary yellow turmeric paper, or, if it has been browned by an alkali, they simply restore its original colour; but boracic acid behaves like an alkali, turning the yellow of the paper to a reddish brown. The suspected borate is mixed with hydrochloric acid, and into the mixture a small piece of turmeric paper is placed. The test is applied in a white porcelain dish.

γ. Sulphuretted hydrogen and ferrocyanide of potassium produce no characteristic actions upon boracic acid or soluble borates.

SALTS OF THE SILICIC RADICAL, OR SILICATES.

These salts are of universal distribution in nature: they form a very large proportion of the rocks constituting the earth's crust, and enter into the composition of many minerals.

Heated before the blowpipe, most silicates fuse to a colourless or coloured *glass*.

THE HYDROGEN SALT ($HSiO_2$), or silicic acid, is not very well known; it is believed that the body termed gelatinous silica has, when air-dried, this formula, but when dried at 100° the formula $H_2Si_4O_7$, *i. e.* $2HSiO_2 + Si_2O_3$: at a higher temperature it is resolved into water and silicic anhydride (Si_2O_3). This body (Si_2O_3), which bears the same relation to silicic acid ($HSiO_2$) as boracic anhydride (Bo_2O_3) bears to boracic acid ($HBoO_2$), is of very common occurrence, and is familiar to every one under the forms of quartz, amethyst, siliceous sand, flint, and chalcedony. Silicates are as various in their constitution as they are great in number; but, as we have seen in the tungstates, chromates, and especially in the borates, a number of acid-radicals may be built up by the assimilation of successive additions of the body which has been termed the anhydride, into which and water all these complex acids are capable of splitting.

Silicates are best recognized, not by the formation of insoluble salts, but by certain characteristic products of decomposition which they yield.

Silicates are very generally insoluble in water, the neutral and basic silicates of the first subdivision being almost the only exceptions.

The Potassium Salts $KSiO_2$, $K_2Si_4O_7$, and $K_2Si_8O_{13}$ are soluble in water; the salts $K_2Si_{16}O_{25}$, $K_2Si_{36}O_{55}+9aq$, and $K_2Si_{48}O_{73}+16aq$ are insoluble.

The Sodium Salts $NaSiO_2+3aq$, $Na_2Si_4O_{10}$, and $Na_2Si_8O_{13}+12aq$ are soluble in water; those containing a larger addition of silicic anhydride are insoluble.

The Barium, Calcium, and Magnesium Salts are white. They are insoluble in water, but soluble in acids.

The Ferrous and other Salts of the third and fourth subdivisions are insoluble in water.

The Cupric Salt is green; the Silver and Mercurous Salts white.

The Mercuric Salt is tolerably soluble: it occurs in small dark crystals.

The Lead Salt is precipitated from silicofluoride of lead by hydrate of ammonium: it is a white precipitate, insoluble in water.

This acid-radical is invariably recognized by the decomposition and behaviour of its salts.

a. Many silicates, insoluble in water, are readily dissolved by acids; others, again, are insoluble both in water and in all acids, the hydrofluoric excepted. The latter class of silicates may be converted into compounds quite soluble in acids and even in water, by the following process:—The insoluble silicate is mixed with four times its weight of hydrate or carbonate of potassium, or of the mixed carbonates of sodium and potassium, and the mixture fused for 15 minutes; the mass should remain quite liquid for 10 minutes; this fusion of course yields the alkaline silicate by ordinary double decomposition. By the preceding process, a mass will be obtained which, in most cases, will dissolve slowly in water, or at least the alkali and alkaline silicate will dissolve, leaving a residue of metallic carbonate or oxide. In acids the fused mass will dissolve readily; and then, if to the solution we proceed to add excess of acid (*e.g.* hydrochloric acid), a precipitate of silicic acid will be formed, which, on the addition of a further portion of acid, again dissolves. If now the clear solution be evaporated to perfect dryness on a water-bath (at 100°), then moistened with water, and again evaporated to ensure the expulsion of all free acid and moisture, the decomposition of the silicic acid into water and silicic anhydride will have taken place, and the resulting white powder will be found perfectly insoluble in water and in all acids except hydrofluoric. So perfect is this decomposition, that the most minute trace of silicic acid may be thus detected, and it is employed in the quantitative estimation of this substance.

β. An experiment already given on page 66, and also described as one of the tests for the presence of fluorine, serves for the detection of silicon. A small tube of lead closed at one end, perfectly dry, and fitted with a dry cork and leaden delivery-tube, is employed; and into this vessel a mixture of equal weights of the substance to be tested for silicon and of fluoride of calcium is introduced, together with about twice the bulk of oil of vitriol. The delivery-tube should then be dipped under the surface of a small quantity of water contained in a cup of lead, and heat applied to the mixture: if silicon be present, the gaseous terfluoride of silicon (SiF_3) will be disengaged, which, coming in contact with water, will yield a gelatinous precipitate of silicic acid, and the solution will contain hydrofluosilicic acid, recognizable by the usual tests.

γ. When gelatinous silicic acid is dried, it yields, as has been stated, the anhydride (Si_2O_3), a fine white scaly powder of extreme lightness. If now a bead of carbonate of sodium be made on a platinum wire, and, when it is red-hot, silicic anhydride be added little by little, fusing the bead between each addition of substance, a period will arrive at which the bead no longer presents the opacity of fused carbonate of sodium when cold, but *remains perfectly pellucid.*

δ. If a bead of microcosmic salt be made, and some silica (Si_2O_3) fused with it, the anhydride will remain undissolved, and float about the bead as a network or skeleton.

ε. Hydrosulphuric acid and ferrocyanide of potassium give no characteristic reactions with silicic acid.

This radical is usually detected by the tests α, β, and γ.

Of compound acid-radicals containing tantalum and oxygen, two are known: they occur in a mineral termed "Tantalite," one variety of which consists of ferrous tantal*ite*, $Fe_2Ta_2O_3$; other varieties are composed of ferrous tantal*ate*, $FeTaO_2$.

SALTS OF THE TANTALIC RADICAL, OR TANTALATES.

Tantalic acid, and many tantalates, when heated, yield tantalic anhydride (Ta_2O_3).

The Hydrogen Salt ($HTaO_2$), or tantalic acid, is known: it is obtained as a snow-white bulky precipitate, quite insoluble in water, and, when washed, but slightly soluble in many acids, except sulphuric acid, from its solution in which, water reprecipitates it, and hydrochloric acid, which dissolves it somewhat more abundantly. It dissolves readily in the hydrate or the acid oxalate of potassium, in boiling solutions of alkaline carbonates, and in hydrofluoric acid. The formula of the precipitate is $HTaO_2+aq$.

The tantalic radical is detected by the formation of insoluble salts, but especially by processes of decomposition.

The alkaline tantalates are soluble in water, but are precipitated by ordinary salts of ammonium. The sodium salt is also precipitated by the addition of excess of hydrate or carbonate of sodium,—a behaviour whereby tantalic acid is distinguished from all other acids (except niobic and pelopic), particularly from tungstic acid, to which, in many points, it bears a great resemblance.

The Potassium Salt is soluble in pure water, nearly insoluble in cold carbonate of potassium solution.

The Sodium Salt is sparingly soluble in cold water; when the solution is boiled, it deposits a bitantalate.

The Barium and Calcium Salts are white and insoluble. The Calcium, Magnesium, and Copper Salts are unknown.

The Silver Salt is white and insoluble.

The Mercury and Lead Salts are unknown.

This acid-radical is detected by the following tests:—

a. From soluble tantalates, hydrochloric acid precipitates tantalic acid

($HTaO_2$), which, on addition of excess of the precipitant, is redissolved, but again *separates on the addition of sulphuric acid* and subsequent ebullition, a compound of that acid with tantalic acid being produced.

β. If into the sulphuric acid precipitate (just mentioned) still remaining in the slightly acid liquid a strip of zinc be plunged, as it dissolves, a fine blue colour will be imparted to the liquid; this tint will, however, change to a brown, and, finally, brown flakes will separate, which, after some time, will become oxidized, and converted into tantalic acid.

γ. Precipitated tantalic acid is insoluble after ignition, in all acids, and must, like ignited silica (Si_2O_3), be fused with hydrate or carbonate of sodium.

δ. Hydrosulphuric acid does not precipitate an acid solution of tantalic acid.

ϵ. In a slightly acidified solution of tantalic acid, ferrocyanide of potassium produces a yellow precipitate, and ferricyanide a white.

Of compound acid-radicals containing niobium and oxygen, one is known, the radical of niobic acid. Of its salts, the niobiates, almost all that has been said regarding the tantalates equally well applies. The acid is, however, more completely separated from its salts than tantalic acid is from tantalates, on the addition of sulphuric acid, not requiring the aid of heat.

Of compound acid-radicals containing pelopium and oxygen, one is known, that existing in pelopic acid. Its salts bear the closest resemblance to the tantalates and niobiates.

SALTS OF THE TITANIC RADICAL, OR TITANATES.

Two combinations of titanium with oxygen are known; the lower oxide has not, however, been observed to manifest any tendency to pass into an acid-radical. The titanic radical occurs in numerous minerals. In Titanite it occurs as titanate of calcium ($Ca_2Ti_2O_3$) associated with silicate of calcium, while it is most frequently found in the varieties of titaniferous iron, one of which, Ilmenite, is the ferrous titanate ($Fe_2Ti_2O_3$).

Titanic acid when heated before the blowpipe yields the infusible titanic oxide Ti_2O_2. The titanates are not generally decomposed by fusion, but, on the contrary, many salts of this radical are prepared by fusing titanic oxide with metallic carbonates.

The Hydrogen Salt is prepared just as the analogous compound of silicon, by the gradual addition of an acid. It is a white, flocculent, and bulky precipitate, and consists (when dried *in vacuo* over sulphuric acid) of the pure substance $H_2Ti_2O_3$. The acid thus obtained, if washed with cold, not with hot water, dissolves readily in acids, but not in the hydrates of the first subdivision, and only to a trifling extent in alkaline carbonates. When the acid solution of titanic acid is diluted with much water and boiled, a precipitate occurs, probably of the body (Ti_2O_2) already mentioned as obtained by the ignition of the acid. It is a white precipitate, becoming yellow on heating. It is quite insoluble in water, and in all acids except hydrofluoric and boiling sulphuric acids. It occurs naturally in the minerals Rutile and Anatase.

The titanates are, for the most part, insoluble in water. The monotitanates of the first subdivision are decomposed by water into a basic salt, which dissolves, and an acid salt, which is precipitated. The barium, calcium, silver, mercury, and lead salts are unknown.

This acid-radical is recognized by the following processes of decomposition:—

α. When the hydrochloric solution of titanic acid is diluted and boiled, the oxide or anhydride (Ti_2O_2) separates as a white powder.

β. The oxide Ti_2O_2 requires fusion with carbonate of sodium to render it soluble.

γ. If into the hydrochloric solution of titanic acid a strip of zinc be introduced, a blue solution will be obtained; and from this a reddish or violet precipitate will separate, which gradually oxidizes into the white titanic acid.

δ. Titanic anhydride (Ti_2O_2), when fused with microcosmic salt in the reducing flame, gives a violet-blue bead on cooling: the colour is rendered more evident after the addition of tin. If iron be present, a yellow or blood-red bead will be produced in the reducing flame.

ε. Hydrosulphuric acid does not precipitate an acid solution of titanic acid.

ζ. Ferrocyanide of potassium gives a dense orange brown precipitate in a solution of titanic acid in weak hydrochloric acid. The precipitate is soluble in excess of the precipitant.

SALTS OF THE SULPHOCARBONIC RADICAL, OR SULPHOCARBONATES.

These salts are usually of a yellow, red, or brown colour; many of them decompose with rapidity into sulphides. They closely resemble the carbonates in constitution, the oxygen of those salts being replaced by sulphur, thus—

$K_2C_2O_3$,	$K_2C_2S_3$.
carbonate of potassium.	sulphocarbonate of potassium.

On a slight increase of temperature, the sulphocarbonates decompose into bisulphide of carbon (CS_2) and metallic sulphides.

THE HYDROGEN SALT ($H_2C_2S_3$) or sulphocarbonic acid, is a reddish brown, transparent, oily liquid, denser than water; it has a very peculiar odour, and is prone to decompose into hydrosulphuric acid and the body CS_2, which is the sulphocarbonic anhydride, and bears to sulphocarbonic acid the same relation that carbonic anhydride (CO_2) bears to carbonic acid (H_2CO_3).

The sulphocarbonates may be recognized by certain insoluble compounds, and also by their products of decomposition.

The soluble sulphocarbonates have a saline and somewhat sulphureous taste; those of the first and second subdivisions are soluble in water, as are also some members of the third subdivision.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE CUPRIC SALT is red-brown when precipitated from sulphocarbonic acid, dark brown when from sulphocarbonate of calcium (Ca_2CS_3); it is soluble in excess of its precipitants; it becomes black on drying.

THE SILVER SALT is produced by the action of sulphocarbonate of calcium on silver salts: it is a dark brown precipitate, which becomes black on drying. It is soluble in excess of its precipitant.

The Mercuric Salt is yellow when precipitated by sulphocarbonate of ammonium ($[NH_4]_2CS_3$), black when the calcium salt is employed. The yellow salt passes from yellow to orange red and black, with evolution of bisulphide of carbon.

The Lead Salt is dark brown when precipitated by sulphocarbonate of calcium, but red when sulphocarbonic acid or the ammonium salt is employed; it rapidly becomes black from separation of sulphide of lead (Pb_2S).

The sulphocarbonic radical may be readily distinguished by the following tests:—

α. When to the solution of a sulphocarbonate a strong acid is added, the sulphocarbonic acid liberated is at once decomposed into hydrosulphuric acid and the oily body, bisulphide of carbon (CS_2), both products being easily identified not only by their reactions but by their unmistakeable and unpleasant odour:

$$H_2CS_3 = H_2S + CS_2.$$

β. If the aqueous solution of a sulphocarbonate be evaporated two or three times with excess of sulphide of ammonium, and the resulting mass dissolved in water, filtered, and the solution then tested with ferric chloride (Fe_2Cl_3), *the magnificent blood-red colour* of sulphocyanide of iron will be produced.

This radical is perhaps best recognized by the formation, &c. of the mercuric and lead salts, and by the tests α. and β.

SECTION III.—*The cyanides, cyanates, and sulphocyanides; the ferrocyanides, ferricyanides, and cobalticyanides; the formiates, acetates, benzoates, succinates, tartrates, lactates, citrates, gallates, tannates, and urates.*

SALTS OF THE COMPOUND ACID-RADICALS WHICH CONTAIN CARBON AND NITROGEN; CARBON, NITROGEN, AND OXYGEN; CARBON, NITROGEN, AND SULPHUR; CARBON, NITROGEN, AND METALS; CARBON, OXYGEN, AND HYDROGEN; AND CARBON, OXYGEN, HYDROGEN, AND NITROGEN.

To these salts the term "*organic*" is generally applied, from their naturally occurring almost solely in the organic kingdoms of nature. Many of these bodies do not, however, occur actually in nature, but are the artificial products of a chemical action upon natural substances. It was thought till recently that the building up of complex molecules from the common and simpler bodies at his disposal was not within the power of the chemist: but the experiments of recent years have shown this to be a fallacy; for, by skilful manipulation and ingenuity of contrivance, many most complicated substances have been artificially constructed. Numerous bodies have not yet been thus produced; but their number is constantly diminishing. By a consideration of the members of this section, it will be seen that they are often arranged in series, somewhat after the manner of the borates, already alluded to; and it needs but little discernment to predict that, if by a certain process one member of such a series can be formed, by a slight variation of the experiment to suit the circumstances of the special case, every member of the group may probably be produced at will. The invention of a method is a discovery; but the production of all subsequent members of the series is but the application of a principle.

Of acid-radicals formed by the union of carbon with nitrogen, one only is of any analytical importance, viz. cyanogen.

SALTS OF CYANOGEN, OR CYANIDES.

These bodies occur in some few organic products; and the radical may also be formed directly from its elements by exposing hydrate or carbonate of potassium to the joint action of carbon (or carbonic oxide) and nitrogen, at a high temperature. This action has been made to take place by employing charcoal saturated with the salts just mentioned, and heating it strongly in a vertical shaft to which the nitrogen, &c. of a furnace-flue was admitted by appropriate openings. The radical is thus obtained in combination with potassium. It may also be obtained by the decomposition of ferrocyanide of potassium. (See p. 53.)

The cyanides of the first subdivision may be fused without decomposition, excepting the ammonium salt, which volatilizes unchanged; the fusion may be effected on charcoal. The cyanides of the second subdivision also sustain a high temperature without change. Many other cyanides, however, decompose into cyanogen gas and metal, or into cyanogen gas and a mixture of the metal with a *paracyanide*: such cyanides are the silver and mercuric salts. Others, again, are resolved into their elements—carbon, nitrogen, and metal; *e.g.* cyanide of lead (PbCN *or* PbCy).

The Hydrogen Salt (HCN *or* HCy), hydrocyanic or prussic acid, is remarkable as being one of the most terrible poisons known. It is a transparent, colourless, mobile liquid of sp. gr. 0·705—0·710 at 6° C.; it freezes at −15°, boils at 27°·5, and volatilizes in the air with such rapidity, that the cold produced by the evaporation of a portion freezes the remainder: it is inflammable, burning with a pale blue flame. In a state of great dilution, it is used in medicine. Pure hydrocyanic acid and its aqueous solution, if tolerably concentrated, rapidly decomposes, yielding ammonia and a brownish black powder. The presence of a trace of mineral acid prevents this change; but a large quantity of a strong acid itself causes a decomposition, the hydrocyanic acid then yielding an ammonium salt and formic acid, thus—

$$\underset{\text{hydrocyanic acid.}}{HCN} + HCl + 2H_2O = NH_4Cl + \underset{\text{formic acid.}}{HCHO_2}.$$

This radical may be detected both by the formation of insoluble salts and by its products of decomposition; also by certain complex bodies which it may be made to yield.

Regarding the solubility of cyanides, it may be stated that the salts of the first and second subdivisions are readily soluble in water: for the bases of the first half of the third subdivision this radical exhibits little affinity; but the cyanides of iron, manganese, cobalt, nickel, and zinc, and those of the fourth subdivision, are for the most part insoluble in water. The insoluble cyanides all exhibit the peculiarity of dissolving in excess of alkaline cyanide, to form compounds in which a new, and often very stable, compound acid-radical is believed to exist. Such a change is represented, in the case of iron, by the following equations:—

$$\mathrm{KCy} + \mathrm{FeCl} = \underset{\text{ppt.}}{\mathrm{FeCy}} + \mathrm{KCl};$$

$$\mathrm{FeCy} + 2\mathrm{KCy} = \underset{\substack{\text{double cyanide}\\ \text{of potassium}\\ \text{and iron.}}}{2\mathrm{KCy}, \mathrm{FeCy}} = \underset{\substack{\text{ferrocyanide}\\ \text{of potassium.}}}{\mathrm{K_2FeCy_3}}.$$

The ferrocyanides are usually written M_2Cfy. These changes have already been alluded to under iron and cobalt, pp. 120, 132.

The Potassium, Sodium, Barium, Strontium, Calcium, and Magnesium Salts are soluble.

The Ferrous Salt ($FeCy$) is a light reddish brown precipitate. (See p. 120.)

The Cuprous Salt is white: it is generally produced by adding to a soluble cupric salt, first, sulphurous acid, and then hydrocyanic acid or cyanide of potassium. Its formula is Cu_2Cy. It is soluble in cyanide of potassium, in the hydrate and many other ammonium salts, and in concentrated hydrochloric acid.

The Cupric Salt is brownish yellow. It decomposes spontaneously into cupro-cupric cyanide and cyanogen gas. Its formula is $CuCy$. It is soluble in excess of cyanide of potassium.

The Silver Salt is a white curdy precipitate. Its formula is $AgCy$. It is soluble in alkaline cyanides and hyposulphites, in ferrocyanide of potassium, and in hydrate of ammonium. It is decomposed by strong hydrochloric, nitric, and sulphuric acids, more especially on boiling; the dilute acids act but slightly on it.

The Mercurous Salt is unknown: mercurous nitrate produces with cyanide of potassium a grey precipitate of metallic mercury, mercuric cyanide being formed and dissolved.

The Mercuric Salt ($HgCy$) is soluble.

The Lead Salt is white. Its formula is $PbCy$. It appears to be insoluble in the cyanides of calcium and potassium. It is decomposed by cold dilute sulphuric acid, but not by dilute nitric acid.

This acid-radical is also recognized by the following changes and decompositions:—

a. When hydrocyanic acid is set free by the action of a dilute acid on its salts (dilute hydrochloric acid is found to answer best*), and heat applied to the liquid, the acid, as it escapes, may be seen to be inflammable by applying a light to the mouth of the tube. It burns with a blue flame. This vapour has also a most peculiar smell, resembling, when diluted with much air, the odour of peach-blossoms; it also produces *a singular sense of heat at the back of the throat a few seconds after inhalation.* These experiments, and the others about to be described, if performed at all, should be tried on a very small scale, and with the greatest precaution.

β. If the mercuric or silver salt be obtained, dried, and carefully ignited in a short and very narrow tube, *the gas cyanogen* is disengaged, which, though generally considered to be the acid-radical itself, is, as we have previously shown, more probably the cyanide of cyanogen, CyCy. This gas, upon the application of a light, burns with a *violet flame.*

γ. If a cyanide be decomposed by a drop or two of acid, in a watch-glass over which is inverted a second watch-glass moistened with a trace of sulphydrate of ammonium solution containing sulphur in excess, placed in the centre of its concave surface (the circumferences of the two glasses accurately fitting), the hydrocyanic acid evolved will be found, after the lapse of a few minutes, to have given rise, by its action on the sulphide, to the salt known as sulphocyanide of ammonium, thus—

$$HCy+NH_4HS+S=NH_4CyS+H_2S.$$

The sulphocyanide thus produced may be recognized by a ferric salt; but, in order to ensure success, the upper watch-glass should be placed in a water-bath (that all remaining sulphydrate of ammonium may evaporate), and to the residue a small quantity of a solution of ferric chloride added: *the magnificent blood-red colour* of ferric sulphocyanide will be at once produced, and is indicative of the presence of cyanogen in the original substance tested.

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* When it is desired to distinguish the odours of acids, concentrated reagents should not in general be employed as liberators of the acids; for nitric, hydrochloric, and several other acids, being themselves volatile, may completely mask all other odours by their own pungent vapours.

δ. If we take an alkaline cyanide (which may be made from any other cyanide by boiling the latter with hydrate or carbonate of potassium and filtering), and add to it a solution containing a ferrous and a ferric salt, warming the liquid at the same time, the excess of alkali present will of course produce a dense precipitate, consisting apparently of ferrous and ferric hydrates only; but if to the precipitate an excess of dilute hydrochloric acid be added, the presence of *a blue compound*, previously masked, will be rendered manifest. This precipitate is Prussian blue ($[Fe_2]_2Cfy_3$), or ferric ferrocyanide; and its production is an excellent indication of the original presence of cyanogen.

A word of explanation with regard to the formation of the ferrocyanogen salts just described may be introduced here. The ferrous and ferric salts, though added simultaneously, may be more conveniently considered as acting separately; and the changes may be regarded as taking place in the following order:—

$$1. \begin{cases} KCy + \underset{\text{ferrous hydrate.}}{FeHO} = FeCy + KHO \\ 2KCy + FeCy = K_2FeCy_3 = \underset{\text{ferrocyanide of potassium.}}{K_2Cfy.} \end{cases}$$

$$2. \quad 3K_2Cfy + \underset{\text{ferric hydrate.}}{2Fe_2H_3O_3} = \underset{\text{prussian blue.}}{(Fe_2)_2Cfy_3} + 6KHO.$$

ε. Mixed solutions of hydrate and cyanide of potassium dissolve mercuric oxide (Hg_2O) with great facility; and since this oxide is quite insoluble in a solution of hydrate of potassium which has been mixed with any other salt but an alkaline cyanide, this solvent power is therefore an indication of the presence of cyanogen.

Cyanogen is most usually identified by the tests β, γ, and δ.

Of acid-radicals formed by the union of carbon, nitrogen, and oxygen, one is known, the cyanic.

SALTS OF THE CYANIC RADICAL, OR CYANATES.

The salts are commonly obtained by the action of oxidizing agents upon cyanides. The potassium salt may be readily produced by fusing cyanide of potassium with the oxides of lead or copper; "red lead" is frequently employed for the purpose.

Alkaline cyanates are not decomposed by simple fusion; but, like all other cyanates, they are instantly decomposed when heated on charcoal.

The Hydrogen Salt (HCyO), or cyanic acid, is a colourless liquid which has a peculiar odour intermediate between that of acetic acid and that of sulphurous anhydride (SO_2). It presents the peculiarity of spontaneously changing into a white solid called cyamelide. An aqueous solution of the acid yields, at ordinary temperatures, acid carbonate of ammonium, thus—

$$HCNO + 2H_2O = NH_4HCO_3.$$

Most of the cyanates are more or less soluble in water, those of the first and second subdivisions dissolving readily.

The Potassium, Sodium, Barium, Strontium, Calcium, and Magnesium Salts are soluble.

The Ferrous Salt does not exist.

The Cupric Salt is a greenish brown precipitate.

The Silver Salt is a white precipitate. Its formula is AgCyO. It is soluble in cyanide of potassium and in hydrate of ammonium; it dissolves sparingly in boiling water, and is almost insoluble in cold water. It is decomposed by dilute nitric acid.

The Mercurous Salt is white.

The Lead Salt is white. Its formula is PbCyO. It is slightly soluble in boiling water, and is dissolved, with decomposition, by dilute nitric acid.

This radical may also be detected by its decomposition.

a. When cyanic acid is set free by the action of an acid on a cyanate, it decomposes with an effervescence due to the escape of carbonic anhydride (CO_2): the pungent odour of cyanic acid, which in part escapes undecomposed, will be very perceptible. If the liquid be tested for ammonium, additional evidence will be obtained of the original presence of the cyanic radical: the two reactions, which occur simultaneously when a cyanate is decomposed by an acid, may be represented in one equation,—

$$H_2O + 2KCNO + 2H_2SO_4 = \overset{\nearrow}{HCNO} + KHSO_4 + KNH_4SO_4 + \overset{\nearrow}{CO_2}.$$

β. Hydrosulphuric acid is said to decompose cyanic acid.

The cyanic radical is generally recognized by the test *a*.

Of acid-radicals produced by the union of carbon, sulphur, and nitrogen, one is well known, viz. the sulphocyanic. Its soluble salts are very useful as tests.

SALTS OF SULPHOCYANOGEN, OR SULPHOCYANIDES.

The sulphocyanides are prepared much in the same way as the cyanates, substituting sulphur for oxygen: the potassium salt, for instance, is generally obtained by fusing ferrocyanide of potassium with carbonate of potassium and sulphur. (See p. 54.)

The sulphocyanides are all more or less easily decomposed when heated, and yield very varied and very numerous products.

THE HYDROGEN SALT ($HCNS$ *or* $HCsy$), hydrosulphocyanic acid, may be produced by saturating hydrocyanic acid with hydrosulphuric acid, and exposing the liquid to the air. When pure, it is a colourless oily liquid, having a pungent odour like that of acetic acid: it freezes at 12°·5, boils at 102°·5. It is very poisonous. On keeping, it is speedily resolved into a new acid, hydropersulphocyanic acid, with evolution of hydrocyanic acid, thus—

$$3HCNS = HCN + \underset{\text{yellow ppt.}}{H_2C_2N_2S_3}.$$

Sulphocyanogen may be recognized by the insoluble salts which it forms, by the remarkable colour of the ferric salt, and by the products of decomposition which its compounds yield.

The majority of the sulphocyanides of the three first subdivisions are soluble in water. The chief insoluble compounds are the silver, mercurous, and lead salts.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

The Ferric Salt, though soluble, is very characteristic: it imparts to water a magnificent blood-red colour.

THE CUPROUS SALT is a white precipitate. Its formula is Cu_2CNS ($=Cu_2Csy$). It is scarcely altered by hydrochloric acid; but nitric and sulphuric acids decompose it.

THE CUPRIC SALT does not separate from dilute solutions; if concentrated solutions be employed, a precipitate is obtained which is grey from the admixture of cuprous sulphocyanide. The pure cupric salt may be produced by adding some sulphuric acid to a concentrated solution of sulphocyanide of potassium, and then a saturated solution of cupric sulphate. A black crystalline precipitate, of the formula $CuCNS$ *or* $CuCsy$ will slowly separate. This substance is decomposed by pure water, but dissolved by ammonia water. Nitric, sulphuric, and hot hydrochloric acids dissolve it.

The Silver Salt is a white precipitate. Its formula is $AgCNS$. It is soluble in hydrate of ammonium, very sparingly dissolved by boiling water, and insoluble in dilute nitric acid.

THE MERCUROUS SALT is white. Its formula is Hg_2CNS. It is scarcely attacked by nitric acid.

THE MERCURIC SALT is soluble.

The Lead Salt separates gradually from the mixed solutions of plumbic acetate and sulphocyanide of potassium; it is more rapidly deposited on agitation: it is a pale yellow crystalline precipitate. Its formula is $PbCNS$. It is decomposed by pure water: warm nitric acid converts it into sulphate of lead.

This acid-radical may also be detected by the decompositions which its compounds suffer.

α. When a sulphocyanide (that of potassium, for instance) is boiled with nitric acid, or when chlorine gas is passed into the aqueous solution of a sulphocyanide, a yellow precipitate is produced, to which the name "pseudo-sulphocyanogen" has been given: the probable constitution of this body is $HC_3N_3S_3$.

β. Most sulphocyanides, when heated in a closed tube, yield a sublimate of sulphur, together with many other products. The ammonium suffers very remarkable changes, and yields, among other volatile bodies, bisulphide of carbon, sulphide of ammonium, hydrosulphuric acid, and sulphur.

This acid-radical may be recognized by its insoluble silver and lead salts, and by the decomposition described under *α*.

Of acid-radicals formed by the union of cyanogen with metals, there are three which more especially demand notice: they are known respectively as ferrocyanogen, ferricyanogen, and cobalticyanogen. The number of these compounds of carbon, nitrogen, and metals, or rather of cyanogen and metals, is, however, very great. They are generally formed by the direct union of two metallic cyanides, which, instead of combining to form a double salt, appear to undergo a total change in the arrangement of their constituent molecules:—

$$2KCy + FeCy = K_2(FeCy_3).$$

Some few of these compounds do, however, appear to partake far more of the characters of double salts than of simple salts which contain compound acid-radicals: such compounds are those formed by the cyanides of zinc and copper—$KCy, ZnCy$, and KCy, Cu_2Cy; while in other compounds, such as those of iron, manganese, cobalt, and platinum, so complete a metamorphosis has been effected, that no hesitation can be felt in ascribing to them a constitution differing from that of the others. The two compounds containing cyanogen and iron—ferrocyanogen ($FeCy_3$) and ferricyanogen (Fe_2Cy_6)—are well known in combination with basic radicals, forming very stable salts: the former of these radicals is bibasic, the latter tribasic. Chromium and manganese yield several radicals; but their salts are not stable. The best known of these last mentioned compound radicals are chromicyanogen (Cr_2Cy_6) and manganicyanogen (Mn_2Cy_6), which are each tribasic. Cobalt forms a radical of the formula Co_2Cy_6, the salts of which (cobalticyanides) are very stable. The metals allied to platinum yield several radicals by union with cyanogen.

SALTS OF FERROCYANOGEN, OR FERROCYANIDES.

A ferrocyanide is produced when an alkaline cyanide meets with iron, or an iron salt, under appropriate conditions.

Ferrocyanides are decomposed by heat: in most cases nitrogen gas is evolved, and a residue of iron and carbon left.

THE HYDROGEN SALT (H_2Cfy), or hydroferrocyanic acid, is produced when hydrochloric acid is added to a concentrated solution of ferrocyanide of potassium. It separates on the addition of ether, in the form of minute white, yellowish, or bluish crystals floating in the ether. It is soluble in water.

This radical is best recognized by the formation of certain characteristic salts; but it may also be identified by the products of its decomposition.

The chief insoluble ferrocyanides are the calcium, ferrous, ferric, cupric, argentic, and lead salts.

THE POTASSIUM and SODIUM SALTS are soluble.

THE BARIUM SALT dissolves in about 36 parts of cold water.

THE STRONTIUM SALT is soluble.

The Calcium Salt is a white precipitate.

Its formula is $KCaCfy + 1\frac{1}{2}aq$.

It requires about 800 parts of cold water for its solution, and is even less soluble in water containing ammonium salts.

The Magnesium Salt is a white precipitate.

Its formula is $Mg_2Cfy + 6aq$; but when an ammonium is present in the solutions employed, the precipitate appears to be $MgNH_4Cfy$.

It is insoluble in chloride of ammonium, readily soluble in hydrochloric acid.

The Ferrous Salt is a white, or more usually a pale blue precipitate, which is rapidly converted by the air or oxidizing agents into the ferric salt, becoming a deep blue in consequence.

Its formula is KFe_3Cfy_2, *or* $KFeCfy, Fe_2Cfy$.

It is nearly insoluble in water.

The Ferric Salt is produced by the action of ferric salts on a solution of ferrocyanide of potassium. It is a deep blue precipitate, known as Prussian blue.

Its formula is $(Fe_2)_2Cfy_3$.

It is insoluble in water, and in dilute hydrochloric acid (see p. 126).

THE CUPROUS SALT is a white precipitate. Its formula is $(Cu_2)_2Cfy$. It is soluble in the hydrate, but insoluble in the other salts of ammonium.

The Cupric Salt is a brownish red precipitate.

Its formula is Cu_2Cfy.

It is insoluble in water, ammonium salts, and acids.

THE SILVER SALT is white. Its formula is Ag_2Cfy. It is soluble in cyanide of potassium, in the hydrate but not in the other salts of ammonium. Hydrochloric acid does not act upon it; but nitric acid dissolves out one-fourth of its silver, converting it into ferricyanide. Sulphuric acid dissolves it. It is insoluble in water.

THE MERCUROUS SALT is not known; ferrocyanide of potassium precipitates yellowish white flakes (which contain no mercury) from solutions of mercurous salts.

THE MERCURIC SALT is white.

THE LEAD SALT is white. Its formula is Pb_2Cfy. It is sparingly soluble in hot hydrate of ammonium, and entirely in chloride of ammonium, but not in the other common ammonium salts. It is insoluble in water, but partially soluble in sulphuric acid.

This acid-radical may also be detected by the following processes of decomposition:—

a. If ferrocyanide of potassium or sodium be made by boiling any other ferrocyanide* with the hydrates or carbonates of potas-

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* Insoluble ferrocyanides may be thus decomposed, an alkaline salt of the radical, and an insoluble carbonate of the base being formed. Thus, to take two examples—

$$(Fe_2)_2Cfy_3+6KHO=3K_2Cfy+2Fe_2H_3O_3; \text{ or}$$
$$Ba_2Cfy+Na_2CO_3=Na_2Cfy+Ba_2CO_3.$$

sium or sodium and filtering, and the resulting solution then evaporated to dryness and ignited in a small covered crucible, a fused mass will be obtained, and, in that part of it soluble in water, an alkaline *cyanide* will be found, which may be identified by any of the usual tests, while the residue, insoluble in water, may, after due washing, be dissolved in hot hydrochloric or nitric acid and tested for *iron*.

β. When an alkaline ferrocyanide is heated with dilute sulphuric acid, the characteristic odour of hydrocyanic acid is perceptible.

γ. But when powdered ferrocyanide of potassium (or of sodium) is heated with concentrated sulphuric acid, scarcely a trace of hydrocyanic acid is evolved, but only carbonic oxide gas (CO), according to the following equation :—

$$\begin{aligned} &2K_2FeC_3N_3+6H_2O+6H_2SO_4 \\ &=2K_2SO_4+Fe_2SO_4+3[NH_4]_2SO_4+6CO. \end{aligned}$$

Ferrocyanogen is usually recognized by the formation of the ferrous and ferric salts; occasionally also the cupric and uranium compounds are employed for this purpose, as well as the process given under a.

SALTS OF FERRICYANOGEN, OR FERRICYANIDES.

The potassium salt is obtained by passing chlorine into a solution of ferrocyanide of potassium, until a drop of the solution no longer produces a blue precipitate with a ferric salt.

When heated, ferricyanides undergo decompositions very similar to those of the ferrocyanides.

The Hydrogen Salt ($H_3Fe_2Cy_6$ *or* H_3Cfdy), or hydroferricyanic acid, is obtained by the action of hydrofluosilicic acid upon ferricyanide of potassium.

This radical may be recognized by the formation of the ferrous, ferric, zinc, and silver salts.

The Potassium, Sodium, Barium, Strontium, Calcium, and Magnesium Salts are soluble.

The Ferrous Salt is produced by the action of ferricyanide of potassium: it is a blue precipitate. Its formula is Fe_3Cfdy. It is insoluble in water and in hydrochloric acid.

The Ferric Salt is thought to be produced by the action of ferricyanide of potassium. It is a very soluble salt, and only appears in the form of a brownish green solution.

THE ZINC SALT is produced by the action of ferricyanide of potassium: it is an orange brown precipitate. Its formula is Zn_3 Cfdy. It dissolves in ammonium salts.

THE CUPROUS SALT is reddish brown. Its formula is $(Cu_2)_3$ Cfdy. It is soluble in the hydrate, but not in other salts of ammonium; it is insoluble in hydrochloric acid.

THE CUPRIC SALT is brownish or greenish yellow. Its formula is Cu_3 Cfdy. It is soluble in the hydrate and carbonate of ammonium, but not in other ammonium salts, unless with the aid of heat.

THE SILVER SALT is orange yellow. Its formula is Ag_3 Cfdy. It dissolves in the hydrate, and in a hot solution of the carbonate of ammonium, but is insoluble in other ammonium salts.

THE MERCUROUS and MERCURIC SALTS are yellow.

THE LEAD SALT is deposited gradually in dark brownish red crystals. Its formula is Pb_3 Cfdy. It is somewhat soluble in water. It is decomposed by dilute sulphuric acid into sulphate of lead and hydroferricyanic acid.

The constituents of this radical may be detected by its decomposition, in the manner described under ferrocyanogen; but the formation of the characteristic ferricyanides above mentioned must be relied on for its distinction.

SALTS OF COBALTICYANOGEN, OR COBALTICYANIDES.

These salts are produced by the direct action of an alkaline cyanide upon cyanide of cobalt. 4 eqs. of cyanide of potassium with 2 eqs. of cyanide of cobalt only differ from 1 eq. of cobalticyanide of potassium by 1 eq. of potassium, which in the reaction decomposes 1 eq. of water, producing 1 eq. of hydrogen and 1 eq. of hydrate of potassium:

$$4KCy+2CoCy+H_2O=K_3(Co_2Cy_6)+KHO+H.$$

Cobalticyanogen, it will be observed, is analogous to ferricyanogen; the cobalt compound corresponding to ferrocyanogen is unknown, or at least its existence is very doubtful.

THE HYDROGEN SALT ($H_3Co_2Cy_6$ *or* H_3 Cocy), or hydrocobalticyanic acid, crystallizes in deliquescent needles. Heated above 100°, it is decomposed. It is soluble in water and in alcohol, but does not dissolve in ether.

This acid-radical may be recognized both by the formation of insoluble salts, and by its decomposition.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE FERROUS SALT is a white precipitate. Its formula is Fe_3 Cocy.

THE FERRIC SALT is soluble.

THE ZINC SALT is a white precipitate.

THE CUPROUS SALT is unknown.

THE CUPRIC SALT is produced by the action of soluble cupric salts on cobalticyanic acid: it is a sky-blue precipitate. Its formula is Cu_3 Cocy + $3\frac{1}{2}$aq. It is soluble in hydrate of ammonium, insoluble in water and acids.

The Silver Salt is a white curdy precipitate. Its formula is Ag_3 Cocy. It is insoluble in water and acids.

The Mercurous Salt is a white precipitate.

The Mercuric Salt is soluble.

The Lead Salt is readily dissolved by water, but is insoluble in alcohol.

Cobalticyanide of potassium gives with manganese and stannous salts white precipitates, and with cadmium salts a brown precipitate which becomes white. It does not yield any results with titanic, uranic, and chromic salts.

Cobalticyanogen may be recognized by its decomposition in a similar manner to the two preceding acid-radicals.

Of acid-radicals containing carbon, oxygen, and hydrogen, a very large number is known; we shall, however, describe the salts of those only which are likely to come in the way of the student, viz. the acetates, benzoates, lactates, succinates, tartrates, citrates, gallates, and tannates.

SALTS OF THE ACETIC RADICAL, OR ACETATES.

The radical under consideration is an exemplar of a new class or order of compounds: it is a member of what is called "a homologous series." Some approach to this form of combination has already been noticed in the case of the borates; but among the compounds of carbon with hydrogen and oxygen, it is more completely and extensively developed. An immense number of acid-radicals has been discovered by degrees, each requiring the same amount of base for its saturation, and each differing, from the term of the series next above or below it, only by the molecule CH_2. The following list shows a few of the hydrogen compounds or acids of these radicals:—

Formic acid	$HC\,H\,O_2$.
Acetic acid	$HC_2H_3O_2=HCHO_2+CH_2$.
Propionic acid	$HC_3H_5O_2=HCHO_2+2CH_2$.
Butyric acid	$HC_4H_7O_2=HCHO_2+3CH_2$.
Valerianic acid	$HC_5H_9O_2=HCHO_2+4CH_2$.

The series of which acetic acid is a member, is called "the series of fatty acids," because, as the amount of CH_2 increases in them, they no longer exhibit the limpidity and perfect miscibility with water characteristic of formic and acetic acids, but become more and more oily, until, finally, the higher terms of the series reach the condition of solid fats. All these acids have certain features in common: they are volatile without decomposition; their boiling point increases regularly with each increment of CH_2; they all yield similar products of decomposition, which vary only by CH_2; and they may all be formed by the same agencies from a series of "alcohols" containing basic radicals, which bear a fixed and constant relation to the radicals of the acids.

The acid of the acetic series is produced by the imperfect combustion of most organic bodies; as "vinegar" it is produced by the slow oxidation of alcohol, and as "pyroligneous acid" by the distillation of wood at a high temperature in iron retorts.

The acetates of the first and second subdivisions, when heated, yield carbonates, and, if out of contact of air, a volatile liquid of peculiar odour, called *acetone* (C_3H_6O). Alkaline acetates, if mixed with excess of alkaline hydrate and heated, are completely decomposed into the combustible gas known as "marsh-gas" and alkaline carbonates.

THE HYDROGEN SALT ($HC_2H_3O_2$), or acetic acid, is a colourless crystalline solid at temperatures below 15° C.; on this account it has received the name of *glacial acetic acid*.* It boils at 120° C. It has the well-known taste and smell of vinegar in a most marked degree, and acts as an acrid poison.

The normal or neutral acetates are almost without exception soluble in water; the basic acetates are for the most part insoluble.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM SALTS are soluble.

THE FERROUS and **Ferric Salts** are soluble; the latter, however, if produced by adding a drop of ferric chloride to the solution of an alkaline acetate, imparts a distinct brownish red colour to the liquid. If the coloured solution be then boiled, the neutral ferric acetate will be decomposed, a mixed hydrate

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* The hydrate of this acid, having the formula $C_2H_4O_2, H_2O$, boils at 104° C.

and acetate, or basic acetate, being produced, and the solution becoming gradually colourless.

THE ZINC and CUPRIC SALTS are soluble.

THE MERCUROUS SALT is obtained by adding mercurous nitrate to acetic acid or a soluble acetate: it is a white, scaly, crystalline precipitate. Its formula is $Hg_2C_2H_3O_2$. It dissolves readily in excess of its precipitant: it is slightly soluble in water or acetic acid, especially on warming; but a slight decomposition of the salt into mercuric acetate and mercury then occurs.

The Silver Salt is produced by the action of soluble silver salts on the solution of an acetate: it is a white, beautifully crystalline precipitate, which becomes discoloured by exposure to light.

Its formula is $AgC_2H_3O_2$.

It is soluble in hydrate of ammonium, but dissolves very sparingly in cold water or acetic acid, although it dissolves more abundantly in these liquids when hot, crystallizing out again on cooling.

THE MERCURIC SALT is soluble.

THE LEAD SALT ($PbC_2H_3O_2$) is soluble. THE BASIC LEAD SALT is soluble, and is remarkable for having an alkaline reaction. Its formula is $PbC_2H_3O_2, Pb_2O$.

This acid-radical may also be detected by the following special processes:—

a. When an acetate is warmed with dilute sulphuric acid, acetic acid is liberated, and, being volatile without decomposition, may be recognized by its peculiar odour and inflammability.

β. If an acetate be mixed with a small quantity of alcohol (C_2H_5HO *or* EHO, the hydrate of the compound basic radical ethyle) to which an equal bulk of sulphuric acid has been previously added, a true salt will be formed, containing a compound basic and a compound acid-radical: this product is termed acetate of ethyle, or acetic ether, and may be at once recognized by its peculiar and agreeable aromatic odour. The reaction is as follows:—

$$EHO+H\bar{A}=H_2O+E\bar{A}.$$

γ. When an acetate of the first or second subdivision is heated in a test-tube, acetone, remarkable for its odour and inflammability, is evolved; the reaction is as follows:—

$$2BaC_2H_3O_2 = Ba_2CO_3 + \underset{\text{acetone.}}{C_3H_6O}$$

The acetic radical is generally recognized by the formation of the silver salt, and the test β.

SALTS OF THE BENZOIC RADICAL, OR BENZOATES.

Just as acetic acid is the representative of the series of fatty acids, so benzoic acid is the type of "the series of aromatic acids." This group is by no means so numerous as the former; but its members present the same regular differences of composition, and the same relations to other groups of connected bodies. Benzoic acid, though itself somewhat rare, is the member of this series most commonly met with.

Benzoates when heated decompose, generally giving rise to the formation of a volatile solid body termed *benzophenone*, which is in reality the benzoate of phenyle (C_6H_5, $C_7H_5O_2$).

This radical may be recognized by the formation of insoluble salts, and by processes of decomposition.

THE HYDROGEN SALT ($HC_7H_5O_2$), or benzoic acid, is generally obtained by exposing "gum benzoin" and several other resins to heat, or by boiling them with an alkaline hydrate. It crystallizes in plates, and has an aromatic odour. At 120° C. it fuses, sublimes at 145°, and boils at 239°. Its vapour, if inhaled, provokes coughing. It is but slightly soluble in cold, more readily in hot water. In alcohol it is soluble.

Nearly all benzoates are soluble in water; the ferric salt is the most characteristic insoluble benzoate.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, and FERROUS SALTS are soluble.

The Ferric Salt is produced by the action of ferric chloride upon solutions of benzoates. It is of a reddish yellow colour, and has the composition of a basic salt. It is dissolved by most acids.

THE ZINC SALT is soluble. THE CUPROUS SALT is unknown.

THE CUPRIC SALT is produced by the action of soluble cupric salts upon solutions of benzoates, as a blue precipitate. Its composition is $CuC_7H_5O_2$ with some water of crystallization. It is soluble in many acids.

THE SILVER SALT is produced by adding a soluble silver salt to a solution of a benzoate, as a white curdy precipitate. Its formula is $AgC_7H_5O_2$. It dissolves in boiling water and in many acids.

THE MERCUROUS SALT is a curdy precipitate. THE MERCURIC SALT is a white curdy precipitate, slightly soluble in water and alcohol.

THE LEAD SALT is a white precipitate of the formula $PbC_7H_5O_2$ with water of crystallization.

This acid-radical may also be detected by the following methods:—

α. When an acid is added to a soluble benzoate, a precipitate of benzoic acid is produced, which, if boiled in water, dissolves, and crystallizes out again on cooling. The acid, when separated, may be recognized by its fusibility, volatility, and remarkable odour.

β. The dry cupric benzoate, when heated in a test-tube, decomposes, with the formation, among other products, of the benzoate of phenyle (C_6H_5, $C_7H_5O_2$), which is a body possessing an odour resembling that of the geranium.

SALTS OF THE LACTIC RADICAL, OR LACTATES.

This radical is bibasic; and the lactates known belong to the two series of acid and neutral salts: for the most part they dissolve sparingly in water or alcohol, and are insoluble in ether.

The Hydrogen Salt, or lactic acid, occurs in sour milk, in which it is produced by a fermentive action upon the milk-sugar that liquid naturally contains, thus—

$$C_{12}H_{20}O_{10}+2H_2O=\underset{\text{lactic acid.}}{2C_6H_{12}O_6}.$$

It is produced by the fermentation of other kinds of sugar. Its formula is $H_2C_6H_{10}O_6$. It is a colourless syrupy liquid, which does not solidify at 24° C. It is inodorous, but has a biting acid taste. In presence of platinum it volatilizes without decomposition at about 200° C. Heated alone, it decomposes at about 130° C. into water and lactic anhydride ($C_{12}H_{20}O_{10}$). The latter is a pale yellow, bitter, and easily fusible solid. At high temperatures, lactic acid decomposes into a great variety of products. Lactic acid dissolves in water in all proportions.

The lactates of the first subdivision are very soluble in water; those of the second subdivision require from 20 to 30 parts of water for solution, while the majority of the remaining salts dissolve easily.

The Potassium, Sodium, Barium, Strontium, Calcium, and Magnesium Salts are soluble.

The Ferrous Salt is a nearly white precipitate. Its formula is $Fe_2\bar{L}$. It is soluble in 48 parts of water at 10° C., or in 12 of boiling water; it is insoluble in strong alcohol.

The Ferric Salt is brown and soluble.

The Zinc Salt is white, and crystallizes in four-sided prisms belonging to the right prismatic system. Its formula is $Zn_2\bar{L}$. It is soluble in 58 parts of cold, or 6 of boiling water; it is insoluble in alcohol.

The Cupric Salt is very soluble.

The Silver Salt is soluble in 20 parts of cold water, nearly insoluble in cold, but very soluble in hot alcohol.

The Mercurous Salt is a white precipitate consisting of fine needles. Its formula is $(Hg_2)_2\bar{L}+aq$. It is sparingly soluble in cold, and is decomposed by boiling water.

The Mercuric Salt is soluble.

THE LEAD SALT is soluble.

Lactates may also be recognized by the following processes:—

α. When the hydrogen compound, lactic acid, is heated to 130° C., water containing a little lactic acid distils, and the residue, on cooling, becomes a yellowish white solid, of very bitter taste, almost insoluble in water, but easily soluble in alcohol or ether. It is called "lactide," and has the formula $C_6H_{10}O_5$, and by long boiling with water is converted again into lactic acid.

β. If lactic acid be heated with concentrated sulphuric acid, almost pure carbonic oxide gas is given off, and a body resembling humin remains behind.

SALTS OF THE SUCCINIC RADICAL, OR SUCCINATES.

To the series of which succinic acid is a member, the name "oxalic acid series" has been applied. Oxalic acid, the first member, has been already described as a volatile and bibasic acid; succinic acid and the other terms of the series, or *homologues* of oxalic acid, present the same characteristics. Succinic acid is obtained in many ways; the most important of these are the dry distillation of amber, and the fermentation of malate of calcium.

Succinates when heated yield numerous products of decomposition, carbonic anhydride and acetic acid being among the number.

THE HYDROGEN SALT ($H_2C_4H_4O_4$ *or* $H_2\overline{S}$), or succinic acid, crystallizes in colourless prisms belonging to the oblique prismatic or monoclinic system. It is inodorous. It melts at 180° C., and boils at 235°, forming a most pungent vapour, which, if inhaled, excites violent coughing. It dissolves in 5 parts of water at 16° C., in 2·2 parts of boiling water, and in 1·37 part of strong alcohol.

Many succinates are soluble in water; the insoluble salts dissolve readily in acetate of potassium.

THE POTASSIUM and SODIUM SALTS ($K_2C_4H_4O_4$ and $Na_2C_4H_4O_4$) are soluble.

THE BARIUM and STRONTIUM SALTS are sparingly soluble in water, but dissolve in acids; in alcohol they are insoluble.

THE CALCIUM SALT is precipitated on boiling concentrated solutions of chloride of calcium and succinate of ammonium. Its formula is $Ca_2C_4H_4O_4 + aq$. It is soluble in succinic, acetic, and most other acids, but insoluble, or nearly so, in alcohol.

THE MAGNESIUM SALT is soluble.

THE FERROUS SALT is a grey-green precipitate, insoluble in water, but soluble in acids.

The Ferric Salt is a reddish brown precipitate of very variable constitution. It is insoluble in water, soluble in hot solutions of succinic or acetic acid, and in most other acids.

THE CUPRIC SALT is green or blue. Its formula is $Cu_2C_4H_4O_4$. It is soluble with difficulty in water or solution of succinic acid; it dissolves in acetic and other acids.

The Silver Salt is a white precipitate, produced by nitrate of silver in neutral or alkaline solutions. It is soluble in hydrate of ammonium, and dissolves slowly in water or acetic acid. It dissolves in most mineral acids.

The Mercurous Salt appears to be soluble. The Mercuric Salt is a white precipitate.

The Lead Salt is a white precipitate. Its formula is $Pb_2 C_4 H_4 O_4$. It is but sparingly soluble in water, in acetic, or boiling solution of succinic acid. In alcohol it is insoluble.

The radical of the succinates may be recognized by the following tests:—

α. Succinic acid, when heated in the air, evolves suffocating vapours, which burn with a pale flame. It may be sublimed in great part unchanged.

β. Succinates are not blackened when heated with strong sulphuric acid.

SALTS OF THE TARTARIC RADICAL, OR TARTRATES.

The potassium salt of this radical is found in the deposit which occurs in wine casks, and which is termed "Tartar," or "Argol." This radical is not at present known to be a member of any homologous series; it is bibasic; none of its inorganic salts are volatile without decomposition.

Tartrates when heated evolve the peculiar odour of burnt sugar, decomposing with formation of carbonic anhydride, carburetted hydrogen gas, acetic acid, pyrotartaric acid, and other bodies.

The Hydrogen Salt ($H_2 C_4 H_4 O_6$ *or* $H_2 \bar{T}$), or tartaric acid, is a substance which crystallizes in fine colourless prisms belonging to the oblique prismatic system. It melts at 170° C. to a transparent colourless liquid, but does not volatilize without decomposition. When heated to a high temperature, new acids are obtained from tartaric acid. 1 part dissolves in $\frac{7}{13}$ part of cold, and in a less quantity of boiling water. This acid has the property, in common with several others, of preventing the precipitation of many oxides by hydrate of potassium or ammonium.

This radical may be recognized both by the formation of insoluble salts and by processes of decomposition.

The neutral tartrates of the first subdivision are almost the only soluble neutral salts of this radical, and their acid salts almost the only insoluble acid salts.

The Barium Salt is produced by the addition of chloride of barium to the neutral or alkaline solution of a tartrate: it is a white precipitate. Its formula is $Ba_2C_4H_4O_6$. It is easily soluble in all ammonium salts except the hydrate; it is also soluble in hydrochloric acid.

THE STRONTIUM SALT is comparatively soluble in water, readily so in chloride of ammonium.

The Calcium Salt is produced by the addition of even the hydrate or sulphate of calcium in aqueous solution to tartrate of sodium; it is produced in larger quantity by chloride of calcium. Its formula is $Ca_2C_4H_4O_6$. Its precipitation is prevented, or at least retarded, by the presence of ammonium salts, in which it is easily soluble. This salt, if filtered and washed, is remarkable for its solubility in cold hydrate of potassium, its reprecipitation on boiling the alkaline solution, and its re-solution on the cooling of the liquid.

THE MAGNESIUM SALT is comparatively soluble.

THE FERROUS SALT is a green precipitate.

THE FERRIC SALT appears to be soluble.

THE ZINC SALT is soluble.

THE CUPRIC SALT is a green precipitate. Its formula is $Cu_2C_4H_4O_6 + 3aq$. It is soluble in a boiling solution of carbonate of sodium and in acids.

The Silver Salt is a white and crystalline precipitate. Its formula is $Ag_2C_4H_4O_6$. It is insoluble in water; in hydrate of ammonium it dissolves, forming a solution which, when boiled, deposits a great portion of the silver it contains upon the sides of the containing vessel. With proper modifications, this constitutes Petitjean's silvering process.

THE MERCUROUS and MERCURIC SALTS are white precipitates, insoluble in water, but soluble in acetic, tartaric, and mineral acids.

THE LEAD SALT is white. Its formula is $Pb_2C_4H_4O_6$. It is soluble in chloride of ammonium, nearly insoluble in water; it dissolves in acids.

This acid-radical may be distinguished by processes of decomposition.

a. Tartaric acid and tartrates, when heated on platinum foil, char, and evolve inflammable gases and the peculiar odour of burnt sugar. The experiment may be performed in a test-tube open at both ends.

β. When a tartrate is boiled with concentrated sulphuric acid, besides the odour of burnt sugar which is evolved, and the carbon which separates rapidly, carbonic oxide gas is also formed, and may be detected by the blue flame with which it burns when a lighted taper is applied to the mouth of the test-tube employed.

The tartaric radical is usually recognized by the formation of the insoluble or sparingly soluble barium, calcium, and silver salts, and by the tests α. and β.

SALTS OF THE CITRIC RADICAL, OR CITRATES.

The citric radical belongs to no ascertained homologous series. It is tribasic. The acid is found in many plants, especially in the fruit of the *Citrus medica*, or lemon, and of the *Citrus aurantium*, or orange.

The citrates, when heated, begin to decompose at about 230° C., evolving many volatile products, and leaving a large quantity of charcoal.

The Hydrogen Salt ($H_3C_6H_5O_7$ *or* $H_3\overline{Ci}$), or citric acid, is a colourless crystalline body of the same form as the commercial acid $H_3\overline{Ci}+aq$, which occurs in prisms belonging to the right prismatic system: these hydrated crystals effloresce in the air, and form the true acid. When heated to a high temperature, citric acid yields several new acids.

The radical may be recognized both by the formation of insoluble salts and by its decomposition.

The majority of the citrates are insoluble in water. The salts of the first subdivision are, however, soluble.

The Barium Salt is a white precipitate. Its formula is $Ba_3C_6H_5O_7$. It is soluble in ammonium salts, in a large proportion of water, and in acids.

The Strontium Salt is a white precipitate of the formula $Sr_3C_6H_5O_7$, soluble in many acids.

The Calcium Salt is a white crystalline precipitate, which is produced in dilute solutions only on boiling; the salt partially redissolves on the cooling of the solution. Its formula is $Ca_3C_6H_5O_7$. It is soluble in chloride of ammonium solution; it dissolves more sparingly in boiling than in cold water; it is soluble in acids and in most ammonium salts, excepting the hydrate.

The Magnesium Salt is soluble. The Zinc Salt is but slightly soluble in water.

The Ferric Salt is soluble.

The Cupric Salt is precipitated on boiling as a green crystalline powder. Its formula is $Cu_3\overline{Ci}$, $CuHO+aq$.

The Silver Salt is a white precipitate. Its formula is $Ag_3C_6H_5O_7$. It is soluble in boiling water.

The Mercurous and Mercuric Salts are white precipitates.

The Lead Salt is a white precipitate, soluble in ammonium salts.

This acid-radical may be distinguished by the following tests:—

a. Citric acid, when heated in a tube open at both ends, evolves irritating acid vapours; heated on platinum foil, it chars and evolves combustible gases.

β. When boiled with concentrated sulphuric acid, citric acid evolves a trace of acetic acid and a large quantity of carbonic oxide, which may be kindled. A gradual separation of carbon also takes place.

SALTS OF THE GALLIC RADICAL, OR GALLATES.

The radical of these salts is obtained by the decomposition which tannic acid undergoes when exposed in a moist condition to the action of the air or to the influence of a fermenting body. It is said to occur in the vegetable kingdom. Recent researches have shown it to be a tribasic radical.

The radical is remarkable on account of the behaviour of its hydrogen salt (gallic acid) under the influence of heat: at a temperature of from 210° to 215° C. it loses 1 eq. of carbonic anhydride, and is converted into *pyrogallic acid*, thus—

$$\underset{\text{gallic acid.}}{H_3, C_7H_3O_5} = CO_2 + \underset{\text{pyrogallic acid.}}{H, C_6H_5O_3}.$$

The latter body sublimes in flattened needles: it is remarkable for its great affinity for oxygen, which it absorbs (especially when in solution), either from the atmosphere or from oxidizing agents, with the greatest avidity, becoming brown and ultimately black.

THE HYDROGEN SALT, or gallic acid ($H_3, C_7 H_3 O_5$), is a solid body, crystallizing in silky needles, which have no odour, but an astringent taste: 1 part dissolves in 100 parts of cold, or in 3 of boiling water; it is very soluble in alcohol, but less so in ether.

The gallates generally formed are those which have the formulæ

$$H_2 M, C_7 H_3 O_5 \text{ and } H M_2, C_7 H_3 O_5 ;$$

those represented by $M_3 C_7 H_3 O_5$ are but rarely produced.

THE POTASSIUM and SODIUM SALTS are soluble; those of BARIUM, STRONTIUM, and CALCIUM are but slightly soluble in water. They all have the general formula $H_2 M, C_7 H_3 O_5$.

THE MAGNESIUM and ZINC SALTS are white precipitates, of the formula $HM_2, C_7 H_3 O_5$, and very slightly soluble in water.

THE FERROUS SALT does not appear to have been obtained.

The Ferric Salt is produced by the addition of a ferric salt to a solution of a gallate; the liquid instantly becomes of a bluish black colour. If this liquid be boiled, it decolourizes with escape of carbonic acid gas and formation of a *ferrous* salt.

THE COPPER, MERCURY, and SILVER SALTS appear to be unknown.

THE LEAD SALT is produced by the action of a solution of acetate of lead upon a solution of gallic acid, as a white precipitate having the composition $HPb_2, C_7 H_3 O_5$, with water of crystallization. It dissolves easily (when recently precipitated) in concentrated acetic acid. Excess of this reagent is a perfect means of precipitating gallic acid.

This acid-radical may be still further recognized by—

a. Its rapid oxidation, with formation of a brown colouring matter, when an alkaline solution containing it is freely heated in contact with air.

β. It may be distinguished from tannic acid by its not producing a precipitate in solution of gelatine, unless previously mixed with a solution of gum.

SALTS OF THE TANNIC RADICAL, OR TANNATES.

Tannin or tannic acid is a name given to that large class of bodies which form the astringent principle in various parts of many plants. The individual acid here to be described, as most commonly met with, is that to which the name of gallotannic acid has been given, from its occurrence in nutgalls, from which it is always extracted by the joint action of ether and water.

THE HYDROGEN SALT, tannic or gallotannic acid ($H_3 C_{27} H_{19} O_{17}$), is obtained as a white or slightly yellow spongy mass, glistening frequently from being an aggregation of crystals. It is very soluble in water, alcohol, or anhydrous ether.

The gallotannates generally contain 2 eqs. of metal, but sometimes 3 eqs.; consequently their radical must be regarded as tribasic.

THE POTASSIUM and SODIUM SALTS are very soluble in water.

THE BARIUM SALT is white, almost insoluble in water.

THE CALCIUM SALT dissolves in pure water.

THE MAGNESIUM SALT is but slightly soluble.

THE FERROUS SALT is white and gelatinous, and sufficiently soluble in water not to be precipitated from dilute solutions.

The Ferric Salt is produced by adding a ferric salt to a solution of a gallotannate: it is a bluish black precipitate. Its formula is probably $Fe_2 H, C_{27} H_{19} O_{17}$.

THE ZINC SALT is white. THE CUPRIC SALT is brownish yellow.

THE SILVER SALT is reddish brown.

THE MERCUROUS SALT is yellow, and THE MERCURIC SALT brick-red.

THE LEAD SALT is white. Its composition is probably $Pb_3, C_{27} H_{19} O_{17}$.

This radical may also be recognized and distinguished from that of the gallates by its property of precipitating gelatine: when an aqueous solution of gallotannic acid is mixed with an aqueous solution of gelatine, a fine filmy or gelatinous precipitate immediately forms. This is the reason of the employment of oak-bark, and other substances which contain these astringent principles, in the process of tanning.

Of acid-radicals produced by the union of carbon with nitrogen, hydrogen, and oxygen, one only needs description here, viz. the uric.

SALTS OF THE URIC RADICAL, OR URATES.

This radical is of animal origin: the chief source from which its salts are prepared is the excrement of serpents, which consists almost wholly of urate of ammonium. This radical is bibasic.

Uric acid and urates, when heated, in common with nearly all organic bodies containing nitrogen, evolve the odour of burning feathers.

The Hydrogen Salt ($H_2C_5N_4H_2O_3$ *or* $H_2\bar{U}$), or uric acid, occurs in delicate white needles; it dissolves very sparingly in cold water; in sulphuric acid it is soluble, forming a brown solution, from which water reprecipitates the uric acid.

Urates, with the exception of the Potassium and Sodium Salts, are almost all insoluble in water: it is very remarkable that the Ammonium Salt is extremely insoluble in water; it is, however, dissolved by chloride or phosphate (Na_2HPO_4) of sodium, the sodium salt being formed.

The Calcium Salt is white; the Ferric Salt brown; the Cupric Salt green; the Silver Salt white, rapidly becoming black if the liquid be heated; the Mercuric and the Lead Salts are white.

The uric radical may be easily identified by the following processes of decomposition:—

a. Uric acid, if heated alone, evolves the odour of burnt hair together with that of cyanide of ammonium, a carbonaceous residue being left.

β. If uric acid or a urate be mixed with solid hydrate of potassium and heated in a narrow tube, ammonia will be evolved, and cyanide or cyanate of potassium remain in the tube. The two latter products may be identified in the manner already pointed out (pp. 338-341).

γ. If uric acid be dissolved in dilute nitric acid, the solution evaporated just to dryness in a porcelain dish, and a glass stopper moistened with strong ammonia water be held over the residue in the dish, the magnificent purple colour of *murexide* is produced, which is quite characteristic.

TABLE OF REACTIONS.

SALTS.	CO_3. (p. 320)	C_2O_4. (p. 323)	BoO_2. (p. 326)	SiO_2. (p. 329)	$C_2H_3O_2$. (p. 348)	$C_4H_4O_6$. (p. 354)
Potassium ...	—	—	—	—	—	white cryst.
Sodium	—	—	—	—	—	—
Barium	white	white	white	white	—	white
Strontium ...	white	white	white	white	—	white
Calcium	white	white	white	white	—	white
Magnesium ..	white	—	white gelat.	white	—	—
Ferrous	greenish white	yellow	pale yellow	greyish green	—	green
Ferric.........	red	yellow	yellow	?	red solution	—
Zinc	white	white	white	white	—	—
Cupric	blue	pale blue	pale green	greenish blue	—	green
Silver	white	white	white	?	white crystal.	white
Mercurous ...	—	—	—	white	white	white
Mercuric ...	white	white	—	—	—	white
Lead	white	white	white flaky	white	—	white

In the Table which immediately follows, as indeed in all similar Tables, reference must be made to the reactions for confirmatory and discriminatory tests.

Analysis of Subdivision III.

The acid-radicals of somewhat common occurrence only being included, the salt may be a CARBONATE, OXALATE, BORATE, SILICATE, CYANOGEN-COMPOUND, ACETATE, BENZOATE, SUCCINATE, TARTRATE, CITRATE, GALLATE, TANNATE, or URATE.

Some of these acid-radicals may be satisfactorily detected by the addition of concentrated sulphuric acid to the solid, or to its strong solution. The odours may, however, be better detected by using dilute hydrochloric acid, aided by a gentle heat.

Immediate effervescence indicates a carbonate.
Effervescence with *odour of peach-blossoms* indicates a cyanide.
The *same odour* (of HCy) may indicate a ferro- or ferricyanide.
An *odour of vinegar* (of $HC_2H_3O_2$) indicates an acetate.
Separation of crystals from the solution may indicate a borate.
" " with *aromatic odour* indicates a benzoate.
" " with *irritating vapour* indicates a succinate.
Blackening on warming, with *odour of burnt sugar*, indicates a tartrate.
" " " *in a less degree* indicates a citrate.
Evolution of *carbonic oxide gas without blackening* indicates an oxalate.

Further Analysis.

Carefully neutralize the solution with carbonate of sodium, then add one drop of hydrate of ammonium. Add solution of chloride of calcium until no more precipitate is formed.

<table>
<tr><td colspan="4">A precipitate would indicate the presence of $\bar{O}$, BoO_2, SiO_2, or $\bar{T}$.
Wash thoroughly and divide into two parts.</td><td colspan="3">If no precipitate occurs, boil the solution for some minutes.</td></tr>
<tr><td rowspan="3">I.
Shake with cold solution of hydrate of potassium; if the precipitate dissolves, and is thrown down again on boiling the solution, $\bar{T}$ is indicated.</td><td colspan="3">II.
If no solution takes place with I., add to the remainder of the precipitate acetic acid, and warm.</td><td rowspan="3">The formation of a precipitate indicates $\overline{Ci}$, or perhaps $\bar{S}$ or Cfy.</td><td colspan="2">If no precipitate is produced, add to the solution perchloride of iron.</td></tr>
<tr><td rowspan="2">An undissolved residue indicates $\bar{O}$.</td><td colspan="2">If it dissolves entirely, add hydrochloric acid, and evaporate to perfect dryness. Redissolve in hydrodrochloric acid.</td><td rowspan="2">A pale red precipitate indicates $\overline{Be}$ or $\bar{S}$. A bluish or greenish black indicates $\bar{G}$ or $\overline{Qt}$. A bright blue indicates Cfy.</td><td rowspan="2">If no precipitate, the solution may be coloured. A red colour indicates $\bar{A}$ or Csy. A green colour indicates Cfdy.</td></tr>
<tr><td>A residue indicates SiO_2.</td><td>If entirely dissolved, BoO_2 is indicated</td></tr>
</table>

SUBDIVISION IV.

SALTS OF NITROGEN, PHOSPHORUS, ARSENIC AND ANTIMONY, AND OF THE CHIEF COMPOUND ACID-RADICALS INTO THE COMPOSITION OF WHICH THEY ENTER.

The three latter members of this subdivision present a remarkable similarity in properties; nitrogen, although closely allied to them in many respects, exhibits, as we shall presently see, important differences, which may nevertheless be cleared away by future observations. In the preliminary observations made upon each section, we shall enter more into detail concerning the chemical peculiarities of the radicals considered, since, although not strictly important in an analytical point of view, their knowledge will be of extreme use and interest to the student. This subdivision is divided into two sections :—

Section I.—SALTS OF NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY.

The nitrides, phosphides, arsenides, and antimonides.

Section II.—SALTS OF THE ACID-RADICALS WHICH CONTAIN NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY COMBINED WITH OXYGEN OR SULPHUR.

The nitrites, nitrates, hypophosphites, phosphites, phosphates, arsenites, arseniates, antimoniates; sulpharsenites, sulpharseniates, and sulphantimoniates.

Section I.—*The nitrides, phosphides, arsenides, and antimonides.*

SALTS OF NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY.

The elements considered in this group have the property of combining with many basic radicals, and are usually found to be triatomic, uniting with 3 equivalents of a monatomic molecule; a few circumstances have, however, raised great obstacles to these combinations being considered truly saline. Their hydrogen compounds, in the first place, are not possessed of manifestly acid properties—they do not redden litmus; this may, nevertheless, be accounted for by supposing that hydrogen, when combined in the proportion of 3 equivalents with the weak acid-radicals, nitrogen, phosphorus, or arsenic, forms a basic radical sufficiently powerful, in its counteraction, entirely to mask the acid properties of the nitrogen, phosphorus, or arsenic. These hydrogen compounds are also all gaseous bodies at common temperatures; this is a great barrier to the perfect investigation of the properties of a substance; and, what is more perplexing, they all (and the compound NH_3 in the most marked manner) have a tendency to unite with a fourth equivalent of hydrogen to form a compound base, which again combines with acid-radicals to form stable saline compounds. With regard to the compounds produced by the union of these acid-radicals directly with metals, little is known; and (as might be readily conjectured from the fact that hydrogen saturates their acid tendency so completely) those are the most stable, in which the weaker basic radicals exist combined.

SALTS OF NITROGEN, OR NITRIDES.

These bodies have not been hitherto obtained by the action of ammonia (H_3N) either as gas or in solution upon saline bodies at ordinary temperaratures; the only method which has successfully resulted in their production is that of passing the dry gas (H_3N) over the heated metal, the molecules of which we desire to substitute for those of hydrogen in the body H_3N. This, as might be expected when the triatomic character of nitrogen is considered, does not always result in the formation of the substance M_3N; but occasionally, as in the case of potassium, a compound is obtained, the formula of which represents a partial replacement. The olive-green substance which potassium yields when gently heated in ammonia gas, has the composition H_2KN; it is known as *amide of potassium*, a name given by chemists who believed its constitution to be $K(NH_2)$,—NH_2 being a hypothetical acid-radical which they called *amidogen*. This body, when heated to redness in a close vessel, decomposes into nitride of potassium and nitride of hydrogen, with the consequent separation of the latter (ammonia):

$$3H_2KN = K_3N + 2H_3N.$$

When, again, dry ammonia gas is passed over iron wire heated to redness in a tube for six or eight hours, a white brittle substance is obtained, the composition of which nearly corresponds to the formula Fe_9N_2, that is, to a mixture of equivalents of nitride and dinitride of iron; for $Fe_9N_2=Fe_3N+(Fe_2)_3N$: this has no analogue among the combinations of iron with other acid-radicals, although the probable existence of a disulphide of iron $(Fe_2)_2S$ *or* Fe_4S, and the well-known tendency of iron salts of different series to combine together, removes the improbability of its existence. The di- or subnitride of copper may be made by heating the precipitated oxide in dry ammonia gas; its formula is Cu_6N, that is, $(Cu_2)_3N$. Mercuric nitride is similarly produced; it is a brown powder having the composition Hg_3N, which explodes with great violence when struck or heated.

THE HYDROGEN COMPOUND of nitrogen (H_3N), or ammonia, is almost always found in combination or union with water: its great source is the decomposition of nitrogenized organic matters; any such compounds, when heated with the hydrates of potassium or calcium, yield the whole of their nitrogen in the form of ammonia. The analogous compounds of phosphorus, arsenic, and antimony will be seen to be produced by the action of nascent hydrogen upon the element under experiment. This is not the case when the same agent meets with already eliminated nitrogen; the gaseous condition of the latter body is, however, perhaps unfavourable to the success of the reaction. The gas ammonia has a very pungent odour, but is not corrosive; it is slightly combustible, burning when a candle is applied to it, but the combustion ceasing upon the removal of the ignited body: when intensely heated it decomposes into its elements. It may be condensed to the liquid and even to the solid state by cold and pressure. The solid is colourless and crystalline, and melts at $-75°$ C.: the liquid is colourless and very mobile, of specific gravity 0·76; it boils at $-33°\cdot7$ C. at about the ordinary pressure ($0\cdot7493^{m}$). The gas is absorbed by water with the greatest rapidity; and, according to Ure, when the specific gravity of the solution is 0·8914 it holds 27·94 per cent. of H_3N in solution.

No decomposition with formation of nitrides takes place when ammonia gas is passed into saline solutions, or when its aqueous solution is added to them: this may, perhaps, be accounted for by the change which is very generally believed to occur whenever H_3N meets with H_2O, and which certainly takes place when it meets with more powerful acids—namely, its direct union with the acid, and formation of the corresponding salt of the basic radical ammonium:

$$H_3N+H_2O=NH_4HO; \qquad H_3N+HCl=NH_4Cl.$$

SALTS OF PHOSPHORUS, OR PHOSPHIDES.

These are more numerous than the analogous compounds of nitrogen, and may be more readily obtained by reason of the occurrence of phosphorus in the solid, liquid, and gaseous forms within a convenient range of temperature, which is a circumstance most favourable for a full investigation of the chemical properties of a body. The phosphides may be produced similarly with the nitrides; but some are also formed by the action of phosphuretted hydrogen, H_3P (the ammonia of this series), upon saline solutions. The potassium salt is formed when its components are gently heated in an atmosphere of nitrogen; it is a substance of a chocolate-brown colour. The calcium salt is produced, together with hypophosphite of calcium, when the vapour of phosphorus acts on lime (Ca_2O). Others, again, as the phosphides of iron, copper, and lead, are prepared by throwing phosphorus on the melted or red-hot metal, or by igniting the filings of the metal with *glacial phosphoric acid* (HPO_3). These compounds may also be formed by heating the metal in the gas H_3P; and in some cases, by the passage of that gas through the aqueous solution of the metallic salt, the phosphide is slowly formed: thus cupric salts yield black phosphide of copper (Cu_3P), mercuric salts a whitish yellow precipitate of a basic salt, and lead salts a brown precipitate. One thing is to be remarked in the phosphides, viz. that two distinct series of them are known, in one of which phosphorus plays the part of a bibasic, in the other of a tribasic radical; thus we have two series of salts :—

		Ferrous.	Ferric.	Cuprous.	Cupric.
Bibasic	Ca_2P	$(Fe_2)_2P$	—	—	Cu_2P
Tribasic	—	—	$(Fe_2)_3P$	$(Cu_2)_3P$	Cu_3P.

It is interesting to know that whilst the majority, if not all, of the tribasic phosphides are produced by the vapour of α phosphorus (ordinary phosphorus, see p. 34) upon metals, the bibasic cupric phosphide (Cu_2P) is obtained by the reducing action of hydrogen gas at a high temperature upon the bibasic cupric phosphate ($Cu_4P_2O_7$): it may be, that in the bibasic phosphides the β variety of phosphorus occurs.

THE HYDROGEN COMPOUND (H_3P), or phosphuretted hydrogen, is usually obtained by the action of solution of hydrate of potassium upon phosphorus, or by the decomposing influence which water exerts upon the calcium salt (Ca_2P); it is not obtained by the action of nascent hydrogen on solid phosphorus. As usually prepared, it is spontaneously inflammable in the air. In addition to this gaseous body, there is another which is liquid, having the composition H_2P: this latter it is which is said to result from the action of water or other acids on the phosphide of calcium (Ca_2P); but by the agency of light it almost immediately splits up into the gas H_3P, and a yellowish solid body, insoluble in water, which has the formula HP_2: this decomposition is as follows :—

$$5H_2P = HP_2 + 3H_3P.$$

The liquid H_2P possesses an intense spontaneous inflammability in the air; and the presence of a small portion of it is said to impart its inflammability to the gas H_3P, which is prepared from the phosphide of calcium: this is by no means improbable, since, when mixed with any combustible gas, it renders it spontaneously inflammable when exposed to the air. The gas H_3P is very slightly absorbed by water, but sufficiently so to impart to it a disagreeable smell and taste. The liquid H_2P is insoluble in water.

Solutions of Manganese, Zinc, or Iron Salts are not precipitated by solution of phosphuretted hydrogen; but this liquid does precipitate solutions of the salts of Copper, Silver, Mercury, Lead, and Gold.

SALTS OF ARSENIC, OR ARSENIDES.

These also are both a numerous and important class of salts, although they have not yet been much studied; together with the phosphides, silicides and other similar compounds, they are of the utmost importance to the metallurgist, since their presence in minute quantity so much affects the character of the metals he produces. Arsenic occurs frequently combined with metals in nature; and these compounds begin to partake more of the characters of metallic alloys than those previously mentioned. The arsenides may be produced artificially, just as the phosphides—namely, by heating the acid-radical itself or its oxygen compound As_2O_5 with the metal,—by heating the metal under experiment with the gaseous hydrogen compound H_3As, or by passing the latter into solutions of some metallic salts. The constitution of the arsenides varies even more than that of the phosphides; and they may be grouped into three series, in which a molecule of arsenic of the same atomic weight plays the part of a monobasic, a bibasic, or a tribasic radical respectively. Our surprise at such peculiarities is prevented by the remarkable instances of allotropy occurring among the elements, and of isomerism and polymerism among compound bodies. A few examples of arsenides may be given, the whole of which here quoted occur as minerals in nature—

		Ferrous.		Cuprous.	Cupric.
Monobasic	—	$FeAs$	$NiAs$	—	—
Bibasic	Mn_2As	—	Ni_2As	$(Cu_2)_2As$	—
Tribasic	—	—	Ni_3As	—	Cu_3As.

The compound acid-radicals into the composition of which arsenic enters retain this variable basicity, just as the well known and investigated compound acid-radicals containing phosphorus.

The Hydrogen Compound ($H_3 As$), or arseniuretted hydrogen, has been already spoken of at some length (p. 211); we will, however, here recapitulate its leading properties and characters.

It is produced when an alkaline arsenide is dissolved in water, or the arsenide of a metal insoluble in water is dissolved in an acid; it is formed most commonly by acting with nascent hydrogen upon one of the oxygen compounds of arsenic. It is a colourless gas, of which the composition is $H_3 As$; it possesses a very offensive and peculiar odour, and is excessively poisonous when inhaled. The gas does not redden litmus. At a temperature of —40° C. it condenses to a colourless liquid; but it has not yet been solidified. Its specific gravity is 2·695; water dissolves one-fifth of its volume; and the solution darkens solutions of many metallic salts. When heated, this gas is resolved into its elements, hydrogen and arsenic; and when a light is applied to it in contact with the air, it burns with a bluish white flame, forming the oxide of arsenic ($As_2 O_3$) and water: if sufficient air is not present for the oxidation of the arsenic, the latter is deposited upon the sides of the containing vessel as a metallic film; and the same end may be compassed by depressing a cold porcelain surface upon a jet of the burning gas. These features have already been spoken of as tests for arsenic (p. 212).

In the decomposition of arsenide of potassium by water, a solid arseniuretted hydrogen is formed, which presents itself as a brown powder. Its formula appears to be $H_2 As$.

The salts of the two first subdivisions of basic radicals are not precipitated by the passage of arseniuretted hydrogen gas through their solutions; those of iron also are not precipitated; those of Manganese, Zinc, and Tin are very slowly decomposed; but most salts of the fourth subdivision are precipitated, some in the form of arsenides, as Copper and Platinum, whilst in other cases, as in those of Silver and Gold, the metal is thrown down, and arsenious oxide formed, which remains in solution,—thus, when this gas is passed into nitrate of silver—

$$12AgNO_3 + 2H_3As + 5H_2O = 12HNO_3 + 12Ag + H_4As_2O_5.$$

Organic acid-radicals have some influence in preventing this precipitation, as is shown in the instances of the acetate of lead and of the tartrate of antimonyle and potassium (tartar-emetic) which are not acted upon by arseniuretted hydrogen.

SALTS OF ANTIMONY, OR ANTIMONIDES.

The body antimony, as has been already stated, partakes almost more of the characters of a basic than of those of an acid-radical, and in its combinations with metals it produces bodies which far more nearly resemble alloys (or combinations of metals with each other) than true saline bodies, in which no physical characteristics of the basic or acid-elements are perceptible. It is thus not an easy matter to obtain definite compounds, upon the formulæ of which an opinion may be safely pronounced.

The Hydrogen Compound (H_3Sb), or antimoniuretted hydrogen, is a very well defined body: it has been fully treated of at p. 200, and need be here but slightly noticed. It is obtained by the action of water on the antimonide of potassium, or by the action of nascent hydrogen on solutions of antimony salts. It is a gas which closely resembles H_3As; its composition is H_3Sb: when ignited it burns with formation of antimonious oxide (Sb_2O_3) and water; and if a cold porcelain surface be depressed upon the flame, a metallic spot is obtained: it is decomposed by a temperature below redness, into its elements antimony and hydrogen. This gas is not sensibly absorbed by water. A solid antimonide of hydrogen is also known.

When passed into alcoholic solutions of alkaline hydrates, a dark colour is produced, and, finally, brownish black flakes separate: *this peculiarity distinguishes it from arseniuretted hydrogen.* Solutions of salts of COPPER, SILVER, MERCURY, and PLATINUM are precipitated by it more or less readily, with formation of bodies of the formula M_3Sb, thus—

$$3AgNO_3 + H_3Sb = 3HNO_3 + Ag_3Sb.$$

SECTION II.—*The nitrites, nitrates, hypophosphites, phosphites, phosphates, arsenites, arseniates, antimoniates; sulpharsenites, sulpharseniates, sulphantimoniates.*

SALTS OF THE ACID-RADICALS WHICH CONTAIN NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY COMBINED WITH OXYGEN OR SULPHUR.

Of acid-radicals containing nitrogen combined with oxygen, two only are of sufficient importance to demand attention; these are the nitrous and the nitric radicals (NO_2 and NO_3): several other compounds of nitrogen and oxygen exist, but are of trivial importance in an analytical point of view.

SALTS OF THE NITROUS RADICAL, OR NITRITES.

This radical is usually obtained in combination with potassium by heating the nitrate of potassium (KNO_3) in a crucible, by which means the nitrite (KNO_2) and oxygen are produced. Nitrites detonate when heated with combustible bodies; they are either colourless or yellow, and generally crystallizable: the nitrite of silver is almost the only insoluble salt. This radical appears to have the property of assuming oxygen and transforming itself into monobasic, bibasic, and tribasic radicals, after the manner of the phosphoric acid-radical.

THE HYDROGEN SALT (HNO_2), or nitrous acid, is known only in solution in water, forming a blue liquid; its anhydride (N_2O_3) is obtained as a gas when 1 part of starch is heated with 8 parts of nitric acid of specific gravity 1·25: if the vapour is first dried by chloride of calcium, and then passed through a tube cooled to —20° C., a very volatile liquid is obtained, green at the ordinary temperature, but colourless when exposed to extreme cold; the vapour of this body is yellowish red.

THE POTASSIUM, SODIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, IRON, and COPPER SALTS of this radical are soluble.

The Silver Salt is obtained by adding nitrate of silver to a soluble nitrite (as the potassium salt); it is a yellowish white crystalline precipitate, the formula of which is probably $AgNO_2$.

It requires 300 parts of cold water for its solution, but is more soluble in hot water; and from its hot solution it crystallizes on cooling. It is insoluble in alcohol.

THE MERCURIC SALTS are of doubtful existence; and the LEAD SALT is soluble.

This radical is also detected by the following experiments:—

a. By its liberation, even by weak acids (as acetic acid), in the form of the hydrogen compound, and the instantaneous decomposition of the latter, with formation of nitric oxide gas, which reddens on contact with air.

β. By the addition of a solution of ferrous sulphate and sulphuric acid to the solution of a nitrite, a deep red liquid is obtained.

γ. Nitrites, when added to solutions of auric chloride or mercurous nitrate, cause the precipitation of gold or mercury; from solutions of manganous or ferrous salts, they precipitate manganic or ferric hydrate.

δ. When to a solution containing pure sulphuric acid, iodide of potassium, and starch, a minute portion of a nitrite is added, the characteristic blue iodide of starch is at once produced.

SALTS OF THE NITRIC RADICAL, OR NITRATES.

The abundant forms in which this radical occurs are its potassium, sodium, and calcium salts; they are produced whenever nitrogenized organic matter is allowed to decompose in the presence of the hydrates of those basic radicals. Nitrates in general have a peculiar cooling taste; they are all decomposed at a red heat: some, as the alkaline nitrates, yield nitrites in the first place; but ultimately all are converted into oxides, with evolution of nitrogen and oxygen. Nitrate of ammonium (NH_4NO_3) undergoes a peculiar decomposition under these circumstances, water and the gas called nitrous oxide (N_2O) or *laughing-gas* being formed:

$$NH_4NO_3 = 2H_2O + N_2O.$$

Nitrates when fused on charcoal *deflagrate,* their oxygen uniting with the carbon to form carbonic acid gas, which then takes oxygen, and converts the metal into a carbonate, if that salt is capable of withstanding the temperature to which it is exposed. When heated before the blowpipe with carbon and sulphur, with carbon and phosphorus, or with cyanide of potassium, a very violent and dangerous detonation ensues.

THE HYDROGEN COMPOUND (HNO_3), or nitric acid, is an exceedingly corrosive liquid, and forms a most powerful solvent for metals, by reason of its ready decomposability. When acting as a solvent, however, it differs from most acids hitherto considered, which simply part with their hydrogen and receive the replacing molecule of metal: nitric acid undergoes a more radical change; for so comparatively feeble is the affinity which the nitrogen has for its 3 equivalents of oxygen, that the hydrogen of the acid in escaping decomposes a part of the acid-radical with the formation of water and the evolution of one of the gaseous lower oxides of nitrogen. Thus, when it acts upon copper—

$$8HNO_3 + 6Cu = 6CuNO_3 + \underset{\text{nitric oxide.}}{N_2O_2} + 4H_2O.$$

This property it is which imparts such a peculiar energy to the mixture of nitric and hydrochloric acids known by the names nitrohydrochloric acid and aqua regia: the oxygen of the nitric radical unites with the hydrogen of the hydrochloric acid; and among other products of decomposition, chlorine is set free, and, like all other *nascent* elements, exerts upon the body submitted to its action the most powerful effect:

$$2HNO_3 + 2HCl = 2H_2O + N_2O_4 + 2Cl.$$

In this way it is that this mixture of acids will dissolve the precious metals gold and platinum, which are attacked by chlorine, although not affected by either hydrochloric or nitric acids separately. The same reaction of course takes place when either hydrochloric acid is added in excess to a nitrate, or nitric acid in excess to a chloride; for

$$2MNO_3 + 4HCl \quad = 2MCl \quad + 2H_2O + N_2O_4 + 2Cl$$

$$\text{or } 2MCl \quad + 4HNO_3 = 2MNO_3 + 2H_2O + N_2O_4 + 2Cl;$$

and it should be remembered that we always have it in our power to convert one of these salts into the other by adding *excess of the acid which we wish to retain*, since the other, becoming decomposed into gaseous constituents, may be entirely removed by warming the solution.

The nitric acid usually called "fuming" is generally red from the presence of N_2O_4, one of the products of its decomposition: its specific gravity is 1·536; and it solidifies at —49° C. to a very dark red mass.

All nitrates are soluble in water; and therefore this radical cannot be recognized by the formation of any insoluble salts.

It may, however, be identified by other processes:—

a. By setting free the hydrogen compound (nitric acid) by the addition of concentrated sulphuric acid to a nitrate, and subjecting it to the immediate action of copper turnings, which must be added simultaneously with the sulphuric acid, decomposition of the nitric acid ensues, with disengagement of nitric oxide gas (N_2O_2). The latter is recognized by being itself colourless but capable of acquiring a peculiar brownish red colour by mixture with air; it absorbs the atmospheric oxygen, and is converted into nitrous and hyponitric anhydrides (N_2O_3 and N_2O_4).

β. When nitric acid is produced from a nitrate by the action of concentrated sulphuric acid, the mixture cooled by immersion of the test-tube containing it in cold water, a crystal of ferrous sulphate added, and the whole allowed to rest, a dark halo is observed to form around the crystal, which, upon the application of heat, disappears with a kind of effervescence. This is due to the formation of a very singular combination of ferrous sulphate and nitric oxide having the formula $4Fe_2SO_4, N_2O_2$: heat decomposes this combination. The cause of its production is the decomposition of a portion of the nitric acid consequent upon the passage of the ferrous into the ferric salt, thus—

$$10Fe_2SO_4 + 4H_2SO_4 + 2KNO_3 = 3(Fe_2)_2(SO_4)_3 + K_2SO_4 + \underset{\text{brown compound.}}{4Fe_2SO_4, N_2O_2} + 4H_2O.$$

γ. The nitrates do not reduce gold or mercurous salts; but when mixed with hydrochloric acid, they acquire the power of dissolving gold leaf.

δ. Upon adding to a nitrate sulphuric acid and sulphindigotic acid, the colour of the latter is destroyed.

Of the acid-radicals containing phosphorus combined with oxygen, those existing in the phosphites and phosphates are of great analytical importance. The hypophosphites are rare.

SALTS OF THE HYPOPHOSPHOROUS RADICAL, OR HYPOPHOSPHITES.

This acid-radical is of rare occurrence, being only produced by artificial means. It is obtained in the decomposition of phosphide of barium by water, or by boiling phosphorus with an alcoholic solution of hydrate of potassium, or with the aqueous solutions of hydrate of barium or calcium, until it disappears, and the vapour has no longer the odour of phosphuretted hydrogen. The phosphuretted hydrogen evolved during the process frequently causes dangerous explosions, which may be moderated by employing only a gentle heat. The barium or calcium salts thus obtained (BaH_2PO_2 *or* CaH_2PO_2) are very crystallizable.

THE HYDROGEN SALT (H_3PO_2), or hypophosphorous acid, is a viscid, uncrystallizable, very acid liquid, which when heated decomposes into phosphuretted hydrogen and phosphoric acid, thus—$2H_3PO_2=H_3P+H_3PO_4$. Although hypophosphorous acid is thus tribasic, one series of salts only is known, namely, the series of acid salts represented by the general formula MH_2PO_2; they generally occur with water of crystallization, and are all soluble in water, and many of them also in alcohol.

This radical may nevertheless be recognized by several processes of decomposition:—

a. When any dry hypophosphite is rather gently heated in a test-tube, decomposition of its radical occurs; phosphuretted hydrogen is evolved, which may be recognized by its odour and ready inflammability; and a pyrophosphate of the metal remains behind. The lead salt exhibits this decomposition best:

$$4MH_2PO_2=\underset{\text{pyrophosphate.}}{M_4P_2O_7}+H_2O+2H_3P.$$

β. When mixed with an acid, hypophosphites reduce silver and gold salts, precipitating silver and gold; they also reduce mercuric and cupric salts. The same reactions take place more slowly with concentrated solutions of hypophosphites.

γ. When boiled with excess of hydrate of potassium, alkaline hypophosphites evolve pure hydrogen gas:

$$KH_2PO_2+2KHO=K_3PO_4+4H.$$

SALTS OF THE PHOSPHOROUS RADICAL, OR PHOSPHITES.

This acid-radical is obtained in combination with hydrogen by the decomposition of terchloride of phosphorus (PCl_3) by water, or by the slow oxidation of phosphorus in the air.

The Hydrogen Salt (H_3PO_3 ?), or phosphorous acid, is known in the liquid and also in the crystallized state; when heated, it decomposes, thus—

$$4H_3PO_3 = 3H_3PO_4 + \overset{\nearrow}{H_3}P.$$

The Alkaline Phosphites are soluble in water; most other salts are insoluble or nearly so. The acid salts of the formula MH_2PO_3 are soluble in water; the acid salts having the composition M_2HPO_3 are less so, whilst the neutral phosphites M_3PO_3 are insoluble.

The Barium and Calcium Salts are slowly precipitated by the addition of alkaline phosphites to soluble barium or calcium salts, as white precipitates having the formula M_2HPO_3: by boiling, the precipitation is accelerated; but the precipitate which then falls is M_3PO_3,—MH_2PO_3 (the acid salt) remaining in solution. They are soluble in most acids, and by nitric acid are converted into phosphates.

The Magnesium Salt is not precipitated when *a dilute solution* of a magnesium salt is added to a soluble phosphite in the presence of the chloride and hydrate of ammonium.

The Ferrous Salt is white, changing to red basic ferric phosphate. The Ferric Salt is white.

The Zinc Salt is soluble.

The Cupric Salt is blue.

The Mercurous, Mercuric, and Silver Salts do not exist.

The Lead Salt is white.

This radical may also be recognized as follows:—

a. The majority of the phosphites do not evolve phosphuretted hydrogen, but pure hydrogen slightly contaminated with it, when the dry salts are heated. The lead salt is an exception.

$$2Ba_2HPO_3 + H_2O = Ba_4P_2O_7 + \overset{\nearrow}{4H}.$$

β. Soluble phosphites reduce solutions of cupric, silver, mercuric, or gold salts, and precipitate the metal. This takes place especially on boiling.

γ. Phosphites, when boiled with excess of hydrate of potassium, are not altered, nor does any evolution of hydrogen occur.

SALTS OF THE PHOSPHORIC RADICAL, OR PHOSPHATES.

The phosphates occur somewhat abundantly in nature; they are found distributed in small quantities through the mineral and vegetable kingdoms, whence they pass into the bodies of animals, to which they are absolutely essential for the formation and renewal of their skeleton.

The Hydrogen Salt (H_3PO_4), or phosphoric acid, is produced by the decomposition of these, or by the solution of phosphoric anhydride (the body P_2O_5, which is the white crystalline solid obtained when phosphorus is burnt in oxygen or air) in water. The substance P_2O_5, when combining with water, produces three distinct acids, thus—

$P_2O_5 + H_2O = 2HPO_3$, meta- or monobasic phosphoric acid.

$P_2O_5 + 2H_2O = H_4P_2O_7$ pyro- or bibasic phosphoric acid.

$P_2O_5 + 3H_2O = 2H_3PO_4$, ordinary or tribasic phosphoric acid.

These are each the representative of three distinct classes of salts, called respectively the metaphosphates, pyrophosphates, and phosphates, or the mono-, bi-, and ordinary phosphates: whether in these the three allotropic varieties of phosphorus exist, we do not know; but they singularly correspond to the two classes of phosphides previously mentioned (p. 366). The phosphates which ordinarily occur in nature are the tribasic phosphates. When the anhydride P_2O_5 is dissolved in abundance of water, and the solution heated, the latter of these acids is produced; but if the phosphoric anhydride be allowed to dissolve in cold water, the second is obtained,—whilst, again, if the aqueous solution of either acid be evaporated in a platinum dish until water no longer is expelled, the residue solidifies on cooling into a glassy substance, which is called "glacial" phosphoric acid, and which is in reality HPO_3, or the monobasic acid. This will volatilize altogether at a red heat. The solution of the ordinary acid (H_3PO_4) may be evaporated without decomposition up to a temperature of 149° C., when it becomes of a syrupy consistence; between that temperature and 213° C. it loses the elements of water, and is converted into pyrophosphoric acid; and if cooled from that point, it solidifies in the form of a soft glass, or in small granular crystals; if heated further, it again loses the elements of water, and is converted into the monobasic acid, as has before been stated.

Many phosphates behave in a characteristic manner when heated, owing to their peculiar constitution: thus with the tribasic radical PO_4, which forms the three series of salts,

MH_2PO_4	M_2HPO_4	M_3PO_4.
acid salt.	acid salt.	neutral salt.

If heat is applied to the second of these acid salts, it decomposes into water and a neutral pyro- or bibasic phosphate, thus—

$$2M_2HPO_4 = M_4P_2O_7 + H_2O:$$

and again, if the first acid salt be heated, water is again obtained and a meta- or monobasic phosphate; for

$$MH_2PO_4 = MPO_3 + H_2O.$$

The pyrophosphates exhibit similar features. Notwithstanding, however, that the acid salts of the various phosphoric radicals are thus unstable, all neutral salts are but little affected by heat: the generality fuse to a glassy mass, and yield to few decomposing agents except carbon, which, at a high temperature, removes the oxygen from most phosphates except those of potassium and sodium, and eliminates the phosphorus, which then distils and is suitably collected. (See p. 33.)

Of neutral phosphates, those of the first subdivision are almost the only soluble ones; many of the acid phosphates, especially those of the formula MH_2PO_4, are soluble in water; most are soluble in acids.

The Barium, Strontium, and Calcium Salts are white precipitates of the formula M_2HPO_4 when produced by the action of ordinary phosphate of sodium (Na_2HPO_4). They are soluble in chloride of ammonium, insoluble in water, but soluble in acids, even in acetic.

The neutral meta- and pyrophosphates of barium are insoluble in chloride of ammonium, or water, and the latter also in acetic acid. The same salts of strontium are insoluble in water, and the former also in acids, the latter in acetic acid. The metaphosphate of calcium is a white viscous precipitate; and the pyrophosphate does not dissolve in acetic acid.

THE MAGNESIUM SALT is formed but slowly by the addition of a salt of magnesium alone to a soluble phosphate—the precipitate under such circumstances has the formula $Mg_2 HPO_4$; if, however, chloride of ammonium and ammonia have been previously added, the subsequent mixture with a magnesium salt gives rise to an immediate crystalline precipitate, which forms more rapidly on stirring: its formula is $Mg_2 NH_4 PO_4$.

It is soluble in 7548 parts of chloride of ammonium, in 44,330 parts of hydrate of ammonium, and in 15,627 parts of chloride of ammonium solution containing hydrate of ammonium. It is insoluble in water which contains any phosphate in solution, but dissolves in 15,293 parts of pure water, from which it may be precipitated by the addition of ammonia. It dissolves in acids.

The meta- and pyrophosphates are scarcely produced except in the presence of hydrate of ammonium.

THE FERROUS phosphate and pyrophosphate are white.

The Ferric Salt is white; its formula is uncertain. It is insoluble in ammonium salts, except the carbonate and sulphite, and it dissolves also in hydrate of ammonium in the presence of phosphate of sodium. It partially dissolves in carbonate of sodium. It is soluble in 1500 parts of water, and is easily dissolved by dilute acids, even by sulphurous, but not by cold acetic acid.

The metaphosphate is white, insoluble in water or dilute acids, but soluble in strong sulphuric acid.

The pyrophosphate is white, and is soluble in hydrate or carbonate of ammonium or in phosphate of sodium; it is insoluble in chloride of ammonium, and in hydrochloric or sulphurous acids.

THE ZINC SALT is a gelatinous precipitate which becomes crystalline on standing. It formula is $Zn_3 PO_4$. It dissolves in the hydrate and most ammonium salts, is insoluble in water, but soluble in acids.

The metaphosphate is soluble in water. The pyrophosphate is white, soluble in ammonia, but insoluble in water.

THE CUPRIC SALT is bluish green; of the formula $Cu_2 HPO_4$, slightly soluble in ammonium salts, insoluble in water, but soluble in acids.

The metaphosphate is bluish white, insoluble in water or in dilute acids, but soluble in strong sulphuric acid. The pyrophosphate ($Cu_4 P_2 O_7$) is greenish white, soluble in ammonia, phosphate of sodium, and acids.

The Argentic or Silver Salt is yellow.

Its formula is $Ag_3 PO_4$.

It dissolves easily in the hydrate or carbonate of ammonium, but less so in other ammonium salts; it is insoluble in water, but soluble in most acids.

The metaphosphate is white, decomposed by water, soluble in nitric acid. The pyrophosphate is white, of the formula $Ag_4 P_2 O_7$, soluble in hydrate of ammonium, insoluble in water or acetic acid, soluble in nitric acid, which, by boiling, converts it into the ordinary phosphate ($Ag_3 PO_4$).

THE MERCUROUS SALT is white, of the composition $(Hg_2)_4 P_2 O_7$, insoluble in water and in many acids. By some acids it is decomposed.

The pyrophosphate is white, and is decomposable by hydrochloric acid.

THE MERCURIC SALT is white, it appears to be the pyrophosphate ($Hg_4 P_2 O_7$). It dissolves in many ammonium salts, but very slightly in the hydrate. It is insoluble in water, but soluble in many acids.

THE LEAD SALT is white, and variable in composition, being sometimes $Pb_2 HPO_4$, and at other times $Pb_3 PO_4$. It dissolves in hydrate of potassium or chloride of ammonium, is insoluble in water or acetic acid, but soluble in nitric acid. This salt exhibits a great peculiarity: when heated on charcoa before the blowpipe even the inner flame fails for some time to reduce it; and upon removal from the flame, the colourless and transparent bead becomes opaque and crystalline on cooling; the crystalline form is the dodecahedron.

The metaphosphate is white, insoluble in ammonia. The pyrophosphate ($Pb_4 P_2 O_7$) is white, soluble in hydrate of potassium or pyrophosphate of sodium, insoluble in hydrate of ammonium and in many acids, but soluble in nitric acid.

Other means of proving the existence of this radical are wanting, owing to its great stability; it may, however, be recognized by adding to the nitric solution of a phosphate (an alkaline phosphate is the best) some molybdate of ammonium ($NH_4 MoO_2$), evaporating to dryness, and just redissolving in nitric acid: *a yellow crystalline residue* is an evidence of the presence of a phosphate.

Of acid-radicals containing arsenic and oxygen, two only are known, those occurring in the arsenites and arseniates.

SALTS OF THE ARSENIOUS RADICAL, OR ARSENITES.

The arsenites are considered bibasic, and have the general formula $M_4 As_2 O_5$; they are sometimes colourless, but occasionally of beautiful colours. Most arsenites, when heated alone, decompose and leave the oxide of the basic radical, whilst the anhydride ($As_2 O_3$) volatiles; some, as the alkaline arsenites, decompose into an arseniate and arsenic.

THE HYDROGEN SALT ($H_4 As_2 O_5$) is unknown; for when its supposed aqueous or acid solution is evaporated, the arsenious anhydride ($As_2 O_3$) crystallizes out.

THE ALKALINE ARSENITES are soluble in water; but most others are insoluble, although dissolved by acids and frequently by ammonium salts.

THE BARIUM and STRONTIUM SALTS are precipitated only after being allowed to rest for some time.

THE CALCIUM SALT is precipitated immediately on mixing a soluble arsenite, or arsenious acid, with excess of the hydrate or other salt of calcium. It is a white precipitate.

Dried in the air, its composition is $Ca_4 As_2 O_5 + aq$.

It dissolves in ammonium salts, but is only slightly soluble in water; in dilute acids, and even in an aqueous solution of arsenious acid, it is soluble.

The Magnesium and Zinc Salts are scarcely known.

The Cupric Salt is bright green. Its formula is $Cu_4\,As_2O_5$; it dissolves in ammonium salts and in acids.

The Argentic or Silver Salt is lemon-yellow, of the formula $Ag_4\,As_2O_5$. It dissolves in ammonium salts and in acids.

The Mercurous, Mercuric, and Lead Salts are white precipitates, insoluble in ammonium salts, but soluble in nitric acid.

In addition to these means of detection, this radical may be recognized by other methods, previously detailed (p. 209), but which may be here briefly recapitulated:—

α. By heating the arsenite in a bulb-tube with carbonate of sodium or charcoal, and observing the arsenical mirror.

β. By the action of nascent hydrogen, which produces the gas H_3As, by the subsequent decomposition of which the arsenical mirror may also be obtained.

γ. By the action of hydrosulphuric acid gas, which, when passed through the hydrochloric solution of an arsenite, yields the arsenious sulphide, which may be further tested by the method of Fresenius and Von Babo (p. 213).

SALTS OF THE ARSENIC RADICAL, OR ARSENIATES.

The arseniates are tribasic, and bear a great resemblance to the phosphates; they are produced by the action of nitric acid or other oxidizing agents on arsenious anhydride or arsenites. The arseniates when heated are not so prone to decompose as the arsenites.

The Hydrogen Salt ($H_3\,AsO_4$?) is known; it occurs in large crystals. By heating this body to fusion, a glassy substance, arsenic anhydride (As_2O_5), is obtained.

The Alkaline Arseniates are soluble; most others are insoluble.

The Barium, Strontium, Calcium, and Magnesium Salts are white, insoluble in water, but soluble in acids.

The Zinc Salt is similar.

The Cupric Salt is bluish green, insoluble in water, but soluble in ammonia water and in the stronger acids.

The Argentic or Silver Salt is dark brick-red; its formula is Ag_3AsO_4; it is insoluble in water, but soluble in ammonium salts and in many acids.

THE MERCUROUS SALT is white, changing to a fine red, a double salt being at first precipitated. Its composition is $(Hg_2)_2 HAsO_4 + aq$. It is insoluble in most ammonium salts and in water, but soluble in nitric acid.

THE MERCURIC SALT is yellow, soluble in nitric and arsenic acids.

THE LEAD SALT is white, of the formula $Pb_3 AsO_4$, insoluble in ammonium salts and in water, but soluble in nitric acid.

This radical may be recognized in precisely the same manner as the preceding one, by processes of decomposition, a few precautions being taken.

a. Arseniates should be mixed with carbon, or carbon and boracic anhydride, before introducing into the bulb-tube in the blowpipe experiment. (See p. 210.)

β. With nascent hydrogen they act as arsenites.

γ. But before passing hydrosulphuric acid into their acid solution, the latter should be invariably treated with a current of sulphurous acid gas, in order to reduce the arsenic to an arsenious salt. This is necessary because the arsenic sulphide ($As_2 S_5$) forms and separates very slowly, whilst the arsenious sulphide ($As_2 S_3$) is much more rapidly produced. The liquid must be boiled until every trace of sulphurous acid gas is evolved, before any attempt is made to pass sulphuretted hydrogen.

Of acid-radicals formed by the union of antimony and oxygen, two only are known—those existing in the antimoniates and metantimoniates; but of their combinations we are almost wholly ignorant. (See p. 207.)

Of acid-radicals formed by the union of arsenic and antimony with sulphur, three are well defined—those existing in the sulpharsenites, in the sulpharseniates, and in the sulphantimoniates; but they are not of sufficient importance to demand a separate notice. (See pp. 208 and 217.)

TABLE OF REACTIONS.

SALTS.	NO_2. (see p. 370)	NO_3. (p.371)	PO_4. (p. 376)	As_2O_5. (p. 380)	AsO_4. (p. 381)
Potassium Sodium...	—	—	—	—	—
Barium	—	—	white	white	white
Strontium ...	—	—	white	white	white
Calcium	—	—	white	white	white
Magnesium...	—	—	white crystalline	?	white
Ferrous	—	—	white changing to blue	?	white
Ferric.........	—	—	buff-white or white	yellowish brown	brown
Zinc	—	—	white gelatinous	—	white
Cupric	—	—	bluish green	bright green	bluish green
Silver	yellowish white	—	yellow	lemon-yellow	brick-red
Mercurous ...	—	—	white	white	white changing to red
Mercuric	—	—	white	white	yellow
Lead.........	—	—	white	white	white

Analysis of Subdivision IV.

The acid-radicals of more common occurrence only being included, the salt may be a NITRATE, PHOSPHATE, ARSENITE, or ARSENIATE.

<table>
<tr><td colspan="3">Evidence of the presence of the first of these acid-radicals may be obtained by adding concentrated sulphuric acid to the solid, or its strong solution, and heating.
Pungent *orange brown* vapours indicate a nitrate.
Proof of the presence of arsenic will have been obtained in the examination for the basic radical, which in analysis always precedes the search for the acid-radical. If the salt, when heated with carbonate of sodium and charcoal in a bulb tube (see p. 210), yields
a *metallic mirror*, an arsenite or arseniate is indicated.</td></tr>
<tr><td colspan="3">*Further Analysis.*
Acidify a portion of the solution of the salt with a few drops of dilute sulphuric acid, and pass hydrosulphuric acid gas.</td></tr>
<tr><td rowspan="2">A yellow precipitate of As_2S_3 or As_2S_5 would indicate the presence of As_2O_5 or AsO_4. To distinguish between these, the silver test must be resorted to, being applied to a *perfectly neutralized* part of the original solution.
$Ag_4As_2O_5$ is *yellow* ;
Ag_3AsO_4 is *brick-red.*</td><td colspan="2">If no precipitate, or only a white one of sulphur (due to nitric acid), warm the solution, to expel every trace of hydrosulphuric acid; add excess of acetate of potassium, and a drop or two of perchloride of iron.</td></tr>
<tr><td>A white precipitate of Fe_2PO_4 would indicate the presence of PO_4.</td><td>If no precipitate, a fresh portion of the original solution of the salt should be mixed with concentrated sulphuric acid (the test-tube being cooled at the time of mixture by immersion in water), a crystal of ferrous sulphate then added, and the whole allowed to rest: the formation of a reddish brown halo around the crystal, consisting of $4Fe_2SO_4, N_2O_2$, would indicate the presence of NO_3.</td></tr>
</table>

PART II.—THE METHOD OF ANALYSIS.

CHAPTER I.

INTRODUCTION.

TERRESTRIAL matter, although consisting primarily of a definite number of elements, is found, as the student will now have learnt, in an almost infinite variety of combinations. These combinations or salts are formed, it will be remembered, by the union of two classes of bodies, which may be either simple or compound, and are distinguished as basic radicals, and acid-radicals. To *test* these combinations, that is, to *identify* their basic or acid constituent, is easily accomplished by the employment of any appropriate reaction which may elicit some characteristic feature of colour, odour, insolubility, &c.; but to *analyse* such a combination, that is, to *separate* its basic and acid-radical either in an isolated condition or in a new form, is a more difficult task. And this difficulty is, of course, enhanced when the process of separation has to be performed upon a complicated *mixture of salts.*

Although complex bodies of mineral origin, almost without exception, as well as a vast majority of those derived from vegetables and animals, are reasonably believed to be definite saline combinations of basic and acid-radicals, still several substances which occur abundantly in organic structures, such as albumen, fibrine, starch, and gelatine, are composed of molecules so complex as to baffle all attempts made to catch a glimpse only of their constitution. These bodies, therefore, are not subjects for chemical analysis; at least, they cannot be resolved, like the *saline* combinations of compound radicals, into their *proximate,* but only into their several *elementary* constituents.

Since, therefore, the processes of qualitative analysis to which the present work is confined have for their object the separation, recombination, and recognition of certain forms of elementary or of definite compound matter, *i.e.* the separate identification, in the bodies termed salts, of their acid- and basic radicals, it is obvious that all indefinite compounds, to which ultimate analysis only is applicable, are excluded from consideration. All salts commonly met with (using the term salt in its widest sense, as including bases, oxides, acids, &c.) may, however, be considered as fit subjects for qualitative chemical analysis.

It will be at once seen that the certainty of analysis depends much upon the simplicity or complexity of the bodies with which it has to deal. Thus, chemical analysis is most likely to be successful with bodies of mineral origin; for in them, generally speaking, the elements exist in the simplest forms of combination. These constituent elements of mineral substances are, moreover, possessed of most powerful chemical affinities, and, above all, are usually neither themselves gaseous at ordinary temperatures, nor do they yield gaseous products. On the other hand, the bodies derived from the animal and vegetable kingdoms are compounds in which, for the most part, the four elements, carbon, hydrogen, nitrogen, and oxygen, exist in large proportion. The ready decomposability of these organic bodies depends in great measure upon the gaseous character, *i. e.* the volatility of their constituent elements, and upon the remarkable tendency which carbon and hydrogen, or carbon, hydrogen, and oxygen present, to unite in endless and ever-varying proportions. Other causes combine to render these substances unstable, such as the great affinity of carbon and of hydrogen for oxygen (CO_2 and H_2O being thus formed), and of nitrogen for hydrogen (NH_3 being the product): the gaseous character or ready volatility of the simpler compounds thus produced is also to be taken into account. But the causes of the instability of these organic substances is not now the object of discussion; it is merely adduced to show how small a hold upon them chemical analysis possesses, when we consider that its object is to separate a particular compound, which in these substances may slip, by a Protean metamorphosis, through the fingers of the experimenter in the very process of detection. The action of reagents, themselves the means of analysis, is sufficient to decompose bodies such as these.

But it is far otherwise with the elementary or simpler forms of matter which constitute mineral bodies. These are not so affected by reagents; and if isolated, there is in most cases no danger of their volatilization at ordinary temperatures, and none of their decomposition: neither is their presence so concealed as to be undiscoverable; for no known means, however energetic, can destroy their identity. It matters not whether they exist dissolved in mineral waters, crystallized as distinct substances in masses of mineral, or diffused in minute quantity through various soils; their recognition and separation is a matter of almost equal certainty. It is thus that mineral poisons are so much more easy of detection than those of vegetable or animal origin. The latter poisons are, in the majority of cases, easily destroyed, and often cannot be satisfactorily pronounced to be the poison supposed without a quantitative determination of the proportions in which the carbon, hydrogen, nitrogen, and oxygen are present. Arsenic, lead, and copper, on the other hand, are subject to no such accidents. Whatever stage of decomposition the body poisoned by these substances may have reached, these minerals can still be recognized and separated from the mouldering remains.

So far for the limits and the scope of qualitative analysis; we will now speak of its method.

The student will now have become acquainted with a certain number of tests, the application of which, either singly or combined, cannot fail to assure him of the presence or absence of every basic or acid-radical. To analyse successfully, there is, however, one point to which he must invariably attend; and that is, to preserve a well-ordered sequence in the application of the tests at his disposal. By the tables which have been appended to each subdivision of the basic and acid-radicals (in Chapters

VI. and VII.), the student has been somewhat prepared for this system, which, although at first sight it may appear to be a waste, is in reality an economy of time. The only true source of certainty in analysis consists, in fact, in this application of tests in a certain fixed order. The first step must always be to separate a group of substances (such as a subdivision of basic radicals) the members of which may always be removed together as one precipitate by the employment of a certain reagent. The labour is thus simplified: for if such a reagent fail to produce a precipitate, we know that an entire group of bodies is absent; if, on the contrary, a precipitate is produced, we have an assurance that it can only contain certain members, and know therefore the limit of our search in that direction. This accomplished, a second group-test is applied, and the same course followed, until, having exhausted group-tests, we have ascertained in what subdivision or subdivisions the substance or substances sought for exist. Then, by the application of less general tests, we continually subdivide the groups until the isolation of the individual members is accomplished. This principle applies to the analysis of simple salts or mixtures—to the detection of basic or acid-radicals. And the student cannot be warned too early of the extreme folly of what may be termed analytical "angling"—of the promiscuous employment of tests which, when properly applied, are extremely effective in detecting individual substances. Complicated results may thus ensue, to unravel which may baffle all the ingenuity of the student; many substances, too, may thus be entirely overlooked, in consequence of the special test employed acting upon bodies other than the one sought for, and in a way not remembered.

To take an instance from a frequent occurrence in the laboratory. The student has a solution to analyse, the colour of which is green. He instantly concludes that the base is copper; and instead of employing the ordinary sequence of group-tests, he devises a short and easy method. Knowing that hydrate of ammonium gives a characteristic reaction with copper salts, he adds it: a green precipitate is formed, and then redissolved; but the solution does not present the deep blue colour of cuprammonium salts. Thus he is disappointed; but, still under the impression that he is dealing with a copper salt, he tries the action of hydrate of potassium: a green precipitate occurs, somewhat pale, it is true, but the student nevertheless regards it as confirmatory of his original supposition. Ferrocyanide of potassium is next added; and the green precipitate which follows is a new perplexity. In despair at these results so conflicting and so contradictory of his original idea, he adds sulphide of ammonium: the black sulphide formed confirms his first supposition; the doubts consequent upon the previous reaction clear away; and he definitely pronounces the solution to contain copper. Why has nickel been thus obviously mistaken for copper? Because the experimenter, in defiance of the conflicting evidence which the special tests have afforded, has entirely neglected all proper sequence of experiment, and omitted to apply the test which claims precedence of all—the group reagent, hydrosulphuric acid in an acid solution, by the employment of which he would at once have been able to decide the question about which so much time has been wasted.

The student, however, should be equally careful not to trust too implicitly to a mechanical familiarity with the routine of analysis, and should learn by repeated trials to assign to each indication no more than its due value. The accumulation of evidence is also of the highest importance.

Next to the accurate recollection of reactions characteristic of each basic and acid-radical, a scrupulous attention to the orderly application of tests is, as we have seen, most necessary to success in analysis; and so, in order that the student may be well practised in this method, it is advisable that he should at first test substances for basic radicals only, reserving for a second stage the analysis of salts with a view to the detection of their acid-radicals: for these latter are, for the most part, identifiable only by a chain of circuitous evidence. And it must be remembered that, upon the knowledge of the basic radical present in a salt, the mode of testing for its acid constituent is frequently founded; indeed, the presence of the latter is often ascertained in the examination for the former constituent. We now proceed, therefore, to details.

CHAPTER II.

QUALITATIVE ANALYSIS OF A SINGLE SALT.

SECTION I.—*Examination for the basic constituent.*

THE student will have learned, from the analytical schemes already given (Part I. Chapter VI., pp. 81, 97, 150, 190, 245), what basic radicals he should be prepared to find in any salt. In order to facilitate analysis, it has been found advisable to perform in the first place a few experiments, chiefly with the blowpipe, upon the dry salt. These experiments constitute what has been termed "the preliminary examination;" and the results which it yields with a simple salt are often so decisive as at once to determine the nature of the basic radical present. Skill in this blowpipe analysis is of great service to the travelling mineralogist, since the apparatus necessary for conducting it may be packed in a small compass, and the results obtained afford a tolerably certain and valuable guide in examining the minerals of the country through which he passes. The student, however, who has the means of controlling these results by further analysis of a solution of the substance, or "analysis by the wet method," should always consider the latter, as in truth it is, the mode of procedure most to be relied on, and should then employ the blowpipe examination only as the preliminary step to a more accurate analysis. A convenient form of this examination is given in the following Table, in which, and in the other Tables which succeed, symbols are often employed in the place of words.

Simple soluble salts for analytical examination may be selected from those mentioned under each basic radical in Chapter VI. For acid-radicals, their combinations with sodium, potassium, or ammonium may in general be used. Examples of insoluble salts may be obtained from those printed in antique type.

Preliminary examination for the detection of the basic radical.

EXPERIMENT.	OBSERVATION.		INFERENCE.
Heat the powdered substance by the blowpipe flame, allowing the flame to spread, on a flat surface of charcoal; begin with a gentle heat, and increase to intense ignition.	**A.** Entirely volatile.		**A.** NH_4, Cd, Hg, As, certain salts of tin.
	B*†. Not volatile; no reduction of metal.		[Al, Zn.
	1. Residue white on cooling.		**B.** 1. Subd. I. & II.
	†*a*. Fusible when heated.		*a*. K, Na, perhaps Subd. II.
	b. Infusible when heated.		*b*. Subd. II., Al, Zn.
	2. Residue coloured on cooling.		2. Cr, Fe, Mn, Co, Ni.
	C. Not volatile; reduction of metal.		
	1. Metallic globules malleable.		**C.** 1. Pb, Ag, Sn, Cu, Au.
	2. Metallic globules brittle.		2. Bi, Sb.
	3. Black metallic powder.		3. Pt.
Allow the residue (if any) to be heated by the central part of the flame.	Brilliant incandescence.		Ca, Mg, Al, Zn.
	Less briillancy.		Ba, Sr.
Colour imparted to the blowpipe flame in the first experiment.	1. Green; 2. Red; 3. Crimson; 4. Yellow-green; 5. Yellow; 6. Violet.		1. Cu, 2. Ca, 3. Sr, 4. Ba, 5. Na, 6. K.
Incrustation on the charcoal; its distance from that end of the charcoal on which the substance has been placed; its colour.	1. Dense white; very distant.		1. Hg_2Cl, $HgCl$, NH_4Cl.
	2. White and crystalline; distant.		2. As_2O_3.
	3. Bluish white; distant.		3. Sb_2O_3, $SnCl$.
	4. Yellowish white when hot, almost or quite white when cold; less distant.		4. Zn_2O, Bi_2O_3.
	5. Orange hot, yellow cold; less distant.		5. Pb_2O.
	6. Dense white; less distant.		6. Sn_2O.
	7. Reddish brown; less distant.		7. Cd_2O.
If **A** (see above), Heat with Na_2CO_3 in bulb-tube (see pp. 169, 210).	1. Sublimate is a black mirror.		1. As.
	2. Sublimate is grey globules.		2. Hg.
Heat with solution of KHO in test-tube (see p. 78).	Pungent ammoniacal odour.		NH_4.
If **B** 1. *b* (see above), Heat with $CoNO_3$ on charcoal in oxidizing flame.	Residue, originally white, becomes— 1. pink; 2. blue; 3. green.		1. Mg, 2. Al, 3. Zn.
If **B** 2 (see above), Heat with borax on platinum wire in both flames, and observe the colour of the bead, both when hot and when cold.	O.F.	R.F.	
	1. *Green*.	*Green*.	1. Cr.
	2. *Green* when hot. *Blue-green*, cold.	Colourless when hot. *Reddish*, cold.	2. Cu.
	3. *Orange*, hot. Yellow, cold.	Colourless, hot. *Bottle-green*, cold.	3. Fe.
	4. *Blue*.	*Blue*.	4. Co.
	5. *Amethyst*.	Colourless.	5. Mn.
	6. *Red-brown*.	Grey.	6. Ni.

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* We cannot be sure that the substance belongs to **B**, and not to **C**, until we have also heated it on charcoal with Na_2CO_3 or KCy.

† Most salts containing water of crystallization fuse as soon as heated, from the solvent action of the water; but the substance under examination can only be pronounced fusible when it continues so under the prolonged action of heat.

The student should make careful and ample notes of all observations made, drawing up his results in the tabular form given above; and having done this, he should proceed to make a solution of the substance under examination, preparatory to the actual analysis.

ACTUAL ANALYSIS FOR THE DETECTION OF ONE BASIC RADICAL.

If the substance be soluble in water, that liquid is the best solvent that can be employed, since all others entail more or less trouble in the subsequent treatment; and so desirable is it that water should if possible be used, that in analysing a substance known to be a single salt only, if it is but slightly soluble in water, that aqueous solution may be taken in preference to an acid one. The solubility or insolubility of any substance in a given liquid may be ascertained very readily by boiling the solid and liquid together, allowing the mixture to cool, and then filtering it. A drop of the filtrate is now evaporated on a bright piece of platinum foil or in a watch glass, when, if a tolerable residue be visible, enough substance is contained in the solution for the purposes of the analyst. But if the residue be scarcely appreciable, or if none be present, the substance must be considered insoluble, and another course adopted.

If water fails to dissolve the substance, acids must be employed. The incautious use of acids, however, leads not unfrequently to failure in analysis; great judgment is therefore necessary in dealing with these solvents. The acids most commonly employed are hydrochloric and nitric, or a mixture of these; but before proceeding to the selection of one of these solvents, the student must recall the results of his preliminary examination, if indeed the substance has been found insoluble in water. If, in the blowpipe experiments, a malleable globule of the lustre and colour of silver or lead, or a sublimate indicative of mercury has been obtained, nitric, not hydrochloric acid, must be employed. The reason of this is apparent. Hydrochloric acid, in dissolving silver, mercurous, or lead salts, produces an insoluble chloride of those metallic radicals, which will baffle the student's attempts at analysis. The following equations represent the different results of acting upon an insoluble silver salt with hydrochloric and with nitric acid:—

$$Ag_2C_2O_4+2HCl=H_2C_2O_4+\underset{\text{ppt.}}{2AgCl}.$$

$$Ag_2C_2O_4+2HNO_3=H_2C_2O_4+\underset{\text{sol.}}{2AgNO_3}.$$

Again, if a globule and incrustation indicative of tin or antimony has been obtained in the blowpipe examination, hydrochloric, and not nitric acid, must be employed as the solvent of the compound, since soluble chlorides of the above-named metals will be thus produced, but with nitric acids the insoluble compounds, metastannic acid and antimonic anhydride. (See pp. 197, 207.)

Sulphuric acid is but rarely employed as a solvent; for when in the concentrated form, it is somewhat unmanageable, and when dilute, it is not so advantageous as nitric or hydrochloric acid.

A mixture of nitric and hydrochloric acids is seldom used. It is, however, the common solvent for certain alloys, and for the metals platinum and gold.

It may be remarked that in most cases it is well to act with as small a quantity as possible of a tolerably strong acid, and, after boiling the substance with it, to dilute with water and repeat the ebullition; for many of the salts formed by the action of acids under these circumstances are easily soluble in dilute, although insoluble in strong acids: take the following instance—

$$\underset{\substack{\text{carb. of lead,}\\\text{insol. in water.}}}{Pb_2CO_3}+2HNO_3=\underset{\substack{\text{nitrate of lead,}\\\text{insol. in strong acid.}}}{2PbNO_3}+H_2O+CO_2;$$

the nitrate of lead here formed would remain as a white crystalline powder in the presence of excess of strong nitric acid, but on the addition of water would dissolve.

But there exist substances insoluble in water and all acids, or which, if soluble in hot concentrated acids, are immediately precipitated on dilution with water or cooling. All such substances require a special treatment to bring them into a condition fit for analysis. The following are some of the more usual bodies of this class, arranged under their respective basic radicals:—

Sn as stannic oxide, Sn_2O_2.
Ag as chloride, bromide, or iodide.
Fe, Cr, Al as sesquioxides.
Sb as antimoniate of antimony, Sb_4O_8.
Pb as sulphate.
Ba, Sr, Ca as fluorides and sulphates.
Almost all basic radicals as silicates.

To obtain these salts in a soluble form, it is necessary to mix the dry substance with five or six times its weight of $Na_2CO_3 + K_2CO_3$; and to fuse the mixture on a fragment of porcelain, or, better, on a piece of platinum* foil for about ten minutes. If the body is a silicate, it should be fused with hydrate of barium in a silver* crucible at a low temperature.

The fusion described in the preceding paragraph may produce several results.

1°. It may produce a double decomposition, and transference of the acid-radical—

$$\underset{\substack{\text{insol. in } H_2O\\ \text{and in acids.}}}{Ba_2SO_4} + Na_2CO_3 = Na_2SO_4 + \underset{\substack{\text{insol. in } H_2O,\\ \text{but sol. in acids.}}}{Ba_2CO_3}.$$

In this case we simply treat the fused mass with cold water, washing the residual Ba_2CO_3 perfectly free from soluble salts, and then dissolving it in dilute HCl.

2°. One of the salts produced in the decomposition may be itself decomposed—

$$\underset{\substack{\text{insol. in water}\\ \text{and nitric acid.}}}{2AgCl} + Na_2CO_3 = 2NaCl + \underset{\substack{\text{sol. in}\\ \text{nitric acid.}}}{2Ag} + O + CO_2.$$

The fused mass is treated as in 1°; but the residue is dissolved in dilute HNO_3.

3°. The body may be unchanged in composition, but rendered soluble in acids—

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* Previous to the employment of platinum or silver vessels, the absence of reducible metals in the substance under examination must be ascertained.

$$\underset{\text{ignited oxide, insol. in acids.}}{(Fe_2)_2O_3} + Na_2CO_3 = \underset{\text{soluble in acids.}}{(Fe_2)_2O_3} + Na_2CO_3.$$

The mass is treated as in 1°.

4°. The body yields an acid-radical, and unites with the sodium or potassium present—

$$Sn_2O_2 + Na_2CO_3 = Na_2\,Sn_2O_3 + CO_2.$$

In this case the fused mass will entirely dissolve in water: the aqueous solution must be acidified with HCl, and H_2S passed; in fact, the proper group-test for Sn must be applied. In the case of the compound Sb_4O_8 the actions 1° and 4° will occur together.

As a general rule, the nature of the salt-radical in union with the base is perfectly immaterial, the cases being quite exceptional in which it affects the action of the tests employed.

1. Many organic acid-radicals, however, such as those of tartaric and citric acids, entirely prevent the precipitation by hydrate of ammonium of certain metals, as aluminium, chromium, and iron, from solutions in which they exist. In the cases where these acid bodies interfere (and we always have an indication of their presence by the salt blackening when its solution is evaporated to dryness, and the residue heated), it is better, if no volatile metal be present, to ignite the substance so as thoroughly to carbonize it, to redissolve by boiling in hydrochloric acid, and to filter from the carbonaceous residue. In cases (as of poisoning) in which a volatile metal, as mercury or arsenic, is mixed with organic acids or organic matter which obstruct the occurrence of the reactions, it is usual to destroy the organic matter by the powerful oxidizing agents, nitric acid or hydrochloric acid with chlorate of potassium, which converting the carbon into carbonic anhydride, and the hydrogen into water, break up the constitution of the organic matter.

2. Another class of saline compounds requires peculiar treatment also; it is the large class of cyanogen compounds—the cyanides, ferrocyanides, ferricyanides, and sulphocyanides. These salts, if dissolved in acids, behave frequently in so peculiar a

manner with reagents, as to involve the analyst in endless perplexity. It is better to decompose them at once by boiling them with hydrate of potassium solution to which a little carbonate of sodium has been added, in case of the presence of metals belonging to the second subdivision. The first solution thus obtained should be poured off the residue, which latter should then be boiled twice or thrice with the same reagents as at first. The substance left should be washed with water, and dissolved in acid. The decompositions in this process are extremely simple; Prussian blue (the ferric ferrocyanide) may be taken as an instance—

$$(Fe_2)_2Cfy_3 + 6KHO = 3K_2Cfy + (Fe_2)_2O_3 + 3H_2O.$$

3. There is yet a third class of salts which may perplex the student, viz. such as, being insoluble in water, dissolve in acids without decomposition, and are reprecipitated in their original form when the acid is removed by neutralization. Thus, when phosphate of calcium is dissolved by hydrochloric or nitric acid, we have at least 2 saturating eqs. of acid-radical to every eq. of calcium present; and in all such cases we cannot tell with certainty with which radical the metal is combined. The salt may be simply dissolved; or a double decomposition may have taken place, thus—

$$Ca_2\,HPO_4 + 2HNO_3 = H_3\,PO_4 + 2CaNO_3.$$

At all events, no sooner is the acid removed by neutralization, than the elements originally in combination appear as a precipitate of the original salt. Thus, if simple solution occurs, the reaction may be given thus—

$$\underbrace{Ca_2\,HPO_4 + 2HNO_3}_{\text{in solution.}} + 2NH_4\,HO = \underbrace{Ca_2\,HPO_4}_{\text{reprecipitated.}} + 2NH_4\,NO_3 + 2H_2O;$$

while, if a double decomposition is believed to take place, the equation will be as follows:—

$$H_3\,PO_4 + 2CaNO_3 + 2NH_4\,HO = \underbrace{Ca_2\,HPO_4}_{\text{reprecipitated.}} + 2NH_4\,NO_3 + 2H_2O.$$

In the ordinary process of analysis, these salts therefore are precipitated as soon as the acid solution is rendered neutral; and by a reference to the Tables which follow, this condition of things will be found to occur at the precipitation of Group III. in the analytical arrangement of the metals. Consequently the precipitate which should contain only the hydrates of iron, chromium, and aluminium, may include all the insoluble salts of the kind just described which may be present in the solution. In the Tables for Group III., the influence which they exert, and the mode of dealing with them, will be found described.

Thus we have endeavoured to point out the various means at our disposal for effecting the solution of a salt previous to its analysis; we now proceed to the plan of analysis.

GENERAL TABLE SHOWING THE APPLICATION OF GROUP-TESTS.

<table>
<tr><td colspan="6">To the solution add dilute HCl in excess, and warm gently.</td></tr>
<tr><td rowspan="5">A precipitate indicates the presence of
Pb,
Ag,
Hg.
Examine by Table for Group I.</td><td colspan="5">If no precipitate occurs, pass excess of H_2S through the solution, and warm gently.</td></tr>
<tr><td rowspan="4">A precipitate indicates the presence of
Hg, Sn,
Pb, Sb,
Bi, As,
Cu, Pt,
Cd, Au,
Pd.
Examine by Table for Group II.</td><td colspan="4">If no precipitate occurs, boil the solution to expel H_2S, add a little HNO_3 to peroxidize the Fe, boil again, evaporate to perfect dryness, ignite, redissolve in HCl; then add some quantity of NH_4Cl solution, and lastly excess of NH_4HO.</td></tr>
<tr><td rowspan="3">A precipitate indicates the presence of
Ur,
Al,
Fe,
Cr.
Examine by Table for Group III.</td><td colspan="3">If no precipitate occurs, add $(NH_4)_2S$ in small quantity.</td></tr>
<tr><td rowspan="2">A precipitate indicates the presence of
Zn,
Ni,
Co,
Mn.
Examine by Table for Group III. *a*.</td><td colspan="2">If no precipitate occurs, boil off the $(NH_4)_2S$, filter if necessary from precipitate of S, add NH_4Cl and $(NH_4)_2CO_3$, and warm.</td></tr>
<tr><td>A precipitate indicates the presence of
Ba,
Sr,
Ca.
Examine by Table for Group IV.</td><td>If no precipitate occurs, the solution may contain
NH_4,
Mg,
K,
Na.
Examine by Table for Group V.</td></tr>
</table>

The student having now ascertained to which group the basic radical of the simple salt under examination belongs, must proceed to discover which member of the group is present. The groups above given are almost identical with the subdivisions of the basic radicals described in Part I., the chief differences being the reversion of their order, and the division of the hydrosulphuric acid (Subdivision IV.) and sulphide of ammonium (Subdivision III.) groups respectively into two. The reason for reversing the order is obvious—it being far easier to separate at first those bodies which form the larger number of insoluble compounds, whilst, in the study of the reactions, it is simpler to begin with those bodies which yield the smallest number of insoluble salts.

The student may now proceed to examine the precipitates belonging to the various groups, somewhat according to the following Tables, in each case referring to the reactions given in Chapter VI. for confirmatory tests.

TABLE FOR GROUP I.

<table>
<tr><td colspan="3">The precipitate produced by hydrochloric acid may contain PbCl, AgCl, or Hg_2Cl. Collect on a filter, transfer the precipitate to a large test-tube, and heat with much water: if it entirely dissolves,</td></tr>
<tr><td rowspan="2">the solution will contain PbCl.
The presence of lead must be confirmed by the addition of H_2SO_4; a white precipitate of Pb_2SO_4 indicates
Pb.</td><td colspan="2">If a residue is left (it may be either AgCl or Hg_2Cl), collect on a filter, remove to a test-tube, add NH_4HO and warm: if the residue dissolves entirely,</td></tr>
<tr><td>the solution will contain AgCl.
The presence of silver must be confirmed by the addition of slight excess of HNO_3; an insoluble white precipitate indicates
Ag.</td><td>If a black residue is left, it will consist of $(Hg_2)_2O$.
The presence of mercury must be confirmed by collecting the precipitate, drying it at 100° C., and mixing it with Na_2CO_3 and heating in a bulb-tube (see p. 169); a sublimate of grey globules indicates
Hg.</td></tr>
</table>

TABLE FOR GROUP II.

<table>
<tr><td colspan="6">The precipitate produced by hydrosulphuric acid may be Hg_2S, Bi_2S_3, Pb_2S, Cu_2S, Cd_2S, Pd_2S, Sn_2S, Sn_2S_2, Sb_2S_3, Sb_2S_5, As_2S_3, As_2S_5 *Pt_2S_2, *Au_2S_3, or S (if a ferric salt or chromate were present).
Collect on a filter, transfer to a test-tube, and boil with $(NH_4)_2S$ for five minutes: if a residue remains, it indicates—</td></tr>
<tr><td colspan="3">if brown or black, the presence of Hg_2S, Pb_2S, Bi_2S_3, Cu_2S, or Pd_2S; if yellow, of Cd_2S (presence of Cd).
Wash the brown or black precipitate free from HCl, and boil in HNO_3.</td><td colspan="3" rowspan="2">If the precipitate entirely dissolves, Sn, Sb, or As must be sought for.
Add slight excess of HCl and some H_2S water; collect the precipitated sulphide on a filter, wash, and dry it at 100° C. Mix the dried precipitate with KNO_3 and Na_2CO_3, and fuse in a crucible. Digest the fused mass with cold water, neutralize <i>exactly</i> with HNO_3: complete solution of the mass indicates</td></tr>
<tr><td rowspan="3">A residue will be a <i>trace</i> of Pb_2S, or will consist of Hg_2S. Confirm (p. 169) the presence of Hg.</td><td colspan="2">If the precipitate entirely dissolves, add excess of NH_4HO.</td></tr>
<tr><td rowspan="2">A precipitate formed and not redissolved, will indicate Bi.</td><td rowspan="2">If the solution is blue, it indicates the presence of Cu; if colourless, it contains PdCl. Add H_2S: a brown precipitate indicates Pd.</td><td rowspan="2">the presence of K_2HAsO_4. Confirm by adding $AgNO_3$: a precipitate of Ag_3AsO_4 indicates As.</td><td colspan="2">If a residue and precipitate exist, collect and wash both, dry, mix with KCy, and fuse in a porcelain crucible. Wash the metallic globules or powder, boil them with HNO_3, wash the white residue with water, and then digest it in $H_2\overline{T}$ solution: if entirely dissolved, it indicates</td></tr>
<tr><td>the presence of $HSbO_3$. Add H_2S: an orange precipitate indicates Sb.</td><td>If a residue exists, it consists of Sn.</td></tr>
</table>

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* A separate examination must be made for platinum and gold, according to the plan given on page 245.

TABLE FOR GROUP III.

<table>
<tr><td colspan="4">The precipitate produced by hydrate of ammonium may be $Ur_2H_3O_3$, $Fe_2H_3O_3$, $Cr_2H_3O_3$, or $Al_2H_3O_3$; it may also be a phosphate or fluoride of Ba, Sr, Ca, or Mg, or a phosphate of Ur, Fe, Cr, or Al. The oxalates will have been destroyed by ignition; and the borates do not occur.
It will be sufficient to ascertain the presence of the phosphoric radical by dissolving a small portion of the precipitate in the least possible quantity of dilute HNO_3 in a watch-glass, adding a trace of NH_4HO, to neutralize as far as possible the excess of HNO_3 without reprecipitating the salt dissolved, and then introducing a few drops of $AgNO_3$: the presence of H_3PO_4 is ascertained by the immediate precipitate of the yellow Ag_3PO_4.
The mass of the precipitate is then treated with <i>sesquicarbonate</i> of ammonium in the cold: complete solution indicates</td></tr>
<tr><td rowspan="3">the presence of $Ur_2H_3O_3$. Evaporate to dryness; dissolve the yellow residue in $H\bar{A}$, and add K_2Cfy: a brownish red precipitate or colour indicates
Ur.</td><td colspan="3">If a residue is left, it is to be examined for Fe, Cr, or Al.
Boil for five minutes with $H_2\bar{O}$, to separate Ba, Sr, and Ca as oxalates; filter, allow to cool, and add excess of KHO.</td></tr>
<tr><td rowspan="2">A red or buff precipitate consists of $Fe_2H_3O_3$ or Fe_2PO_4. Confirm the presence of iron by dissolving the precipitate in $H\bar{A}$, and adding K_2Cfy: a blue precipitate indicates
Fe.</td><td colspan="2">Perfect solution indicates the presence of the chromic or aluminic hydrate or phosphate. Boil the solution.</td></tr>
<tr><td>A green precipitate will be $(Cr_2)_2O_3$. Confirm by fusion with borax: a grass-green bead indicates
Cr.</td><td>If no precipitate occurs, the solution will contain $Al_2H_3O_3$. Add NH_4Cl: a white precipitates indicates
Al.</td></tr>
</table>

TABLE FOR GROUP III. *a*.

<table>
<tr><td colspan="4">The precipitate produced by sulphide of ammonium may be Zn_2S, Mn_2S, Ni_2S, or Co_2S.
Dissolve it in concentrated HCl, adding one or two drops of concentrated HNO_3 when boiling. To the solution add excess of KHO. Perfect solution indicates</td></tr>
<tr><td rowspan="3">the presence of Zn_2S: add H_2S to the solution, a white precipitate of Zn_2S indicates
Zn.</td><td colspan="3">A precipitate of a flesh colour consists of Mn_2S; a black precipitate, of Ni_2S or Co_2S.
Dissolve in concentrated HCl, add excess of $K\bar{A}$, and pass H_2S gas: the non-formation of a precipitate indicates</td></tr>
<tr><td rowspan="2">the presence of Mn_2S. Confirm by the addition of NH_4HO, which will form NH_4HS, and give a flesh-coloured or buff precipitate of Mn_2S, indicating
Mn.</td><td colspan="2">The occurrence of a precipitate proves the existence of Ni_2S, or Co_2S.
Dissolve in concentrated HCl; add one drop of concentrated HNO_3 when boiling, then KCy in excess. Boil the solution, and acidify with dilute HCl: a precipitate indicates</td></tr>
<tr><td>the presence of nickel, which must be confirmed by fusion with borax: a red-brown bead indicates
Ni.</td><td>The absence of a precipitate indicates cobalt, the presence of which must be confirmed by evaporating the solution to dryness, and fusing a portion of the residue with borax: a blue bead indicates
Co.</td></tr>
</table>

TABLE FOR GROUP IV.

<table>
<tr><td colspan="3">The precipitate produced by carbonate of ammonium, in the presence of NH_4HO and NH_4Cl, may be Ba_2CO_3, Sr_2SO_3, or Ca_2CO_3.
Dissolve in the smallest quantity of dilute HCl, add $KCrO_2$ in solution: the formation of a precipitate, after the lapse of a few minutes, indicates</td></tr>
<tr><td rowspan="2">the presence of
Ba.</td><td colspan="2">The absence of any precipitate indicates the presence of strontium or calcium.
Divide the solution into two parts, dilute it with a small quantity of water.</td></tr>
<tr><td>1.
Add a saturated solution of Ca_2SO_4: a precipitate, after standing fifteen minutes, indicates
Sr.</td><td>2.
If no precipitate occurs in 1. after fifteen minutes standing, add to 2. $(NH_4)_2\bar{O}$: a white precipitate indicates
Ca.</td></tr>
</table>

TABLE FOR GROUP V.

If the various group-tests have produced no precipitate in the solution under examination, either NH_4, Mg, K, or Na is present. Of these basic radicals, NH_4 will have been already detected in the preliminary examination (p. 391).

Divide the solution into two portions, one being thrice the bulk of the other.

1.	2.
To the smaller portion add Na_2HPO_4 and NH_4HO, agitate well, and allow to stand some time: a white crystalline precipitate indicates **Mg.**	Evaporate the larger portion to dryness, ignite and test a small portion of the residue before the blowpipe: a yellow colour imparted to the flame indicates **Na.** The remainder of the residue is to be dissolved in water, and then HCl and $HPtCl_3$ added: a yellow crystalline precipitate indicates **K.**

Having now considered the method of detecting the basic radical in a simple salt, we proceed to give the details of—

SECTION II.—*The examination for the acid constituent.*

The student must have already perceived that, although *compound basic* radicals are extremely rare, the *compound acid*-radicals which occur in the course of analysis are very numerous. The latter bodies, though easily detected if they yield characteristic products of decomposition, are, however, in many cases recognized with great difficulty, particularly when of very great complexity. The recognition of the basic radicals by means of the blowpipe is comparatively easy, because in the majority of cases the acid-radical of the salt is expelled, or its basic constituent is left in combination with oxygen only as an oxide, the characters of which are easily recognized; but when we wish to detect the acid-radical present by the same means, the ready decomposability of the latter forms an insuperable obstacle.

We have, however, at our disposal a method of Preliminary Examination which is of the greatest service in enabling us to form an idea concerning the nature of the acid-radical present, and occasionally, indeed, affording us decisive proof of its existence. One of the reactions thus employed consists in the decomposing influence which concentrated sulphuric acid exerts upon almost all saline combinations. The sulphuric radical unites with the basic constituent of the salt to form a sulphate, while the acid-radical in the substance either unites with the hydrogen to form a new acid which is liberated, or else splits up into characteristic products of decomposition. Whichever result takes place, its occurrence generally affords sufficient evidence of the nature of the acid constituent originally present.

In addition to the experiment with concentrated sulphuric acid, decisive information concerning the nature of the acid-radical present in the substance under examination may often be obtained by gently warming the substance, or its solution, with *dilute* hydrochloric acid. All *concentrated* acids, particularly concentrated nitric and hydrochloric, when heated, themselves evolve pungent vapours, which mask the otherwise characteristic odour of the newly liberated acid.

In observing the action of sulphuric or hydrochloric acid upon a salt, it must be borne in mind that the nature of the basic radical present greatly influences the reaction. Thus the salts containing basic radicals of the first and second subdivisions united with weak acid-radicals, or with acid-radicals the hydrogen salts of which are gaseous at ordinary temperatures, are much more readily decomposed by strong acids than are the salts of other subdivisions.

To take an example of this difference in the behaviour of salts. NaCl *or* BaCl is instantly decomposed by the addition of $H_2\,SO_4$, the HCl escaping with effervescence,—while AgCl is not acted upon. $K_2\,S$ or $Ca_2\,S$ is decomposed in a similarly rapid manner by HCl even when dilute, while $Fe_2\,S$ is but slowly acted upon, and $Pb_2\,S$ remains wholly intact. The varying solubility of the different compounds doubtless here influences the play of affinities. Carbonates and sulphites, the acids of which split, as soon as liberated, into water and carbonic and sulphurous anhydrides, are decomposed, perhaps without exception, even by weak acids, whatever may be the solubility of the individual salt operated on; but here it is obvious that the decidedly gaseous character of the chief product of the action must exert a powerful influence in determining the decomposition.

Preliminary examination for the detection of the acid-radical.

EXPERIMENT.	OBSERVATION.	INFERENCE.
Heat the substance in a tube open at both ends, and held obliquely (fig. 13). Fig. 13. 	1. Odour of burning sulphur at A.	1. Presence of a sulphide, or free S.
	2. Drops of liquid, neutral to test-paper, condense about B.	2. Presence of a hydrate, or water of crystallization.
	3. The substance carbonizes, with odour of burnt sugar.	3. Presence of $M_2\overline{T}$.
	4. The substance carbonizes, with odour of burnt feathers.	4. Presence of $M_2\overline{U}$.
	5. Substance changes colour, regaining its first tint on cooling.	5. Probable presence of oxides or chromates.
	6. Yellow sublimate at B.	6. Presence of a volatile or other sulphide, or of free S.
	7. Red sublimate at B.	7. Presence of Hg_2S.
	8. Evolution of red fumes.	8. Presence of certain nitrates.
Add to the solid salt, or its aqueous solution, in a test-tube, dilute HCl, or dilute H_2SO_4.	1. Effervescence in the cold, gases of characteristic odours being evolved.	1. Presence of MCyO, M_2CO_3, M_2SO_3, or sulphides and cyanides of Subdivisions I. and II.
	2. Occurrence of peculiar odour, without effervescence.	2. Presence of $M\overline{A}$, certain cyanides, sulphides, selenides, and sulphites.
Add to the solid salt, or its aqueous solution, in a test-tube, concentr. H_2SO_4; boil for some minutes.	*α*. No blackening occurs.	
	1. Crystals separate.	1. Presence of $MBoO_2$, $M\overline{Bz}$, or M_2S.
	2. The liquid effervesces, pungent gases being evolved.	2. Presence of $M\overline{A}$, MNO_3, MNO_2, M_2CO_3, M_2SO_3, MCyO, and frequently MCl, MBr, MI, MF, MCy, M_2S, or M_2Se.
	3. Evolution of CO_2 and CO.	3. Presence of $M_2C_2O_4$.
	4. Evolution of Cl.	4. Presence of MClO, or $MClO_3$.
	5. Evolution of Cl, together with peculiar crackling explosion.	5. Presence of $MClO_3$.
	6. Evolution of O.	6. Presence of $MCrO_2$.
	7. Evolution of gas which etches glass.	7. Presence of MF.
	8. Evolution of red vapours.	8. Presence of MBr, or MNO_3.
	β. The substance blackens.	
	1. Evolution of violet vapours.	1. Presence of MI.
	2. Evolution of CO, with odour of burnt sugar.	2. Presence of tartrates or citrates.
	3. No evolution of CO or peculiar odour.	3. Presence of gallates or tannates.

Many acid-radicals being by no means distinctly recognized by analysis in the wet way, it will be well for the student to follow up the evidence he has elicited by the foregoing preliminary examination, by testing specially for various acid-radicals before undertaking the actual analysis.

SPECIAL TESTS.

Any suspicion of the presence of **Chlorine** may be followed by direct testing (with H_2SO_4 and Mn_2O_2) of the original substance (see p. 255); of **Bromine,** by the starch test (see p. 259); **Iodine,** by the starch test (see p. 263); **Fluorine,** by the etching test (see p. 265); the **Hypochlorous** radical, by the lead test (see p. 268); the **Chloric** radical, by the action of concentrated H_2SO_4 (see p. 269); **Sulphur,** by its odour, blue flame, and coloured salts; **Selenium,** by its horse-radish odour (see p. 286); **Sulphocyanogen,** by ebullition with HNO_3 (see p. 343); the **Sulphurous** radical, by the odour and action on H_2S, of SO_2 the product of its decomposition (see p. 293); the **Carbonic** radical, by the action on BaHO solution of CO_2, the product of its decomposition; **Cyanogen,** by passing the vaporized acid, which burns with a blue flame, into a test-tube containing a drop of KHO solution, dividing the solution of KCy thus obtained into two parts, and applying to one the Prussian-blue, and to the other the sulphocyanide test (see p. 342); the **Acetic** radical, by the acetic-ether test (see p. 350); the **Nitric** radical, by mixing with a fresh portion of the strong solution of the substance an equal bulk of concentrated H_2SO_4, cooling the mixture, and then dropping in a crystal of $FeSO_4$—on standing quietly for some seconds, a brown halo will appear.

We may remind the student that every result obtained in the above preliminary examination should be as carefully recorded as those observed in the examination for basic radicals. It is, indeed, more necessary to do this in the present case, since the detection and distinction of acid-radicals is more dependent on the preliminary analysis and the special testings consequent thereon, than is the recognition of the basic radicals, previously treated of.

ACTUAL ANALYSIS FOR THE DETECTION OF ONE ACID-RADICAL.

Attention to several points connected with this branch of the analysis of a salt is necessary to ensure success; and—

1. With regard to the solution of the substance under examination. If it dissolve in water, one great source of difficulty is evaded; but if not, it becomes a question in what acid it shall be dissolved. To the use of HCl is presented a great objection—that it produces a dense precipitate with $AgNO_3$, which is one of the principal reagents employed in the detection of acid-radicals. To the adoption, on the other hand, of HNO_3 as the solvent for salts insoluble in water, a scarcely diminished objection exists; for with many complex acids, if employed in sufficient strength to dissolve the salt, it oxidizes, and thus completely changes, the acid-radical. H_2SO_4 too is rejected, because, if concentrated, it acts powerfully as an oxidizer, and even when dilute it produces precipitates with BaCl and CaCl, two reagents frequently employed in this course of analysis. Other acids, such as HF, $H\bar{A}$, $H_2\bar{O}$, &c., are either too energetic, too weak, or too rare to be employed; or else they form insoluble salts with the reagents used; or, lastly, by their often complex constitution or ready decomposability they increase the difficulties of the analysis. Thus something may be urged against the use of each solvent acid; and the student must bear in mind the evils and advantages which attach to each, and use his judgment in all cases, by employing that solvent to which the fewest objections are attached. It is well that he should early learn that no strict rule can be laid down for his guidance in chemical analysis, and that this science demands of its practiser not only his whole manual skill, but also his best mental faculties. On the whole, the best acid solvent for general use is dilute HNO_3; in this form the acid does does not oxidize very rapidly, and has the immense advantage over most others, of not forming any insoluble salts. The salts of organic acid-radicals should not be boiled, but only heated gently with this acid. In addition to dilute HNO_3. HCl, con-

centrated HNO_3, and $H\bar{A}$ are advantageously employed in many special instances.

2. It will be seen presently that the method already adverted to in the detection of basic radicals may be employed for the recognition of the acid-radical also, in the analysis of salts insoluble in water. We allude to the mode mentioned (p. 395, § 2.) in which the decomposition is effected, and a soluble salt of the acid-radical thus obtained, by boiling the insoluble salt with a solution of NaHO or KHO. This method is frequently applicable where the attempt to make an acid solution would fail, and is especially used in the examination of cyanides, ferrocyanides, &c. The solid salt boiled with a concentrated solution of KHO, to which a little Na_2CO_3 has been added in order to precipitate any metal of Subdivision II. present as a carbonate, gives the following result:—

$$\underset{\substack{\text{an insol.}\\\text{cyanide.}}}{NiCy}+KHO=\underset{\substack{\text{a sol.}\\\text{cyanide.}}}{KCy}+\underset{\text{ppt.}}{NiHO};$$

$$\underset{\substack{\text{an insoluble}\\\text{ferrocyanide.}}}{2CaKCfy}+Na_2CO_3=\underset{\text{soluble ferrocyanides.}}{K_2Cfy+Na_2Cfy}+\underset{\text{precipitate.}}{Ca_2CO_3}.$$

This mode of decomposition may be very advantageously employed in the case of salts containing a complex acid-radical liable to decomposition if treated with HNO_3. It is better to boil such salts with Na_2CO_3, and not with the more powerful KHO. $NaCO_3$, too, is an agent which almost invariably produces an insoluble precipitate: for nearly all carbonates are insoluble in neutral solutions; and in most other cases where an insoluble carbonate is not produced, an equally insoluble hydrate is the result, thus—

$$\underset{\substack{\text{an insoluble}\\\text{oxalate.}}}{Mn_2C_2O_4}+Na_2CO_3=\underset{\substack{\text{a soluble}\\\text{oxalate.}}}{Na_2C_2O_4}+\underset{\text{precipitate.}}{Mn_2CO_3}.$$

$$\underset{\text{an insoluble citrate.}}{2Ba_3C_6H_5O_7}+3Na_2CO_3=\underset{\text{a soluble citrate.}}{2Na_3C_6H_5O_7}+\underset{\text{precipitate.}}{3Ba_2CO_3}.$$

By such means we obtain a *soluble* in the place of an *insoluble* salt of the acid-radical we wish to detect: nor is this the only object attained; we have an *alkaline* salt, *i. e.* a salt containing a metal belonging to the first subdivision. And this fact brings us to the consideration of a point of great consequence, viz.—

THE ABSENCE OF ALL BASIC RADICALS EXCEPT POTASSIUM AND SODIUM.

It has been already stated that the presence of acid-radicals often interferes most materially with the detection of the basic constituent of a salt; the converse of this statement is true in even a more extended sense. The presence of metallic radicals other than potassium or sodium is found extremely inconvenient, chiefly on account of the insoluble salts which they form by union with the acid-radicals of the salts added as reagents or tests. Ammonium indeed should, as a general rule, be excluded, on account of the interference which its salts (*e.g.* NH_4Cl, $NH_4 NO_3$, and $[NH_4]_2 SO_4$) frequently exert by their solvent action on other saline combinations. Thus the borates and phosphates, the citrates and tartrates of barium and calcium (salts characteristic of their respective acid-radicals) are held in solution when reagents appropriate for their formation are added, if a salt of ammonium also be present in the liquid. It must, however, be stated here, that stable ammonium salts ($NH_4 HO$ and $[NH_4]_2CO_3$ being thus excepted) do not inferfere with the action of two frequently employed reagents, viz. $AgNO_3$ and Fe_2Cl_3.

The separation of the original basic constituent of a salt is sometimes very difficult, and in other cases very easy of accomplishment.

1. If the salt is soluble in water, and the basic constituent belongs to Subdivision I., no such separation is needed, except in the special cases just mentioned, where the radicals of borates, phosphates, and organic salts are present, and we intend to employ BaCl or CaCl as a test; then, if ammonium be the base, it must be removed. This is accomplished by adding to the solution some KHO, and boiling the liquid until the addition of a few drops more of the alkali no longer produces an odour of NH_3.

2. If the salt is soluble in water, and contains for its basic constituent a member of Subdivision II., it may be immediately

converted to the requisite condition of a suitable alkaline salt by boiling its solution with a solution of Na_2CO_3:

$$2BaBr+Na_2CO_3=2NaBr+Ba_2CO_3.$$

3. If the salt contains a member of Subdivision II. as its basic radical, but is insoluble in water though soluble in acids, the treatment with Na_2CO_3 may be employed. Care must, however, be taken to add a quantity of Na_2CO_3 sufficient not only to neutralize the acid employed as solvent, but also to effect the decomposition of the original salt. If this precaution be not observed, the reagent will simply neutralize the solvent acid, and reprecipitate the original salt, thus—

$$\underset{\substack{\text{salt sol. in}\\ \text{acid only.}}}{Ba_2R}+\underset{\substack{\text{acid}\\ \text{solvent.}}}{2HNO_3}+Na_2CO_3=\underset{\substack{\text{reprecipi-}\\ \text{tated salt.}}}{Ba_2R}+\underbrace{2NaNO_3+H_2CO_3}_{\text{solution.}};$$

the search for the desired salt (Na_2R) in the solution will therefore in this case fail. But if enough Na_2CO_3 has been added, the reaction is as follows:—

$$Ba_2R+2HNO_3+2Na_2CO_3=Na_2R+2NaNO_3+H_2CO_3+Ba_2CO_3,$$

where the desired salt (Na_2R) is obtained. In these experiments the smallest possible quantity of acid solvent should be used.

Moreover, in certain instances where Na_2CO_3 does not effect a rapid decomposition of the salt (*e.g.* $BaCrO_2$, Ba_2HPO_4), it is well to filter off the precipitate first formed, and to boil it with a fresh portion of Na_2CO_3.

4. These observations and methods of treatment apply also generally to all salts, whatever basic radicals they contain, provided that their acid constituent is not a complex organic radical containing C, H, and O, *or* C, H, N, and O.

5. But when we try to decompose salts containing the metallic radicals of the third and fourth subdivisions united with a complex organic constituent, we find that complete decomposition is not effected, that a perfect precipitation of the basic radical as carbonate is not made, but that in the filtrate the acid-radical to be detected exists in combination partly with Na, and partly with the original basic radical. Nor can this latter be removed by successive repetitions of the process; here the

analyst must use his judgment and the knowledge previously acquired. These organic radicals do not allow of the perfect precipitation of many bases belonging to the third and fourth subdivisions by any reagents except certain combinations of sulphur (H_2S or NH_4HS). Some of the sulphides thus formed are, it will be remembered, soluble in alkaline solutions, some in acids, while others are soluble in none of these reagents. The method of separation must therefore be adapted to the nature of the basic constituent present, which the student will have already recognized. If the sulphide of the radical be insoluble in acids, it is better to make a solution of the salt in HNO_3 as dilute as possible, and to pass H_2S through the acid solution till no more precipitate is formed. The sulphide should then be removed by filtration, and the residual H_2S expelled by gently warming the filtrate. The solution thus treated may then be immediately tested for acid-radicals. Should the sulphide of the radical in the salt be soluble in acids, but insoluble in alkaline solutions, H_2S is to be passed into the solution obtained by boiling the original salt with Na_2CO_3 (this plan is better, though longer, than adding NH_4HS); thus the removal of the small quantity of metallic radical retained in the alkaline solution is effected. Having filtered off the precipitate thus formed, the student must acidify the filtrate with dilute HNO_3, to decompose the NaHS present, and then gently warm the solution, to expel H_2S.

By the means just described, or by a combination of them, acid-radicals may be separated from their original saline combinations, and obtained in the form of an alkaline salt, the base of which will not interfere with the effects produced by the reagents employed.

We now proceed to the method of testing the solution for acid-radicals—the actual analysis. But first it may be useful to give a list of the acids whose salts we may expect to be present, distinguishing by small type those which are of rarer occurrence. These, when they occur, are often reduced to simpler forms, or else are separated, in the preparation of the solution. They generally require for their recognition the employment of the special tests detailed in Chapter VII., although evidence of their existence is occasionally obtained in the preliminary examination for the acid constituent (which see):—

Subdivision I.—HCl, HBr, HI, HF; $HClO$, $HClO_3$, $HClO_4$, $HBrO_3$, HIO_3, HIO_4, $HPtCl_3$, &c.

Subdivision II.—H_2O, H_2S, H_2Se, H_2Te; H_2SO_3, H_2SO_4, H_2SeO_3, H_2SeO_4, H_2TeO_3, H_2TeO_4; $HCrO_2$, HWO_2, $HMoO_2$, HVO_2.

Subdivision III.—$H_3Si_2F_9$; H_2CO_3, $H_2C_2O_4$, $HBoO_2$, $HSiO_2$; HCy, $HCyO$, $HCyS$, H_2Cfy, H_3Cfdy, H_3Cocy; $H\overline{A}$, $H\overline{Bz}$, $H_2\overline{L}$, $H_2\overline{S}$, $H_2\overline{T}$, $H_3\overline{Ci}$, $H_3\overline{G}$, $H_3\overline{Qt}$, $H_2\overline{U}$.

Subdivision IV.—HNO_2, HNO_3, H_3PO_2, H_3PO_3, H_3PO_4, $H_4As_2O_5$, H_3AsO_4.

Of these acid-radicals, some, as has been previously observed, can be detected in the preliminary examination, or by tests based upon the results of that examination. These are the radicals the acids of which are represented by the formulæ $HClO$, $HClO_3$; H_2S, H_2Se, H_2SO_3; $HCyO$ and HNO_3. Some radicals, again, though found in analysing by the moist way, are best detected in the previous examination: the acids of these radicals are HCl, HBr, HI, HF, HCy, and $H\overline{A}$.

From the solution prepared as above directed, the original basic radical has been separated; CO_2 has also been expelled by a gentle heat applied to the liquid after it has been slightly acidified with dilute HNO_3[*]: this expulsion of the CO_2 is necessary, for its presence in the liquid would falsify the results. The next step should be to exclude another class of metallic acids: they may all be removed by the passage of H_2S through the liquid; but if this has been already done, it need not be here repeated. The H_2S gas is passed through the solution, which has been very slightly acidified with HNO_3. By this means we remove the radicals[†]

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[*] Unless the solution be very dilute, and the nitric acid very weak, $H\overline{Bz}$ and $H_2\overline{S}$ may be here precipitated, while $H_2\overline{U}$ and $H_3\overline{Qt}$ will certainly separate.

[†] Chromic acid, and the other metallic acids in general, are detected and separated among the basic radicals by their behaviour with H_2S.

$PtCl_3$, CrO_2, Sn_2O_3, WO_2, MoO_2, VO_2, As_2O_5, AsO_4; we also convert BrO_3, IO_3, and IO_4 into the types MBr and MI; and if cyanogen compounds be present, they will generally be found to produce a sulphocyanide, while ferricyanogen is changed to ferrocyanogen: these facts must be borne in mind when testing. The H_2S remaining in the liquid must now be removed by gently warming the solution placed in an evaporating dish.

The list of radicals now existing as acids will be as follows:—

Subdivision I.—HCl, HBr, HI, HF.

Subdivision II.—H_2SO_4, H_2SeO_4.

Subdivision III.—$H_3Si_2F_9$, $H_2C_2O_4$, $HBoO_2$, $HSiO_2$; HCy (if not all expelled by warming the acid solution), HCsy; H_2Cfy, H_3Cfdy, H_3Cocy; $H\bar{A}$ (if not all expelled), $H\overline{Bz}$, and the other organic acids.

Subdivision IV.—H_3PO_4.

No really good plan of detecting and separating the various acids has been yet devised; and the Tables we are about to give must not be deemed in any way faultless. More reliance must be placed on the preliminary examination and special testings, than upon the actual analysis.

To detect, then, with more or less certainty, in a single salt, the radical of any one of the above-mentioned acids, we may employ the following plan:—

Actual analysis for the detection of the acid constituent.

<table>
<tr><td colspan="4">To the solution add excess of HNO_3.</td><td colspan="2" rowspan="2">To a fresh portion of the original solution, after careful neutralization with NH_4HO, add Fe_2Cl_3.</td></tr>
<tr><td rowspan="3">A precipitate indicates the presence of
BoO_2
SiO_2
$\overline{Bz}$
$\overline{S}$
or $\overline{U}$.
If the plan described in the introductory remarks has been followed, the absence of a precipitate here might arise from the previous separation of the acid by the addition of dilute HNO_3.</td><td colspan="3">To the solution add $BaNO_3$.</td></tr>
<tr><td rowspan="2">A dense precipitate indicates the presence of
SO_4
SeO_4;
a gelatinous precipitate indicates
Si_2F_9.</td><td colspan="2">To the solution add slight excess of Na_2CO_3 and warm.</td><td>A precipitate indicates the presence of
Cfy
$\overline{Bz}$
$\overline{G}$
or $\overline{Qt}$.</td><td>A coloured solution indicates the presence of
Csy
$\overline{A}$
or Cfdy.</td></tr>
<tr><td>A precipitate indicates the presence of
C_2O_4
BoO_2
SiO_2
$\overline{T}$
$\overline{Ci}$
or PO_4.
Examine by Table for Group I.</td><td>To the solution add HNO_3 and $AgNO_3$.
A precipitate indicates the presence of Cl, Br, I, Cy, Csy, Cfy, or Cfdy.
Examine by Table for Group II.</td><td colspan="2">See Table for Group III.</td></tr>
</table>

TABLE FOR GROUP I.

<table>
<tr><td colspan="5">The precipitate may be BaF, $Ba_3Si_2F_9$, $Ba_2\overline{O}$, $Ba_2\overline{T}$, $Ba_3\overline{Ci}$, Ba_3PO_4, $BaBoO_2$, or $BaSiO_2$.
To the solution add dilute HCl, and then divide the liquid into two parts.</td></tr>
<tr><td rowspan="4">I.
Evaporate to dryness, add HCl, introduce a slip of turmeric-paper. A brown colouration indicates
BoO_2
(or the green-alcohol flame may be obtained, see p. 329);
An insoluble residue indicates
SiO_2.</td><td colspan="4">If no results are obtained with I., boil the second portion with Na_2CO_3; filter from the precipitate of Ba_2CO_3, acidify with $H\overline{A}$, and add CaCl.</td></tr>
<tr><td rowspan="3">A precipitate indicates
F or
$\overline{O}$
(also indicated in the Prelim. Exam.).</td><td colspan="3">The solution may contain $CaBoO_2$, $Ca_2\overline{T}$, $Ca_3\overline{Ci}$, or Ca_3PO_4. Divide into two parts.</td></tr>
<tr><td rowspan="2">I.
Add Fe_2Cl_3.
A white precipitate indicates
PO_4.</td><td colspan="2">II.
Boil the solution.</td></tr>
<tr><td>A white precipitate ($Ca_3\overline{Ci}$) indicates
$\overline{Ci}$.</td><td>Solution may contain
$Ca_2\overline{T}$
(indicated in prelim. ex.).</td></tr>
</table>

TABLE FOR GROUP II.

<table>
<tr><td colspan="4">The precipitate may be AgCl, AgBr, AgI, AgCy, AgCsy, Ag_2 Cfy, or Ag_3 Cfdy. Add NH_4HO, and warm.</td></tr>
<tr><td colspan="2">A residue may be AgI, AgCsy, or Ag_2Cfy. Boil it with concentrated KHO and a fragment of sugar; filter, neutralize with dilute HNO_3, and divide into two parts.</td><td colspan="2">The solution may contain AgCl, AgBr, (traces of AgI,) AgCy, Ag_3Cfdy.
Add slight excess of dilute HNO_3; collect the precipitate, wash, dry, and ignite it in a porcelain crucible: the Cy compounds are thus almost entirely reduced to the metallic state. Boil the residue in dilute HNO_3.</td></tr>
<tr><td>I.
Test with HgCl. A scarlet precipitate of HgI indicates
I.</td><td>II.
Test with Fe_2Cl_3. A red colouration indicates
Csy;
a blue precipitate
Cfy.</td><td>A residue may be AgCl or AgBr. Wash; add a fragment of zinc and a drop of dilute H_2SO_4; allow to stand a quarter of an hour, filter: to the filtrate (neutralized and then concentrated) apply the starch-test. An orange colour indicates
Br;
the absence of colour indicates
Cl
(to be confirmed as usual).</td><td>The solution may contain $AgNO_3$. Add HCl. A precipitate indicates the previous existence of
Cy or
Cfdy.</td></tr>
</table>

TABLE FOR GROUP III.

The precipitate may be				The solution may contain			
Fe_2Cfy_3, which is a *blue* ppt. and indicates . . .			**Cfy.**	Fe_2Csy_3, which is a soluble *_red_ salt, and indicates . .			**Csy.**
$Fe_2\overline{Bz}_3$	,,	*buff* ,,	**$\overline{Bz}$.**	$Fe_2\overline{A}_3$	,,	*_brown red_	**$\overline{A}$.**
$Fe_3\overline{G}$	,,	*blue black*	**$\overline{G}$.**	FeCfdy	,,	*brown green*	**Cfdy.**
$Fe_3\overline{Qt}$	,,	*blue black*	**$\overline{Qt}$.**				

* These reds may be distinguished by adding HgCl; when the colour of Fe_2Csy_3 is discharged, and that of $Fe_2\overline{A}_3$ remains.

CHAPTER III.

ANALYSIS OF MIXED SALTS.

In the recognition of the various basic and acid-radicals which may be present in a mixture of salts, the plans described in the following Tables are to be adopted, with, however, such modifications as the preliminary examinations may suggest. To the methods of preliminary examination already given (see pp. 391, 404) recourse must again be had; indeed, the indications which they afford are often of extreme value in the analysis of complicated mixtures. The methods for preparing the solution of the substance to be analysed will be the same as those already described. (See pp. 392, 408.)

A few words may here be introduced concerning those combinations and mixtures of basic radicals with one another, known as alloys and amalgams. When once in solution, the manner of recognizing their constituents is identical with that adopted in the case of salts; but nitric acid, moderately concentrated, which is usually employed as the solvent for alloys, leaves many metals unacted upon and undissolved (*e. g.* platinum, gold, &c.), which require further treatment with hydrochloric or nitrohydrochloric acid. Nitric acid, moreover, partly separates tin and antimony in the form of insoluble compounds, which must then be treated according to the plan described on p. 394.

Throughout the Tables of the present and preceding chapter, the more common radicals are indicated by a conspicuous type. For the detection, &c. of the acid-radicals contained in a mixture of salts, the Tables already given may be employed (see pp. 413, 414); from these Tables, the rarer organic radicals, the reactions of which have been detailed in Chapter VII., are for the most part omitted, since they seldom occur together in the course of analysis, and generally require the employment of very special methods of separation. For these methods, reference must be made either to Chapter VII. or to a comprehensive treatise on Organic Chemistry.

The preliminary examination of the mixture of salts having been accomplished, and its results recorded, the student will then proceed to the actual analysis.

GENERAL TABLE FOR THE

<table>
<tr><td colspan="3">If HCl has been used for the solution of the substance, and no precipitate
be assumed to be absent; but if the substance has been dissolved in water
addition as long as any precipitate is produced: when the precipitate ceases,
ride of Bi or Sb, or any $HSiO_2$, which may have been thrown down. Agitate</td></tr>
<tr><td rowspan="2">The precipitate may contain
PbCl, AgCl, or Hg_2Cl;
and also by thus acidifying their alkaline solutions, the anhydride
W_2O_3
and the acids
$HSbO_3$
$H_4Sb_2O_7$
$HBoO_2$
$H\overline{Bz}$
$H_2\overline{S}$ and
$H_2\overline{U}$
may be here precipitated, since they are but slightly soluble in water or acids.
Examine according to Table for GROUP I.</td><td colspan="2">The filtrate is first freed from HNO_3 by one or two
separate Pt and the mass of the rarer allied metals,
given in Table for Group II. If extremely acid, it
suspected to contain As in the form of arsen*ic* com-
of the latter is expelled*, when a rapid stream of H_2S
pitation of Pb, As, and Mo, it is well to warm the fil-
time, with H_2S. A blue colour on the first passage of
precipitate may be only S, due to the oxidizing action
ever, a mass of S might easily mask a small but impor-
suffered to pass unexamined. Collect and wash the</td></tr>
<tr><td>The precipitate may contain
Pb_2S Sn_2S_2
Hg_2S Sb_2S_3
Bi_2S_3 Sb_2S_5
Cu_2S As_2S_3
Cd_2S As_2S_5
Pd_2S Mo_2S_3 †
Sn_2S
Examine according to Table for GROUP II.</td><td>If the filtrate is of a
previously formed, or
evaporated to dryness at
moistened with water and
separation of $HSiO_2$ as
sent, the residue should
not be interfered with.
a current of air: the only
dered insoluble in acids;
bonaceous mass is left,
well to burn the insoluble</td></tr>
</table>

TABLE FOR THE ANALYSIS OF GROUP I.

<table>
<tr><td colspan="4">The precipitates produced by the addition of HCl, and remaining undissolved in excess of that reagent, may contain
PbCl, AgCl, and Hg_2Cl; the anhydride W_2O_3; and the acids $HSbO_3$, $H_4Sb_2O_7$, $HBoO_2$, $H\overline{Bz}$, $H_2\overline{S}$, and $H_2\overline{U}$.
Boil the precipitate with several fresh portions of water, and wash it, when on the filter, with hot water.</td></tr>
<tr><td rowspan="3">The solution may contain PbCl,
$HBoO_2$, $H\overline{Be}$ and $H_2\overline{S}$.
Add dilute H_2SO_4; a white precipitate indicates the presence of
Pb.
The acids will be found in the analysis for acid-radical.</td><td colspan="3">The residue may contain
AgCl and Hg_2Cl; W_2O_3; $HSbO_3$, $H_4Sb_2O_7$, and $H_2\overline{U}$.
Warm with solution of KHO, filter and wash.</td></tr>
<tr><td rowspan="2">The solution may contain
KWO_2
$KSbO_3$
$K_2H_2Sb_2O_7$
and
$K_2\overline{U}$.
The W may be detected by the blowpipe reactions; the Sb by the H_3Sb series of experiments.</td><td colspan="2">The residue may contain AgCl and $(Hg_2)_2O$.
Warm with solution of NH_4HO.</td></tr>
<tr><td>The solution will contain
AgCl.
If a reprecipitation occurs on addition of HNO_3, it indicates
Ag.</td><td>The residue will consist of
$(Hg_2)_2O$,
the presence of which may be proved by heating the dried substance with Na_2CO_3 in a bulb-tube, and obtaining the metallic globules of
Hg.</td></tr>
</table>

EXAMINATION FOR BASIC RADICALS.

either immediate or on cooling has been the result, the first group may
or in HNO_3 or H_2SO_4, add a few drops of concentrated HCl, and repeat the
add yet a few drops more of the concentrated acid, to redissolve any oxychlo-
until the solution is clear, and then filter.

evaporations on a water-bath with HCl; it is then treated with NH_4Cl, to
and subsequently with $H_2C_2O_4$ to precipitate Au, according to the details
should then be partially neutralized with Na_2CO_3, still keeping it acid; and if
pounds, it must be saturated with SO_2 gas: it is then warmed until all excess
gas is passed through it for at least half an hour. To ensure the perfect preci-
trate from the first H_2S precipitate, and to saturate it a second, and even a third
H_2S should lead the student to look for Mo. A white or very pale yellow
of unexpelled HNO_3, of $HCrO_2$, or of ferric salts upon the H_2S. Since, how-
tant quantity of Sb_2S_3 or As_2S_3, or other bodies, no such precipitate must be
precipitate completely.

fine blue colour, special search for Ru should be made in the Pt precipitate
Mo may be looked for again in the following group. The filtrate should be now
100° C. with HNO_3; this process should be repeated, and the residue finally just
again evaporated to perfect dryness: absolute desiccation ensures the complete
Si_2O_3; it would otherwise be mistaken for $Al_2H_3O_3$. If organic matter is pre-
be more highly heated, in order that the detection of Al, Cr, Fe, Mn, &c. may
It is well to burn organic bodies off entirely, by igniting the residue strongly in
danger is, that by exposing sesquioxides to so high a temperature they are ren-
a compromise is therefore frequently effected by heating until merely a car-
which is boiled repeatedly with HCl, and the solution filtered. It would be
residue white, to ascertain whether Si_2O_3 is present.

To the HCl solution add some quantity of NH_4Cl; then almost neutralize with NH_4HO; place in a flask, and add $(NH_4)_2S$ until no more precipitate is produced: warm gently, allow to rest for some time in the corked flask, and filter, washing with water slightly impregnated with $(NH_4)_2S$.

<table>
<tr><td rowspan="2">The precipitate may contain
Zn_2S $Al_2H_3O_3$
Mn_2S $Cr_2H_3O_3$
Co_2S $Gl_2H_3O_3$ $MphH_2O$
Ni_2S $Zr_2H_3O_3$ QuH_2O
Fe_2S $Ce_2H_3O_3$ $SchH_2O$
U_2S_3 YHO
$ThHO$
$Ti_2H_2O_3$
TaH_3O_3.
Examine according to Table for GROUP III.</td><td colspan="2">If the filtrate is brown, the presence of Ni may be inferred. First acidify with HA; warm, filter, and add the new precipitate to the one previously produced. The filtrate should be evaporated to expel excess of $(NH_4)_2S$, and any precipitate of S resulting from its decomposition ascertained to be only S by its entire volatility. Solution of $(NH_4)_2CO_3$ is then added until the precipitation ceases; the liquid warmed (not boiled, lest the precipitate should redissolve in the NH_4Cl) and filtered.</td></tr>
<tr><td>The precipitate may contain
Ba_2CO_3
Sr_2CO_3
Ca_2CO_3.
Examine according to Table for GROUP IV.</td><td>The filtrate, containing NH_4, Mg, K, and Na, is examined according to Table for GROUP V.</td></tr>
</table>

---

* Certain sulphates, as those of Ba, Sr, and Ca, may be precipitated here, the SO_2 being converted into H_2SO_4. If insoluble in acids, such precipitate must be examined by fusion.

† Mo is not perfectly precipitated unless H_2S is passed into its alkaline solution, which is afterwards acidified.

TABLE FOR THE

<table>
<tr><td colspan="3">The filtrate from Group I. may contain all other basic Pb, Hg, Bi, Cu, Cd, Pd, Sn, Sb, As, It must be freed from HNO_3: this may be done by evaporating with slight To the HCl solution, which should be concentrated if it has been rendered too agitated, and allowed to rest for some hours.</td></tr>
<tr><td rowspan="2">A yellow crystalline precipitate of $KPtCl_3$ indicates **Pt.** The largest part of the rare metals R, Ru, Ir, and also some PdCl, would separate here in the same form.</td><td colspan="2">The filtrate should be mixed with a reasonable quantity of</td></tr>
<tr><td>A precipitate consisting of yellow spangles, or of a brown yellow sponge, indicates **Au.**</td><td>Through the filtrate a current of second and even a third stream of thoroughly washed with hot water S; the undissolved portion must be</td></tr>
</table>

<table>
<tr><td colspan="6">The residue may contain Hg_2S, Pb_2S, Bi_2S_3, Cu_2S, Cd_2S, and Pd_2S: it must be washed until quite free from Cl, then boiled in concentrated HNO_3 until all red fumes cease. The liquor is diluted with H_2O, the residue allowed to settle, and dilute H_2SO_4 added until precipitation is complete; it is then agitated and filtered.</td></tr>
<tr><td colspan="2">The residue and precipitate may contain Hg_2S and Pb_2SO_4. Divide it into two portions.</td><td colspan="4" rowspan="2">The filtrate may contain Bi, Cu, Cd, and Pd. Add some quantity of solution of KCl; evaporate to dryness on a water-bath, adding a little nitrohydrochloric acid towards the end of the operation. Redissolve in a solution of KCl, adding one drop of HCl; filter and wash with KCl.</td></tr>
<tr><td rowspan="4">I.
Boil in HCl; add one or two drops of HNO_3, and continue to boil. Drop in a bright fragment of copper foil. A silvery film on the foil indicates **Hg.**</td><td rowspan="4">II.
Ignite on a fragment of porcelain. A white non-volatile residue of Pb_2SO_4 indicates **Pb.**</td></tr>
<tr><td rowspan="3">A reddish yellow crystalline precipitate of $KPdCl_3$ indicates **Pd.**</td><td colspan="3">To the filtrate add excess of NH_4HO.</td></tr>
<tr><td rowspan="2">A white precipitate of BiH_3O_3 indicates **Bi.** Confirm by the oxychloride test (see p. 182).</td><td colspan="2">The filtrate may contain Cu and Cd. Acidify with HCl, and saturate with H_2S; filter and wash the precipitate with H_2O impregnated with H_2S. Boil the precipitate with dilute H_2SO_4, and filter quickly.</td></tr>
<tr><td>To the solution add excess of H_2S. A yellow precipitate indicates **Cd.**</td><td>The precipitate is Cu_2S. Dissolve, and confirm by the NH_4HO and K_2Cfy tests for **Cu.**</td></tr>
</table>

ANALYSIS OF GROUP II.

radicals; in the present Group we separate the following:—
Pt, R, Ru, Ir, Os*, Au, and Mo.
excess of HCl once or twice; in so doing, any Os would escape as osmic anhydride*.
dilute, a reasonable quantity of NH_4Cl solution should be added, the liquid well

concentrated solution of $H_2C_2O_4$, and moderately heated for some hours.

H_2S should now be passed for a considerable time, the liquid warmed, and a H_2S passed to ensure perfect precipitation. The precipitate must be collected, containing a little H_2S, then boiled for a few minutes with $(NH_4)_2S$ containing filtered off.

The filtrate may contain
Sn, As, and Sb, combined with S,
in the form of acid-radicals. Reprecipitate them as sulphides by acidulating with HCl; and, to prevent the HCl from decomposing a portion and dissolving it as chloride, pass a few bubbles of H_2S through the solution. Collect and wash the precipitate; boil it in HCl, and add, when boiling, a very little HNO_3, drop by drop, until it is dissolved. Introduce the solution into an apparatus from which H is being evolved by the action of H_2SO_4 upon Zn, both of these reagents having been ascertained to be free from As; pass the evolved gases through a wash-bottle containing solution of $Pb\bar{A}$, and thence into a test-tube containing a somewhat strong solution of $AgNO_3$, continuing the passage as long as any precipitate is produced in the $AgNO_3$ solution. When the action has ceased, a black residue will be found upon the surface of the Zn in the generator †.

<table>
<tr><td rowspan="3">The black residue consists partly of Pb and other impurities in the Zn; but it also contains the Sn and part of the Sb. It must be collected, boiled with HCl, filtered, diluted with H_2O, and tested with a few drops of HgCl, when the formation of a white or grey precipitate indicates
Sn.</td><td colspan="3">The solution of $AgNO_3$ is filtered, in order to collect the suspended precipitate.</td></tr>
<tr><td rowspan="2">The filtrate may contain
As
as $Ag_4As_2O_5$ dissolved in excess of HNO_3. Exactly neutralize with NH_4HO, when a yellow precipitate indicates
As.</td><td colspan="2">The precipitate may be Ag only, or Ag_3Sb.
Boil with $H_2\bar{T}$ and filter.</td></tr>
<tr><td>the residue will be Ag.</td><td>The filtrate may contain
Sb.
Acidify with HNO_3 and pass H_2S, when an orange precipitate indicates
Sb.</td></tr>
</table>

---

* The separation of these four metals is most difficult: the process will be described in an Appendix to the present Table.

† This process was, we believe, originated by Dr. Hofmann, and is employed by him in the Royal College of Chemistry.

TABLE FOR THE

The precipitate produced by $(NH_4)_2S$ in the
Zn_2S, Mn_2S, Fe_2S, Co_2S, Ni_2S, U_4S_3; $Cr_2H_3O_3$, $Al_2H_3O_3$,
together with certain phosphates of this group, and certain
Boil the precipitate with HCl, and add a few drops of HNO_3, drop by drop,
excess of KHO solution;

The solution may contain Zn, Cr, Al, Ta, and G. It is divided into two portions.

I. is acidified with $H_2C_2O_4$, and infusion of galls added, when an orange colour or precipitate indicates the presence of **Ta.**

II. is boiled for some time.

A green precipitate indicates the presence of **Cr.** This may contain Fe, for which it must be examined.

The solution may be acidified with HCl, then rendered alkaline with NH_4HO, and the precipitate digested with $(NH_4)_2CO_3$.

The undissolved residue is $Al_2H_3O_3$, or Al_2PO_4, and indicates **Al.** To ascertain whether the phosphoric radical is present, dissolve the precipitate in $H_2\bar{T}$, add NH_4HO in excess, then add NH_4Cl and Mg_2SO_4, when the formation of a white crystalline precipitate would indicate the presence of **PO_4.**

The solution will contain the **G**, which, if it is boiled, will be precipitated as $G_2H_3O_3$.

Fe, Mn, and Y, and
Dissolve in a few
solution, previously

The precipitate would contain the Fe as hydrate; also Mn, Y, Ba, Sr, Ca, and Mg as carbonates. Dissolve in HCl, avoiding any excess, warm, and add $(NH_4)_2S$; filter.

The filtrate will contain the Ba, Sr, Ca, and Mg, and must be examined according to the two succeeding Tables.

The precipitate will contain the Fe, Mn, and Y. Dissolve in HCl, with the cautious addition of a few drops of HNO_3; add excess of $K\bar{A}$, and boil until all the Fe is precipitated.

The precipitate consists of **Fe** as basic acetate. This precipitate should be examined for Cr.

The solution contains the Mn and Y. Add NH_4Cl and excess of NH_4HO; filter off any YHO which may precipitate, and add to the filtrate a few drops of Br. Allow to rest for twenty-four hours.

The brown precipitate contains the **Mn.**

The solution contains any dissolved **Y**, which may be precipitated as oxalate.

ANALYSIS OF GROUP III.

filtrate from the H_2S precipitate may contain
TaH_3O_3, $Ti_2H_2O_3$, $G_2H_3O_3$, $Zr_2H_3O_3$,, $Ce_2H_3O_3$, LaHO, DiHO, ThHO, YHO,
phosphates, borates, and fluorides of Ba, Sr, Ca, and Mg.
to the boiling liquid; filter from any residue of S. Add to the cooled solution
filter, and wash with cold water.

The precipitate may contain
Mn, Fe, Co, Ni, U, Ti, Zr, Ce, La, Di, Y, and Th, together with the phosphates, borates, and fluorides.
First dissolve in HCl, avoiding excess, and boil the solution for some time; filter.

A white precipitate of Ti_2O_2 indicates the presence of **Ti.**

To the filtrate, some quantity of a saturated solution of K_2SO_4 is added, the liquid allowed to rest for some hours, filtered, and the precipitate washed with cold saturated solution of K_2SO_4.

The formation of a white, yellow, or red crystalline precipitate of double sulphate would indicate the presence of

Zr, Ce, La, Di, and Th.

As all these rare bodies are never known to occur together, their separation is not a matter of practical importance.

The solution is boiled with a few drops of HNO_3, slight excess of NH_4HO added, and then a warm and concentrated solution of $(NH_4)_2CO_3$, with which the precipitate formed is digested at a moderate heat for some time. It is then filtered rapidly while hot, and the digestion with $(NH_4)_2CO_3$ repeated.

The precipitate will contain the
also the phosphates, borates, and fluorides.
drops of HCl, and drop into boiling KHO
mixed with a little Na_2Co_3.

The solution should be examined for phosphoric, boracic, and hydrofluoric acids, by the appropriate tests.

The filtrate will contain the
U, Ni, and Co,
and, if concentrated, will, on cooling, deposit fine lemon-yellow crystals of
$(U_2O)_2CO_3$, $(NH_4)_2CO_3$,
which may be separated. Add some NH_4Cl solution, and boil for some time.

The precipitate will consist of $(U_2O)_2O$. Test by means of the blowpipe for **U.**

To the filtrate add Na_2CO_3, and boil until all odour of NH_3 has ceased, then almost neutralize the Na_2CO_3 with HCl. Add now, gradually, such a quantity of a weak solution of KCy as shall be exactly sufficient to redissolve the precipitate at first produced by it. Boil until HCy ceases to be evolved; filter, if necessary, and, when cold, add some excess of a strong solution of NaClO*. If no black precipitate or colour appears after the lapse of ten minutes, add a drop of HCl to facilitate its formation. Warm and filter.

The precipitate will consist of $(Ni_2)_2O_3$. Test by means of the blowpipe for **Ni.**	The filtrate will contain the Co. Evaporate to dryness, and test by means of the blowpipe for **Co.**

---

* This mode of separation was, we believe, first practised by Dr. Hofmann.

TABLE FOR THE ANALYSIS OF GROUP IV.

<table>
<tr><td colspan="4">The filtrate from the $(NH_4)_2S$ precipitate freed from $(NH_4)_2S$ by boiling and filtration, having been mixed with $(NH_4)_2CO_3$ and warmed in the presence of NH_4Cl, may have yielded a precipitate consisting of the carbonates of Ba, Sr, and Ca.
The precipitate is dissolved in a few drops of HCl and divided into two portions.</td></tr>
<tr><td colspan="2">I.
is mixed with some quantity of $H_3Si_2F_9$, and evaporated to dryness. The mass is then treated with EHO.</td><td colspan="2">II.
is mixed with some quantity of solution of K_2SO_4, evaporated to dryness, and the mass boiled with water and filtered.</td></tr>
<tr><td>A residue consists of $Ba_3Si_2F_9$, and indicates
Ba.</td><td>The filtrate is again mixed with $H_3Si_2F_9$, and again evaporated to dryness to ensure the complete separation of Ba. The solution in EHO is repeated, the liquid evaporated to dryness, and the residue dissolved in water and tested with solution of Ca_2SO_4, when a white precipitate indicates
Sr.</td><td>The residue consists of Ba_2SO_4 and Sr_2SO_4.</td><td>To the filtrate, excess of NH_4HO is added, and a few drops of $(NH_4)_2\bar{O}$, when a white precipitate indicates
Ca.</td></tr>
</table>

TABLE FOR THE ANALYSIS OF GROUP V.

<table>
<tr><td colspan="2">The filtrate from Group IV., or the solution in which the various group-reagents have failed to produce any precipitate, may contain NH_4, Mg, K, and Na. Evaporate and ignite to expel NH_4 salts, which will have been already detected in the preliminary examination; mix the residue with mercuric oxide (Hg_2O) in excess, and a drop of water; ignite, extract with boiling water, and filter whilst hot.</td></tr>
<tr><td>A residue will consist of MgHO, and indicates the presence of
Mg.</td><td>Evaporate the filtrate to dryness, test one portion of the residue before the blowpipe for
Na;
dissolve the remainder in dilute HCl, and add $HPtCl_3$. A yellow crystalline precipitate of $KPtCl_3$ indicates
K.</td></tr>
</table>

APPENDIX TO TABLE FOR THE ANALYSIS OF GROUP II.,

Exhibiting the general outline of the method of dealing with the metals Pd, Ir, R, Ru, and Os, which, together with some Fe and Cu, are found in platinum ore.

The mineral is dissolved in a retort by means of a mixture of 5 parts of the most concentrated HCl with 1 part of fuming HNO_3, and the acid which distils over as the liquid boils, collected in a receiver; the distillate is returned and redistilled.

The distillate will contain the Os as Os_2O_4. Saturate with solution of KHO; add EHO, and warm gently, when a fine red crystalline precipitate forms, which is $KOsO_2$.

The syrupy residue in the retort is then filtered off from certain dark steel-coloured grains, which are not acted upon by the acid.

The insoluble grains are called Osm-iridium, and contain Os, Ir, and Ru. These are powdered in a steel mortar, and fused with a mixture of equal parts of KHO and $KClO_3$. The mass is treated with water.

The solution contains KOsO and KRuO, from which the Os may be separated by distillation with nitrohydrochloric acid.

The residue consists of Ir_2O_3 and grains unattacked, which must be again fused.

The concentrated filtrate is mixed with about twice its bulk of EHO, and then with a warm solution of KCl until no more precipitate is formed. It should be allowed to rest for some time, filtered, and washed with weak EHO containing KCl.

The yellow or red crystalline precipitate consists of $KPtCl_3$ and $KIrCl_3$, with traces of $K_2R_2Cl_5$ and $KPdCl_3$. It is gently heated with an equal weight of Na_2CO_3 in a porcelain crucible until the mass becomes quite black. It is then boiled with water acidified with HCl, and the residual black powder of Pt and Ir_2O washed. It is then digested with dilute nitrohydrochloric acid, in order to extract part of the Pt; and this solution being preserved, the insoluble residue of Pt (yet undissolved) and Ir_2O is mixed with NaCl and concentrated nitrohydrochloric acid, and evaporated to dryness. Water is then added, to dissolve the $PtCl_2$, and the solution filtered, the filter being washed with NaCl solution, and finally with NH_4Cl, to prevent the Ir_2O passing through the pores of the paper.

The residue consists of Ir_2O_3, which may be reduced to metal by heating in a current of H.

The solution contains $NaPtCl_3$ and some Ir, which may be separated by a repetition of the ignition with Na_2CO_3, &c. &c.

The solution contains the R, Pd, and some Ir, together with the Fe and Cu. It is evaporated to dryness, the mass digested with concentrated nitrohydrochloric acid, KCl added, and the evaporation repeated. The mass is then washed with alcohol.

The solution will contain Fe_2Cl_3 and CuCl.

The residue, consisting of $K_2R_3Cl_5$, $KPdCl_3$, and $KIrCl_3$, is fused with $K_2Cr_4O_7$, and the mass boiled with H_2O.

The residue contains a portion of Ir_2O_3.

The solution is acidified with HCl, and a piece of pure Zn introduced. The black precipitate is washed and treated with HNO_3.

The solution contains the Pd.

The residue consists of the R.

The examination for acid-radicals is to be conducted in accordance with the plans given on pp. 413, 414.

Suitable mixtures for analysis may easily be made. For instance, at first two salts should be taken containing a common acid-radical and different basic radicals belonging to different groups; then a mixture may be made, the basic constituents of which are four in number, two belonging to one group, and two to another. The student should then exercise himself in effecting the more difficult and delicate methods of separation, gradually increasing the number and variety of the basic and acid-radicals to be detected. Trials should also be made with mixtures of soluble and insoluble salts, with alloys, with salts incapable of remaining dissolved in the same solution, and with some of the substances met with in commerce or in common life.

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