Notes on qualitative analysis: concise and explanatory / by H.J.H. Fenton.

Contributors

Fenton, Henry John Horstman, 1854-1929.

Publication/Creation

Cambridge [England]: University Press, 1883.

Persistent URL

https://wellcomecollection.org/works/ydz5y2f3

License and attribution

This work has been identified as being free of known restrictions under copyright law, including all related and neighbouring rights and is being made available under the Creative Commons, Public Domain Mark.

You can copy, modify, distribute and perform the work, even for commercial purposes, without asking permission.



Norws

QUALITATIVE ANALYSIS

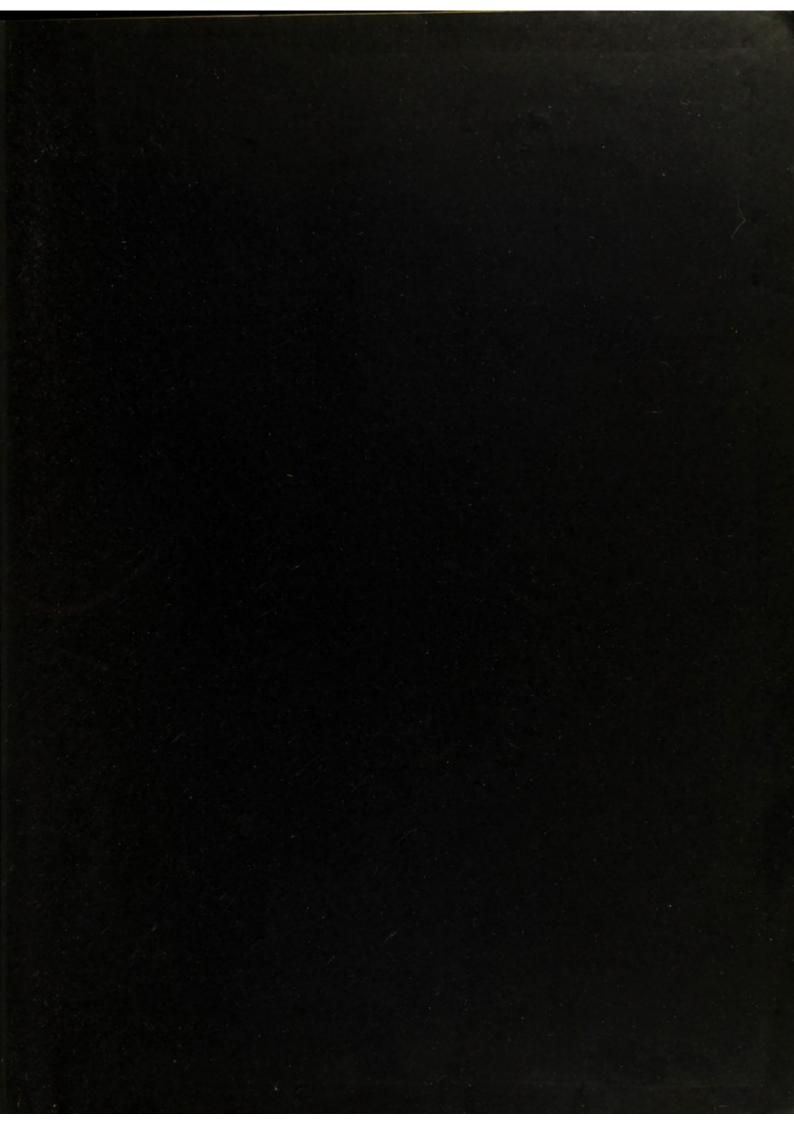
* N T D N

K821

Med K821



22102071547



N.VII.e

P. D. Saint.

January. 29°1903

NOTES ON QUALITATIVE ANALYSIS

CONCISE AND EXPLANATORY.

Mondon: C. J. CLAY AND SONS,
CAMBRIDGE UNIVERSITY PRESS WAREHOUSE,
AVE MARIA LANE.

Slasgow: 50, WELLINGTON STREET.



Leipzig: F. A. BROCKHAUS. Dew York: THE MACMILLAN COMPANY. Bombay and Calcutta: MACMILLAN AND CO., Ltd.

NOTES ON

QUALITATIVE ANALYSIS

CONCISE AND EXPLANATORY

BY

H. J. H. FENTON, M.A., F.I.C., F.C.S.,

DEMONSTRATOR OF CHEMISTRY IN THE UNIVERSITY OF CAMBRIDGE;
LATE SCHOLAR OF CHRIST'S COLLEGE.

STEREOTYPED EDITION.

CAMBRIDGE AT THE UNIVERSITY PRESS

1902

3 511 444

First Edition 1883.
Reprinted 1886, 1888, 1890, 1892, 1894, 1895.
1899, 1902.

WELLCOME INSTITUTE LIBRARY

Coll. welMOmec

Call

No.

PREFACE TO THE THIRD EDITION.

In revising the present edition, a few minor corrections and alterations have been made in matters of detail, and some additional foot-notes added. Beyond these I have not considered it necessary or advisable to make any material change in the scope or arrangement of the book.

H. J. H. F.

January, 1888.

PREFACE TO THE FIRST EDITION.

THE principal object of the present work, while setting forth the usual methods of Qualitative Analysis in their most concise form, is to direct, and if possible to enforce, attention to the rationale of each operation performed, and the nature of each reaction which takes place.

It is hoped that the system adopted will tend to some extent to check the prevailing tendency, common even among more advanced students, to regard Chemical Analysis as a mere routine of mechanical operations, and entirely to overlook its scientific aspect.

It has been my endeavour in drawing up the Analytical Tables, with their Explanations, to render each one comprehensive, avoiding as far as possible the necessity of reference to remote sections or pages.

The scheme of analysis recommended is in substance the same as that given in the standard text-books, but considerable changes have been introduced in many important matters of detail, and in arrangement, such as experience has shewn to be advantageous. The reactions of some of the more important Organic Substances have been stated in a short form, to meet the requirements of commencing Medical Students.

I am greatly indebted to my friend W. J. Sell, M.A., for his kindness in revising the proof-sheets, and in making some useful suggestions.

H. J. H. F.

April, 1883.

PREFACE TO THE SECOND EDITION.

But few alterations or additions have been made in the present edition of these Notes. They have been exhaustively tested in the hands of many hundreds of students of various classes, and have been found satisfactorily to fulfil the objects with which they were written. It has been suggested that the detection and reactions of the "rare" elements should be included; but such would be quite without the scope or intention of the work. It appears to me that in the so-called "common" elements we have ample material—if not too much—wherewith to set forth the principles of Qualitative Analysis on a scientific basis.

Much has been written and said of late calling in question the utility of Qualitative Analysis as a method of scientific training. If the object be solely the identification of unknown substances, and the directions for so doing consist merely of a sequence of bare recipes—like those in a cookery book—it is probable that it has but little value in this respect. But if, while keeping the analytical object ostensibly in view, the processes be employed as means of bringing the student face to face with, and fixing his attention on, various important types and characters of chemical change, Qualitative Analysis becomes a most useful aid in the scientific teaching of Chemistry. The operations are, for the most part, easily performed and successful even in the hands of a beginner. It is of course admitted that these desirable objects may be more directly attained by a series of specially devised experiments, but such are, as a rule, without the reach of the average teacher and student.

CONTENTS.

	PAGE			P	AGE
		Ammonium			21
PRINCIPAL REACTIONS OF THE MORE COM-		Potassium			22
MON METALS	1	Sodium			22
Silver	1				
Lead	2	PRINCIPAL REACTIONS OF THE MO.	RE Co	M-	
Mercury. General Reactions	3	MON ACID RADICLES .			23
" Mercurous Salts	3	Sulphates			23
" Mercuric Salts	4	Sulphites			24
Copper. Cupric Salts	4	Thiosulphates. Formerly called			
,, Cuprous Salts	. 5	sulphites			24
Cadmium	. 5	Sulphides			25
Bismuth	6	Silicofluorides			26
Arsenic. General Reactions	. 6	Fluorides			26
" Arsenious Compounds	7	Oxalates			27
" Arsenic Compounds	. 7	Phosphates, Orthophosphates		200	27
Antimony, General Reactions	. 8	" Metaphosphates			28
,, Antimonious Compounds.		" Pyrophosphates			28
,, Antimonic Compounds .		Arsenates			29
Tin. General Reactions	. 9	Borates		1/25	29
" Stannous Salts	. 9	Silicates			29
" Stannic Salts	. 10	Carbonates	202		30
Iron. Ferrous Salts	11	Tartrates		1000	30
Ferric Salts	. 11	Citrates			31
Chromium	12	Chlorides			32
Chromic Salts	. 12	Hypochlorites			32
CI .	13	Chlorates			33
Aluminium	. 13	Iodides			33
701	. 14	Iodates			34
	. 14	Bromides			34
35 (1.1)	. 15	Bromates			35
Mangania Salta	. 15	Consider			35
,, Manganates and Perman		Cyanates			36
ganates	. 16	Ferrocyanides			36
Nickel	. 17	Ferricyanides			37
Cobalt	. 18	Sulphocyanates			37
D	. 19	Nitrates			38
Calcium	. 20	Nitrites			38
Strontium	. 20	Acetates			39
Magnesium	91	Formatas			40

CONTENTS.

	PAGE		PAGE
Analytical Tables	41	REACTIONS OF SOME OF THE MORE COMMON	
Preliminary Examination of Solid in		Organic Bodies	77
the Dry Way		Methyl Alcohol. Wood Spirit	77
To Dissolve a Substance for Analysis .		Ethyl Alcohol. Alcohol. Spirits of	
Examination for One Metal	44	Wine	77
General Table for Mixtures of Metals .	46	Ethyl Ether	78
Explanation of General Table	47	Acetaldehyde. Aldehyde. Ethaldehyde	78
Table I. Ag, Pb, Hg'	49	Chloral. Trichlor-acetaldehyde	79
Table II. A. Hg", Pb, Bi, Cu, Cd .		Chloroform. Trichloromethane	79
Explanation of Table II. A	51	Glycerin	80
Table II. B. Method 1. As, Sn, Sb .		Fats	
Explanation of Table II. B, Method 1 .	53	Soaps	
Table II. B. Method 2. As, Sn, Sb .	54	Carbohydrates. I. Saccharons	
Explanation of Table II. B, Method 2.	55	" II. Glucoses	82
Table III. Fe, Cr, Al, &c	56	" III. Carbohydrates of	
Explanation of Table III	57	the composition (C ₆ H ₁₀ O ₅),	83
Table IV. Ni, Co, Zn, Mn	60	Lactic Acids	84
Explanation of Table IV	61	Urea	85
Table V. Ba, Sr, Ca	64	Uric Acid	
Explanation of Table V	65	Strychnine. Strychnia	86
Table VI. Mg, K, Na, NH,	66	Quinine. Quinia	86
Explanation of Table VI	67	Morphine. Morphia	87
Preliminary Examination for Acid Ra-		Brucine. Brucia	87
dicles	68	Benzene. Benzol	88
Explanation of Preliminary Acid Table	70	Phenol. Carbolic Acid. Phenic Acid.	
Examination for Acid Radicles. Pre-		Aniline. Phenylamine	89
paration of Solution	71	Salicylic Acid. Orthoxybenzoic Acid.	89
Examination for One Acid Radicle .		Benzoic Acid	90
Detection of More than One Acid		Hippuric Acid. Benzamidacetic Acid.	
Radicle		Succinic Acid	
Examination for Acid Radicles. Expla-		Proteids	91
nation	. 76	Gelatin or Glutin	92

PRINCIPAL REACTIONS OF THE MORE COMMON METALS.

SILVER.

Solutions of silver salts (e.g. AgNO,) give with

Hydrochloric acid, white ppt. of silver chloride soluble in NH_s , insoluble in HNO_s , $AgNO_s + HCl = AgCl + HNO_s$.

This precipitate is turned violet on exposure to sunlight.

Potassium chromate, crimson ppt. of silver chromate, soluble in HNO₅, $2 \text{AgNO}_3 + \text{K}_2 \text{CrO}_4 = \text{Ag}_2 \text{CrO}_4 + 2 \text{KNO}_3.$

Caustic potash, brown ppt. of silver oxide Ag2O, soluble in NH3 and in acids.

Potassium iodide, yellow ppt. of silver iodide Agl, insoluble in NH3 and in dil. HNO3.

Potassium Cyanide, white ppt. of silver cyanide AgCy, soluble in NH3 and in excess of KCy, insoluble in dil. HNO3.

Sodium phosphate, yellow ppt. of silver phosphate Ag₃PO₄, soluble in NH₃ and in acids.

Hydrosulphuric acid, black ppt. of silver sulphide Ag2S, soluble in hot HNO3

Heated on charcoal, before the blow-pipe, with Na₂CO₂, solid silver compounds give brilliant white metallic mass or globules.

LEAD.

Solutions of lead salts, e.g. Pb(NO3)2, give with

Hydrochloric acid, white ppt. of lead chloride, soluble in boiling water, insoluble in ammonia,

Hydrosulphuric acid, black ppt. of lead sulphide*,

$$Pb(NO_s)_s + H_sS = PbS + 2HNO_s$$
.

This ppt. dissolves in hot dilute HNO, forming lead nitrate. Strong nitric acid converts it chiefly into white insoluble lead sulphate.

Dilute sulphuric acid, white ppt. of lead sulphate, soluble in strong solution of ammonium acetate,

$$\mathrm{Pb}(\mathrm{NO_3})_2 + \mathrm{H_2SO_4} = \mathrm{PbSO_4} + 2\mathrm{HNO_3}.$$

Potassium chromate, yellow ppt. of lead chromate, insoluble in acetic acid, soluble in KHO,

Potassium iodide, yellow ppt. of lead iodide Pbl₂.

Caustic potash, white ppt. of hydrated lead oxide 2PbO . H₂O, soluble in excess.

Ammonia, white ppt. of basic salt, insoluble in excess.

Solid lead compounds heated on charcoal before the blow-pipe give yellow or orange incrustation, and, in the reducing flame, with Na₂CO₃, metallic beads which are malleable.

If much HCl is present the ppt. is often dark red and consists of PbS. PbCl₂.

MERCURY.

General Reactions.

Solutions of mercury compounds heated with metallic copper and dilute hydrochloric acid (free nitric acid must be absent) give a bright deposit of metallic mercury on the copper. On heating the two metals in a dry narrow test-tube, the mercury sublimes, forming a grey ring which may be united into globules by rubbing with a glass rod.

Solid mercury compounds heated on charcoal volatilize entirely. Heated in a bulb-tube with dry Na₂CO₂ a ring of metallic mercury is obtained.

Mercurous Salts.

Solutions of mercurous salts, e.g. $Hg'_{g}(NO_{g})_{g}$, give with $Hydrochloric\ acid$, white ppt. of mercurous chloride, $Hg_{g}(NO_{g})_{g} + 2HCl = Hg_{g}Cl_{g} + 2HNO_{g}$.

This ppt. is blackened by ammonia, owing to the formation of dimercurous-ammonium chloride—

 $\begin{aligned} \mathbf{Hg_2Cl_2} + 2\mathbf{NH_3} &= (\mathbf{NHg'_2H_2})\mathbf{Cl} + \mathbf{NH_4Cl}. \\ Caustic \ potash, \ black \ ppt. \ of \ mercurous \ oxide, \ insoluble \ in \ \mathbf{NH_3}, \\ \mathbf{Hg_2(NO_3)_2} + 2\mathbf{KHO} &= \mathbf{Hg_2O} + 2\mathbf{KNO_3} + \mathbf{H_2O}. \end{aligned}$

Ammonia, black ppt. of a basic mercurous salt.

Potassium iodide, greenish-yellow ppt. of mercurous iodide Hg₂l₂.

Hydrosulphuric acid, black ppt. of mercurous sulphide Hg₂S (perhaps a mixture of HgS+Hg).

Stannous chloride, ferrous sulphate, or sulphurous acid, grey ppt. of metallic mercury.

Potassium chromate, orange ppt. of basic mercurous chromate Hg₂CrO₄. Hg₂O.

Mercuric Salts.

Solutions of mercuric salts (e.g. Hg"Cl,) give with

Hydrosulphuric acid, black ppt. of mercuric sulphide,

$$HgCl_{\bullet} + H_{\bullet}S = HgS + 2HCl.$$

This ppt. is insoluble in ammonium sulphide and in dilute HNO₃. Strong HNO₃ converts it into a white mixture of 2HgS and Hg(NO₃)₂.

Caustic potash, yellow ppt. of mercuric oxide,

$$HgCl_{\bullet} + 2KHO = HgO + 2KCl + H_{\bullet}O.$$

Potassium iodide, red ppt. of mercuric iodide Hgl₂, soluble in excess, forming the double iodide (Hgl₂.2Kl). Ammonia, white ppt. of mercuric-ammonium chloride (NHg"H₂)Cl.

Stannous chloride, first a white ppt. of mercurous chloride, which is afterwards further reduced to metallic mercury, if sufficient SnCl₂ is present.

COPPER.

Cupric Salts (usually green or blue).

Solutions of cupric salts (e.g. CuSO4) give with

Hydrosulphuric acid, black ppt. of cupric sulphide,

$$CuSO_4 + H_sS = CuS + H_sSO_4$$
.

This ppt. is nearly insoluble in ammonium sulphide. Soluble in hot dilute HNO₃, forming cupric nitrate Cu(NO₃)₂. Insoluble in dilute H₂SO₄. [The precipitation by H₂S is prevented by the presence of potassium cyanide owing to the formation of a double cyanide Cu₂Cy₂. 2KCy.]

Potassium ferrocyanide, chocolate ppt. of cupric ferrocyanide,

$$2\mathrm{CuSO_4} + \mathrm{K_4}(\mathrm{FeCy_6}) = \mathrm{Cu_2}(\mathrm{FeCy_6}) + 2\mathrm{K_2SO_4}.$$

Ammonia, pale greenish-blue ppt. of a basic cupric sulphate (such as CuSO₄. 2Cu(OH)₂), readily soluble in excess of NH₃, forming a dark blue solution. This solution contains a compound having the composition (CuSO₄ + 4NH₃ + H₂O) or {(N₂H₆Cu)O + (NH₄)₂SO₄}.

Caustic potash, pale blue ppt. of cupric hydroxide Cu(OH)₂, which turns black on boiling, CuO being formed.

Potassium iodide, dirty white ppt. of cuprous iodide Cu₂l₂, free iodine being liberated.

Potassium cyanide, brownish-yellow or olive-green ppt. of cupric cyanide Cu"Cy2, which rapidly loses cyanogen, becoming (2Cu"Cy2. Cu'2Cy2) or Cu'2Cy2.

These cyanides dissolve in excess of KCy, forming double cyanides CuCy2. 2KCy and Cu2Cy2. 2KCy respectively.

Many reducing agents such as glucose, aldehyde, &c. in presence of caustic potash, precipitate red cuprous oxide Cu₂O, on heating.

Cuprous Salts (usually white, and insoluble in water).

Solutions of cuprous salts (e.g. Cu, Cl, dissolved in HCl) give with

Caustic potash, yellow ppt. of cuprous hydroxide Cu, (OH).

Potassium iodide, white ppt. of cuprous iodide without separation of iodine, $Cu_{s}Cl_{s} + 2Kl = Cu_{s}l_{s} + 2KCl.$

Water gives a white ppt. of Cu2Cl2, this being soluble only in strong HCl.

Solid copper compounds heated with Na₂CO₃ on charcoal before the blow-pipe give red globules or spangles of metallic copper.

Borax bead, in oxidizing flame, green when hot, blue when cold.

CADMIUM.

Solutions of cadmium salts (e.g. CdCl.) give with

Hydrosulphuric acid, bright yellow ppt. of cadmium sulphide,

$$CdCl_g + H_gS = CdS + 2HCl.$$

This ppt. is insoluble in ammonium sulphide and in potassium cyanide. Soluble in hot dilute HNO₃ forming cadmium nitrate Cd(NO₃)₂. Soluble in dilute H₂SO₄.

Caustic potash, white ppt. of cadmium hydroxide, insoluble in excess,

$$CdCl_{2} + 2KOH = Cd(OH)_{2} + 2KCl.$$

Potassium cyanide, white ppt. of cadmium cyanide,

$$CdCl_{g} + 2KCy = CdCy_{g} + 2KCl.$$

This ppt. dissolves in excess forming CdCy₂. 2KCy from which solution H₂S precipitates cadmium sulphide.

Ammonia gives same ppt. as caustic potash (from a sufficiently strong solution) easily soluble in excess.

Solid cadmium compounds heated on charcoal in the reducing flame with Na₂CO₃ give a brown incrustation.

BISMUTH.

Solutions of bismuth salts (e.g. Bi(NO₃)₃), give with

Hydrosulphuric acid, blackish-brown ppt. of bismuth sulphide,

$$2\mathrm{Bi}(\mathrm{NO_s})_s + 3\mathrm{H_sS} = \mathrm{Bi_sS_s} + 6\mathrm{HNO_s}$$
.

This ppt. is insoluble in ammonium sulphide. Soluble in hot dilute HNO, forming bismuth nitrate Bi(NO,).

Ammonia, white ppt. of bismuth hydroxide,

$$Bi(NO_s)_a + 3NH_a + 3H_2O = Bi(OH)_a + 3NH_4NO_a$$
.

This ppt. dissolves in HCl, forming bismuth chloride BiCl₃. Much water added to the solution precipitates white bismuth oxychloride Bi₂O₃. BiCl₃,

$$3BiCl_a + 3H_aO = Bi_aO_a$$
. $BiCl_a + 6HCl$.

Bismuth oxychloride dissolves in hydrochloric but not in tartaric acid.

Stannous chloride + caustic potash, black ppt. of bismuth dioxide Bi2O2.

Potassium chromate, yellow ppt. of basic bismuth chromate 3Bi₂O₃. 2CrO₃, insoluble in KHO, soluble in dilute HNO₃.

Potassium iodide, brown ppt. of bismuth iodide BiI3, soluble in excess. Caustic potash, white ppt. of bismuth hydroxide Bi(OH)3.

ARSENIC.

General Reactions.

Compounds of arsenic in solution acidified with HCl (free HNO₃ should be absent) and introduced into a vessel in which bydrogen is being generated (e.g. by the action of Zn+dil. H₂SO₄), give-off arseniuretted hydrogen AsH₃, which burns with a bluish-white flame. If a piece of cold porcelain be held in the flame, a black stain of metallic arsenic is deposited on it. This stain dissolves at once in sodium hypochlorite. [Marsh's test.]

[AsH₃ is also slowly evolved if Zn and KOH (strong sol.) are used instead of Zn and H₂SO₄.]

If arseniuretted hydrogen be passed into a solution of silver nitrate, it is decomposed as follows:

$$\label{eq:asH_3} AsH_{\mathfrak{g}} + 6AgNO_{\mathfrak{g}} + 3H_{\mathfrak{g}}O = 6Ag + H_{\mathfrak{g}}AsO_{\mathfrak{g}} + 6HNO_{\mathfrak{g}}.$$
 black ppt.

On carefully neutralizing the clear liquid with ammonia (and adding a drop more AgNO₃, if necessary), a yellow ppt. of silver arsenite is obtained (see below).

Solid arsenic compounds heated on charcoal with Na₂CO₃ (or KCy) in the reducing flame give a characteristic (poisonous) odour of garlic.

Heated in a bulb-tube with Na₂CO₃ and charcoal, a black ring of metallic arsenic is obtained. This ring when heated in a dry test-tube gives a crystalline sublimate of arsenic trioxide As₂O₃.

Arsenious Compounds.

Solutions of arsenious compounds (e.g. KaAsOa) give with

Hydrosulphuric acid in presence of dilute HCl, yellow ppt. of arsenious sulphide,

$$2\mathrm{K_{s}AsO_{s}} + 6\mathrm{HCl} + 3\mathrm{H_{2}S} = \mathrm{As_{s}S_{s}} + 6\mathrm{KCl} + 6\mathrm{H_{2}O}.$$

This ppt. dissolves in ammonium sulphide, forming an ammonium sulpharsenite, e.g. (NH₄)₃AsS₃ (or 3(NH₄)₂S. As₂S₃); and in ammonium carbonate giving a mixture of arsenite and sulpharsenite. From either of these solutions dilute acids reprecipitate As₂S₃, thus:

$$2(\underbrace{\mathrm{NH_4}}_{3})_{3} \underbrace{\mathrm{AsS}}_{3} + 6 \underbrace{\mathrm{HCl}} = \underbrace{\mathrm{As_2S}}_{3} + 6 \underbrace{\mathrm{NH_4Cl}}_{4} + 3 \underbrace{\mathrm{H_2S}}_{2}$$
 sulpharsenite

and

$$\underbrace{\left(\underbrace{\mathbf{NH_4}} \right) \mathbf{AsO}_g}_{\text{arsenite}} + \underbrace{3 \left(\mathbf{NH_4} \right) \mathbf{AsS}_g}_{\text{sulpharsenite}} + 4 \\ \text{HCl} = 2 \\ \mathbf{As_gS_g} + 4 \\ \mathbf{NH_4Cl} + 2 \\ \mathbf{H_2O}.$$

Silver nitrate, yellow ppt. of silver arsenite, soluble in ammonia and in acids,

$$K_aAsO_a + 3AgNO_a = Ag_aAsO_a + 3KNO_a$$
.

Copper sulphate, yellowish-green ppt. of cupric hydrogen arsenite CuHAsO3, which, when heated with caustic potash, gives red cuprous oxide Cu2O.

Magnesium sulphate, in presence of NH4Cl and NH2, no ppt.

Metallic copper, in presence of dilute HCl, steel-grey deposit of copper arsenide, which, when heated in an open tube, gives crystalline sublimate of As₂O₃.

Oxidizing agents, such as nitric acid, sodium hypochlorite, &c., convert arsenious compounds into the arsenic form.

Arsenic Compounds.

Solutions of arsenic compounds (e.g. K3AsO4) give with

Hydrosulphuric acid, in presence of dilute HCl, on heating, at first, white ppt. of sulphur,

$$K_aAsO_a + 3HCl + H_oS = H_aAsO_a + 3KCl + H_oO + S_a$$

and, after some time, yellow ppt. of As₂S₃,

$$2\mathbf{H}_{s}\mathbf{AsO}_{s}+3\mathbf{H}_{s}\mathbf{S}=\mathbf{As}_{s}\mathbf{S}_{s}+6\mathbf{H}_{s}\mathbf{O}.$$

[If first boiled with SO, As, S, is at once precipitated (see below).]

Silver nitrate, brick-red ppt. of silver arsenate,

$$\label{eq:K_3AsO_4+3AgNO_3=Ag_3AsO_4+3KNO_3,} K_3AsO_4+3KNO_3,$$

soluble in ammonia and in acids.

Copper sulphate, greenish-blue ppt. of cupric hydrogen arsenate CuHAsO₄ (not reduced on heating with KHO).

Magnesium sulphate+ammonia, in presence of NH₄Cl, white crystalline ppt. of magnesium ammonium arsenate Mg(NH₄)AsO₄.

Ammonium molybdate, in presence of HNO3, yellow ppt. on heating.

Ferric chloride, yellowish-white ppt. of ferric arsenate FeAsO4.

Calcium chloride, white ppt. of calcium arsenate Ca,(AsO,) a.

Many reducing agents, such as SO2, convert arsenic compounds into the arsenious form

$$As_2O_5 + 2SO_2 + 2H_2O = As_2O_3 + 2H_2SO_4$$
.

ANTIMONY.

General Reactions.

Compounds of antimony in solution acidulated with HCl, and poured on to a piece of zinc in contact with platinum foil, give a black stain of metallic antimony on the platinum.

In Marsh's apparatus they behave similarly to compounds of arsenic, but the black stain produced does not dissolve in sodium hypochlorite, [nor is SbH₃ evolved if Zn and KOH be employed].

Antimoniuretted hydrogen SbH, passed into a solution of silver nitrate is decomposed as follows:

$$SbH_3 + 3AgNO_3 = \underbrace{SbAg_3}_{black ppt} + 3HNO_3$$
.

The Sb may be dissolved out of this ppt. with tartaric acid, and confirmed by HCl + H₂S, as below.

Solid antimony compounds heated on charcoal before the blow-pipe with Na₂CO₃, in the reducing flame, give brittle grey metallic globules, and a white incrustation of Sb₂O₃.

Antimonious Compounds.

Solutions of antimonious compounds (e.g. SbCl,) give with

Hydrosulphuric acid (in presence of dilute HCl), orange ppt. of antimonious sulphide, $2\mathrm{SbCl_a} + 3\mathrm{H_oS} = \mathrm{Sb_oS_a} + 6\mathrm{HCl}$.

This ppt. dissolves in ammonium sulphide, forming an ammonium sulph-antimonite, e.g. (NH₄)₅SbS₅, from which it is reprecipitated by dilute acids; and in strong boiling HCl, forming antimonious chloride SbCl₅. It is almost insoluble in ammonium carbonate.

Silver nitrate, in presence of caustic potash, black ppt. of argentous oxide (?) which is insoluble in ammonia,

$$SbCl_3 + 4AgNO_3 + 8KHO = Ag_4O(?) + KSbO_3 + 4KNO_3 + 3KCl + 4H_2O.$$

Water gives white ppt. of antimonious oxychloride Sb₂O₃. SbCl₃, soluble in tartaric acid and in HCl. HCl gives a similar ppt. from many antimonious compounds (e.g. tartar emetic) readily soluble in excess.

Caustic potash, white ppt. of antimonious oxide Sb_2O_3 , soluble in excess, forming potassium antimonite K_2O . Sb_2O_3 .

Ammonia gives same ppt. as KHO, nearly insoluble in excess.

Potassium iodide+HCl gives no iodine on heating.

Antimonic Compounds.

Solutions of antimonic compounds (e.g. KSbO3 = K2O . Sb2O3) give with

Hydrosulphuric acid, in presence of dilute HCl, orange ppt. consisting chiefly of antimonic sulphide,

$$K_{a}O$$
. $Sb_{a}O_{b} + 2HCl + 5H_{a}S = Sb_{a}S_{b} + 2KCl + 6H_{a}O$.

This ppt. dissolves in ammonium sulphide, forming ammonium sulph-antimoniate (NH₄)₈SbS₄, from which it is reprecipitated by dilute acids; and in strong boiling HCl, forming antimonious chloride and free sulphur,

$$Sb_{g}S_{s} + 6HCl = 2SbCl_{g} + 3H_{g}S + S_{g}$$

Heated with potassium iodide and hydrochloric acid, iodine is set free:

$$\mathrm{KSbO_3} + 6\mathrm{HCl} + 2\mathrm{KI} = \mathrm{SbCl_3} + 3\mathrm{KCl} + 3\mathrm{H_2O} + \mathrm{I_2}.$$

The precipitate produced by silver nitrate and caustic potash is soluble in ammonia.

These last two reactions distinguish antimonic from antimonious salts,

TIN.

General Reactions.

If a small piece of zinc be added to a solution containing tin acidulated with dilute HCl, a grey deposit of metallic tin is obtained on the zinc. On dissolving this deposit (with the zinc, if necessary) in strong hot HCl, stannous chloride is obtained, which may be confirmed, as below, with mercuric chloride.

Solid tin compounds heated on charcoal with Na₂CO₃ and KCy in the reducing flame give malleable beads of metallic tin. Oxides of tin moistened with cobalt nitrate and heated in the oxidizing flame give a bluish-green mass.

Stannous Salts.

Solutions of stannous salts (e.g. SnCl.) give with

Hydrosulphuric acid, in presence of dilute HCl, dark brown ppt. of stannous sulphide, $SnCl_{\circ} + H_{\circ}S = SnS + 2HCl$.

This ppt. dissolves in yellow ammonium sulphide*, forming ammonium sulphostannate (NH₄)₂SnS₃[=(NH₄)₂S.SnS₂] from which dilute HCl precipitates dirty yellow stannic sulphide SnS₂. Stannous sulphide is soluble in strong boiling HCl, forming stannous chloride. Insoluble in ammonia.

^{*} The yellow "ammonium sulphide" used in laboratories contains an excess of sulphur, being a mixture of polysulphides of ammonium, ammonium thiosulphate, &c.

Stannous Salts (continued).

Mercuric chloride, white ppt. of mercurous chloride, turning to grey metallic mercury if sufficient stannous salt is present, especially on heating,

$$SnCl_g + 2HgCl_g = Hg_2Cl_g + SnCl_4$$

 $SnCl_g + Hg_gCl_g = 2Hg + SnCl_4$.

Auric chloride, purple ppt. of aurous stannate (purple of Cassius) Au'₂Sn"(SnO₃)₂ (or perhaps Au₂+3SnO₂).

Caustic potash, white ppt. of hydrated stannous oxide SnO.2H₂O, soluble in excess, forming potassium stannite K₂SnO₂(=K₂O.SnO).

Ammonia, same ppt. as KHO, insoluble in excess.

Stannous salts act as reducing agents, becoming converted into the stannic form; thus potassium chromate or permanganate (in acidulated solution) are at once reduced, giving a green chromium salt, and a colourless manganous salt respectively. Silver nitrate gives a black ppt. of metallic silver. Ferric and cupric salts are reduced to the ferrous and cuprous state.

Stannic Salts.

Solutions of stannic salts (e.g. SnCl4) give with

 $Hydrosulphuric\ acid$, in presence of dilute HCl, dirty yellow ppt. of stannic sulphide, $SnCl_4 + 2H_2S = SnS_2 + 4HCl.$

This ppt. dissolves in ammonium sulphide, forming ammonium sulphostannate (NH₄)₂SnS₃, from which HCl reprecipitates SnS₂. Soluble in strong boiling HCl, forming stannic chloride. Slightly soluble in ammonium carbonate. Soluble in ammonia.

Mercuric chloride, no ppt. (Distinction from stannous salts.)

Many neutral salts (e.g. Na_2SO_4 or KNO_3) give, in dilute solutions, on heating, white ppt. of metastannic acid $H_2Sn_6O_{11}$. $4H_2O(=5SnO_2$. $5H_2O)$.

Caustic potash, white ppt. of hydrated stannic oxide SnO_2 . H_2O_3 , soluble in excess, forming potassium stannate $K_2SnO_3(=K_2O_3,SnO_2)$.

Ammonia, a similar ppt. incompletely soluble in large excess.

Stannic salts may be reduced to the stannous form by metallic copper or tin, or by reducing to metal by zinc and dissolving in strong HCl.

IRON.

Ferrous Salts.

Solutions of ferrous salts (e.g. FeSO,) give with

Ammonia, dirty green ppt. (white, if pure) of ferrous hydroxide, $FeSO_4 + 2NH_3 + 2H_2O = Fe(OH)_2 + (NH_4)_2SO_4$.

This precipitation is partly prevented by NH₄Cl. The ppt. rapidly absorbs exygen from the air, becoming reddish-brown hydrated Fe₂O₂.

Potassium ferricyanide, dark blue ppt. of ferrous ferricyanide (?) "Turnbull's blue," 3Fe"SO, + K_a(Fe₂Cy₁₂)^{vi} = Fe"₄(Fe₂Cy₁₂)^{vi} + 3K₂SO, *.

Potassium ferrocyanide, pale blue ppt. of ferrous potassium ferrocyanide (white, if quite pure),

•
$$FeSO_4 + K_4(FeCy_6) = FeK_9(FeCy_6) + K_9SO_4$$
.

Nitric acid, potassium permanganate, potassium bichromate, and other oxidising agents, convert ferrous into ferric compounds,

$$\begin{split} &6\text{FeSO}_4 + 2\text{HNO}_3 + 3\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} + 2\text{NO} \\ &10\text{FeSO}_4 + \text{K}_2\text{O} \cdot 2\text{MnO} \cdot \text{O}_5 + 8\text{H}_2\text{SO}_4 = 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} \cdot \text{O}_4 \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} \cdot \text{O}_4 \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} \cdot \text{O}_4 \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} \cdot \text{O}_4 \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O} \cdot \text{O}_4 \\ &6\text{FeSO}_4 + \text{K}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot \text{O}_3 + 7\text{H}_2\text{SO}_4 = 3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}$$

Potassium sulphocyanate, no colouration with pure ferrous salts.

Caustic potash, same result as ammonia.

Ammonium sulphide, black ppt. of ferrous sulphide FeS.

Ferric Salts.

Solutions of ferric salts (e.g. Fe Cl) give with

Ammonia, reddish-brown ppt. of hydrated ferric oxide,

 $Fe_{g}Cl_{g} + 6NH_{3} + 5H_{g}O = Fe_{g}O_{3} \cdot 2H_{g}O + 6NH_{4}Cl.$

Potassium ferrocyanide, dark blue ppt. of "Prussian blue." Usually represented † $2\text{Fe}_2\text{Cl}_6 + 3\text{K}_4(\text{FeCy}_6) = \text{Fe}''_4(\text{FeCy}_6)^{\text{Iv}}_3 + 12\text{KCl}.$

Potassium sulphocyanate, blood-red colouration, due to ferric sulphocyanate, Fe₂(CyS)_e.

Bleached by mercuric chloride.

• Perhaps $2\text{FeSO}_4 + K_6(\text{Fe}_2\text{Cy}_{12}) = \text{Fe}'_2K_2(\text{Fe}_2\text{Cy}_{12}) + 2K_2\text{SO}_4$.

[†] But the ppt. always contains potassium. If excess of ferrocyanide be employed, the reaction appears to be $Fe'''_2Cl_6 + 2K_4(FeCy_6)^{l_7} = K_2Fe''_2(Fe_2Cy_{12})^{r_1} + 6KCl$.

Ferric Salts (continued).

Sodium phosphate, yellowish-white ppt. of ferric phosphate, Fe₂Cl₆ +2 Na₂HPO₄ = 2FePO₄ + 4NaCl + 2HCl.

This ppt. is soluble in HCl, but insoluble in acetic acid. If an acid phosphate be used, as above, the precipitation is incomplete unless the free acid be neutralized, or replaced by acetic acid.

Potassium ferricyanide, no ppt. (brown or green colouration).

Ammonium sulphide, black ppt. of ferrous sulphide, free sulphur separating.

Caustic potash, same ppt. as ammonia.

Reducing agents such as H2S, SO2, SnCl2, Zn, &c., convert ferric into ferrous compounds.

Compounds of iron heated in the borax bead, give, in the oxidizing flame, an orange yellow while hot, pale yellow when cold. In reducing flame, bottle-green bead, especially with ferrous salts.

CHROMIUM.

Any chromium compound fused with Na₂CO₃ on platinum foil in presence of air (or with addition of a little KNO₃) gives a yellow mass of sodium chromate; e.g.

$$Cr_gO_s + 2Na_gCO_s + O_s = 2Na_gCrO_s + 2CO_g$$
.

This may be dissolved in water acidified with acetic acid, and tested for chromate as below with lead acetate.

Before the blow-pipe, chromium compounds give a green borax bead in both flames.

Chromic Salts.

Solutions of chromic salts (e.g. Cr. Cl.) give with

Ammonia, bluish-green ppt. of chromic hydroxide,

$$\operatorname{Cr_{2}Cl_{6}} + 6\operatorname{NH_{3}} + 6\operatorname{H_{2}O} = \operatorname{Cr_{2}(OH)_{6}} + 6\operatorname{NH_{4}Cl}.$$

This ppt. is partly soluble in excess of ammonia, giving a pink solution, but is completely reprecipitated by boiling for some time.

Caustic potash gives same result as ammonia, easily soluble in excess, forming a green solution. Reprecipitated by continued boiling.

Many oxidizing agents, e.g. NaClO, PbO₂, K₂Mn₂O₈, (in presence of caustic potash), convert chromic salts into chromates.

Ammonium sulphide, bluish-green ppt. of chromic hydroxide Cr₂(OH)₆, with evolution of H₂S. Sodium phosphate, green ppt. of chromic phosphate CrPO₄, sparingly soluble in acetic acid.

Chromates.

Solutions of chromates (e.g. K, CrO4) give with

Lead acetate, yellow ppt. of lead chromate, insoluble in acetic acid,

$$K_gCrO_4 + (CH_3CO_g)_2Pb = PbCrO_4 + 2CH_3CO_gK.$$

Hydrosulphuric acid, in presence of HCl, gives a green solution of chromic chloride, and a white ppt. of sulphur,

$$2K_{o}CrO_{a} + 10HCl + 3H_{o}S = Cr_{o}Cl_{a} + 4KCl + 8H_{o}O + 3S.$$

Many other reducing agents, e.g. stannous chloride, sulphur dioxide, alcohol, ferrous salts, likewise give green solutions of chromic salts.

$${}^{*}(K_{3}O)_{2} \cdot Cr_{2}O_{3} \cdot O_{3} + 3SnCl_{2} + 16HCl = Cr_{2}Cl_{6} + 3SnCl_{4} + 4KCl + 8H_{2}O$$

$$(K_{2}O)_{2} \cdot Cr_{2}O_{3} \cdot O_{3} + 3SO_{2} + 2H_{2}SO_{4} = Cr_{2}(SO_{4})_{3} + 2K_{2}SO_{4} + 2H_{2}O$$

$$(K_{2}O)_{2} \cdot Cr_{2}O_{3} \cdot O_{3} + 3C_{2}H_{5}OH + 5H_{2}SO_{4} = Cr_{2}(SO_{4})_{3} + 3CH_{3}COH + 2K_{2}SO_{4} + 8H_{2}O$$

$$(K_{2}O)_{2} \cdot Cr_{2}O_{3} \cdot O_{3} + 6FeSO_{4} + 8H_{2}SO_{4} = Cr_{2}(SO_{4})_{3} + 3Fe_{3}(SO_{4})_{3} + 2K_{3}SO_{4} + 8H_{2}O$$

Peroxide of Hydrogen, added to a dilute solution, acidified with dilute H₂SO₄ and shaken up with ether, gives a deep blue solution (due to perchromic acid H₂Cr₂O₈(?))

Silver nitrate, crimson ppt. of silver chromate Ag2CrO4, soluble in dilute HNO3.

Barium chloride, yellow ppt. of barium chromate, insoluble in acetic acid.

Dry chromates, heated with concentrated H_2SO_4 and sodium chloride, give off red vapours of chromyl chloride CrO_2Cl_2 .

Mercurous Nitrate, brick red ppt. of basic mercurous chromate 2Hg₂O . CrO₃, which, on heating, gives off Hg and O, leaving Cr₂O₃.

ALUMINIUM.

Solutions of aluminium compounds, e.g. Al₂(SO₄)₃, give with

Ammonia, white gelatinous ppt. of aluminium hydroxide (or basic salt),

This ppt. is somewhat soluble in excess, unless NH₄Cl is present, and the solution boiled.

Caustic potash, same ppt. as ammonia, easily soluble in excess, forming potassium aluminate, 3K₂O.Al₂O₃; reprecipitated by ammonium chloride,

$$3K_2O \cdot Al_2O_3 + 6NH_4Cl = Al_2O_3 \cdot 3H_2O + 6KCl + 6NH_3$$

Ammonium sulphide, white ppt. of aluminium hydroxide Al₂(OH)₆ (often discoloured).

Sodium phosphate, white ppt. of aluminium phosphate AlPO₄, insoluble in acetic acid.

Many solid aluminium compounds when heated on charcoal leave a white infusible mass, which, when moistened with cobalt nitrate and again heated, gives a sky-blue colour.

ZINC.

Solutions of zinc salts (e.g. ZnSO,) give with

Ammonium sulphide, white ppt. of zinc sulphide (often discoloured),

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$
.

Soluble in dilute HCl, forming zinc chloride ZnCl₂. Insoluble in acetic acid. (Distinction from Mn.)

Caustic potash, white ppt. of zinc hydroxide,

$$ZnSO_4 + 2KHO = Zn(OH)_a + K_aSO_4$$

easily soluble in excess of *cold* caustic potash, forming potassium zincate K₂O. ZnO, from which H₂S precipitates white zinc sulphide ZnS. On boiling the solution of K₂O. ZnO, Zn(OH)₂ is reprecipitated, especially if dilute.

Ammonia, same ppt. as caustic potash, soluble in excess, and in ammonium chloride.

Hydrosulphuric acid, white ppt. of ZnS in alkaline solution, or one containing only acetic acid. No ppt. in presence of sufficient free HCl, H₂SO₄, or HNO₃.

Potassium ferrocyanide, white ppt. of zinc ferrocyanide, insoluble in dilute HCl.

Potassium ferricyanide, orange ppt. soluble in HCl.

Solid zinc compounds heated on charcoal before the blow-pipe with Na₂CO₃ give a residue which is yellow while hot, white when cold. This residue, when moistened with cobalt nitrate and again heated, gives a bright green mass.

MANGANESE.

General Reactions.

Any compound of manganese when fused in platinum foil with Na₂CO₃ in presence of air (or with addition of a little KNO₃) give a blue-green mass of sodium manganate, e.g.

$$MnSO_4 + 2Na_2CO_3 + O_9 = Na_9MnO_4 + Na_2SO_4 + 2CO_9$$

All compounds of manganese after boiling with HCl, give the reactions of manganous salts.

Traces of manganese compounds (in absence of Cl and Br) when boiled with nitric acid and peroxide of lead, give a pink colour, due to permanganic acid H₂Mn₂O₈.

In the borax bead manganese compounds give a violet colour in the oxidizing flame, colourless in reducing flame.

Manganous Salts.

Solutions of manganous salts (e.g. MnCl2) give with

Ammonium sulphide, buff or pinkish ppt. of manganous sulphide,

$$MnCl_2 + (NH_4)_2S = MnS + 2NH_4Cl.$$

This ppt. dissolves in dilute HCl, forming manganous chloride MnCl₂. Soluble also in acetic acid. Not precipitated in presence of large excess of ammonia.

Caustic potash, white ppt. of manganous hydroxide, insoluble in excess,

$$MnCl_o + 2KHO = Mn(OH)_o + 2KCl.$$

This ppt. rapidly absorbs oxygen from the air, forming brown hydrated sesquioxide $Mn_{\bullet}O_{a}$. $H_{\bullet}O$.

Ammonia, same ppt. as caustic potash. No ppt., however, in presence of ammonium chloride, which forms the soluble double chloride MnCl₂. 2NH₄Cl. This solution readily absorbs oxygen from the air, brown Mn₂O₃. H₄O being precipitated.

Sodium hypochlorite, dark brown ppt. of hydrated manganese dioxide MnO2. H.O.

Hydrosulphuric acid gives no ppt. in presence of a free acid, even acetic. In alkaline solution MnS is precipitated.

Manganic Salts.

These are very unstable, and usually decompose when dissolved in water. They form red or violet solutions in acids.

Heated with Hydrochloric acid they evolve chlorine, e.g.

$$\mathbf{Mn_{\mathfrak{g}}(SO_{\mathfrak{q}})_3} + 2\mathbf{HCl} = 2\mathbf{MnSO_{\mathfrak{q}}} + \mathbf{H_{\mathfrak{g}}SO_{\mathfrak{q}}} + \mathbf{Cl_{\mathfrak{g}}}.$$

Caustic potash gives a dark brown ppt. of hydrated manganese sesquioxide, $Mn_s(SO_s)_s + 6KHO = Mn_sO_s \cdot H_sO + 3K_sSO_s + 2H_sO.$

Manganates and Permanganates.

Solutions of manganates (e.g. $K_2MnO_4 = K_2O \cdot MnO_3$) are green; those of permanganates (e.g. $K_2Mn_2O_3 = K_2O \cdot Mn_2O_3$) rose or purple.

Manganates in solution are very unstable, except in presence of free alkali. In neutral solution they decompose as follows:

$$3\underbrace{(\text{K}_2\text{O}.\text{MnO}_3)}_{\text{green solution}} + 3\text{H}_2\text{O} = \underbrace{\text{K}_2\text{O}.\text{Mn}_2\text{O}_7}_{\text{pink solution}} + \underbrace{\text{MnO}_2.\text{H}_2\text{O}}_{\text{brown ppt.}} + 4\text{KHO}.$$

Chlorine converts manganates into permanganates,

$$2K_{e}MnO_{\bullet} + Cl_{e} = K_{e}Mn_{e}O_{e} + 2KCl.$$

Permanganates boiled with alkalis, become manganates, oxygen being evolved,

$$2K_2Mn_2O_8 + 4KHO = 4K_3MnO_4 + 2H_2O + O_2$$
.

Permanganates (or manganates) when heated with strong sulphuric acid evolve oxygen,

$$2(K_2O.2MnO.O_s) + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2;$$

and with strong hydrochloric acid evolve chlorine,

$$\rm K_2O$$
 , $\rm 2MnO$, $\rm O_6+16HCl=2\,K\,Cl+2Mn\,Cl_2+8\,H_2O+5Cl_3$.

In presence of free acid, they convert-

Ferrous salts into ferric salts,

$$10\text{Fe''SO}_4 + 5\text{H}_8\text{SO}_4 + 5\text{O} = 5\text{Fe''}_8(\text{SO}_4)_8 + 5\text{H}_8\text{O}_8$$

Stannous salts into stannic salts,

Oxalic acid into carbon dioxide and water,

$$5 \begin{cases} \ensuremath{\mathrm{COOH}} + 5 \ensuremath{\mathrm{O}} = 10 \ensuremath{\mathrm{CO}_2} + 5 \ensuremath{\mathrm{H}_2\mathrm{O}}. \end{cases}$$

Nitrous acid into nitric acid,

$$5HNO_0 + 5O = 5HNO_1$$

Sulphurous acid into sulphuric acid,

$$5H_{*}SO_{*} + 5O = 5H_{*}SO_{*}$$

NICKEL.

Solutions of nickel salts (e.g. NiSO,) give with

Ammonium sulphide, black ppt.,

$$\mathrm{NiSO_4} + (\mathrm{NH_4})_2 \mathrm{S} = \mathrm{NiS} + (\mathrm{NH_4})_2 \mathrm{SO_4}.$$

This ppt. is nearly insoluble in dilute HCl. Soluble in aqua regia, forming nickel chloride NiCl_s. Somewhat soluble in excess of ammonium sulphide (especially yellow), forming a dark-coloured solution. [It may be reprecipitated from this solution by adding ammonium acetate and boiling, or by acidifying with acetic acid.]

Caustic potash, pale green ppt. of nickelous hydroxide, insoluble in excess, soluble in ammonium salts,

$$NiSO_4 + 2KHO = Ni(OH)_9 + K_9SO_4$$
.

Potassium cyanide (pure), greenish-yellow ppt. of nickelous cyanide,

$$NiSO_4 + 2KCy = NiCy_2 + K_2SO_4$$
.

This ppt. redissolves easily in excess of potassium cyanide, forming a double cyanide NiCy. 2KCy, which is not altered by boiling with excess of KCy in presence of air.

This double cyanide gives a pale green ppt. with mercuric oxycyanide*, and a black ppt. with sodium hypochlorite on gently warming, thus

$$\begin{aligned} \text{NiCy}_2 + \text{HgO} \cdot \text{HgCy}_2 + \text{H}_2\text{O} &= \underbrace{\text{Ni(OH)}_2}_{\text{greenish ppt.}} + 2\text{HgCy}_2 \\ 2\text{NiCy}_2 + \text{NaClO} + 5\text{H}_2\text{O} &= \underbrace{\text{Ni}_2\text{(OH)}_2}_{\text{black ppt.}} + \text{NaCl} + 4\text{HCy.} \end{aligned}$$

Potassium nitrite, in presence of acetic acid no ppt.

Ammonia, greenish ppt. of nickelous hydroxide, soluble in excess, forming a blue solution. Soluble in ammonium salts.

Hydrosulphuric acid, no ppt. in presence of free HCl.

Potassium ferricyanide, yellowish-brown ppt. of nickel ferricyanide, soluble in ammonia.

Nickel compounds give, in the borax bead, a brownish-violet colour in the oxidizing flame, often grey in the reducing flame.

* Prepared by boiling mercuric oxide (freshly pptd.) with solution of mercuric cyanide and filtering.

COBALT.

Solutions of cobaltous salts, e.g. Co(NO,), give with

Ammonium sulphide, black ppt. of cobalt sulphide, $Co(NO_3)_2 + (NH_4)_2S = CoS + 2NH_4NO_3.$

This ppt. is almost insoluble in dilute HCl. Soluble in aqua regia, forming cobaltous chloride CoCl₂.

Caustic potash, blue ppt. of basic salt, insoluble in excess, becoming green or grey on exposure to the air, owing to formation of sesquioxide. The blue ppt. turns to red cobaltous hydroxide Co(OH)₂ on heating.

Potassium cyanide (pure), brown ppt. of cobaltous cyanide, $Co(NO_3)_2 + 2KCy = CoCy_2 + 2KNO_3$.

This ppt. redissolves easily in excess of potassium cyanide, forming a double cyanide CoCy₂. 2KCy*. This solution, if boiled (with slight excess of KCy) in presence of air, is converted into potassium cobalticyanide†,

$$2\left(\mathrm{CoCy_22KCy}\right) + 4\mathrm{KCy} + \mathrm{H_2O} + \mathrm{O} = \mathrm{K_6Co_2Cy_{12}} + 2\mathrm{KHO}.$$

This compound is not precipitated by sodium hypochlorite (at gentle heat), or by mercuric oxycyanide.

Potassium nitrite (concentrated solution) in presence of acetic acid, yellow crystalline ppt. after a time, probably K₆Co₂(NO₂)₁₂. 3H₂O.

Ammonia in small quantity gives same result as caustic potash. More ammonia dissolves it, forming a brownish-red liquid which absorbs oxygen from the air becoming red.

Potassium ferricyanide, reddish-brown ppt. of cobalt ferricyanide, insoluble in ammonia.

Potassium sulphocyanate in strong solutions, blue colour, soluble in ether.

Cobalt compounds give in the borax bead a blue colour in both flames.

^{*} Derived from 4HCy by replacement of H4 by Co" and K'2.

⁺ Derived from H6Co2Cy12 by replacement of H6 by K6.

BARIUM.

Solutions of barium salts (e.g. BaCl2) give with

Ammonium carbonate, white ppt. of barium carbonate,

BaCl, + (NH,),CO, = BaCO, + 2NH,Cl,

soluble in dilute HCl or HNO.

Calcium sulphate, immediate white ppt. of barium sulphate,

 $\mathrm{BaCl_2} + \mathrm{CaSO_4} = \mathrm{BaSO_4} + \mathrm{CaCl_2}.$

Hydrofluosilicic acid, colourless crystalline ppt. of barium silicofluoride,

BaCl, + H,SiF, = BaSiF, + 2HCl,

somewhat soluble in dilute acids, unless alcohol be added.

Potassium chromate, yellow ppt. of barium chromate, even in dilute solutions,

BaCl, + K, CrO, = BaCrO, + 2KCl,

nearly insoluble in acetic acid. Soluble in HCl.

Barium salts are precipitated from their solutions by strong HCl or HNO₃. Barium chloride is insoluble in alcohol.

Dilute sulphuric acid, or any soluble sulphate, white ppt. of barium sulphate BaSO₄.

Sodium phosphate, white ppt. of barium phosphate, soluble in dil. HCl, HNO₃, and acetic acid.

Ammonium oxalate, white ppt. of barium oxalate Ba(CO₂)₂, soluble in HCl, very sparingly soluble in acetic acid.

Barium compounds moistened with HCl, and held in the edge of a Bunsen flame on platinum wire, give an apple-green colour.

CALCIUM.

Solutions of calcium salts (e.g. CaCl.) give with

Ammonium carbonate, white ppt. of calcium carbonate, CaCl₂ + (NH₄)₂CO₃ = CaCO₃ + 2NH₄Cl

Calcium sulphate, no ppt.

Hydrofluosilicic acid, no ppt.

Potassium chromate, no ppt.

Ammonium oxalate, white ppt. of calcium oxalate, even in very dilute solutions,

$$CaCl_{2} + \begin{cases} CO_{2}NH_{4} \\ CO_{2}NH_{4} \end{cases} = \begin{cases} CO_{2}Ca + 2NH_{4}Cl. \end{cases}$$

This ppt. is insoluble in acetic acid; soluble in dilute HCl or HNO₃.

Calcium chloride and calcium nitrate are both soluble in absolute alcohol.

Sulphuric acid or soluble sulphates, white ppt. of calcium sulphate in strong solutions only. Readily soluble in strong (ammoniacal) solution of ammonium sulphate.

Sodium phosphate, white ppt. of calcium phosphate, soluble in HCl, HNO3, and acetic acid.

Calcium compounds examined by the flame test give an orange-red colour.

STRONTIUM.

Solutions of strontium salts, e.g. Sr(NO3)2, give with

Ammonium carbonate, white ppt. of strontium carbonate,

$$Sr(NO_3)_g + (NH_4)_gCO_3 = SrCO_3 + 2NH_4NO_3.$$

Calcium sulphate, white ppt. of strontium sulphate after a time, or on heating, $Sr(NO_3)_2 + CaSO_4 = SrSO_4 + Ca(NO_3)_2$.

Hydrofluosilicic acid, no ppt.

Potassium chromate, no ppt. in dilute solutions.

Strontium chloride is soluble in absolute alcohol; strontium nitrate insoluble,

Dilute sulphuric acid or soluble sulphates, white ppt. of strontium sulphate insoluble in strong solution of ammonium sulphate (ammoniacal).

Ammonium oxalate, white ppt. of strontium oxalate Sr(CO₂)₂, sparingly soluble in acetic acid, soluble in HCl. Sodium phosphate, white ppt. of strontium phosphate, soluble in HCl, HNO₃, and acetic acid.

Strontium compounds examined by the flame test give a characteristic crimson colour.

MAGNESIUM.

Solutions of magnesium salts (e.g. MgSO4) give with

Sodium phosphate, in presence of ammonia (and ammonium chloride), white ppt. of magnesium ammonium phosphate,

This ppt. is crystalline from dilute solutions.

Ammonia, white ppt. of magnesium hydroxide, (in part)

$$MgSO_4 + 2NH_3 + 2H_2O = Mg(OH)_2 + (NH_4)_2SO_4$$

but no ppt. in presence of sufficient ammonium chloride, since the soluble double chloride MgCl₂. 2NH₂Cl formed is not decomposed by ammonia.

Ammonium carbonate, white ppt. of magnesium carbonate, but no ppt. in presence of sufficient ammonium chloride.

Barium hydroxide, in absence of ammonium salts, white ppt. of magnesium hydroxide Mg(OH)₂. Caustic potash, same ppt.

Some magnesium compounds (e.g. oxide, sulphate, carbonate) heated on charcoal, moistened with cobalt nitrate, and again heated, give a pale rose colour.

AMMONIUM.

Ammonium compounds (e.g. NH₄Cl), when boiled with caustic potash, evolve ammonia, NH₄Cl + KHO = KCl + H₂O + NH₃.

The ammonia may be recognized by its odour, and action on red litmus.

Solutions of ammonium salts give with

Platinic chloride (in presence of HCl if necessary), yellow ppt. of ammonium platinic chloride,

 $2\mathrm{NH_4Cl} + \mathrm{PtCl_4} = (\mathrm{NH_4})_{\mathfrak{g}} \mathrm{PtCl_6}.$

This precipitation is more complete in presence of alcohol.

Nessler's solution (potassium mercuric iodide with excess of caustic potash) gives, even in very dilute solutions, a brown or yellow colouration (or precipitate in stronger solutions) due to dimercuric-ammonium iodide,

$$NH_4Cl + 2(HgI_2 \cdot 2KI) + 4KHO = NHg''_2I \cdot H_2O + 7KI + KCl + 3H_2O.$$

Tartaric acid, white crystalline ppt. on shaking (in strong solutions) of ammonium hydrogen tartrate

CHOH CHOH COOH

Ammonium compounds heated before the blow-pipe volatilize entirely or in part.

POTASSIUM.

Solutions of potassium salts (e.g. KCl), if not too dilute, give with

Platinic chloride (in presence of HCl if necessary), yellow crystalline ppt. of potassium platinic chloride, especially on stirring,

$$2KCl + PtCl_4 = K_2PtCl_6$$
.

Tartaric acid, white crystalline ppt. on shaking, of potassium hydrogen tartrate,

$$KCl + \begin{cases} COOH \\ CHOH \\ CHOH \\ COOH \end{cases} = \begin{cases} COOK \\ CHOH \\ CHOH \\ COOH \end{cases}$$

Hydrofluosilicic acid, white gelatinous ppt. of potassium silicofluoride K₂SiF₆.

Picric acid (in strong solutions), yellow crystalline ppt. of potassium picrate C₆H₂(NO₂)₃.OK.

All of the above reactions of potassium are more complete in the presence of alcohol. Potassium salts examined by the flame reaction, give a violet colour.

SODIUM.

Solutions of sodium compounds give no characteristic reaction with any of the common reagents, nearly all sodium salts being soluble.

Dioxytartaric acid, when neutralized with ammonia, gives a white precipitate of sodium dioxytartrate Na₂C₄H₄O₈. 2½H₂O. A few crystals of the acid should be dissolved in a drop or two of water on a watch-glass, mixed with the solution to be tested, and ammonia added till neutral or alkaline. The precipitate appears in lines on stirring.

Potassium metantimoniate gives in neutral solutions a white ppt. of acid sodium metantimoniate, Na_oO . H_oO . Sb_oO_s . 6H_oO.

This test is not often used. Ammonium, calcium, &c., give a similar reaction.

Sodium compounds, heated on platinum wire in a Bunsen flame, give a strong yellow colouration.

PRINCIPAL REACTIONS OF THE MORE COMMON ACID RADICLES.

SULPHATES.

Heated with strong H2SO4, no result.

Solutions of sulphates (e.g. K2SO4) give with

Barium chloride, white ppt. of barium sulphate, insoluble in HCl or HNO₃,

K₂SO₄ + BaCl₂ = BaSO₄ + 2KCl.

Strontium chloride (or nitrate), white ppt. of strontium sulphate, SrSO₄ (slowly in dilute solutions).

Calcium chloride, white ppt. of calcium sulphate CaSO₄, in strong solutions only; soluble in much water.

Lead acetate, white ppt. of lead sulphate PbSO₄, soluble in ammonium acetate.

Dry sulphates (like all sulphur compounds), when heated with sodium carbonate and charcoal in the reducing flame, give sodium sulphide, which when placed on a silver coin and moistened with water, gives a black stain of silver sulphide Ag₂S.

SULPHITES.

(E.g. Na, SO, .) Heated with HCl, sulphur dioxide is evolved,

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$
.

The evolved gas may be recognized by its odour, and action on K2Cr2O2.

$$\begin{array}{l} {\rm K_{g}Cr_{g}O_{7} + H_{g}SO_{4} + 3SO_{2} = K_{g}SO_{4} + Cr_{g}(SO_{4})_{3} + H_{g}O.} \\ {\rm (orange)} \end{array}$$

Treated with HCl and metallic zinc, hydrosulphuric acid is evolved (detected by lead acetate, &c.),

$$Zn + 2HCl = ZnCl_g + H_g$$

and

$$SO_{a} + 3H_{a} = 2H_{a}O + H_{a}S.$$

Solutions of sulphites give with

Barium chloride, white ppt. of barium sulphite,

$$Na_{g}SO_{g} + BaCl_{g} = BaSO_{g} + 2NaCl_{g}$$

easily soluble in dilute HCl; from this solution oxidizing agents, e.g. chlorine water, precipitate white barium sulphate, insoluble in HCl,

$$BaSO_3 + H_2O + Cl_2 = BaSO_4 + 2HCl.$$

Silver nitrate, white ppt. of silver sulphite, Ag₂SO₃, soluble in dilute HNO₃. This ppt. darkens when heated, metallic silver and sulphuric acid being formed,

$$Ag_2SO_3 + H_2O = 2Ag + H_2SO_4$$
.

Free iodine is decolourized, thus:

$$Na_2SO_3 + H_2O + I_2 = Na_2SO_4 + 2HI$$
.

THIOSULPHATES.

Formerly called Hyposulphites.

(E.g. Na₂S₂O₃.) Treated with HCl, sulphur dioxide is evolved, and yellow sulphur separates, especially on heating,

$$Na_gS_gO_g + 2HCl = 2NaCl + H_gO + SO_g + S.$$

Treated with metallic zinc in excess and HCl, H2S is evolved as with sulphites, especially on heating.

Thiosulphates (continued).

Solutions of thiosulphates give with

Lead acetate, white ppt. of lead thiosulphate,

This ppt. on heating blackens, owing to formation of lead sulphide,

$$\mathrm{PbS_2O_3} + \mathrm{H_2O} = \mathrm{PbS} + \mathrm{H_2SO_4}.$$

Silver and mercurous salts behave similarly.

Free iodine is at once decolourized,

$$2\mathrm{Na_2S_2O_3} + \mathrm{I_2} = \mathrm{Na_2S_4O_6} + 2\mathrm{NaI}.$$

Ferric chloride, transient violet colouration (afterwards reduced to ferrous chloride).

SULPHIDES.

Heated alone in a current of air (e.g. in an open tube) sulphur dioxide is evolved.

Treated with HCl, many sulphides evolve hydrosulphuric acid. [Some require boiling with strong acid; others (e.g. FeS₂) are not decomposed unless zinc be added.]

$$FeS + 2HCl = FeCl_g + H_gS$$
.

The evolved gas is recognized by its odour, action on lead acetate, &c.

Soluble sulphides, e.g. (NH4),S, give with

Lead acetate, black ppt. of lead sulphide,

$$(NH_a)_2S + (CH_aCO_2)_2Pb = PbS + 2CH_aCOO(NH_a)$$
.

Sodium nitroprusside, Na₄Fe₄(NO)₂Cy₁₀, gives a fine purple colouration, probably due to a double salt of the sulphide and nitroprusside. Free H₂S does not give the reaction.

Metallic silver is stained black owing to formation of silver sulphide Ag.S.

SILICOFLUORIDES.

(E.g. K_sSiF₆) when heated in a platinum vessel with strong H₂SO₄, evolve silicon tetrafluoride and hydrofluoric acid gases,

$$K_sSiF_a + H_sSO_4 = K_sSO_4 + SiF_4 + 2HF.$$

SiF₄ deposits white hydrated silica on a wet rod, and HF will etch glass. [See Fluorides.]

Solutions of silicofluorides, or hydrofluosilicic acid, give with

Barium chloride, colourless crystalline ppt. of barium silicofluoride,

$$H_2SiF_6 + BaCl_2 = BaSiF_6 + 2HCL$$

This ppt. is nearly insoluble in dilute HCl.

Strontium chloride, no ppt.

Potassium chloride, gelatinous ppt. of potassium silicofluoride,

$$H_aSiF_a + 2KCl = K_aSiF_a + 2HCl$$
.

FLUORIDES.

(E.g. CaF₂) Heated in a platinum vessel with concentrated H₂SO₄ evolve hydrofluoric acid,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The evolved gas will corrode glass, owing to its action on silica,

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Heated with concentrated H₂SO₄ in presence of silica or silicates, e.g. in a test-tube, silicon tetrafluoride is evolved:

$$2CaF_g + 2H_gSO_4 + SiO_2 = 2CaSO_4 + 2H_gO + SiF_4$$

A wet rod held in this gas becomes coated with hydrated silica,

$$3\mathrm{SiF_4} + 4\mathrm{H_2O} = \mathrm{SiO_2} \cdot 2\mathrm{H_2O} + 2\mathrm{H_2SiF_6}.$$
 white deposit

Solutions of fluorides (e.g. NaF) give with

Calcium chloride, white gelatinous ppt. of calcium fluoride, 2NaF + CaCl_o = CaF_o + 2NaCl.

Sparingly soluble in HCl; nearly insoluble in acetic acid.

Barium chloride, white ppt. of barium fluoride BaF 2.

OXALATES.

 $\left(E.g.\ {
m COOK \atop COOK}.\right)$ Heated with strong H_2SO_4 , carbon monoxide and carbon dioxide are evolved,

$$\begin{cases} \begin{array}{l} \mathrm{COOK} \\ \mathrm{COOK} \end{array} + \mathrm{H_2SO_4} = \mathrm{K_2SO_4} + \mathrm{CO} + \mathrm{CO_2} + \mathrm{H_2O}. \end{cases}$$

The CO will burn with a blue flame, and the CO₂ may be detected by lime water. (See Carbonates.)

Treated with H,SO, and manganese dioxide, carbon dioxide alone is evolved,

$$\begin{cases} \text{COOK} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2. \end{cases}$$

Solutions of oxalates give with

Calcium chloride, white ppt. of calcium oxalate,

$$\begin{cases} \text{COOK} + \text{CaCl}_2 = \begin{cases} \text{COO} \\ \text{COO} \end{cases} \text{Ca} + 2 \text{KCl},$$

soluble in HCl, but insoluble in acetic acid. This ppt. is produced even in very dilute solutions.

Barium chloride and Strontium chloride, white ppts. of barium oxalate (CO2)2Ba and strontium oxalate (CO2)2Br respectively.

Silver nitrate, white ppt. of silver oxalate (COOAg, soluble in dilute HNO3.

PHOSPHATES.

Orthophosphates.

Heated with strong H2SO4, no result.

Solutions of orthophosphates (e.g. Na, HPO,) give with

Calcium chloride, white ppt. of calcium hydrogen phosphate,

soluble in HCl, HNO, and acetic acid.

[If ammonia is added, Ca,(PO,), is precipitated instead of CaHPO,.]

Orthophosphates (continued).

Ferric chloride, yellowish-white ppt. of ferric phosphate,

$$2Na_sHPO_4 + Fe_sCl_s = 2Fe(PO_4) + 4NaCl + 2HCl,$$

soluble in HCl or HNO_s, insoluble in acetic acid. [This precipitation, in case of acid phosphates as above, is therefore incomplete, unless the HCl be neutralized or replaced by acetic acid.]

Magnesium sulphate, in presence of ammonia and ammonium chloride (the latter, to prevent precipitation of Mg(OH)₂ by the ammonia), white ppt. (crystalline in dilute solutions or on standing) of magnesium ammonium phosphate,

$$Na_2HPO_4 + MgSO_4 + NH_3 = Mg(NH_4)PO_4 + Na_2SO_4$$
.

Silver nitrate, yellow ppt. of silver phosphate,

$$Na_gHPO_4 + 3AgNO_8 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

soluble in acids and in ammonia. [The above precipitation is therefore incomplete unless the free HNO₃ be neutralized.]

Ammonium molybdate, (NH₄)₂MoO₄ in presence of strong HNO₃, on heating, canary yellow ppt. of ammonium phosphomolybdate. [Composition uncertain, approximately

The (NH₄) MoO₄ must be added considerably in excess of the phosphate taken.

Free orthophosphoric acid does not coagulate albumin.

Barium, strontium, lead, aluminium, bismuth, &c. salts give white ppts. of their respective normal or acid phosphates.

Metaphosphates.

Solutions of metaphosphates (e.g. NaPO₃) give with

Silver nitrate, white ppt. of silver metaphosphate AgPO.

Magnesium sulphate, in presence of NH, and NH, Cl, no ppt.

The free acid (or a metaphosphate + acetic acid) coagulates albumin.

Pyrophosphates.

Solutions of pyrophosphates (e.g. Na, P2O7) give with

Silver nitrate, white ppt. of silver pyrophosphate Ag, P,O,

Magnesium sulphate, white ppt. of magnesium pyrophosphate Mg, P,O,, soluble in excess. The free acid does not coagulate albumin.

Boiled with water, in presence of acids, both meta- and pyro-phosphates are converted into orthophosphates.

ARSENATES.

Solutions of arsenates (e.g. K₃AsO₄) give the same reactions as phosphates with Ferric chloride, Magnesium sulphate, and Ammonium molybdate. Silver nitrate however gives, in neutral solution, a brick-red ppt. instead of yellow.

Arsenates are also distinguished (and separated) from phosphates by hydrosulphuric acid in presence of HCl, which gives first a white ppt. of sulphur, and afterwards a yellow ppt. of arsenious sulphide, on heating. [See Arsenic.]

BORATES.

(E.g. Na₂B₄O₇.) Mixed with strong H₂SO₄ and alcohol, the latter on being kindled burns with a green-edged flame.

Solutions of borates acidified with dilute HCl, colour turmeric paper orange or brown (in dilute solutions only on drying). This colour is changed to green or blackish by treatment with KHO.

Solutions of borates give with calcium chloride, barium chloride, or silver nitrate, white ppts. (such as 2CaO. H₂O. 3B₂O₃, BaBO₂, AgBO₂, but variable in composition according to relative proportions used, temperature, &c.), readily soluble in dilute acids.

Strong Hydrochloric acid gives white crystalline ppt. of boric acid, in concentrated solutions,

$$Na_{o}O \cdot 2B_{o}O_{a} + 2HCl + 5H_{o}O = 2(B_{o}O_{a} \cdot 3H_{o}O) + 2NaCl.$$

SILICATES.

Insoluble in water, except those of K and Na.

Silica, or insoluble silicates, when fused with excess of K₂CO₃ or Na₂CO₃ in a platinum vessel, give silicates which are soluble in water, e.g.

$$SiO_2 + K_2CO_3 = SiO_2$$
. $K_2O + CO_2$.

These, when dissolved in water and poured into an excess of HCl, give a solution containing silicic acid,

$$SiO_2K_2O + 2HCl + H_2O = SiO_2$$
, $2H_2O + 2KCl$.

A solution of silicic acid, or a solution of any soluble silicate in HCl, when evaporated to dryness, leaves a residue of SiO_e, which is insoluble in all acids except HF.

Silica or silicates treated with a fluoride (e.g. NH₄F, or CaF₂) and concentrated H₄SO₄ give off gaseous silicon tetrafluoride,

$$SiO_{g} + 2H_{g}SO_{4} + 4NH_{4}F = 2(NH_{4})_{g}SO_{4} + SiF_{4} + 2H_{g}O.$$

Solutions of silicates (e.g. K₂SiO₃) give white ppt. with calcium chloride, barium chloride, or silver nitrate, of variable composition; easily decomposed by acids.

CARBONATES.

(E.g. Na2CO3) Treated with acids (either dilute or strong) CO2 is evolved,

$$Na_{g}CO_{g} + 2HCl = 2NaCl + H_{g}O + CO_{g}$$

This gas, when passed into lime water, gives white ppt. of calcium carbonate,

$$CO_2 + Ca(HO)_2 = CaCO_3 + H_2O.$$

Excess of CO, redissolves the ppt.

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2$$

Solutions of carbonates give with

Calcium chloride, white ppt. of calcium carbonate,

easily soluble in acids with effervescence.

Salts of almost all other metals give precipitates of carbonates or basic carbonates.

TARTRATES.

Solid tartrates heated with concentrated H₂SO₄ blacken immediately, owing to separation of carbonaceous matter, and evolve CO and CO₂.

Solutions of neutral tartrates, e.g.
$$KNa\overline{T} = \begin{cases} COOK \\ CHOH \\ CHOH \\ COONa \end{cases}$$
, give with

Calcium chloride, white gelatinous ppt. of calcium tartrate,

$$KNa\overline{T} + CaCl_2 = Ca\overline{T} + KCl + NaCl,$$

soluble in HCl, HNO₃, and acetic acid*. Soluble also in cold KHO (after washing), repptd. by boiling. Neutral cupric chloride converts it into *insoluble* cupric tartrate.

Potassium acetate, in presence of acetic acid, white crystalline ppt. of potassium hydrogen tartrate, especially on shaking,

$$\mathbf{Na_{2}T} + \mathbf{CH_{2}COOK} + \mathbf{CH_{3}COOH} = \mathbf{KH\overline{T}} + 2\mathbf{CH_{3}COONa},$$

more complete in presence of alcohol. Soluble in KHO, forming normal tartrate $K_{\underline{a}}\overline{T}$.

Silver nitrate, white ppt. of silver tartrate,

$$KNa\overline{T} + 2AgNO_3 = Ag_2\overline{T} + KNO_3 + NaNO_3$$

soluble in HNO, and in NH,

^{*} After standing some time calcium tartrate usually becomes crystalline, and will not then dissolve in acetic acid.

Tartrates (continued).

If dissolved in the least possible quantity of NH₃, the solution on heating deposits a bright mirror of metallic silver on the side of the tube*.

Potassium permanganate (one or two drops), in presence of caustic potash, is reduced on heating, first to green manganate,

$$2(K_2O \cdot Mn_2O_7) + 4KHO = 4(K_2O \cdot MnO_3) + 2H_2O + O_2$$

which is rapidly changed to a brown ppt. of hydrated manganese dioxide,

$$2(K_2OMnO_2) + 4H_2O = 2(MnO_2 \cdot H_2O) + 4KHO + O_2$$

the tartrate being oxidized to formate carbonate, &c.

If to a neutral or acid solution of a tartrate (or tartaric acid), a little ferrous sulphate be added, followed by a few drops of hydrogen dioxide, and lastly excess of caustic potash, a deep violet or blue colour is obtained. (Metals other than K, Na, and NH, must be absent.)

CITRATES.

Solid citrates treated with concentrated H₂SO₄, evolve CO, and on heating blacken slowly, evolving CO₂, acetone, &c.

Solutions of normal citrates, e.g. Na₃Ci (= C₃H₄(OH)(COONa)₃), give with

Calcium chloride, white ppt. of calcium citrate,

soluble in dilute acids, and in neutral cupric chloride. Insoluble in cold KHO.

N.B. Normal ammonium citrate gives no ppt. till boiled.

Barium acetate, white ppt. of barium citrate Ba₃Ci₂, especially in presence of alcohol and on long standing. (Tartaric acid must be first removed if present.)

Potassium permanganate, in presence of excess of KHO, is reduced on heating to green manganate, but is not further reduced, except after continued boiling.

Lime water added to free citric acid gives no ppt. (or only slight turbidity) in the cold, but on boiling, white calcium citrate is pptd.

Potassium acetate, no ppt. AgNO₃, white ppt. of Ag₃Ci, which does not behave as with tartrate on dissolving in NH₃ and heating.

FeSO4, H2O2, and KHO, as above, gives only a yellow or brown colour.

* The safest method of trying the "mirror" test is as follows: 1st, add dilute NH₃ to AgNO₃ till the ppt. first formed is nearly redissolved. 2nd, make the solution to be tested neutral or faintly alkaline with KHO. Mix the two solutions and heat gently.

CHLORIDES.

(E.g. NaCl.) Solid chlorides treated with concentrated H₂SO₄, evolve hydrochloric acid in the cold,

colourless gas forming dense white fumes of NH4Cl on coming in contact with NH4.

Heated with manganese dioxide and strong H.SO., chlorine is evolved.

$$2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

yellowish-green gas, bleaches litmus, liberates I from KI.

Distilled with dry potassium dichromate and concentrated H₂SO₄, chromyl dichloride ("chlorochromic acid") is obtained,

orange red gas condensing to a deep red liquid; decomposed on coming in contact with water, giving chromic and hydrochloric acids,

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Solutions of chlorides give with

Silver nitrate, white ppt. of silver chloride which coagulates on shaking.

insoluble in HNO3, soluble in NH3. Turns violet on exposure to sunlight. Not decomposed on heating.

Lead acetate, white ppt. of lead chloride PbCl₂.

Mercurous nitrate, white ppt. of mercurous chloride Hg₂Cl₂.

HYPOCHLORITES.

(E.g. NaClO.) Treated with HCl, chlorine is evolved in the cold,

NaClO + HCl = NaCl + HClO,

and

$$HClO + HCl = H_oO + Cl_2$$
.

Solutions of hypochlorites bleach litmus, indigo, ink, &c. They give with

Manganous chloride, brown ppt. of hydrated manganese dioxide,

$$NaClO + MnCl_{g} + 2NaOH = MnO_{g}$$
. $H_{g}O + 3NaCl$.

Metallic mercury, on shaking, yellow deposit of mercuric oxide,

$$NaClO + Hg = NaCl + HgO.$$

Free hypochlorous acid shaken with metallic mercury gives yellow mercuric oxychloride, HgCl₂. HgO; whereas free chlorine gives white mercurous chloride, Hg₂Cl₂.

CHLORATES.

(E.g. KClO₃.) Treated with concentrated H₂SO₄, the liquid turns yellow, and on heating, chlorine peroxide (yellow explosive gas) is evolved,

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$$

Heated with strong HCl, chlorine peroxide and chlorine are evolved,

$$2KClO_a + 4HCl = 2KCl + 2H_2O + 2ClO_2 + Cl_3$$

Most chlorates, when heated alone to redness, evolve oxygen and leave a chloride,

and at higher temperature,

Solutions of chlorates acidulated with dilute H₂SO₄ bleach indigo only on heating. If a few drops of sulphurous acid be added, however, they do so in the cold (the chlorate being reduced to chlorite or hypochlorite).

IODIDES.

(E.g. KI.) Treated with concentrated H₂SO₄, iodine is liberated as a brown or black ppt. which, on heating, gives violet vapours,

$$2KI + 3H_{g}SO_{4} = 2KHSO_{4} + SO_{2} + 2H_{2}O + I_{2}$$

Free iodine colours starch-paste blue; the colour is temporarily destroyed by heat. Solutions of iodides give with

Silver nitrate, pale yellow ppt. of silver iodide,

$$KI + AgNO_3 = AgI + KNO_3$$

practically insoluble in ammonia. Insoluble in dilute HNO₃. Darkens on exposure to light.

Chlorine water, or nitrous acid, liberates iodine,

$$2KI + Cl2 = 2KCl + I2$$
$$2HI + 2HNO2 = 2H2O + 2NO + I2.$$

If the mixture be shaken up with carbon disulphide, the iodine is dissolved out, giving a violet colour.

Cupric sulphate, dirty white ppt. of cuprous iodide, with liberation of iodine,

In presence of sulphurous acid no iodine is liberated,

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4$$

Lead acetate, yellow ppt. of lead iodide PbI₂, soluble in boiling water, crystallizing out on cooling. Mercuric chloride, red ppt. of mercuric iodide HgI₂, soluble in KI and in HgCl₂. Palladium nitrate, black ppt. of PdI₂.

IODATES.

 $(E.g. \text{ K}_2\text{I}_2\text{O}_6.)$ Boiled with strong HCl, chlorine is evolved, together with iodine trichloride,

$$K_2I_2O_6 + 12HCl = 2KCl + 6H_0O + 2ICl_3 + 2Cl_3$$

Strong H.SO. liberates iodic acid, but no free iodine.

Solutions of iodates give with

Potassium iodide, in presence of a dilute acid (H2SO4, HCl, or CH3COOH), liberation of iodine,

$$10HI + H_2I_2O_6 = 6H_2O + 6I_2$$
.

Silver nitrate, white ppt. of silver iodate,

$$K_2I_2O_6 + 2AgNO_3 = Ag_2I_2O_6 + 2KNO_3$$

sparingly soluble in cold dilute HNO_a. Easily soluble in ammonia, from which solution, SO₂ precipitates AgI, insoluble in ammonia.

Barium chloride, white crystalline ppt. of barium iodate BaI₂O₆. H₂O.

Pyrogallol C₆H₃(OH)₃, brownish-red colour, sometimes ppt. of purpurogallin C₂₀H₁₆O₉.

BROMIDES.

(E.g. KBr.) Heated with concentrated H₂SO₄, bromine is evolved, mixed with hydrobromic acid,

$$KBr + H_2SO_4 = KHSO_4 + HBr$$

 $2HBr + H_0SO_4 = 2H_0O + SO_2 + Br_0$.

Free bromine colours starch-paste yellow.

Heated with concentrated H_2SO_4 and manganese dioxide, bromine alone is evolved, $2KBr + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + 2H_2O + Er_2$.

Solutions of bromides give with

Silver nitrate, yellowish-white ppt. of silver bromide,

$$KBr + AgNO_3 = AgBr + KNO_3$$

sparingly soluble in ammonia. Insoluble in dilute HNO₃. Darkens on exposure to sunlight.

Chlorine water liberates free bromine,

$$2KBr + Cl_g = 2KCl + Br_g$$
.

If the mixture be shaken up with carbon disulphide, the bromine is dissolved out, giving a yellow or orange colour.

BROMATES.

(E.g. KBrO₃.) Heated with acids, bromic acid, HBrO₃, is liberated, which soon decomposes, giving off bromine and oxygen,

$$4 H Br O_3 = 2 H_2 O + 2 Br_2 + 5 O_2$$
.

Solutions of bromates give with

Silver nitrate, white ppt. of silver bromate,

sparingly soluble in dilute HNO₃. Soluble in ammonia.

Potassium bromide, in presence of cold dilute acid, liberation of bromine,

$$HBrO_3 + 5HBr = 3H_2O + 3Br_2$$
.

CYANIDES.

Treated with dilute HCl, many cyanides, (e.g. KCy, or ZnCy2) evolve hydrocyanic acid in the cold; others (e.g. HgCy2, or AgCy) require strong HCl and heating.

$$KCy + HCl = KCl + HCy.$$

The evolved HCy may be absorbed by KHO (on a watch-glass or filter paper) and tested with iron salts as below; (or by $(NH_4)_2S_2$, and tested for *sulphocyanate* with HCl and Fe_2Cl_6 — $(NH_4)_2S_2 + HCy = NH_4CyS + NH_4HS$).

Heated with excess of concentrated HaSO, carbon monoxide is evolved (in part),

$$2\mathrm{KCN} + 4\mathrm{H_{9}SO_{4}} + 2\mathrm{H_{9}O} = 2\mathrm{KHSO_{4}} + 2\mathrm{NH_{4}HSO_{4}} + 2\mathrm{CO}.$$

Solutions of cyanides (not mercuric cyanide) give with

Silver nitrate, white ppt. of silver cyanide,

$$\mathrm{KCy} + \mathrm{AgNO}_{3} \! = \! \mathrm{AgCy} + \mathrm{KNO}_{3},$$

insoluble in cold dilute HNO₂; easily soluble in ammonia, and in KCy. Not darkened by exposure to sunlight. On heating, it decomposes into metallic silver, cyanogen, and paracyanogen.

On adding successively Ferrous sulphate, Ferric chloride, and hydrochloric acid, a dark blue ppt., "Prussian blue," is obtained,

$$\begin{aligned} &6\mathrm{KCy} + \mathrm{FeSO_4} = \mathrm{K_4}\mathrm{FeCy_6} + \mathrm{K_2SO_4} \\ &3\mathrm{K_4}\mathrm{FeCy_6} + 2\mathrm{Fe_2Cl_6} = \mathrm{Fe_4}(\mathrm{FeCy_6})_3 * + 12\mathrm{KCl.} \end{aligned}$$

(If the solution contains free acid to start with, KHO must be added before applying the test. The object of the HCl is to dissolve the hydroxides of iron which may have been precipitated by alkali present.)

CYANATES.

(E.g. KCNO.) Treated with dilute acids, carbon dioxide is evolved, and an ammonium salt formed, which may be identified as usual,

$$KCNO + HCl = KCl + HCNO$$

 $HCNO + H_0O + HCl = NH_cCl + CO_0$

Traces of HCNO escape undecomposed, giving a pungent odour.

Solutions of cyanates treated with ammonium sulphate give ammonium cyanate, by double decomposition, which is soon transformed into urea,

The solution may be evaporated to dryness (on a water bath), the urea extracted with alcohol, and identified as usual.

Silver nitrate gives white ppt. of silver cyanate AgCNO, easily soluble in ammonia. Decomposed by acids as above.

FERROCYANIDES.

 $(E.g. K_{a}FeC_{a}N_{a}=K_{a}FeCy_{a}+K_{a}FCy.)$

Heated with strong H2SO4, carbon monoxide is evolved

$$\mathbf{K_4} \mathbf{FeC_6N_6} + 6\mathbf{H_2SO_4} + 6\mathbf{H_2O} = 2\mathbf{K_2SO_4} + 3(\mathbf{NH_4})_2\mathbf{SO_4} + \mathbf{FeSO_4} + 6\mathbf{CO_4}$$

With dilute H2SO4, hydrocyanic acid is obtained,

$$2\mathrm{K_4FeCy_6} + 3\mathrm{H_2SO_4} = \mathrm{K_2Fe(FeCy_6)} + 3\mathrm{K_2SO_4} + 6\mathrm{HCy}.$$

Solutions of ferrocyanides give with

Silver nitrate, white ppt. of silver ferrocyanide,

$$K_4(FeCy_6) + 4AgNO_3 = Ag_4(FeCy_6) + 4KNO_3$$

insoluble in dilute HNO, and in cold ammonia.

Ferric chloride, dark blue ppt. of "Prussian blue." (See Ferric salts.)

Ferrous sulphate, pale blue (white if quite pure) ppt. of potassium ferrous ferrocyanide,

K_FeCy_s + FeSO_s = K_sFe''FeCy_s + K_sSO_s.

Cupric sulphate in excess, chocolate ppt. of cupric ferrocyanide,

$$\mathbf{K_4FeCy_6} + 2\mathrm{CuSO_4} = \mathrm{Cu_2(FeCy_6)} + 2\mathbf{K_2SO_4}.$$

Oxidizing agents, such as K2Mn2O2 or chlorine, convert ferrocyanides into ferricyanides,

$$10 K_4 FeCy_6 + K_2 O \cdot 2 MnO \cdot O_5 + 8 H_2 SO_4 = 5 K_6 (Fe_2 Cy_{19}) + 6 K_2 SO_4 + 2 MnSO_4 + 8 H_2 O.$$

FERRICYANIDES.

$$(E.g. K_{\epsilon} Fe_{2}C_{12}N_{12} = K_{\epsilon} Fe_{2}Cy_{12} = K_{\epsilon}(FdCy)_{s'})$$

Heated with concentrated H₂SO₄, carbon monoxide is evolved (also CO₂, &c.) and ferric, potassium, and ammonium sulphates remain.

Solutions of ferricyanides give with

Silver nitrate, orange ppt. of silver ferricyanide,

$$K_6(Fe_2Cy_{12}) + 6AgNO_3 = Ag_6(Fe_2Cy_{12}) + 6KNO_3$$

insoluble in dilute HNO, soluble in ammonia.

Ferrous sulphate, dark blue ppt. of ferrous ferricyanide (?) "Turnbull's blue."

$$\mathbf{K}_{\mathrm{e}}(\mathrm{Fe_{2}Cy_{12}}) + 3\mathrm{FeSO_{4}} = \mathrm{Fe_{3}}(\mathrm{Fe_{2}Cy_{12}}) + 3\mathrm{K_{2}SO_{4}}.$$

Potassium iodide (in presence of HCl) reduces ferri- to ferro-cyanides with liberation of iodine,

$$K_{\epsilon}Fe_{2}Cy_{12} + 2KI = 2K_{4}FeCy_{\epsilon} + I_{2}$$
.

Ferric chloride, no ppt. (brown solution, green if not quite pure).

Copper sulphate, yellowish-green ppt., Nickel sulphate, yellowish-green ppt. Cobalt nitrate, reddish-brown ppt. of the respective ferricyanides.

SULPHOCYANATES.

(E.g. KCNS.) Heated with strong HCl or H₂SO₄, carbon dioxide, hydrosulphuric acid, hydrocyanic acid, &c. are evolved,

$$KCNS + H_2SO_4 = KHSO_4 + HCNS$$

 $3HCNS = H_2C_2N_2S_3 + HCN$
(yellow ppt.)
 $HCNS + 2H_2O = CO_2 + H_2S + NH_3$.

Solutions of sulphocyanates give with

Ferric chloride, blood-red colour due to ferric sulphocyanate Feg(CNS). The colour is bleached by mercuric chloride, but not by dilute HCl.

Silver nitrate, white ppt. of silver sulphocyanate,

easily soluble in ammonia, insoluble in dilute HNO3.

NITRATES.

(E.g. KNO_3 .) Heated with concentrated H_2SO_4 , nitric acid is evolved, $KNO_3 + H_0SO_4 = KHSO_4 + HNO_3$.

Part of the HNO₃ usually splits up, giving yellow or brown vapours of lower nitrogen oxides, e.g.

$$4HNO_{3} = 2H_{2}O + 4NO_{2} + O_{2}$$

Heated with concentrated H₂SO₄ and metallic copper, brownish-red fumes of nitrogen peroxide are given off,

$$2KNO_3 + 3H_2SO_4 + Cu = 2KHSO_4 + CuSO_4 + 2H_2O + 2NO_2$$
.

Solutions of nitrates

Treated with excess of ferrous sulphate in the cold, and concentrated H₂SO₄ gradually poured in down the side of the vessel, give a brown ring where the liquids meet,

$$2\mathrm{KNO_3} + 6\mathrm{FeSO_4} + 4\mathrm{H_2SO_4} = \mathrm{K_2SO_4} + 3\mathrm{Fe_2(SO_4)_3} + 4\mathrm{H_2O} + 2\mathrm{NO}$$

$$2\mathrm{FeSO_4} + \mathrm{NO} = \underbrace{(2\mathrm{FeSO_4},\mathrm{NO})}_{\text{brown compound}}.$$

and

Heated gently with amalgamated zinc they are reduced (in part at any rate) to nitrites, $KNO_a + Zn = KNO_e + ZnO$,

which may be detected by the KI+HCl test, &c. [See Nitrites.]

Brucine in presence of concentrated H,SO, gives a red colour.

Mixed with dilute H₂SO₄, solutions of nitrates do not bleach indigo in the cold (even in presence of SO₂), but do so on heating.

"Nascent" hydrogen (from Zn + KHO, &c.) converts them into ammonia. [See Nitrites.]

NITRITES.

(E.g. KNO2.) Treated with dilute acids, nitric oxide is evolved,

$$KNO_g + HCl = KCl + HNO_g$$

 $3HNO_g = HNO_g + 2NO + H_gO.$

and

The evolved gas unites with oxygen from the air, giving brownish-red fumes of NoO4.

Solutions of nitrites give with

Ferrous sulphate, even in neutral solution or in presence of dilute acid, a brown colour,

$$2KNO_{2} + 2FeSO_{4} + 2H_{2}SO_{4} = K_{2}SO_{4} + Fe_{2}(SO_{4})_{3} + 2H_{2}O + 2NO$$

 $2FeSO_{4} + NO = (2FeSO_{4}, NO).$

and

Nitrites (continued).

Potassium iodide, in presence of dilute HCl or H2SO4, liberation of iodine (detected by starch-paste or CS2),

$$2KNO_{o} + 2KI + 4HCl = 4KCl + 2H_{o}O + 2NO + I_{o}$$

Urea, added to free nitrous acid (or a nitrite + dilute H₂SO₄), gives off nitrogen and carbon dioxide,

$$CO(NH_g)_2 + 2HNO_g = CO_g + 3H_gO + 2N_g$$

(complete on heating).

"Nascent" hydrogen, e.g. from zinc (coated with copper) and caustic potash, evolves ammonia from either nitrates or nitrites,

$$Zn + 2KHO = ZnO \cdot K_2O + H_2$$

 $KNO_2 + 3H_2 = KHO + H_2O + NH_2$.

and

Potassium permanganate + dil. H.SO, is at once decolourized.

Meta-diamido-benzene C₆H₄(NH₂)₂ in presence of dilute H₂SO₄, a yellow colour, even in very dilute solutions

Aniline sulphate (one or two drops of solution) triturated with a concentrated solution of a nitrite
gives the odour of phenol C₆H₅OH.

ACETATES.

(E.g. CH₃. COONa.) Heated with concentrated H₂SO₄, acetic acid is given off (recognized by its odour)

$$CH_8$$
. $COONa + H_2SO_4 = NaHSO_4 + CH_3$. $COOH$.

Heated with concentrated H₂SO₄ and alcohol (one or two drops) the characteristic odour of ethyl acetate is produced,

$$CH_a$$
. $COOH + (C_2H_5)OH = CH_a$. $COO(C_2H_5) + H_2O$.

Heated to redness with arsenious anhydride, characteristic (poisonous) odour of cacodyi As_z(CH_s)_z is produced.

Neutral solutions of acetates give with

Ferric chloride, a red colour, due to ferric acetate (CH₂. CO₂)₆Fe₂. On boiling the solution, a brown ppt. is produced of basic ferric acetate (CH₃. CO₂)₆Fe₂. nFe₂O₃. The red colour is bleached by HCl but not by HgCl₂.

FORMATES.

(E.g. H. COONa.) Heated with concentrated H₂SO₄ carbon monoxide is evolved without blackening of the liquid,

 $H \cdot COONa + H_2SO_4 = NaHSO_4 + H_2O + CO.$

Neutral solutions of formates give with

Silver nitrate, on heating, a black ppt. of metallic silver.

Mercuric chloride, on heating, a white ppt. of mercurous chloride, or a grey ppt. of metallic mercury, according to quantity.

Ferric chloride gives a reaction similar to that produced with acetates.

[#] Confirm by fusing with excess of Na, CO, and a little KNO,. Mn bluish-green, Cr yellow,

TO DISSOLVE A SUBSTANCE FOR ANALYSIS.

Boil the finely powdered substance with (1) water, (2) hydrochloric acid, (3) nitric acid, (trying both dilute and strong acids), (4) aqua regia; pouring off the previous solvent in each case. If a part only dissolves, the solution may be examined separately*.

If all the above reagents fail to dissolve the substance[†], fuse it (or that portion which is insoluble) with about 5 times its weight of pure dry sodium carbonate[‡], extract the fused mass with boiling water§.

FILTER

RESIDUE

Wash; dissolve in hot dilute HCl (or in presence of Ag and Pb, HNO₃) and test for metals (and silica) as usual_{||}.

An insoluble residue is probably due to insufficient fusion.

SOLUTION

Examine a portion for acids in the usual way, after acidifying with dilute HNO₃.

Acidify the remainder with HCl and test as usual for silica and metals (Al, Cr, Mn, Zn, As, Sn).

Since cyanides, ferrocyanides, cobalticyanides, &c. often greatly interfere with the ordinary processes of analysis, it is best to destroy them, if present, before proceeding.

This may be done by evaporating to dryness with strong sulphuric acid, and heating, whereby the metals, including those in the acid cyanogen radicle, are obtained as sulphates.

In some cases silver nitrate in excess may be used, followed by excess of nitric acid. In this way the cyanides, &c. are obtained as silver salts, and the metals remain in solution as nitrates.

The solution for analysis is assumed to be neutral or slightly acid. If strongly acid it must be diluted largely, or nearly neutralized with Na₂CO₃. If alkaline it should be just acidified with dilute HNO₃, any precipitate produced being filtered off and examined separately.

* If the substance is a metal or alloy, heat it with strong nitric acid (adding water if necessary), evaporate to small bulk to remove excess of acid, add water and filter.

RESIDUE

Contains antimony and tin [as hydrated SnO₂ and Sb₂O₅, or as arsenates; also possibly Bi as arsenate or phosphate; Au and Pt].

Digest with zinc and dilute HCl. Test evolved gas for AsH₃ by the AgNO₃ reaction. Residue on the zinc consists of metallic Sb and Sn (Bi, Au, Pt).

Boil for some time with strong HCl.

ou for some time with strong an

RESIDUE Sb (Bi, Au, Pt).

Digest with yellow ammonium sulphide. Sb dissolves as sulphosalt.

Evaporate solution just to dryness. Orange red residue ANTIMONY.

SOLUTION

Contains Sn as stannous chloride. Add mercuric chloride.

White ppt. (which usually turns grey on heating) TIN.

SOLUTION

Examine for metals as usual, except for Sn, Sb (Au, Pt).

- † The only common substances likely to remain insoluble in water and acids are:—SiO₂ and silicates. Sulphates of Ba, Sr, Pb (Ca). Fluoride of Ca, &c. Chrome iron ore. SnO₂. Sb₂O₄ and Sb₂O₅. AgCl (and some other Ag salts which are converted into AgCl). Ignited Sesquioxides of Fe, Al, Cr (in part). Ignited lead chromate. Some metaphosphates, arsenates, &c. Carbon. Sulphur. These are all more or less decomposed, or rendered soluble, by fusion with Na₂CO₃. Chrome iron ore is best decomposed by fusion with about 3 parts of Na₂CO₃ and 2 of powdered fused borax (or with a mixture of 2NaF+NaHSO₄). Tin and antimony oxides may also be decomposed by fusion with KCy, whereby they are obtained as metals.
- ‡ A platinum crucible or foil may be used in absence of easily reducible metals (generally indicated in preliminary examination) such as Pb or Ag. If they are present, porcelain must be employed (in which case small quantities of Al, Si, &c. will be introduced), or else they must be first removed. PbSO₄ may be dissolved out with ammonium acetate and ammonia; AgCl with potassium cyanide.
- § The action of sodium carbonate here is, generally speaking, to give an insoluble carbonate or oxide of the metal, and a soluble sodium salt of the acid—e.g.

$$\label{eq:Na2CO3} \operatorname{Na2CO_3} + \operatorname{BaSO_4} = \operatorname{BaCO_3} + \operatorname{Na2SO_4}. \qquad \operatorname{Na2CO_3} + \operatorname{CaF_2} = \operatorname{CaCO_3} + 2\operatorname{NaF}.$$

In case of silicates, potassium and sodium must be looked for in a separate portion of the original substance. This may be done as follows—Heat the finely powdered substance with ammonium or calcium fluoride (pure) and strong H₂SO₄ (in a platinum vessel). In this way the silicon is removed as gaseous tetrafluoride.

$$4NH_4F + SiO_2 + 2H_2SO_4 = 2(NH_4)_2SO_4 + 2H_2O + SiF_4$$

and the metals remain as sulphates. Extract with water and test solution for K and Na in the ordinary way (after removing previous groups, if present, as usual).

Or 1 part of the finely powdered substance may be strongly heated in a covered platinum vessel with about 8 parts of pure CaCO₃ and 1 part of NH₄Cl for about an hour. The mass is then extracted with water, and the calcium removed from the solution by precipitation with ammonium carbonate.

EXAMINATION FOR ONE METAL.

If solid, dissolve in (1) water, (2) HCl, (3) HNO₃ (try both dilute and strong acids), (4) aqua regia. Otherwise fuse with Na₂CO₃. If solution is alkaline, just acidify with HNO₃ (dilute), filter off any ppt., and examine it separately. [See p. 42.] If solution is strongly acid, dilute, or nearly neutralize it, before Group 2. Test portions of the solution as follows:

1	1	1.	io	1		1 4				act	100			ur refer to G	
CONFIRMATORY TESTS in original solution or substance.	(1) K _o CrO, crimton ppt. (2) The HCl ppt, turns violet on exposure to light.	 Dilute H₂SO₄ white ppt. K₂CrO₄ yellow ppt. soluble in boiling water. 	 Heat solid in bulb-tube with dry Na₂CO₃. Grey sublimate of metallic mercury. KHO black ppt. insoluble in NH₃. Same as for Mercuric (1). 			 Try Marsh's test. Black stain on porcelain, soluble in NaClO. Distinguish between As" and As' by adding AgNO₃ (in neutral solution) { yellow = As" } 	 Acidify dilute solution with HCl, pour it on to piece of zinc in contact with platinum foil; black stain on the platinum. Marsh's test; black stain not dissolved by NaClO. Distinguish between Sb" and Sb' by AgNO, test. 	 Add small piece of zinc+dilute HCl. Allow to stand. Pour off liquid, and dissolve residue in strong hot HCl. Add HgCl₂. White ppt. (often turning grey on heating). Distinguish between Sn" and Sn" by adding HgCl₂ to original solution. White ppt. Sn". No ppt. Sn". 	 Acidulate with HCl and add metallic copper. [Nitric acid must be absent.] Bright deposit of metallic mercury on the copper. Wash, dry, and heat in dry test-tube. Grey sublimate of Hg. KHO yellow ppt. (3) Dry test same as for Mercurous (1). 		(1) NH ₃ pale blue ppt. redissolving at once in excess to deep blue solution. (2) K ₄ FeCy ₈ chocolate ppt.	 NH₂ white ppt.; dissolve it in least possible HCl, and add much water; white milky ppt. SnCl₂+KHO black ppt. R.CrO, vellow ppt. insoluble in KHO 	KCy in excess + H ₂ S yellow pp NH ₃ white ppt. easily soluble i		Heated on charcoal usually gives white infusible mass. Treated with Co(NO ₃₎₂ and again heated, blue mass.
ke ppt. with ammonia.	lved	nged	ened	, and digest portions th hot	Ammonium carbonate	Dissolved	Undissolved	Undissolved						solution of original sub- H ₃ ppt.) with ammonium Yellow ppt. on heating T.E.	inous ppt.; soluble in excess; repptd. by NH4Cl
Pour off liquid and shake ppt. with ammonia.	Dissolved	Unchanged	Blackened	Wash ppt. with water, and digest portions of it with hot	Ammonium sulphide‡	Dissolved	Dissolved	Dissolved	Undissolved	Ditto	Ditto (nearly)	Ditto	Ditto	Test a nitric acid solution of original sub- stance (or of the NH ₃ ppt.) with ammonium molybdate in excess. Yellow ppt. on heating shews a PHOSPHATE. Test original solution with Caustic Potash.	White gelatinous ppt repptd. b
Add dilute Hydrochloric Acid.	SILVER	LEAD	MERCURY	Add dilute HCl and pass Hydrosulphuric Acid gas.	Heat.	ARSENIC (yellow)	ANTIMONY (orange)	TIN (-ous dark brown) (-ic dirty yellow)	MERCURY Mercuric (black)	LEAD (black) **	COPPER (brownish-black)	BISMUTH (brownish-black)	(yellow)	Add a few drops of nitric acid d boil. Then add NH ₄ Cl in cess, and Ammonia. Boil.	(white)
Add dilute		White ppt.	indicates*	Add dilt Hydrost					indicatest					Add a few drops of and boil. Then add excess, and Ammonia. Boil.	
-		-						esi Unle	ss the co	ont	rary	is sta	ted,	each reagent	must

Cable n 47 and to specie	al reactions of eac	h met	al										
(2) Distinguish between Cr" and Cr" by lead acetate test in original solusition. [See Acids.] (2) Distinguish between Cr" and Cr" by lead acetate test in original solusition. [See Acids.] (3) KePeCye { dark blue ppt. Ferrous. No ppt. Ferricl. Perrous of Marge excess of sodium acetate and some acetic acid. [Ad large excess of sodium acetate and some acetic acid. [A ppt. here indicates Oxalate or Fluoride of Ca(BaSr), or phosphate of Fe(CrM)].] Add a few drops of Fe ₂ Cl ₂ ; yellowish-white ppt. confirms Phosphate of Sec Ca Ba Sr Mg. In this case add Fe ₂ Cl ₂ until solution is red. Boil. Add ed Sec Ca Ba Sr Mg. Filter. Test filtrate for Ca Ba Sr Mg by 5 and 6.	iginal substance (or NH ₃ ppt.) to low redness. Add acetic acid. scence indicates Oxalate. Filter if necessary. Test solution for Sr) by 5. Fluoride by heating with strong H ₃ SO ₄ . See Acids. Fuse original tee with Na ₂ CO ₃ . Extract fused mass with water. Filter. Test for Ca, &c., and solution for Fluoride, Borate, &c. with HCl. Evaporate to dryness. Digest residue with HCl. insoluble in HCl—Silica.	met	xidizing flame. 1st redissolved. Boil for some time in 7 to stand. Black ppt.	Bo	(2) Distinguish between Mn" and Mn", Mn", Mn", &c., by boiling with HCl Schoeled—Mn", Mn", Mn", &c. HCl Scholed—Mn", Mn", Mn", &c.	 Pass H₂S into the KHO solution. White ppt. Heat on charcoal. Usually, yellow mass when hot, white when cold. Add Co(NO₈)₂ and again heat. Green mass. 		(1) K ₂ GrO ₄ yellow ppt. (2) H ₂ SiF ₆ translucent crystalline ppt. (3) Flame test, green.	 Flame test, crimson. (2) H₂SiF₆, and K₂CrO₄ in dilute solution, no ppts. (1) (In absence of Ba and Sr) Ammonium oxalate + NH₃ white ppt. Soluble in HCl: insoluble in acetic acid. (2) Flame test, orange red. 	tandi	(1) Boil with KHO. Odour of NH ₃ produced. (2) PtCl ₄ yellow ppt. (in lines on stirring). (See Potassium.)	(1) (In absence of NH4.) Acidify strong solution with HCl. Add PtCl4. Stir. Yellow ppt. in lines. (2) Flame test, violet.	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
Green ppt.; soluble in excess; repptd. by boiling† Reddish-brown ppt. Ferric insoluble Dirty green ppt. Ferrous in excess White ppt. insoluble in excess	White ppt. insoluble in excess White ppt. insoluble in excess	Test original solution with caustic potash.	Pale green ppt. insoluble in excess	Blue ppt. insoluble in excess	White ppt. insoluble in excess. Rapidly turning brown when shaken with air	White ppt. soluble in excess	Test original solution with Calcium Sulphate	Immediate white ppt.	White ppt. on standing or heating No ppt.	Stir. White ppt. MAGNESIUM.	AMMONIUM	POTASSIUM	A characteristic of
CHROMIUM§ (bluish-green) IRON§ (reddish-brown) PHOSPHATE of of Ba, Sr, Ca, or Mg (white)	OXALATE of Ca(BaSr) (white) FLUORIDE [or BORATE, &c.] of Ca(BaSr) (white) SHJICA (white)	Add NH ₄ Cl, NH ₃ and Ammonium sulphide.	NICKEL (black)	COBALT (black)	MANGANESE (buff or pink)	(white or greenish)	Add NH,Cl in excess, NH3 and Ammonium carbonate.	BARIUM	STRONTIUM	Add NH,Cl, NH, and Sodium phosphate.		Lest portions of original solution for	
Ppt.	Ad			Ppt. indicates		Add NI Am		ppt. indicates		E			
က်				4			1	5		6	100	7.	

* A white ppt. which dissolves at once in cold water probably indicates a Barium salt. One which readily redissolves in slight excess of HCl probably Antimony or Bismuth. A white or nearly white ppt. which does not settle is probably Sulphur, indicating an exidizing agent.

If a ppt. of Sulphur is obtained, with much change of colour, filter off the ppt., boil filtrate to expel H₂S, and proceed with this, instead of original solution. 'An orange solution changing to green with pptn. of sulphur indicates Chromium as Cr".

‡ Yellow.

§ As phosphate or otherwise.

¶ Ferrous salts almost always contain ferric.

** Lead is sometimes precipitated as red sulphochloride if much free HCl is present.

(1) Flame test, intense yellow. Fixed residue on heating.

POTASSIUM RODIOM

be added until no further effect is produced.

GENERAL TABLES FOR MIXTURES OF METALS.

Add Ammonium Carbo ate and heat gently. BARIUM Ppt. = STRONTIUM CALCIUM Filter. Examine filtre by Table VI. and ppt. Table V.
Add Ammonium Sulphide in slight excess and heat**. Ppt. = Add Ammonium Carb And Ammonium Carb BARIUM COBALT COBALT Filter. Examine filtrate by column (5) and ppt. by Table V. Table V. Table IV.
Boil till H ₂ S is entirely expelled. Add nitric acid drop by drop as long as any change occurs. Then add any change occurs. Then any change occurs. Then and any change occurs. Then any change occurs. Then and any change occurs. The and any change occurs. The and any change occurs. The and any change occurs occurs. The any change occur
trosulphuric Acid gas n, and heat*. GERCURY (dyad) JEAD SISMUTH SOPPER ADMIUM ANTIMONY Examine filtrate by Examine filtrate by Examine filtrate by A Solution (B) By A Solution (B) By A Solution (B) By A Solution (B) By A Table II. B.
Add Hydrochloric Acid (dil.). Ppt. = Sulver Sulver Sulver Sulver Sulver (MERCURY (dyace at the solution by column (2). Appt. which redissolves at once in cold water, is probably due to Antimony or Bismuth. One which redissolves at once in cold water, is probably a Barium salt. Boric, Uric and Benzoic acids some time with hot yellow may be pptd. here if strong acid monium sulphide‡. Filter. Examine by Examine Habit II. A. Residue II. A. Residue II. A. Table III. A.

rate.

* If much acid has been added, the solution should be diluted largely with water, or nearly neutralized, before passing H₂S. If a further pptn. occurs on heating, boil and pass H₆S again.

+ A white or nearly white ppt. which does not settle is probably sulphur, shewing the presence of an oxidizing agent. If the solution turns bright green with pptn. of sulphur, chromic acid is probably present.

Since CuS is somewhat soluble in yellow ammonium sulphide, it is advisable to use sodium sulphide if traces of Cu are being looked for.

§ Test a portion of this solution by evaporating to dryness and heating the residue. A residue which does not dissolve in HCl on heating is probably SILICA. If present, it must be removed from the remainder of the solution in the same way before proceeding. If the residue blackens considerably on heating, organic bodies such as sugar or tartaric acid are probably present. These should be destroyed by ignition, since they prevent the precipitation of this group, wholly or in part.

If complete separation is required, the ppt. produced by ammonia must be redissolved in HCl and reprecipitated by NH₄Cl and NH₃, and this

process repeated until the filtrate gives no ppt. with ammonium sulphide. In presence of chromium it is necessary to boil for a considerable time to ensure its precipitation with ammonia.

I Phosphates of zinc, manganese, nickel and cobalt may also be precipitated here, in part. If it is required to look for them, the ammonia ppt. must be washed and digested with ammonium sulphide, the filtrate tested for phosphate, and the ppt. washed and redissolved in HCl (with a drop of HNO₃ if necessary) and treated as in column (3). It is the safest plan always to treat the precipitate in this manner.

** It is advisable to test a few drops of the filtrate with ammonium sulphide before adding it to the main portion.

++ If a large excess of ammonia is present, manganese may be entirely held in solution, until the solution is boiled for some time.

Possibly also some IRON, if much alkaline phosphate is present.

§§ If the filtrate from the ammonium sulphide ppt. is dark coloured (probably indicating nickel), the solution should be acidified with dilute HCl, boiled, filtered, and again rendered alkaline with NH₃, before proceeding.

EXPLANATION OF GENERAL TABLE.

Hydrochloric acid precipitates silver, lead (in part) and mercury (mercurous) as chlorides, AgCl, PbCl₂ and Hg₂Cl₂, thus separating them from all the other common metals, whose chlorides are soluble. (Bismuth and Antimony are often precipitated here as oxychlorides BiOCl and SbOCl, but the ppt. at once dissolves in more HCl. Strong HCl precipitates barium salts, these being insoluble in strong acids; cold water at once dissolves the ppt.)

These chlorides having been filtered off, Hydrosulphuric acid precipitates mercury (mercuric), lead, bismuth, copper, cadmium, arsenic, antimony and tin, as sulphides, HgS, PbS, Bi₂S₂, CuS, CdS, As₂S₂, Sb₂S₃ or Sb₂S₄, SnS or SnS₂, these being insoluble in dilute HCl.

Arsenic compounds are usually first reduced, in part at any rate, to the arsenious state with separation of sulphur, e.g.

$$As_2O_5 + 2H_0S = As_2O_3 + 2H_2O + 2S.$$

This operation is very slow, requiring continued boiling, and repeated saturations with H₂S, hence arsenic in this state is often overlooked. [Some prefer to reduce the arsenic to the arsenious state by boiling with SO₂ before passing H₂S, but this process is liable to lead to complications, such as precipitation of Ba, Pb, &c. as sulphates.]

A precipitate of sulphur on passing H₂S indicates the presence of an "oxidizing" agent, such as free chlorine, hypochlorites, chromic arsenic or strong nitric acids, ferric salts, &c., e.g.

$$H_2S + Cl_9 = 2HCl + S.$$
pptd.

The ppt. produced by H₂S is well washed, in order to remove the salts which are still in solution, and free HCl, and digested with yellow ammonium sulphide*.

This converts the sulphides of arsenic, antimony, and tin, into soluble sulpho-salts, such as (NH₄)₂AsS₃, (NH₄)₂SbS₃ and (NH₄)₂SnS₃. For instance,

$$3(\mathbf{NH_4})_{g}\mathbf{S} + \mathbf{As_{g}S_{g}} = 2(\mathbf{NH_4})_{g}\mathbf{AsS_{g}}.$$

The remaining sulphides are left undissolved, and are separated by filtration.

The filtrate from the H₂S precipitate is tested with more H₂S to ascertain whether the previous group is entirely precipitated. If this is the case, the excess of H₂S is removed by boiling, and a few drops of nitric acid added, in order to convert any ferrous salt which may be present into the ferric state (since ferrous salts are only partially precipitated by ammonia). Thus

$$6 \text{FeCl}_2 + 2 \text{HNO}_3 + 6 \text{HCl} = 3 \text{Fe}_2 \text{Cl}_6 + 4 \text{H}_2 \text{O} + 2 \text{NO}.$$

The brown colour which is usually observed being due to a compound of NO with unaltered ferrous salt.

Ammonium chloride and ammonia are now added. (NH₄Cl has the property of forming double chlorides with the chlorides of magnesium, manganese, &c. which are not precipitated by NH₃, and are thus kept out of this group. It also renders the precipitation of aluminium hydroxide by ammonia more complete.)

* The yellow "ammonium sulphide" used in laboratories is a mixture consisting chiefly of polysulphides of ammonium (such as (NH₄)₂S₂) and ammonium thiosulphate (NH₄)₂S₂O₃.

EXPLANATION OF GENERAL TABLE (continued).

Ammonia precipitates iron, chromium and aluminium from most of their combinations, as hydroxides, such as Fe₂(HO)₆, Cr₂(HO)₆ and Al₂(HO)₆, e.g.

$$Al_{g}Cl_{e} + 6NH_{a} + 6H_{g}O = Al_{g}(OH)_{e} + 6NH_{g}Cl_{g}$$

and by neutralizing the acid in which they are dissolved, precipitates many salts which are insoluble in water, i.e. phosphates of Fe, Cr, Al, Ca, Ba, Sr, Mg; oxalates (fluorides, borates, silicates, &c. in part) of Ca, Ba, Sr.

(Ferric and aluminium phosphates are very imperfectly precipitated in presence of much alkaline phosphate, and may therefore occur in the next groups.)

In addition to the above, ammonia partially precipitates phosphates of Zn, Mn, Ni, Co. If these are present in any quantity, it is necessary to decompose them by digesting the precipitate with ammonium sulphide, which converts them into sulphides, e.g.

$$Zn_3(PO_4)_g + 3(NH_4)_gS = 2(NH_4)_3PO_4 + 3ZnS.$$

The solution is tested for phosphoric acid with magnesia mixture, which, if found, indicates phosphates of Zn, Mn, Ni, Co, or Fe. The residue containing the sulphides of these metals is dissolved in acids, and treated exactly as before with NH₄Cl, NH₃, &c. The precipitate thus obtained is free from Zn, Mn, Ni, and Co. The filtrate from it may be examined separately for these metals. If present they probably existed as phosphates.

The separation of groups 3 and 4 by ammonium chloride and ammonia is very imperfect, manganese and zinc especially being carried down with the 3rd group. It is therefore necessary, in cases of accuracy, to repeatedly redissolve the ppt. in HCl, and reprecipitate it with NH₄Cl and NH₃.

A more complete separation of Fe", Cr, Al, from Zn, Mn, Ni, Co, is effected by means of barium carbonate, which ppts. only Fe, Cr, Al. This process, although it takes considerable time, is advisable in cases where accuracy is required, especially if traces of zinc have to be searched for.

To the filtrate from the ammonia precipitate, ammonium sulphide is added. This throws down zinc, manganese, nickel and cobalt as sulphides, ZnS, MnS, NiS, CoS, these being insoluble in alkaline solution. Excess of ammonium sulphide dissolves nickel sulphide to a considerable extent, forming a black solution, and must therefore be avoided. In some cases (as when nickel sulphide has been thus dissolved) it is advisable to destroy the excess of ammonium sulphide with a dilute acid before proceeding,

$$(NH_4)_gS_g + 2HCl = 2(NH_4)Cl + H_gS + S.$$
 pptd.

The filtrate from the ammonium sulphide precipitate contains only Ba, Sr, Ca, Mg, and alkali metals. Ammonium carbonate is added, and the solution heated to decompose carbamate, bicarbonate, &c. This precipitates barium, strontium and calcium carbonates, BaCO₃, SrCO₃, CaCO₃. The liquid must not be boiled, since the reaction then tends to reverse, e.g.

$$\mathrm{CaCO_3} + 2\mathrm{NH_4Cl} = (\mathrm{NH_4})_2\mathrm{CO_3} + \mathrm{CaCl_2}.$$

The filtrate, containing only Mg and alkalies, is examined by Table VI.

TABLE I.

Ag, Pb, Hg'.

Wash ppt. with cold water, then boil it for some time with a considerable quantity of hot water.

FILTER

RESIDUE SOLUTION Add potassium chromate. Digest with ammonia. Filter. Yellow ppt. insoluble in acetic acid. RESIDUE (black) SOLUTION MERCURY. Acidify with HNO, white

Confirm by drying ppt. at gentle heat, mixing with dry Na CO, and heating in a bulbtube.

Grey ring united into globules by rubbing with a rod.

SILVER.

ppt. turning violet on exposure

LEAD.

The precipitate produced by hydrochloric acid contains silver, lead, and mercurous chlorides AgCl, PbCl, Hg,Cl,.

The separation of these is based upon the fact that

- (1) PbCl, is soluble in boiling water, AgCl and Hg,Cl, insoluble.
- (2) AgCl is soluble in ammonia, Hg, Cl, insoluble.

to sunlight.

The PbCl, is first extracted with boiling water, and confirmatory tests for lead applied to the solution so obtained.

The AgCl is extracted from the residue by ammonia, from which it is reprecipitated unchanged by nitric acid (the latter merely neutralizing the ammonia).

Hg, Cl, is converted by ammonia into a black substance (NHg', H,)Cl (chloride of dimercurous-ammonium) which remains undissolved, and is confirmed by the dry test for mercury.

TABLE II. A.

Hg", Pb, Bi, Cu, Cd.

Wash well. Heat with moderately dilute nitric acid as long as any action is observed.

FILTER

e of alcohol†.	Boil off the alcohol. Add ammonia in excess. FILTER	Solution. If blue contains COPPER. Confirm by acidifying a portion with acetic acid and adding potassium ferrocyanide. Chocolate ppt. If copper is present, add KCy to the remainder of blue solution until colourless. Pass H ₂ S. Yellow ppt. CADMIUM.
SOLUTION Add dilute H _s SO ₄ and an equal volume of alcohol†. FILTER		Ppt. Dissolve in the least possible quantity of HCl. Add much water. White milky ppt. BISMUTH.
Add dilu	White ppt. LEAD.	Connrm by dissolving the ppt. in ammonium acetate and adding potassium chromate. Yellow ppt. sol. in KHO.
RESIDUE (black*) MERCURY (mercuric) Confirm by drying at a gentle heat, mixing with dry Na, CO.	and heating in a bulb-tube. Grey ring, united into globules by rubbing with a rod.	

[.] It is best to heat the ppt. with water and add strong HNO3 drop by drop till the action commences. If the acid be too strong, lead will be chiefly converted into sulphate and remain in the residue with mercury. The latter may also be converted into a white substance.

⁺ It is advisable to test a small portion for lead in the first instance, since, if absent, sulphuric acid and alcohol need not be added to the remainder.

EXPLANATION OF TABLE II. A.

The residue insoluble in ammonium sulphide contains mercury, lead, bismuth, copper, and cadmium, as sulphides.

Their separation is effected upon the following principles:

 HgS is insoluble in dilute nitric acid*. The remainder dissolve, forming nitrates with separation of sulphur, e.g.

- (2) Dilute sulphuric acid precipitates lead as sulphate PbSO₄ (more completely in presence of alcohol), leaving the remaining metals in solution.
- (3) Ammonia throws down bismuth as hydroxide, Bi(OH)₃, and gives a characteristic blue colour to the solution if copper is present (due to a compound of cuprammonium hydroxide N₂H₂Cu"(OH)₂). The copper may be further confirmed by the ferrocyanide test.

Bismuth hydroxide dissolves in hydrochloric acid, forming the chloride BiCl₃, which is converted by water into the insoluble oxychloride BiOCl—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

An excess of hydrochloric acid must be avoided in dissolving the bismuth hydroxide, since it prevents the formation of the oxychloride.

If copper is present potassium cyanide is added, which forms with it a colourless double cyanide Cu₂Cy₂. 2KCy. Hydrosulphuric acid does not precipitate copper from this compound, whilst it throws down cadmium as yellow sulphide CdS.

Copper may also be separated from cadmium by precipitating the two together as sulphides, and boiling the precipitate with dilute H_2SO_4 . CdS dissolves, CuS remains insoluble. Or, in absence of ammonium salts, by adding a strongly alkaline solution of sodium tartrate and boiling; cadmium is precipitated as oxide, copper remaining in solution.

^{*} Some prefer to use strong nitric acid, in which case the lead is converted into sulphate, and remains in the residue with HgS, the latter being often converted into a white substance Hg(NO₃)₂. 2HgS. They may be then separated by ammonium acetate, which dissolves only lead sulphate.

TABLE II. B. METHOD 1.

Acidify with dil. HCl. Filter. Neglect filtrate. (If ppt. is nearly white and does not settle, it is probably only sulphur, and may be neglected.)

Wash ppt. and digest it for some time with warm ammonium carbonate*.

FILTER

SOLUTION

Acidify with HCl. Yellow ppt.—probably

ARSENIC†.

Confirm by dissolving ppt. in HCl with a drop of HNO₃ and trying Marsh's test[‡].

[Some Tin may also be present in this ppt. To confirm it, roast ppt. in open vessel, and fuse residue with KCy. Metallic Sn remains, which when dissolved in HCl gives white ppt. with HgCl₂.]

RESIDUE

Wash. Heat with strong HCl. Filter if necessary. (Residue is only S and traces of As₂S₃.) Heat gently to remove H₂S. Divide solution into two parts.

1.

Test for Sn.

Add a small piece of zinc. Allow to stand. Pour off clear solution. Dissolve residue in strong hot HCl. Add HgCl₂. White ppt. often turning grey.

TIN †.

2.

Test for Sb.

Pour the solution on to a piece of zinc on platinum foil. Black stain on the platinum.

ANTIMONY +.

Confirm by dissolving stain off in ammonium sulphide, and gently evaporating the solution.

Orange residue if Sb is present.

^{*} Preferably sequi-carbonate, saturated in the cold. Instead of ammonium carbonate, strong boiling HCl may be used, in which case Sn and Sb dissolve as chlorides, while As₂S₃ remains insoluble.

⁺ Ascertain, if possible, whether -ous or -ic (or both) in original solution.

[‡] Or by heating in a bulb-tube with dry Na₂CO₂, and charcoal or KCy.

EXPLANATION OF TABLE II. B. METHOD 1.

The solution after digestion of the mixed sulphides with yellow ammonium sulphide contains arsenic, antimony, and tin, as sulpho-salts.

These are decomposed by dilute HCl, the insoluble sulphides being reprecipitated, e.g.

$$3(NH_4)_eS$$
. $As_2S_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S$. soluble ammonium insoluble arsenious sulphide

Tin will always be reprecipitated as yellow stannic sulphide, since stannous sulphide is converted into stannic by the excess of sulphur in the yellow ammonium sulphide.

[A white ppt. is merely sulphur from the yellow ammonium sulphide,

$$(NH_4)_0S_0 + 2HCl = 2NH_4Cl + H_2S + S.$$

The ppt. (As₂S₃ (or As₂S₅), Sb₂S₃ (or Sb₃S₅), SnS₂ and free S) is washed till free from HCl, and digested with warm ammonium carbonate.

As, S, dissolves; the reaction may be approximately represented thus-

$$4 \operatorname{As_2S_3} + 4 (\operatorname{NH_4})_2 \operatorname{CO_3} = (\operatorname{NH_4})_2 \operatorname{O}. \ \operatorname{As_2O_3} + 3 \{ (\operatorname{NH_4})_2 \operatorname{S}. \ \operatorname{As_2S_3} \} + 4 \operatorname{CO_2}.$$
 soluble arsenite sulpharsenite

Sb,S, (and Sb,S,) are practically insoluble, and SnS, very slightly soluble.

The solution of arsenite and sulpharsenite is acidified with HCl, which precipitates the arsenic as As_oS_a.

$$(NH_4)_2O$$
. $As_2O_3 + 3\{(NH_4)_2S$. $As_2S_3\} + 8HCl = 4As_2S_3 + 8NH_4Cl + 4H_2O$.

Arsenic is confirmed in this precipitate, by dissolving in acids, and trying Marsh's test; or else in the dry way.

The residue insoluble in ammonium carbonate, containing the antimony and tin, is dissolved in strong hot HCl. SnS₂ dissolves, forming SnCl₄; Sb₂S₃ and Sb₂S₅ both form SbCl₃ (the latter with separation of S); H₂S being evolved.

Sulphur and traces of As,S, remain undissolved.

The HCl solution is divided into two parts.

and

One is examined for tin, by adding zinc. This precipitates tin as metal,

$$SnCl_4 + 2Zn = Sn + 2ZnCl_2$$

The deposited tin is dissolved in HCl, which converts it into stannous chloride SnCl₂, and mercuric chloride added. This is reduced first to white mercurous chloride, and afterwards, if sufficient stannous salt be present, to grey metallic mercury.

$$2 \operatorname{HgCl}_2 + \operatorname{SnCl}_2 = \operatorname{Hg}_2 \operatorname{Cl}_2 + \operatorname{SnCl}_4$$

 $\operatorname{Hg}_2 \operatorname{Cl}_2 + \operatorname{SnCl}_2 = 2 \operatorname{Hg} + \operatorname{SnCl}_4$.

The other part is examined for antimony by causing the solution to act upon zinc in contact with platinum foil. Antimony is deposited as metal on the platinum. On digesting with yellow ammonium sulphide, antimony dissolves as a sulpho-salt, and on evaporation of the solution, orange antimony sulphide remains.

TABLE II. B. METHOD 2.

Acidify with HCl (dil.). Filter. Neglect filtrate. (If ppt. is nearly white, and does not settle, it is probably only sulphur, and may be neglected.)

Wash ppt. and dissolve it in strong HCl (with a drop of HNO₃, or a crystal of KClO₃, if necessary). Heat gently to expel chlorine, &c. Reserve a portion. Introduce remainder into a vessel in which hydrogen is being generated by the action of Zn and dil. H₂SO₄.

Pass the evolved gases through a wash-bottle containing solution of lead acetate, and then into a strong solution of silver nitrate. A black ppt. indicates As or Sb.

FILTER

Solution	Ppt. Wash well. Digest with hot tartaric acid on the filter.				
Add a few drops of AgNO ₃ and then dilute ammonia, drop					
by drop. Yellow ppt. where the liquids meet, ARSENIC.	SOLUTION Add HCl dil. and pass H ₂ S. Orange ppt. ANTIMONY.	Residue neglect.			

Examine the other portion of the solution for tin, by adding a small piece of zinc, and allowing to stand. Pour off clear solution. Boil residue with strong HCl. Add HgCl₂. White ppt. often turning grey, TIN.

EXPLANATION OF TABLE II. B. METHOD 2.

This method is based upon the fact that compounds of arsenic and antimony when brought in contact with zinc and dilute acid, (HCl or H₂SO₄) evolve gaseous arsenic and antimony trihydrides, AsH₃ and SbH₃. (A portion of the As and Sb being usually precipitated on the Zn.)

The gases are purified from any H₂S which may be present by passing through a solution of lead acetate, and then led into a solution of silver nitrate. This decomposes them as follows:—

$$\begin{split} \operatorname{AsH_3} + 6\operatorname{AgNO_3} + 3\operatorname{H_2O} &= 6\operatorname{Ag} + \underbrace{\operatorname{H_3AsO_3} + 6\operatorname{HNO_3}}_{\text{Black ppt.}} \\ \operatorname{SbH_3} + 3\operatorname{AgNO_3} &= \operatorname{SbAg_3} + 3\operatorname{HNO_3}. \end{split}$$

The solution therefore contains arsenious acid, nitric acid, and excess of silver nitrate. On carefully neutralizing with ammonia, yellow silver arsenite Ag_aAsO₃ is precipitated. (This ppt. being soluble either in HNO₃ or NH₃, exact neutralization is necessary.)

The residue on the filter consists of metallic silver, and silver stibide Ag₃Sb. Tartaric acid dissolves Sb leaving Ag, and on passing H₂S into the solution, Sb₂S₃ is obtained as an orange precipitate. The Tin is found as in Method 1.

Add a strong

e in the least possible quantity of HCl. acetate in excess, and some acetic acid.

FILTER

TABLE III.

Ppt. may contain Al, Fe, Cr, hydroxides or phosphates. Ca, Ba, Sr, Mg, phosphates. Ca(BaSr) oxalates (fluorides, borates)*. Sometimes Mn and Zn†.

Wash thoroughly.

(Dissolve a small portion in HNOs, add ammonium molybdate in excess, and heat. Yellow ppt. indicates a PHOSPHATE; [If phosphates are absent, those parts of this table in small print may be omitted.]

(Fuse a portion with Na, CO3 (and a little KNO3) on platinum foil. Bluish-green mass indicates MANGANESE. Yellow mass CHROMIUM. Confirm Cr by dissolving mass in water, acidulating with acetic acid, and adding lead acetate. Yellow ppt. shews Cr. CI

(Dissolve remainder in the least possible quantity of HCIS. Test a small portion of the solution by diluting and adding K,FeCys. Blue ppt. indicates IRON. To the remainder add KHO in large excess and boil. [If Cr is present, boil for a

considerable time

FILTER

Wash. Dissolve in the solution of sodium acetat	Ppt. Oxalates (fluorides) of Possibly also phosphates which may be confirmed as ab Wash, dry, heat to Add acetic acid. Effer cates an OXALATE . Te
XCESS and boil.	indicates ALUMINIUM hydroxide or phosphate. Wash and dissolve it in HNO ₃ and dissolve it in HNO ₃ and action phosphoric acid as with (NH ₄) ₂ MoO ₄ . Cates an OXALATE . The part of cates an OXALATE . The part of cates an OXALATE .
Solution Add NH,Cl in excess and boil. FILTER	Solution Test for phosphate by adding indicates ALUMINIUM magnesia mixture. If found, nuclear probably present as Ferric and dissolve it in HNO3 and test for phosphoric acid as above with (NH4)2MoO4.

Solution	Add Fe ₂ Gl ₆ drop by drop. Whitish ppt. indicates PHOSPHATE of Ca, Ba, Sr or Mg. If a ppt. is produced, continue to add Fe ₂ Gl ₆ until the solution is red. Boil, filter while hot.	Solution Substance to Solution Solution Solution Solution Solution Solution Solution Solution Solution Fig. Add NH, Cl and NH, Filler if necessary. Neglect ppt. Examine solution for CaBaSrMg as usual by Table V.
Ppt.	ides) of Ca(BaSr). sosphates of Fe and Cr, red as above 1, 2, 3. eat to low redness. Effervescence indi-	TE . Test acetic solu-

· Fluorides and Borates are only imperfectly precipitated in this group. The metals (Ca, Ba, Sr) will therefore be found in Group V. and the acids + See note (||) General Table.

tion for Ca, &c. as usua

also be tested for FL heating with H,SO.

Arsenate would give a similar reaction, if not previously separated by H.S.

§ If much chromium is present it is advigable, instead of dissolving the ppt. in HCl and adding KHO, to fuse it with Na2CO2 and KNO2, extract with water, and filter. The Cr will remain in solution together with the Al, and will not interfere with the tests for the latter.

| Calcium oxalate may be decomposed to some extent by potash under these conditions, hence, if its presence be suspected, it is advisable to test for it in a portion of the original NH3 ppt. instead of the ppt. produced by potash.

In most cases the original substance may be used instead.

EXPLANATION OF TABLE III.

Since the presence of phosphates renders the analysis of this group more complex, it is advisable to test a portion of the precipitate at once for phosphate. This is done by dissolving in nitric acid (since hydrochloric acid impairs the delicacy of the reaction), adding ammonium molybdate, and heating, which gives a yellow precipitate of "phospho-molybdate of ammonium" (composition doubtful). It is necessary to employ a large excess of the molybdate, since excess of phosphate prevents the formation of the precipitate.

Fusion of the precipitate with sodium carbonate, in presence of air or some oxidizing agent such as KNO₃, converts lower oxides of chromium and manganese into a chromate and manganate respectively, e.g.

$$\begin{split} \operatorname{Cr_2O_3} + 2\operatorname{Na_2CO_3} + 3\operatorname{O} &= 2\operatorname{Na_2CrO_4} + 2\operatorname{CO_2} \\ \operatorname{yellow\ mass} \\ \operatorname{MnO} + \operatorname{Na_2CO_3} + \operatorname{O_2} &= \operatorname{Na_2MnO_4} + \operatorname{CO_2}. \end{split}$$

and

The fused mass is extracted with water. (If much manganate is present, a drop of alcohol may be added, which will precipitate the manganese as Mn₂O₃ (hydrated), leaving the chromate in solution.) Acetic acid is added to remove the excess of alkali, and lead acetate to precipitate the chromate as yellow PbCrO₄.

The remainder of the precipitate is dissolved in hydrochloric acid. The phosphates, oxalates, &c. dissolve potentially as such, whilst the hydroxides are converted into chlorides. A portion of the solution is tested for iron by potassium ferrocyanide, (which gives "Prussian blue" Fe₄(FeCy₆)₃* if iron is present,) and caustic potash added in excess to the remainder This reprecipitates the whole group substantially in the same condition as before, but redissolves aluminium hydroxide and phosphate, the former as potassium aluminate Al₂(OK)₆. Chromium hydroxide and phosphate also redissolve in excess of cold KHO, but are reprecipitated by continued boiling. If much chromium has been indicated however, it is best to convert it entirely into the hexad (or chromic acid) form before proceeding, by fusion with Na₂CO₂, &c. as above. In this condition it will remain in solution and will not interfere with the other reactions.

The filtered solution, after boiling with potash, is boiled with ammonium chloride. This decomposes the KHO as follows:

$$KHO + NH_4Cl = KCl + H_2O + NH_3$$
.

Aluminium hydroxide and phosphate are consequently reprecipitated.

Boiling with KHO usually decomposes ferric phosphate, in part at any rate. Thus $2\text{FePO}_4 + 6\text{KHO} = \text{Fe}_2(\text{OH})_6 + 2\text{K}_2\text{PO}_4$.

If therefore, after the separation of aluminium, much phosphate is found in solution, ferric phosphate was probably present.

The precipitate produced by caustic potash is dissolved again in hydrochloric acid and excess of sodium acetate added. This has the effect of replacing free hydrochloric acid by free acetic acid:—

* See footnote, p. 11.

EXPLANATION OF TABLE III. (continued).

Calcium oxalate and fluoride, ferric and chromic phosphates, are soluble in hydrochloric acid, but insoluble, or nearly so, in acetic acid, and are therefore precipitated. [Oxalates are confirmed by heating the precipitate, which converts them into carbonates. Fluorides by heating with H_2SO_4 , whereby HF is evolved; and ferric and chromic phosphates by testing as above for Fe, Cr, and PO_4 .]

Phosphates of Ca, Ba, Sr and Mg, however, are soluble both in hydrochloric acid and in acetic acid, and therefore remain in solution. The addition of ferric chloride decomposes them as follows:

$$Ca_s(PO_4)_s + Fe_sCl_6 = 2FePO_4 + 3CaCl_s$$
.

If, therefore, a reddish white ppt. is obtained on the addition of the first few drops of Fe₂Cl₆, it proves that phosphate of Ca, Ba, Sr, or Mg, was present. In this case Fe₂Cl₆ must be added until the solution is red, shewing that the decomposition of Ca &c. phosphates is complete. The phosphoric acid is thus entirely got rid of, leaving the Ca, Ba, Sr, Mg, as chlorides, in which form they can be identified as usual.

Oxalates and Phosphates of Ca, Sr, Ba, may also be analysed by dissolving in the least possible quantity of HCl, adding dilute H₂SO₄ and about $\frac{1}{3}$ total volume of alcohol. After standing some hours the metals are obtained as sulphates and the solution contains oxalic and phosphoric acids.

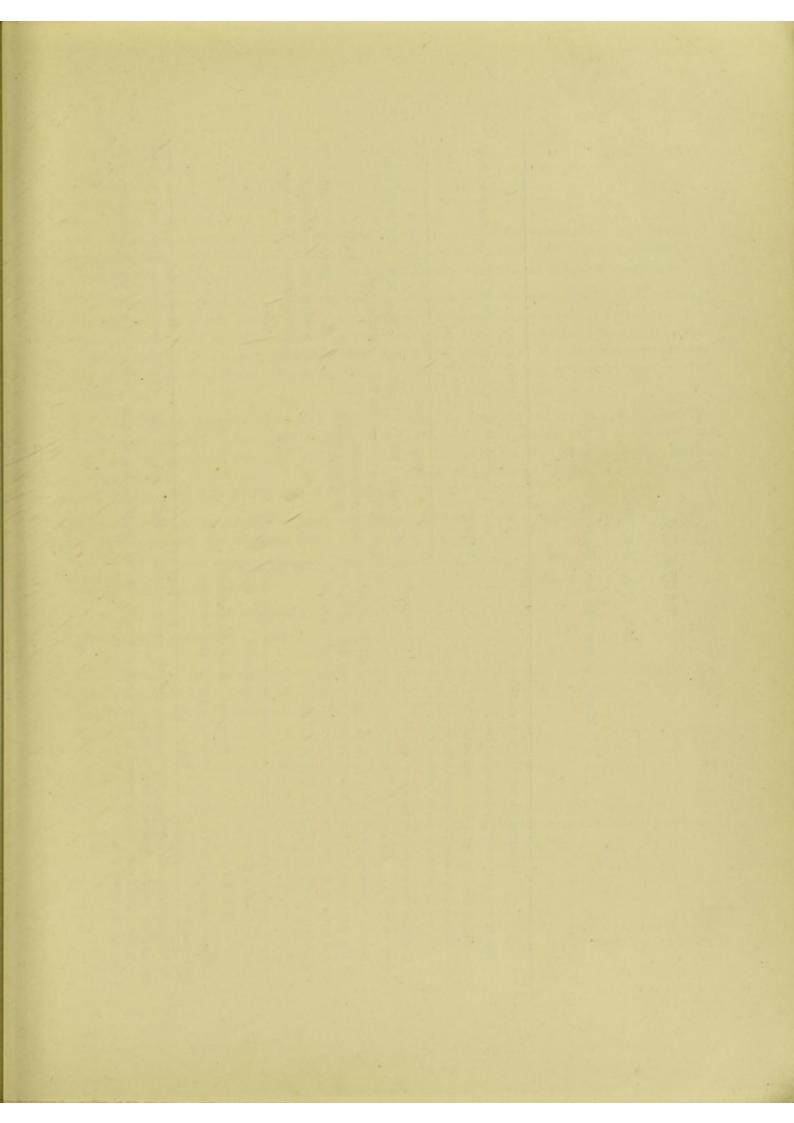


TABLE IV.

NiS, CoS, ZnS, MnS.

Wash; digest with cold dilute hydrochloric acid.

FILTER

Solution†	Boil to expel H _s S. Cool, and add KHO in excess without ing. FILTER	Fuse with Na ₂ CO ₃ (and a tle KNO ₃) on platinum foil. Blue-green mass. MANGANESE. (May be further confirmed by heating ppt. on charcoal with cobalt nitrate. Green mass.)	
	Boil to exp	. E	Solution Evaporate to dryness and test sidue for COBALT by borax ad.
RESIDUE (if not black, neglect)	he borax bead. nes indicates Co. dizing flame	e (arter a time)) least possible quantif S if necessary.) CHO. Add solution cormed is just redisso lish. Filter off any s in HgCy,*. Boil. Filter	re.
RESIDUE (if	Examine a portion with the borax bead. Blue bead in both flames indicates Co. Brownish-violet in oxidizing flame	Dissolve remainder in the least possible quantity of HCl with a drop of HNO ₃ . (Filter off S if necessary.) Nearly neutralize with KHO. Add solution of (pure) KCy till the ppt. which is first formed is just redissolved. Boil for several minutes in an open dish. Filter off any slight ppt., and add a clear solution of HgO in HgCy ₂ *. Boil. FILTER	PPT. (pale green) NICKEL Wash thoroughly and confirm by borax bead.

* Prepared by boiling freshly precipitated HgO in strong solution of HgCy2 and filtering. (NaClO, or bromine+KHO, may be used

instead, but solution must not then be boiled.

+ Some IRON may also be present in this solution if much alkaline phosphate was originally present. Test a few drops therefore with potassium ferrocyanide.

EXPLANATION OF TABLE IV.

Zinc and manganese sulphides dissolve readily in cold dilute hydrochloric acid (forming chlorides ZnCl₂ and MnCl₂, with evolution of H₂S); whilst nickel and cobalt sulphides are only dissolved in traces which do not interfere with the detection of zinc and manganese.

The residue consisting of NiS and CoS is examined with the borax bead. If only nickel is indicated, it is not usually necessary to examine further, but if cobalt is found, the process of separation of nickel and cobalt must be gone through, since the blue given to the borax bead by cobalt may completely mask the nickel colour. It is safer however always to go through the entire process in either case, especially if small quantities have to be looked for.

In order to separate nickel and cobalt, the sulphides are dissolved in aqua regia, whereby they are converted into chlorides NiCl₂ and CoCl₂. The solution is nearly neutralized to remove the excess of free acid, and potassium cyanide added, which precipitates the single cyanides NiCy₂ and CoCy₂. These dissolve in excess of potassium cyanide, forming soluble double cyanides NiCy₂2KCy, and CoCy₂2KCy.

On boiling the solution in presence of air, the latter reacts with the excess of KCy which is present, and oxygen, thus

$$2(\mathrm{CoCy_22KCy}) + 4\mathrm{KCy} + \mathrm{H_2O} + \mathrm{O} = \mathrm{K_6Co_2Cy_{12}} + 2\mathrm{KHO},$$

[or if free acid be present,

$$2(\text{CoCy}_22\text{KCy}) + 2\text{KCy} + 2\text{HCy} + \text{O} = \text{K}_6\text{Co}_2\text{Cy}_{12} + \text{H}_2\text{O}],$$

NiCy.2KCy remaining unaltered.

K_eCo₂Cy₁₂ is tolerably stable, and is not acted upon by mercuric oxide (or oxycyanide*), or by sodium hypochlorite at a gentle heat; whereas NiCy₂. 2KCy is readily decomposed by these reagents as follows:

$$\begin{split} \text{NiCy}_2 + \text{HgOHgCy}_2 + \text{H}_2\text{O} &= \text{Ni(OH)}_2 + 2\text{HgCy}_2, \\ \text{Pale green ppt.} \end{split}$$

$$2 \text{NiCy}_2 + \text{NaClO} + 5 \text{H}_2\text{O} &= \text{Ni}_2(\text{OH)}_6 + \text{NaCl} + 4\text{HCy}. \\ \text{Black ppt.} \end{split}$$

The solution is examined for cobalt by evaporating to dryness and testing with the borax bead [or by neutralizing with dilute HNO₃ and adding mercurous nitrate, whereby white Hg₆Co₂Cy₁₂ is precipitated. This on ignition leaves black Co₃O₄].

^{*} It is preferable to use mercuric oxide dissolved in mercuric cyanide (i.e. mercuric oxycyanide) since it can be added as a solution. If mercuric oxide alone be used, the excess of HgO masks the precipitate of Ni(OH)₂. NiCy₂ which is then produced.

EXPLANATION OF TABLE IV. (continued).

To the solution containing ZnCl₂ and MnCl₂, caustic potash is added. This throws down Zn(OH)₂ and Mn(OH)₂ as white precipitates*. Zn(OH)₂ is soluble† in excess of cold KHO, forming ZnK₂O₂ (Potassium zincate), Mn(OH)₂ remaining insoluble. [If the solution be heated, Zn(OH)₂ will often not redissolve in KHO, especially if dilute.]

H.S passed into the solution precipitates white zinc sulphide,

$$K_gZnO_g + 3H_gS = ZnS + 2KHS + 2H_gO$$
.

(This precipitate is often discoloured owing to traces of impurity.)

The precipitate produced by KHO which does not redissolve in excess is examined for manganese by fusing with sodium carbonate in presence of air (or some oxidizing agent as KNO_a),

$$\begin{aligned} \operatorname{Mn}(\operatorname{OH})_2 + \operatorname{Na_2CO_3} + \operatorname{O_2} &= \operatorname{Na_2MnO_4} + \operatorname{H_2O} + \operatorname{CO_2}. \\ \operatorname{Blue\ green\ mass} \end{aligned}$$

Manganese may also be separated from nickel, cobalt, and zinc, by passing hydrosulphuric acid into an acetic acid solution (containing no other free acid); NiS, CoS, and ZnS, being insoluble in acetic acid, are precipitated, whilst Mn remains in solution.

Nickel may be separated from cobalt by several other methods; for instance:-

- By means of potassium nitrite and acetic acid in a neutral solution, which precipitates all the cobalt, after a time, as yellow K₆Co₂(NO₂)₁₂. 3H₂O, nickel remaining in solution.
- Or by precipitating the metals as *ferricyanides* (in presence of ammonium chloride), and digesting the precipitate with ammonia. Nickel ferricyanide dissolves, cobalt ferricyanide remains.

The white Mn(OH)₂ rapidly turns brown owing to absorption of oxygen and formation of Mn₂O₃. H₂O.
 Incompletely in presence of Mn, Ni, Co.

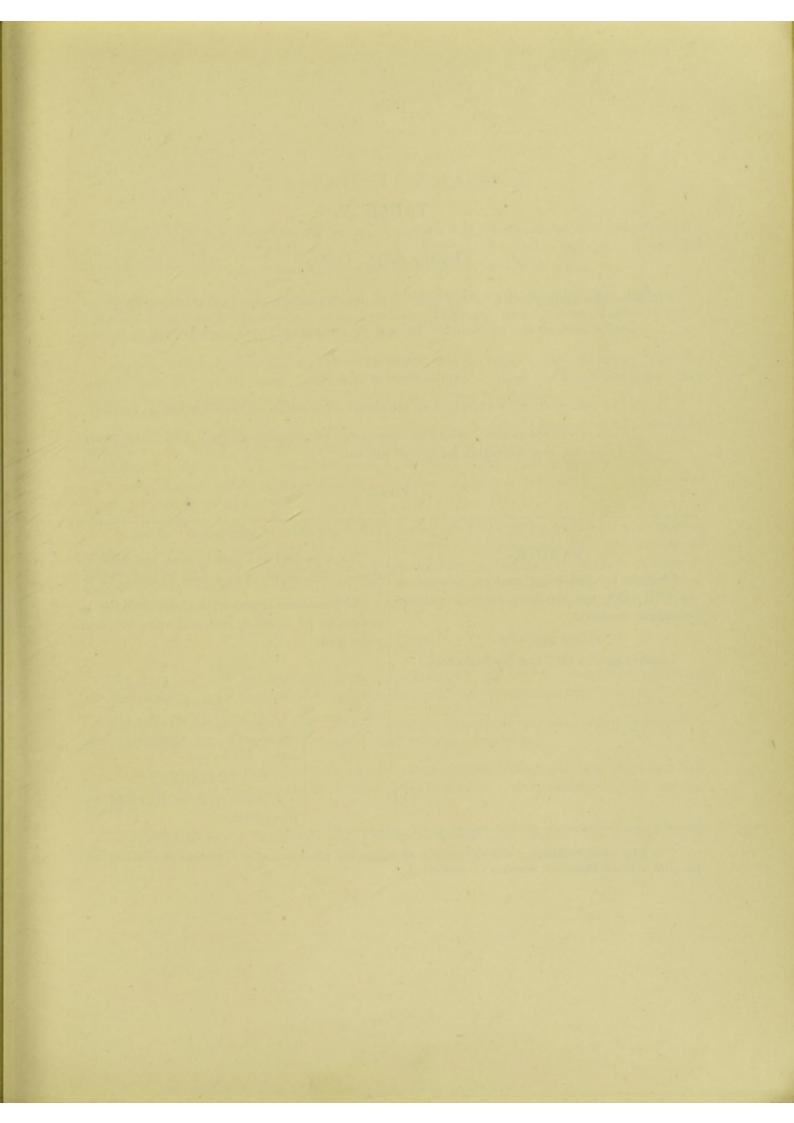


TABLE V.

BaCO, SrCO, CaCO,

Dissolve the main portion of the ppt. in the least possible quantity of dilute HCl*.

Test a part of the solution for Ba and Sr by adding CaSO, and heating.

 ${\rm Immediate\ ppt.=Ba,} \ {\rm ppt.\ after\ a\ time=Sr.}$

If no ppt. even on standing, test remainder of solution at once for Ca as below +.

If Ba or Sr are present, evaporate remainder of solution to small bulk, add H₂SiF₆ in excess, and an equal volume of alcohol.

FILTER

PPT.

BARIUM.

Confirm by dissolving another portion of the (NH₄)₂CO₃ ppt. in acetic acid, and adding potassium chromate.

Yellow ppt. = Ba.

Dissolve ppt. in HCl and try flame-test.

SOLUTION

To a portion add CaSO₄, heat, and allow to stand. White ppt. after a time STRONTIUM.

If Strontium is present, add dilute H₂SO₄ to remainder of solution, boil, and allow to stand some time.

FILTER

PPT.	Solution†
Neglect.	Add NH ₃ till alkaline (filter if necessary), and ammonium oxalate. White ppt.
	CALCIUM.
	Dissolve ppt. in HCl and try flame-test.

^{*} In most cases information can be obtained by trying the flame-test with a portion of this solution. Ba gives a green flame, Sr crimson, Ca orange-red.

EXPLANATION OF TABLE V.

On dissolving the precipitate of barium, strontium, and calcium carbonates in hydrochloric acid, the chlorides, BaCl₂, SrCl₂, and CaCl₂ are obtained, CO₂ being evolved. Dilute HCl must be used, since barium salts are insoluble in strong mineral acids.

Calcium sulphate is sufficiently soluble in water to be used as a test for barium and strontium, whose sulphates are practically insoluble. Sulphuric acid, or other sulphates, would precipitate calcium as well, from a strong solution.

Barium would answer the special tests about to be applied for strontium and for calcium, and, if present, must therefore be removed before these can be looked for. For the same reason, strontium must be removed before testing for calcium.

The barium is separated by means of hydrofluosilicic acid, which gives a translucent precipitate of BaSiF₆ (more complete in presence of alcohol), strontium and calcium remaining in solution. A separate portion of the original precipitate is dissolved in acetic acid, and potassium chromate added, in order to confirm barium, which gives yellow BaCrO₄, insoluble in acetic acid.

A portion of the filtrate from the H₂SiF₆ precipitate is tested for strontium with calcium sulphate. If present, dilute sulphuric acid is added to the remainder. This precipitates all the strontium and may precipitate part of the calcium, as sulphates. Enough calcium is always left in solution to be detected by the ammonium oxalate reaction, which gives, in neutral or ammoniacal solution, a white precipitate of calcium oxalate (CO₂)₂Ca.

Barium may also be separated from strontium and calcium by means of potassium chromate, which, in an acetic acid or dilute neutral solution, precipitates only BaCrO.

Also by converting the metals into *chlorides*, evaporating to dryness, and digesting with absolute *alcohol*. SrCl₂ and CaCl₂ dissolve, BaCl₂ remains insoluble.

Strontium may be separated from calcium by converting the metals into sulphates and digesting with a hot strong solution of ammonium sulphate. CaSO₄ dissolves, SrSO₄ remains insoluble.

Also by converting the metals into nitrates, evaporating to dryness, and digesting with absolute alcohol. Ca(NO_s)₂ dissolves, Sr(NO_s)₃ remains insoluble.

TABLE VI.

Solution may contain Mg, K, Na, NH4.

Evaporate to dryness. Heat residue to low redness until fumes cease to be evolved.

- Dissolve a portion of residue in water (and a drop of dil. HCl if necessary).
 Test the solution with NH₄Cl, NH₃ and sodium phosphate. Warm, shake, and allow to stand. White ppt. (crystalline from dilute solutions or on standing) = MAGNESIUM*.
- Dissolve the remainder in the least possible quantity of water†. Filter if
 necessary. Test a portion of the solution by stirring on a watch glass with
 PtCl₄‡. Yellow ppt. in lines=POTASSIUM.

Examine another portion by the flame-test on a *clean* platinum wire. Strong and persistent yellow colouration = SODIUM. Violet colouration POTASSIUM.

Test a portion of the *original* substance or solution for ammonium by boiling with potash. Fumes of ammonia (recognised by odour and action on red litmus paper) AMMONIUM.

^{*} A slight flocculent ppt. which does not become crystalline on standing may be due to Ba, Ca, Al, &c. In doubtful cases, therefore, add a mixture of ammonium sulphate, ammonium oxalate and ammonia, boil and filter before testing for Mg.

[†] If much Mg is indicated it should be removed before testing for K and Na. This may be done by adding Ba(OH)₂, filtering, removing the excess of Ba salt with ammonium carbonate, evaporating, and igniting to remove ammonium salts.

[‡] If iodides are present, PtCl4 will produce a strong red colour.

EXPLANATION OF TABLE VI.

Before testing for the remaining metals, it is necessary to remove all ammonium salts from the solution; [since PtCl₄ gives the same reaction with them as with potassium salts; and since the precipitation of magnesium by sodium phosphate is rendered less sensitive, and that by barium hydroxide prevented altogether, by their presence.] This is done by evaporating to dryness and igniting the residue, whereby ammonium salts being volatile, are expelled. Too high a temperature must not be used, since sodium and potassium chlorides might then be volatilized also.

A portion of the residue is dissolved in water (and a drop of dilute HCl if necessary, since MgCl₂ leaves a sparingly soluble oxychloride on evaporation of its solution) and tested for magnesium with NH₄Cl, NH₃ and Na₂HPO₄,

[The NH₄Cl prevents the precipitation of Mg(OH)₂ by NH₃, owing to the formation of a soluble double chloride (MgCl₂. 2NH₄Cl).]

The remainder of the residue is dissolved in water (filtered if necessary from MgOMgCl₂) and examined for potassium and sodium; the former by PtCl₄, which gives a yellow precipitate of K₂PtCl₅ (more complete in the presence of alcohol), and the latter by the flame-test, sodium compounds giving a strong yellow flame.

Acid potassium metantimoniate K₂O. H₂O. Sb₂O₅. 6Aq is sometimes employed as a test for sodium salts, with which it produces a white precipitate of Na₂O. H₂O. Sb₂O₅. 6Aq. The solution to be tested must be neutral, and the reagent freshly prepared.

The separation of magnesium from alkali metals may be effected in several ways. In the process here recommended it is precipitated as Mg(OH)₂ by means of barium hydroxide; the barium being then removed as BaCO₃, by adding ammonium carbonate. Mercuric oxide may be used instead of barium hydroxide, and the mercury afterwards got rid of by heating to low redness.

Another method is to precipitate the magnesium by ammonium phosphate, and afterwards remove the excess of phosphate by ferric chloride.

Or the solution (containing the metals as chlorides) may be evaporated to dryness with ammonium oxalate and heated, whereby they are converted into carbonates. On digesting the residue with water, MgCO, remains insoluble.

PRELIMINARY EXAMINATION FOR ACID RADICLES.

Efferescence in the cold with evolution CO ₂ (detected by pouring the evolved gas into lime-water and shaking) "" with evolution of Cl ₂ (detected by odour, colour, and action on KI paper) "" SO ₄ (detected by odour, and by action of sulphur. "" SO ₅ (detected by odour, or by absorbing means as a sulphides are not decomposed by the dilute acid. "" SO ₅ with deposition of sulphur. "" SO ₆ with deposition of sulphur. "" SO ₇ with deposition of sulphur. "" SO ₈ with deposition of sulphur. "" SO ₉ with depos	1. Treat th	Treat the solid substance (or strong solution) with dilute Hydrochloric acid in the cold. Afterwards heat.	tilute Hydrochloric acid	CONFIRMATORY TESTS.
CI, (de- our, and) ction on sction on sction on sction on script (1) ction on sction on subscript (1) bsorbing y test to y test to Sulphuric Acid. CYANIDE ** (1) (1) (1) (1) (1) (1) (1) (Effervescence		CARBONATE * Or Cyanate *	Further confirmation not usually required. If soluble, BaCl ₂ or CaCl ₂ gives white ppt. soluble i acids with effervescence. (N.B. Cyanides usually contain carbonates.)
ction on SULPHIDE; \(\pi\) (1) action on SULPHIDE; \(\pi\) (2) ted with y test to some e acid . Sulphuric Acid. as with as with diliquid (1) GHLORATE (2) (1) (1) (N. (8)	=	" with evolution of Cl, tected by odour, colour, action on KI paper) .	HYPOCHLORITE	 MnCl₂, brown ppt. Solution bleaches litmus, writing-ink, &c. N.B. Hypochlorites always contain chlorides.)
action on SULPHITE \(\psi\) (2) bsorbing ted with y test to y test to caid . Sulpharic Acid. as with as with d liquid centle as with centle as with centle centl	Evolution of	f H ₂ S (detected by odour and action on) lead acetate paper)	SULPHIDE; *	If soluble in water, (1) Sodium nitroprusside, violet colouration. (2) Silver coin stained black.
bsorbing test to y test to Sulphuric Acid. Sulphuric Acid. as with d liquid GHLORATE (2) OHLORATE (2) (1)		SO, (detected by odour, and by action on) K,Cr,O,S)	SULPHITE *	 Zn + dil. HCl. H₂S evolved. Detected as abov AgNO₃, white ppt. Blackens on heating. (N.B. Sulphites usually contain sulphates.)
bsorbing ted with y test to y test to Sulphuric Acid. Sulphuric Acid. as with cHIORATE (1)			THIOSULPHATE	Same as for Sulphite. Distinguished by deposition of yellow sulphur on adding HCl and heating.
as with CHLORATE	" " Repeat test sulphide	HCy (detected by odour, or by absorbing evolved gas on filter paper spotted with KHO, and applying confirmatory test to the spot).	CYANIDE *	 (1) To neutral or alkaline solution, add FeSC Fe₂Cl₈, and HCl; dark blue ppt. or colouratio (Prussian blue.) (2) AgNO₃, white ppt. soluble in NH₃, insoluble dil. HNO₃. (N.B. Cyanides often contain cyanates and cabonates.)
as with cHLORATE			ic Acid.	
CHLORATE	The above i	100		
	Evolution of	f ClO, (yellow explosive gas) and liquid	CHLORATE	 Indigo bleached in the cold, on the addition sulphurous acid. Heated, they evolve O, becoming chlorides.

and als	o s	pecial	reaction	s of th	e respect	ive A	eid Ra	adicles.				
(1) Add FeSO, in excess to cold solution; gradually pour in strong H,SO,. Brown or pink ring where liquids meet.	(2) Brucine in presence of strong H ₂ SO ₄ . Red colour.	(1) KI+dilute HCl. Iodine liberated. Detected by starch.	(1) Fe ₂ Cl _e , red colour, bleached by HCl, not by HgCl _s . This test must be applied in neutral	solution. (2) Heated with strong H ₂ SO ₄ and a drop of alcohol, odour of ethyl acetate.				Proceed to Table on page 72.				
*				*	5	DE	*	(A)			DE	*
NITRATE *		te		ACETATE *	ATE mide)	ANI de te	TARTRATE *	CITRATE (blackens slowly)	DE	EDE e or mite	IDE	CHLORIDE
ITR/	or	Nitrite		CEL	OXALATE (Ferricyanide)	Cyanide Formate	RTR cens	CITRATE ackens slow	IODIDE	BROMIDE Bromate or Hypobromite	FLUORIDE or ICOFLUOR	LOR
Z				Ā	(Fe	FERROCY ANDE Cyanide Formate	TA (black	(blac	Т	BI Br Hy	FLUORIDE or SILICOFLUORIDE	CH
	_	·				<u></u>		~				
	Oxides of nitrogen (yellow or brown, with)			Acetic acid vapour (recognized by odour).	CO (burns with blue flame) and CO (detected by lime-water as above) without blackening				I (violet fumes, which colour starch paste)	Br (brownish-red vapours, condensing to deep red liquid)	SiF, (white clouds which deposit white gelatinous silica on a wet rod)	HCl (colourless pungent fumes, forming white clouds in the air)
	rown			by oc	and (e/w)			. pi	arch	densi	osit	for
	or b			nized	abov	ing		liqu	our st	con .	rod)	fume
	ellow			ecogn	ne fl.	rcken		f the	ich colou	ours	wet	gent ir)
	en (y	lour)		our (r	with blue flame lime-water as abo	ut ble		ing o	whiel	d vaj	nds v	pung
	itrog	11c oc		vapo	wit y lim	vitho		ıcken	mes,	sh-re luid)	clos	rless s in
	s of n	teris		acid	bed by	one,		ch ble	et fu	owni ed li	white	colou
	xide	characteristic odour)		Acetic	CO (burns with blue flame) (detected by lime-water as aborblackening	CO alone, without blackening		CO with blackening of the liquid	I (violet fumes, wh	Br (brownish-red vapours, condeep red liquid).	SiF, (white clouds which der gelatinous silica on a wet rod)	HCl (colourless pungent fun white clouds in the air)
	"	9			2	, ,			b	" d	20 50	# #
	33				2	2			11		2	
	7								12:00-			

If none of these results with the above reagents, the salt may be a phosphate, arsenate, borate, chromate, sulphate, silicate. Proceed to Table on page 72.

^{*} Cyanates treated with dilute acids evolve CO₂, and form an ammonium salt. The latter may be confirmed by adding caustic potash till alkaline, and Nessler's solution, when a yellow or brown colouration is obtained.

⁺ Chlorates may also evolve CI mixed with CIO₂.

\$ Strong HCl vapours will also turn pot bichromate green after a time, and the odour of HCl is sometimes mistaken for that of SO₂; confirmatory test is therefore absolutely necessary.

| Mercuric cyanide must be decomposed by H₂S before applying confirmatory test for cyanide.
| If the substance given is a liquid, it should be evaporated just to dryness (with addition of a little caustic potash if acid). In many cases a strong solution may be used with excess of sulphuric acid; but the effects are not so well marked.

EXPLANATION OF PRELIMINARY ACID TABLE.

The following equations may be taken as typical of the reactions which occur:

 $\begin{aligned} & \text{Carbonate} & \dots \text{Na}_2 \text{CO}_3 + 2 \text{HCl} = 2 \text{NaCl} + \text{H}_2 \text{O} + \textbf{CO}_2. \\ & \text{Hypochlorite} & \dots \begin{cases} \text{NaClO} + \text{HCl} = \text{NaCl} + \text{HClO} \\ \text{HClO} + \text{HCl} = \text{H}_2 \text{O} + \textbf{Cl}_2 \end{cases}. \end{aligned}$ Sulphide $Na_sS + 2HCl = 2NaCl + H_sS$. Sulphite $Na_sSO_a + 2HCl = 2NaCl + H_sO + SO_s$. Thiosulphate ... Na S.O. + 2HCl = 2NaCl + H.O + SO. + S. Cyanide KCy + HCl = KCl + HCy. Cyanate $\text{Cyanate} \quad \text{HCNO} + \text{HCl} = \text{HCNO} + \text{KCl}$ $\text{HCNO} + \text{H}_2\text{O} + \text{HCl} = \text{NH}_4\text{Cl} + \text{CO}_2.$ Chlorate3KClO₃ + $2H_2SO_4 = 2KHSO_4 + KClO_4 + H_2O + 2ClO_2$. $\begin{cases} KNO_3 + H_2SO_4 = KHSO_4 + HNO_3 \\ 4HNO_3 \text{ (in part)} = 2H_2O + 4NO_2 + O_2 \end{cases}$ Nitrate2KNO₂ + 2H₂SO₄ = 2KHSO₄ + N_2O_3 (?) + H₂O (in part). Nitrite AcetateCHaCOOK + HaSO4 = KHSO4 + CHaCOOH. $\cdots = \begin{cases} COOH - H_2O = CO + CO_3. \end{cases}$ Ferrocyanide ... $K_4 \text{FeC}_6 N_6 + 6 H_2 SO_4 + 6 H_2 O = 2 K_2 SO_4 + \text{FeSO}_4 + 3 (NH_2)_2 SO_4 + 6 CO_4$ Formate $HCOOH - H_O = CO$. Cyanide2KCN + 4H,SO, + 2H,O = 2KHSO, + 2(NH,)HSO, + 2CO (in part). Iodide $\begin{cases} \text{KI} + \text{H}_2 \text{SO}_4 = \text{KHSO}_4 + \text{HI} \\ 2 \text{HI} + \text{H}_2 \text{SO}_4 = 2 \text{H}_2 \text{O} + \text{SO}_2 + \mathbf{I}_2 \text{ (in part)*} \end{cases}$ BromideSame reaction as iodide, but much HBr escapes undecomposed. Bromate ${\rm KBrO_3 + H_2SO_4 = KHSO_4 + HBrO_3 \atop 4HBrO_3 - 2H_2O = 2Br_2 + 5O_2 \text{ (in part)}}$ Hypobromite ... Same reaction as for hypochlorite. Fluoride $\operatorname{CaF}_{2} + \operatorname{H}_{2}\operatorname{SO}_{4} = \operatorname{CaSO}_{4} + 2\operatorname{HF}_{4}$ $\operatorname{HF} + \operatorname{SiO}_{2} = 2\operatorname{H}_{2}\operatorname{O} + \operatorname{SiF}_{4}$ Silicofluoride ... K.SiF. + H.SO. = K.SO. + SiF. + 2HF. ChlorideNaCl + HoSO = NaHSO + HCl.

^{*} If the HI were much in excess of the H_2SO_4 , some H_2S might be evolved— $8HI + H_2SO_4 = H_2S + 4H_2O + 4I_2$.

EXAMINATION FOR ACID RADICLES IN THE WET WAY.

Preparation of Solution.

The substance, if solid, must be dissolved if possible in water, since acids are obviously inadmissible. [Dilute nitric acid may however be used in special cases, as for some acids of Group 3.]

If insoluble in water, the most general method is to boil with a strong solution of sodium carbonate for some time (or, in case of acids not decomposable by heat, to fuse with solid sodium carbonate and boil residue with water) and filter. In this way the acid is usually obtained as a soluble sodium salt, while the base remains as an insoluble carbonate or oxide, e.g.

$$CaF_g + Na_gCO_3 = \underbrace{CaCO_3}_{residue} + \underbrace{2NaF}_{solution}$$

If metals are present in solution which would interfere with the tests about to be applied (as a rule, all except K, Na or (NH₄)), they must be removed before proceeding. [The necessity, or otherwise, of removing metals, is roughly indicated by boiling a portion of the solution with Na₂CO₃; if no ppt. is produced, it is usually safe to proceed. The previous examination for metals, however, is a better guide.] This may in most cases be done by boiling or fusing with Na₂CO₃ as above. [Phosphates of Al, Ca, Ba, &c. are very imperfectly decomposed in this way, but they will have been identified during the examination for metals.]

The solution, after boiling or fusing with Na₂CO₃, must be just acidified with dilute HNO₃ to remove the excess of Na₂CO₃, and gently heated to expel CO₂.

Hydrosulphuric acid may be used to remove metals of groups 1 and 2, the filtrate being afterwards heated to expel excess of H₂S. This method is advisable in the cases of mercuric cyanide and tartar-emetic.

Dilute sulphuric acid and alcohol is sometimes employed in case of Pb, Ba, Sr and Ca.

EXAMINATION FOR ONE ACID RADICLE.

[The presence of Carbonate, Hypochlorite, Sulphide, Sulphite, and Thiosulphate, must be concluded from Preliminary Examination

Dissolve substance if possible in water. [If solution is alkaline, just acidify with dil. HNO, and filter off any ppt.†]

Test a portion of the solution by boiling with Na2CO3.

If the substance is insoluble in water, or if the solution gives a ppt. with Na, CO,, boil* with strong solution of Na, CO, for some time. Filter. Add dilute HNO, to the solution till just acid†. Heat gently to expel CO,.

Test separate portions of the solution as follows:

-			
	Add dilute HOI+Barum Chloride. White ppt. indicates		CONFIRMATORY TESTS
-	SULPHATE		Sr(NO ₂) ₂ , white ppt. (slowly in dilute solutions).
	SILICOFLUORIDE		Heated alone, or with H2SO4, in platinum vessel, SiF4 evolved, detected by wet rod.
	Add NH ₃ till alkaline (filter if necessary†) and Calcium Chloride. White ppt. indicates	Digest ppt. with acetic acid	
	OXALATE	Undissolved	Treated with strong H2SO, and MnO2, CO2 is evolved without heating.
	FLUORIDE	n	(1) Heated in platinum vessel with strong H ₂ SO ₄ , HF is evolved; detected by etching glass. (2) Heated in a test-tube with strong H ₂ SO ₄ , SiF ₄ is evolved; detected by wet rod.
	PHOSPHATE	Dissolved	 In neutral solution, AgNO₄, yellow ppt. (2) In NH₂ solution, MgSO₄+NH₄Cl, white ppt. (3) In HNO₃ solution, (NH₄)₂MoO₄, yellow ppt. on heating. (4) In acetic acid solution, Fe₂Cl₆, yellowish ppt.
2.	ARSENATE	"	(1) In neutral solution, AgNO ₃ , brick-red ppt. (2) H ₂ S in presence of HCl, yellow ppt. on heating. (3) MgSO ₄ , Fe ₂ Cl ₆ , and (NH ₄) ₂ MoO ₄ , same as with Phosphate.
	BORATE		(1) Add concentrated H ₂ SO ₄ and alcohol. Set fire to the alcohol. Green-edged flame. (2) Acidulate with dilute HCl. Dip turmeric paper, and dry it at gentle heat. Orange colour, changed to black or green by KHO.
	TARTRATE	**	 Potassium acetate+acetic acid, white crystalline ppt. on shaking (in strong solution). Add KHO in excess and a few drops of K₂Mn₂O₈. Green colour, changing to brown ppt. on heating. Mirror test.
	CITRATES		 To neutral or slightly acid solution, add lime-water in excess. White ppt. on boiling only. (2) Add KHO in excess and a few drops of K₂Mn₂O₈. Green colour, not changed on heating.
	(SILICATE)	Decomposed; often with separation of silica	Evaporate HCl solution to dryness and heat; residue insoluble in HCl.

	Add Silver Nitrate + dilute nitric acid. Ppt. indicates	Digest ppt, with anmonia	
F.	CHLORIDE	Easily soluble	 Heat with MnO₂ and strong H₂SO₄. Cl is evolved; detected by odour, and action on litmus, KI, &c. (2) Heat solid substance with dry K₂Cr₂O₇ and concentrated H₂SO₄. CrO₂Cl₂ is evolved (red gas); which when passed into water gives chromic acid (detected as below) and HCl.
	CYANIDE	u u	Prussian blue test. See Preliminary Table.
	SULPHOCYANATE (white)	*	Fe,Cle, blood-red colouration; bleached by HgCl2, not by dilute HCl.
	FERRICYANIDE (orange)	и	(1) FeSO ₄ , dark blue ppt. (2) KI+dilute HCl, Iodine is liberated on heating. (3) Fe ₂ Cl ₆ , no ppt.
က်	BROMIDE (yellowish white)	Sparingly soluble	 Add a few drops of chlorine water, and shake up with CS₂; the latter is coloured yellow or orange. Heated with strong H₂SO₄ and MnO₂, Bromine is evolved (orange-red gas).
	IODIDE (yellow)	Insoluble	 Add a few drops of chlorine water, and shake up with CS₂; the latter is coloured violet. Heated with strong H₂SO₄ and MnO₂, Iodine is evolved (violet fumes; colour starch-paste blue).
	FERROCYANIDE (white)		(1) Fe ₂ Cl ₆ , dark blue ppt. (2) GuSO ₄ , chocolate ppt. (3) FeSO ₄ , pale blue ppt.
	SULPHIDE (black)	2	See Preliminary Table.
	CHROMATE (crimson) In strong solution only	Soluble	See 5.
	Add Ferric chloride to neutral solution.		
4	Blood-red colour indicates	(Sulphocyanatc Acctate (Todide)	. Bleached by HgCl ₃ ; not by dilute HCl Not bleached by HgCl ₁ ; bleached by HCl Red or brown ppt. with HgCl ₂ . Violet colour with CS ₂ .
	Yellowish white ppt. indicates	Phosphate See above. Arsenate	
9	If no result with the above reagents, test specially for CHROMATE.	agents, test specially	(1) Lead (2) Boil
	Also for NITTE AME and OHIOD AME		since there were here from another on Desired on Perliam

If no acid radicle be found, the substance may be a metallic oxide or hydroxide. These, if soluble in water, give a brown properties of ppt. with silver nitrate soluble in NH, or acids, and are alkaline to test paper. If insoluble, the general the body must be considered and compared with those of the oxide of the metal which has been found. Also for NITRATE and OHLORATE, since these may have been overlooked. See Preliminary Table.

* Or fuse with excess of dry Na₂CO₃, extract fused mass with water and filter. This is preferable in many cases (minerals, &c.) but is inapplicable with organic acids and others decomposable by heat.

† A ppt. on neutralization is probably SiO₂ or Al₂O₃.

† Calcium tartrate often becomes crystalline, especially after a time, and will not then dissolve in acetic acid.

§ Citrate often gives no ppt. with CaCl₂ till boiled.

DETECTION OF MORE THAN ONE ACID RADICLE.

Preliminary examination as before. Make solution and remove bases if necessary, as directed on page 71. Divide solution into several parts and test as below.

Dissolve ppt. in dilute HCl, boil, pass H₂S for some time, and again boil. Yellow ppt. indicates ARSENATE. If arsenate is present, it must be entirely removed by H,S before testing for PHOSPHATE by ammonium molybdate. If Silicofluoride is suspected (Preliminary Table), confirm by heating this ppt. with con SILICOFLUORIDE Confirm Sulphate in another portion of solution by adding HCI (dil.) and strontium nitrate. (Sulphide) (black) Insoluble in NH, (C) White ppt. indicates Oxalate, Fluoride, Phosphate, Arsenate, Borate, Tartrate, Citrate. (Sulphate, Carbonate, Silicate.) Upigest ppt. with excess of NH, for some time. Filter. Residue = (C). Acidulate filtrate with HNO, Ppt. = (A) + (B). Dark blue ppt. FERROCYANIDE. Blood-red colouration bleached by HgCl, SULPHOCYANATE. If no effect, to another portion add Ferrous Sulphate. Dark blue ppt. FERRICYANIDE. Ferrocyanide Yellowish-white ppt. indicates Arsenate Iodide (yellow) SOLUTION Add NH, till alkaline (filter off any ppt.*) and Calcium Chloride-Acidulate with dilute HCl, and to a portion add Ferric Chloride. Sparingly soluble in NH3 (B) Acidulate with dilute HCl, and add Barium Chloride Filter†, wash ppt. and digest it with acetic acid. (yellowish-white) Add Fe₂Cl₂ drop by drop. centrated H,SO, in a platinum vessel. Add Silver Nitrate and dilute HNO,-FILTER Cyanide Sulphocyanate Ferricyanide (orange) for Wash, heat to low redness and treat with acetic acid. Easily soluble in NH, (A) acetic acid (white) Oxalate, Fluoride; (Sulphate) Examine residue insoluble in Effervescence indicates OXALATE. (white) SULPHATE Chloride (white) RESIDUE. White ppt. indicates Ppt. indicates FLUORIDE 48 CV

Also by turmeric test. Test specially for BORATE by adding concentrated H₂SO₄ and alcohol, and setting fire to the mixture. Also by If blackening occurred in the preliminary examination, test specially for TARTRATE and CITRATE as below. Test specially also for ACETATE, CHROMATE, NITRATE and CHLORATE, as in detecting one acid radicle (or as below).

Results obtained with the above tests will indicate which, if any, of the following separations are necessary:

NITRATE and NITRITE

To one portion add KI+dilute HCl. Iodine liberated indicates nitrite.

HNO2+HI=H2O+NO+I.

If nitrite is present, to another portion add urea + dilute H₂SO₄ and heat; nitrite is thus destroyed,

Test residual solution for nitrate as usual 2HNO2+CO(NH2)2 = CO2+3H2O+2N2. with FeSO, and concentrated H2SO.

NITRATE and CHLORATE.

Heat solid to redness. Nitrate becomes nitrite, chlorate becomes chloride,

$$KNO_3 = KNO_2 + O$$

 $KCIO_3 = KCI + 30$.

Dissolve residue in water; test one portion for nitrite by KI and dilute HCl as above, and another for chloride by AgNO3+HNO3.

SULPHITE and CARBONATE.

Cr2O, acidulated with H2SO4. SO2 is ab-Add HCl. SO₂ and CO₂ are evolved. Pass the gases through a solution of sorbed, and the solution turns green.

= K,SO4+Cr,(SO4)3+H,0. KcCr.O7+H2SO4+3SO,

Test residual gas for CO2 by lime-water.

SULPHATE, SULPHITE and THIOSULPHATE.

FERROCYANIDE, FERRICYANIDE and

SULPHOCYANATE II.

To a portion acidulated with dilute HCl add

To a dilute neutral solution add BaCl2 in excess, Filter.

Wash with HgCl2; if Blood-red bleached by Fe₂Cl₆ in excess. Filter. dark blue, odour of SO, indicates Add HCl and boil; yellow ppt. of S and Solution Thiosulphite

Digest with dilute HCl. Filter.

Sulphate, Sulphite.

Wash.

H.S.03 = H.0+SO2+S. Sulphate Add chlorine water. White ppt.

BaSO₃+Cl₂+H₂O=BaSO₄+2HCl.

indicates Sulphite

Solution

Residue

To another portion add KI+dilute HCl and tr. Iodine liberated (detected by shaking with

Sulphocyanate.

Ferrocyanide.

Solution

CHLORIDE, BROMIDE and IODIDE.

To neutral solution add CuSO4 in excess, and H2SO3, cuprous iodide is precipitated

2KI + 2CuSO₄ + H₂SO₃ + H₂O = Cu₂L₂ + 2KHSO₄ + H₂SO₄.

CuO. Filter, evaporate solution to dryness. Mix dry residue with sium acetate dissolved in alcohol, and if necessary, dry K₂Cr₂O₇ and concentrated H₂SO₄. Distil. Bromine and chromyl a few drops of acetic acid. Add an equal bulk of Filter, confirm *iodide* in ppt. by heating with concentrated H₂SO₁. To filtrate, add KHO in excess and boil, to remove excess of Cu as CuO. Filter, evaporate solution to dryness. Mix dry residue with dichloride are evolved,

To a concentrated solution add excess of potas-

TARTRATE and CITRATE.

H₆Fe₂Cy₁₂ + 2HI = 2H₄FeCy₆ + I₂.

CS2) indicates Ferricyanide,

heat.

alcohol, shake, stir, and allow to stand for some

time. Filter.

6KBr + KgCr2O7 + 7HgSO4 = 4KgSO4 + Cr2(SO4)3 + 7HgO + 3Br2 4KCl + K2Cr2O7 + 3H2SO4 = 3K2SO4 + 2CrO2Cl2 + 3H2O. Pass the gases into water. Br dissolves. CrO, Cl2 is decomposed thus, CrO2Cl2+2H20=H2CrO4+2HCl.

sequently chloride) by neutralizing, adding acetic acid and lead acetate Confirm Bromine by shaking up with CS2; and chromate (and con-

hering to the sides of CaCl_a test after boiling vessel) indicates Tar. off alcohol and neutral-

Confirm citrate by the

crystalline, often ad-

Solution

izing with NH3. Or by Barium acetate after

Dissolve it in least Barium acetate

trate.

possible KHO, and con- neutralizing.

(or FeSO4 + H2O2 firm by "mirror"

test).

IODIDE and IODATE.

Confirm iodide in one portion by adding chlorine water + CS2. If iodide is present, add dilute HCl (+starch or CS2) to another portion. Iodine liberated indicates Iodate.

5HI+HIO3=3H20+3I2.

* Probably SiO₂ or Al₂O₃. † A ppt. on boiling filtrate is probably Citrate. ‡ See note ‡, page 73. § Unnecessary if no ppt. in (3). | Cyanide may be detected in presence of Ferrocyanide, &c. by distilling with solution of potassium hydrogen tartrate, which causes HCy to be evolved from cyanide only.

10

EXAMINATION FOR ACID RADICLES.

Explanation.

The method of examination here recommended depends upon the following principles:

1. The insolubility of Sulphate and Silicofluoride of Barium in dilute HCl.

These two acid radicles are easily distinguished in presence of one another, since silicofluorides heated with concentrated H_oSO₄ evolve SiF₄ and HF,

$$BaSiF_6 + H_2SO_4 = BaSO_4 + SiF_4 + 2HF$$

whilst sulphates give a white ppt. of SrSO, with a strontium salt.

The insolubility (or sparing solubility) of the following calcium salts in water.
 Oxalate, Fluoride, Phosphate, Arsenate, Borate, Tartrate, Citrate, (Carbonate).

Of these, calcium oxalate and fluoride are insoluble, or nearly so, in acetic acid, the rest being soluble.

Calcium oxalate on heating to redness is converted into carbonate,

$$Ca(CO_g)_g = CaCO_g + CO,$$

and the residue after heating therefore effervesces when treated with a dilute acid. Calcium fluoride remains unaltered.

From the solution of the remaining calcium salts in acetic acid, ferric chloride precipitates phosphate and arsenate,

Tartrate, citrate, and borate are looked for in separate portions, the two former however only if indicated in the preliminary examination.

 The insolubility of the following silver salts in dilute nitric acid. Chloride, Cyanide, Sulphocyanate, Ferricyanide, Bromide, Ferrocyanide, Iodide, (Sulphide). (If silver nitrate were added in neutral solution, nearly all other acid radicles would likewise be precipitated as silver salts.)

These can be further subdivided into groups owing to their different solubilities in ammonia.

4. Ferric chloride, in dilute acid or neutral solution, precipitates ferrocyanide as "Prussian blue" (usually represented as Fe₄(FeCy₆)₃) and gives a blood-red colour with sulphocyanate due to ferric sulphocyanate Fe₂(CyS)₆; whilst ferrous sulphate precipitates ferricyanide as "Turnbull's blue" Fe₂(Fe₂Cy₁₂). If ferrocyanide is present, ferricyanide must be looked for in some other way, such as by adding potassium iodide and starch (see Special Separations), (or by the solubility of its silver salt in ammonia, but this is not satisfactory, since there is danger of reduction to ferrocyanide).

Having so far divided the acids which are present into groups, special tests or separations must be applied as the results obtained dictate. By carefully noting the effect of each test applied, and excluding those acid radicles shewn to be absent, there will usually remain but few which require further separation or confirmation. The identification of one acid radicle will, moreover, often indicate the presence or absence of another. For example, if a hypochlorite is found, a chloride is almost certain to be present (since pure hypochlorites are very rare and unstable; so-called hypochlorites being usually mixtures of hypochlorite and chloride), whereas sulphite must necessarily be absent, if in solution (since sulphite + hypochlorite = sulphate + chloride).

REACTIONS OF SOME OF THE MORE COMMON ORGANIC BODIES.

METHYL ALCOHOL.

Wood Spirit. CH, OH.

Colourless, limpid, volatile, inflammable liquid. Boils at 66° C. Miscible with water, ether, and ethyl alcohol.

Heated with potassium dichromate and dilute sulphuric acid in excess, it yields formic acid, which may be distilled off and identified as usual,

$$\begin{cases} \mathbf{H} \\ \mathbf{CH}_{\circ}\mathbf{OH} + \mathbf{O} = \begin{cases} \mathbf{H} \\ \mathbf{COOH} + \mathbf{H}_{\circ}\mathbf{O}. \end{cases}$$

Iodine and caustic potash yields no iodoform.

ETHYL ALCOHOL.

Alcohol. Spirits of Wine. $(C_sH_s)OH$ or ${CH_s \choose CH_sOH}$.

Colourless volatile inflammable liquid. Boils at 78°.4°C. Miscible with water and with ether.

1. Heated with potassium dichromate and dilute sulphuric acid, not in excess, it vields acetaldehyde—

$$\begin{cases} \mathrm{CH_{a}} \\ \mathrm{CH_{a}OH} + \mathrm{O} = \begin{cases} \mathrm{CH_{a}} \\ \mathrm{COH} \end{cases} + \mathrm{H_{2}O}. \end{cases}$$

The aldehyde may be distilled off and identified by the usual tests.

- A dilute solution of ethyl alcohol gently heated, and a colourless strong solution
 of iodine in caustic potash added, gives gradually a yellow crystalline ppt. of
 iodoform CHI₃. Examined under the microscope, this ppt. is seen to consist of
 hexagonal plates or six-rayed stars. [Lieben's test.]*
- 3. Heated with sodium acetate and strong sulphuric acid, the characteristic odour of ethyl acetate (acetic ether) is produced,

$$(C_2H_3)OH + CH_3 \cdot COOH = CH_3 \cdot COO(C_2H_3) + H_2O.$$

[•] This reaction is also produced by aldehyde, acetone, ethylidene-lactic acid, &c. but not by chloroform, chloral, methyl or amyl alcohol, acetic or formic acids, glycerin or ether.

ETHYL ETHER.

Ordinary Ether. "Sulphuric" Ether. (C,H,),O.

Colourless, very mobile liquid. Penetrating odour. Highly volatile, its rapid evaporation causing great reduction of temperature. Boils at 35°C. Highly inflammable. Miscible in all proportions with alcohol, but only to a limited extent with water. Dissolves various fats, oils, resins, &c.

By slow oxidation, e. g. with air under certain conditions, it yields aldehyde, acetic acid, hydrogen dioxide, &c.

Heated with nitric acid it gives acetic acid, oxalic acid and carbon dioxide.

ACETALDEHYDE.

Aldehyde. Ethaldehyde. ${}^{\text{CH}_3}_{\text{COH}}$.

Colourless mobile inflammable liquid. Boils at 20°. 8 C. Characteristic odour. Miscible with water, alcohol, and ether.

- Solution of silver oxide in ammonia gives a bright mirror of metallic silver on warming. (More delicate in presence of KHO.)
- Fehling's solution gives, on heating, a red ppt. of Cu₂O.
 In these cases the aldehyde is converted into acetic acid,

$$\begin{cases} CH_{3} \\ COH \end{cases} + O = \begin{cases} CH_{3} \\ COOH \end{cases}.$$

- 3 Heated with caustic potash the liquid turns brown, owing to the formation of so-called aldehyde-resin.
- 4. If dissolved in ether, and ammonia gas be passed into the liquid, white crystals of CH₃ "ammonia-aldehyde" NH² are obtained.
- 5. A solution of a rosaniline salt, which has been bleached by sulphur dioxide, gives a violet or pink colour.

CHLORAL.

Trichlor-acetaldehyde. $\begin{cases} CCl_s \\ COH \end{cases}$.

Colourless mobile liquid. Boils at 97°. 2 C. Combines readily with water, forming crystalline chloral hydrate,

$$\left\{ \begin{matrix} \text{CCl}_3 \\ \text{COH} \end{matrix} \right. \left. \begin{matrix} \text{H}_2\text{O} \end{matrix} \right. \text{or} \left. \left\{ \begin{matrix} \text{CCl}_3 \\ \text{CH(OH)}_2 \end{matrix} \right. \right.$$

1. Caustic potash (aqueous solution) converts it into chloroform and potassium formate,

$$\begin{cases} {\rm CCl}_{_3} + {\rm KHO} = {\rm CHCl}_{_3} + \begin{cases} {\rm H} \\ {\rm COOK} \end{cases}.$$

These products may be identified as usual.

2. Silver oxide, Fehling's solution, and ammonia-gas, behave as with acetaldehyde.

CHLOROFORM.

Trichloromethane. CHCl3.

Colourless limpid volatile liquid. Boils at 61°.2 C. Soluble in alcohol and in ether; nearly insoluble in water.

1. Heated with an alcoholic solution of caustic potash, it gives potassium formate and potassium chloride,

$$\mathrm{CHCl_{3}} + 4\mathrm{KHO} = \left\{ \begin{matrix} \mathbf{H} \\ \mathrm{COOK} \end{matrix} + 3\mathrm{KCl} + 2\mathrm{H_{2}O}. \right.$$

These products may be identified as usual.

2. Heated with a primary amine (e.g. aniline) and an alcoholic solution of caustic potash, the characteristic odour of carbamines is produced,

$$\begin{aligned} \text{CHCl}_{\mathfrak{s}} + (\text{C}_{\mathfrak{s}}\text{H}_{\mathfrak{s}})\text{NH}_{\mathfrak{s}} + 3\text{KHO} &= (\text{C}_{\mathfrak{s}}\text{H}_{\mathfrak{s}})\text{NC} + 3\text{KCl} + 3\text{H}_{\mathfrak{s}}\text{O}. \\ \text{Phenyl carbamine} \end{aligned}$$

Fehling's solution is readily reduced on heating, red Cu₂O being precipitated,
 CHCl₂ + 2CuO + 5KHO = Cu₂O + K₂CO₂ + 3KCl + 3H₂O,

GLYCERIN.

$$(C_3H_5)^{\prime\prime\prime}(OH)_3$$
 or $\begin{pmatrix} CH_2OH\\ CHOH\\ CH_2OH \end{pmatrix}$

Colourless viscid liquid. Sweet taste. Miscible with water and with alcohol.

 Heated with dehydrating agents (e.g. KHSO₄ or concentrated H₂SO₄), characteristic irritating odour of acrolein is obtained,

$$C_3H_5(OH)_3 - 2H_2O = C_2H_3$$
. COH.

2. A borax bead immersed for a few minutes in a solution of glycerin (made slightly alkaline with KHO) and held in a Bunsen flame, gives a green colour to the flame.

FATS.

E.g. Tri-stearin (Mutton fat)
$$\binom{C_{17}H_{35}}{CO_2}_3 \cdot (C_3H_5)'''$$
.

Soluble in ether, and in carbon disulphide. Practically insoluble in water.

1. Heated with caustic soda or potash*, a soap is produced and glycerin separates,

$$\begin{pmatrix} C_{17}H_{38} \\ CO_{9} \end{pmatrix}_{3} \cdot C_{3}H_{5} + 3NaOH = 3 \begin{cases} C_{17}H_{85} \\ CO_{2}Na + C_{3}H_{5}(OH)_{3}. \end{cases}$$

2. And with lead oxide, insoluble lead stearate and glycerin are produced,

$$2 \begin{pmatrix} C_{17}H_{35} \\ CO_{2} \end{pmatrix}_{3} C_{3}H_{5} + 3PbO + 3H_{2}O = 3 \begin{pmatrix} C_{17}H_{35} \\ CO_{2} \end{pmatrix}_{2} Pb + 2C_{3}H_{5}(OH)_{3}.$$

 Heated alone they decompose, evolving acrolein C₂H₃. COH, and other offensive vapours.

^{*} Best in alcoholic solution.

SOAPS.

$$E.g.$$
 Sodium Stearate. $\left\{ egin{matrix} \mathbf{C}_{17}\mathbf{H}_{as} \\ \mathbf{COONa} \end{smallmatrix} \right.$

Soluble in pure water; reprecipitated by a strong solution of sodium chloride. Soluble in alcohol. Aqueous solution "lathers" when shaken.

1. From alcoholic or aqueous solution, calcium or magnesium salts (e.g. hard water) precipitate white calcium or magnesium stearates,

$$\mathrm{CaSO_4} + 2 \left\{ \begin{matrix} \mathrm{C_{17}H_{35}} \\ \mathrm{CO_oNa} \end{matrix} \right. = \left(\begin{matrix} \mathrm{C_{17}H_{35}} \\ \mathrm{CO_o} \end{matrix} \right)_{\mathrm{g}} \mathrm{Ca} + \mathrm{Na_gSO_4}.$$

2. Dilute hydrochloric acid gives a white ppt. of stearic acid,

$$\begin{cases} C_{17}H_{as} \\ COONa \end{cases} + HCl = \begin{cases} C_{17}H_{as} \\ COOH \end{cases} + NaCl.$$

CARBOHYDRATES.

I. Saccharons. (C18H28O11.)

Cane Sugar. Saccharon (Sucrose). C12H22O11.

Soluble in water. Insoluble in cold absolute alcohol. Dextrorotatory.

- 1. Does not directly reduce Fehling's solution *.
- 2. Boiled with dilute acids (H₂SO₄ or HCl) it takes up the elements of water, forming a mixture of dextrose and lævulose ("inverted sugar"),

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
.

- 3. In contact with yeast it passes first into a mixture of dextrose and lævulose, which then undergo alcoholic fermentation.
- Concentrated sulphuric acid, added to a strong warm solution, causes it to blacken
 and swell up, owing to the separation of carbonaceous matter, CO, SO₂, HCOOH,
 &c. being evolved.

[&]quot;Fehling's solution" is made from a cupric salt, an alkaline tartrate, and caustic alkali. The action of glucoses upon it, is virtually the reduction of CuO to Cu₂O, the glucose becoming oxidized to acetic, formic, tartronic, &c. acids, and other bodies. The exact nature of the change is not known.

CARBOHYDRATES (continued).

Milk Sugar. Lacton. C19H29O11.

Less soluble in water than cane sugar. Insoluble in absolute alcohol, Dextrorotatory.

- 1. Readily reduces Fehling's solution on heating, red Cu.O being precipitated.
- Boiled with dilute acids, it takes up the elements of water, forming a mixture
 of galactose (C₆H₁₂O₆), and another glucose (C₆H₁₂O₆), which is probably identical
 with sucrodextrose.
- 3. Not directly fermentable by yeast.
- 4. Concentrated sulphuric acid chars it, but less readily than cane sugar.

Starch Sugar. Malton (Maltose) Amylon. C12H22O11.

Soluble in water and in alcohol.

Dextrorotatory. Diffusible.

- 1. Reduces Fehling's solution on heating, red Cu.O being precipitated.
- 2. Boiled with dilute acids, it is slowly converted into a mixture of two dextroglucoses C.H., O..*
- 3. In contact with yeast it is first converted (probably) into dextroglucoses, which then undergo alcoholic fermentation.

II. Glucoses. (C,H,2O,.)

Dextrose. Sucrodextrose. Grape sugar. C,H,2O6.

Soluble in water and in alcohol.

Dextrorotatory.

Less sweet than cane sugar.

- 1. Reduces Fehling's solution at once on heating, red Cu_oO being precipitated.
- 2. A warm solution in contact with yeast readily undergoes alcoholic fermentation, $C_eH_{12}O_6 = 2(C_2H_6)OH + 2CO_2$.
- 3. Concentrated sulphuric acid does not blacken it.
- 4. Heated with strong solution of caustic potash it turns brown.
- 5. Not affected by boiling with dilute H.SO.

Lævulose. Sucrolævulose. C6H12O6.

Resembles dextrose in the above properties, but is lævorotatory, sweeter, and more soluble in alcohol.

Galactose. Lactose. C.H.,O.

A dextrorotatory glucose, closely resembling dextrose, but having a higher rotatory power, and non-fermentable by yeast.

Or perhaps entirely into ordinary sucrodextrose. Diastase is said to have no action on amylon.

CARBOHYDRATES (continued).

III. Carbohydrates of the composition (C,H,O,),

Starch. (C,H,O,),

Insoluble in cold water. Heated with water it forms a mucilage or paste, and on boiling with much water, a kind of solution which contains "soluble starch". Dextrorotatory. Colloid.

- 1. Iodine colours starch paste, or solution, blue. The colour is temporarily destroyed
- 2. Solid starch when heated to about 150°C. is converted into "British gum" (impure dextrin) which is soluble in cold water, and is not coloured blue by iodine.
- 3. By the action of many unorganized ferments (such as ptyalin, diastase, &c.) or by heating with dilute acids, starch takes up the elements of water, forming a mixture of dextrin (C₆H₁₀O₅), and amylon C₁₂H₂₂O₁₁. These bodies afterwards undergo further hydration, giving dextroglucoses. (See Amylon and Dextrin.)

Dextrin. Amylin. (C,H,O,).

Easily soluble in cold water. Insoluble in alcohol.

Dextrorotatory. Colloid.

Solution is not coloured blue by iodine*.

In contact with many unorganized ferments (or dilute acids), it is converted into amylon C19H22O11,

 $2(C_6H_{10}O_5)_n + nH_2O = nC_{12}H_{22}O_{11}$.

Inulin. (C,H,O,),.

Resembles starch, but is completely soluble in warm water, the solution is lævorotatory, and is not coloured blue by iodine.

In contact with dilute acids it gives a lavorotatory glucose resembling sucrolavulose.

Glycogen. (C,H,O,),

Readily soluble in warm water, forming an opalescent solution. Insoluble in alcohol.

Dextrorotatory.

Iodine colours it reddish-brown. The colour is temporarily destroyed by heating. By dilute acids, and by many unorganized ferments, it is converted first into a kind of dextrin (according to some, into a mixture of amylin and amylon) and then into a dextrorotatory glucose $C_6H_{12}O_6$, perhaps identical with sucrodextrose.

Cellulose. (C,H10Os),

Insoluble in water or alcohol. Soluble in a solution of cuprammonic hydroxide (prepared by dissolving cupric hydroxide in ammonia), from which it is reprecipitated by HCl or CO₂.

Iodine alone does not colour cellulose blue, but it does so in presence of concentrated sulphuric acid, or of zinc chloride.

^{*} There are probably several varieties of dextrin. So-called erythro-dextrin gives a reddish-brown colour with iodine, which permanently disappears on heating.

LACTIC ACIDS.

Fermentation Lactic Acid. (Inactive a Hydroxypropionic or Ethylidene Lactic CH, OH. Acid.)

Colourless syrupy liquid. Very soluble in water, alcohol, or ether.

1. Heated with dilute sulphuric acid, it yields acetaldehyde and formic acid,

- Gentle oxidizing agents (e.g. manganese dioxide and dilute sulphuric acid) convert it
 into acetaldehyde and carbon dioxide. More powerful oxidizing agents yield acetic
 acid and carbon dioxide.
- 3. Heated with concentrated sulphuric acid, carbon monoxide is evolved.

Sarcolactic Acid. (Active a Hydroxypropionic or Ethylidene Lactic Acid.)

CH. OH.

COOH

Identical with fermentation lactic acid in the above properties, but is distinguished by being optically active (feebly dextrorotatory). There is a difference also in the character of the zinc salts.

Ethylene Lactic Acid. (β Hydroxypropionic Acid.) $\begin{cases} \text{CH}_2 \cdot \text{OH} \\ \text{CH}_2 \\ \text{COOH} \end{cases}$

Differs from the above in that, when treated with oxidizing agents (chromic or nitric acids), it yields oxalic acid and carbon dioxide—

$$\begin{array}{l} \mathrm{CH_{2}.\,OH} \\ | \\ \mathrm{CH_{2}.\,COOH} \end{array} + 5\mathrm{O} = \begin{array}{l} \mathrm{CO.\,OH} \\ | \\ \mathrm{CO.\,OH} \end{array} + \mathrm{CO_{2}} + 2\mathrm{H_{2}O} \ ; \end{array}$$

and when heated alone, or with dilute sulphuric acid, it splits up into acrylic acid and water-

$$\begin{array}{ll} \operatorname{CH}_2 \text{. OH} & = & \operatorname{CH}_2 \\ \mid & \mid & \mid \\ \operatorname{CH}_2 \text{. COOH} & = & \operatorname{CH} \text{. COOH} \end{array} + \mathbf{H}_2 \mathrm{O}.$$

UREA.

Carbamide (?)
$$CO \subset_{NH^2}^{NH^2}$$
 or $C = NH^2$.

Prismatic crystals. Easily soluble in water and in alcohol.

- Strong nitric acid throws down, from concentrated solutions, crystals of urea nitrate CO(NH₂)₂. HNO₃. Under the microscope these are seen to consist of rhombic or six-sided tables.
- 2. Heated alone to about 150° C. ammonia is evolved and biuret formed-

$$2\mathrm{CO} \left< \frac{\mathrm{NH_{s}}}{\mathrm{NH_{s}}} = \frac{\mathrm{CO}}{\mathrm{CO}} \right> \frac{\mathrm{NH_{s}}}{\mathrm{NH}} + \mathrm{NH_{s}}.$$

On dissolving biuret in water, adding excess of caustic potash and a drop of copper sulphate, a red-violet colour is produced.

3. A neutral solution heated to about 40°C. with a trace of urine-ferment, turns alkaline after a few minutes, owing to formation of ammonium carbonate—

$$CO < \frac{NH_s}{NH_s} + 2H_sO = CO < \frac{ONH_s}{ONH_s}$$
.

 Sodium hypobromite, in presence of caustic soda*, causes a rapid evolution of nitrogen—

$$CO(NH_{\bullet})_{\bullet} + 3NaBrO + 2NaOH = 3NaBr + Na_{\bullet}CO_{\bullet} + 3H_{\bullet}O + N_{\bullet}.$$

(Sodium hypochlorite only evolves half the nitrogen in the cold— $2CO(NH_2)_2 + 3NaClO + 2NaOH = 2NaCNO + 3NaCl + 5H_2O + N_2$.)

5. Nitrous acid (or a nitrite + dilute acid) evolves nitrogen and carbon dioxide (complete on heating),

$$CO(NH_{\bullet})_{\bullet} + 2HNO_{\bullet} = CO_{\bullet} + 3H_{\bullet}O + 2N_{\bullet}.$$

 Mercuric nitrate (in absence of chlorides), white ppt. of CO(NH₂)₂. 2HgO, or 2CO(NH₂)₂. 3HgO. Hg(NO₃)₂, according to conditions.

^{*} Prepared by gradually adding bromine to strong caustic soda solution, and keeping the mixture cool.

URIC ACID.

H,(C,H,N,O,).

White crystalline powder. Almost insoluble in water. Soluble in caustic potash, forming potassium urate, K₂(C₄H₂N₄O₃), from which hydrochloric acid reprecipitates uric acid.

Evaporated just to dryness with dilute nitric acid, a yellow or pinkish residue is left, which when moistened with ammonia gives a crimson colour, due (in part) to "murexide" or ammonium purpurate, NH₄. (C₈H₄N₅O₆). This colour is changed to a purple by caustic potash.

Heated alone, it blackens, and evolves, amongst other bodies, hydrocyanic acid, carbon dioxide and ammonia, which may be recognized by their odour, &c.

STRYCHNINE.

Strychnia. C21H22N2O2.

Prismatic crystals or white powder. Very slightly soluble in water, the solution having a bitter taste. Sparingly soluble in alcohol and ether. Soluble in chloroform. Soluble in most acids, forming salts.

Dissolved in concentrated sulphuric acid and a fragment of manganese dioxide* added, a purple colour is obtained, which rapidly changes to crimson, and afterwards to pink or orange.

[Curarine gives an exactly similar reaction, but it is almost insoluble in chloroform.] Caustic potash (ammonia, potassium, carbonate, &c.) throws down a white ppt. of strychnine from solutions of its salts (if not too dilute) which is insoluble in excess, and soon becomes crystalline.

QUININE.

Quinia. C,H,N,O,.

White powder or crystals. Very sparingly soluble in water. Easily soluble in alcohol and in chloroform; less so in ether. Soluble in most acids, forming salts.

- 1. Dissolved in dilute sulphuric acid, the solution exhibits well marked blue fluorescence.
- A nearly neutral solution mixed with chlorine or bromine water, and then with ammonia in excess, gives a bright green colouration or precipitate.
- 3. Treated first with chlorine or bromine water, then with a few drops of potassium ferro- or ferri- cyanide, and lastly with ammonia not in excess, a red colouration is produced, destroyed by excess of ammonia.
- 4. Caustic potash gives, in solutions of quinine salts, in white ppt. of hydrated quinine, insoluble in excess.

^{*} Potassium bichromate or permanganate, lead dioxide, &c. answer the same purpose.

MORPHINE.

Morphia. C, H, NO, . H,O.

White powder or small prisms. Almost insoluble in cold water; very sparingly soluble in boiling water, ether, cold alcohol, and chloroform. Dissolves easily in hot alcohol; also in dilute acids, forming salts.

- 1. Neutral ferric chloride gives with dry morphine (or a neutral solution) a deep inky blue colour, changed to green by excess of ferric chloride.
- Iodic acid gives, in neutral morphine solutions, a brown colour, due in part to the liberation of iodine, which may be detected by a starch test. The brown colour is deepened by ammonia.
- 3. Strong nitric acid in excess, gives a deep orange colour. (Unchanged by stannous chloride.)
- 4. Heated to 100°C. with concentrated sulphuric acid, and a crystal of pure potassium perchlorate added, a brown colour is produced.
- 5. From strong solutions of morphine salts, caustic potash (one drop) gives, on stirring, a white ppt. of hydrated morphine, easily soluble in excess.

BRUCINE.

Brucia. C23H26N2O4.

White powder, or crystalline needles or prisms. Slightly soluble in water. Easily soluble in alcohol and in chloroform. Soluble in most acids, forming salts.

- Strong nitric acid gives with solid brucine (or a solution to which strong sulphuric
 acid* has been added) a scarlet colouration changing to orange and yellow.

 Stannous chloride changes the colour to purple or violet, if sufficient brucine is
 present.
- Mercurous nitrate added to a neutral solution, and the mixture heated to 100° gives a crimson colour.
- 3. Caustic potash precipitates brucine from solutions of its salts, insoluble in excess.

^{*} Strong sulphuric acid itself gives a transient rose colour with brucine.

BENZENE.

Benzol. C.H.

Colourless very limpid liquid. Characteristic odour. Gives off highly inflammable vapour when heated. Boils at 80°.5 C. Miscible with alcohol, ether, and chloroform, but not appreciably with water.

Agitated for a few minutes with the strongest nitric acid (not allowing the temperature to rise too high), nitrobenzene C₆H₅NO₂ is formed, which separates in oily drops on pouring the liquid into much water, and has characteristic odour of bitter almonds. On digesting nitrobenzene with a hydrogenizing agent, e.g. zinc and hydrochloric acid, aniline is obtained,

$$C_6H_5NO_g + 3H_g = C_6H_5NH_g + 2H_gO_s$$

which may be detected as usual.

PHENOL.

Carbolic Acid. Phenic Acid. C.H. OH.

Colourless deliquescent crystals. Characteristic odour. Sparingly soluble in water; solution does not redden litmus. Easily soluble in alcohol, ether, chloroform, or alkalies.

Aqueous solutions of phenol give with

- Bromine water, white or yellowish ppt. of tribromophenol C_eH₂Br₃. OH, even in very dilute solutions (1 in 60,000). This ppt. if washed, digested with sodium amalgam and water, and then acidified with HCl, is reconverted into phenol, which may be recognized by its odour.
- 2. Gently heated with ammonia, and a drop of sodium hypochlorite added, a deep blue colour (green in dilute solutions) is produced, changed to red by acids.
- Ferric chloride gives a violet colouration; (not so sensitive as with salicylic acid
 —1 in 3000).
- 4. Phenol added to a mixture of potassium nitrite and strong sulphuric acid, gives a brown colour changing to green and finally to blue.

ANILINE.

Phenylamine. C,H,NH,

Oily liquid, colourless when pure. Boils at 183° 7 C. Slightly soluble in water. Easily soluble in alcohol, ether, and chloroform.

Solutions of aniline or its salts give with bleaching powder solution, not in excess, a violet or purple colouration, soon changing to brown.

Heated with *chloroform* and alcoholic solution of *caustic potash*, characteristic odour of phenyl carbamine C₅H₅NC is evolved. (See Chloroform.)

Treated with sulphuric acid and a fragment of manganese dioxide (or potassium bichromate) added, a blue colouration is obtained, changing to black after a time.

Heated with potassium nitrite and dilute H₂SO₄, phenol is formed, which may be recognized by its odour, &c.

SALICYLIC ACID.

White granular powder or prismatic crystals. Nearly insoluble in cold water. Soluble in hot water, alcohol, ether, or alkalies.

1. Heated with lime, it yields phenol, which may be recognized by its odour, &c.

$$\mathbf{C_6H_4} \leqslant \begin{matrix} \mathbf{OH} \\ \mathbf{COOH} \\ \end{matrix} + \mathbf{CaO} = \mathbf{C_6H_5OH} + \mathbf{CaCO_3}.$$

- Ferric chloride gives a fine violet colour even in very dilute solutions (1 in 100,000).
 The colour is destroyed by acids or alkalies.
- 3. Bromine water gives a white ppt. similar to that produced by phenol, and which behaves similarly with sodium amalgam; but the reaction is far less delicate.

BENZOIC ACID.

COOH.

White feathery crystals. Characteristic odour especially on heating. Sparingly soluble in cold water. (The solubility is much increased by the presence of sodium phosphate.) Easily soluble in boiling water, alcohol, ether, and chloroform. Hydrochloric acid precipitates benzoic acid from strong solutions of its salts.

1. Heated with lime, benzene is evolved, which may be distilled off and identified as usual,

$$C_6H_6$$
, $COOH + CaO = C_6H_6 + CaCO_3$.

- 2. Heated alone to about 120° C. it melts, and afterwards sublimes, giving an irritating vapour which readily condenses to white crystals.
- Neutral ferric chloride gives, in neutral solution, a reddish-white ppt. of basic ferric benzoate Fe₂(C₆H₅CO₂)₆. Fe₂O₃.
- 4. Ammoniacal barium chloride, in presence of alcohol, no precipitate.

HIPPURIC ACID.

 $\label{eq:Benzamidacetic} \textbf{Benzamidacetic Acid.} \quad \left\{ \begin{aligned} & \underbrace{CH_{\mathfrak{g}}NH(C_{\mathfrak{g}}H_{\mathfrak{g}}CO)}_{COOH} = C_{\mathfrak{g}}H_{\mathfrak{g}}NO_{\mathfrak{g}}. \end{aligned} \right.$

Shining prismatic crystals. Nearly insoluble in cold water, ether, and chloroform. Readily soluble in boiling water, and in alcohol.

 Boiled for some time with strong hydrochloric acid, it takes up the elements of water, forming amidacetic acid (glycocol) and benzoic acid—

$$\begin{cases} \mathrm{CH_{2}NH(C_{6}H_{8}\,.\,CO)} + \,\mathrm{H_{2}O} = \begin{cases} \mathrm{CH_{2}NH_{2}} + \begin{cases} \mathrm{C_{6}H_{8}} \\ \mathrm{COOH} \end{cases} \end{cases} \cdot$$

The latter is mostly given off in vapour; and the former may be identified by adding to the solution an excess of caustic potash and a drop of copper sulphate, when a deep blue solution is obtained, which is unaltered by boiling.

Heated alone, it melts, and evolves aromatic odours, due to benzonitrile C_sH_s. CN, benzoic acid, &c. Heated with lime it evolves benzene.

SUCCINIC ACID.

CH COOH

Colourless crystals, easily soluble in water, alcohol, or ether; insoluble in chloroform. Is not precipitated from solutions of its salts by hydrochloric acid.

Heated alone, it gives off a suffocating vapour, easily condensing to crystals. Strongly heated in air it burns with a blue flame.

Ammoniacal barium chloride gives, in presence of alcohol, a white ppt. of barium succinate, CH₂CO₂ Ba.

Neutral ferric chloride gives, in neutral solutions, a brownish-red ppt. of basic ferric succinate, $\operatorname{Fe_2}\left(\overset{\operatorname{CH_2CO_2}}{\operatorname{CH_2CO_2}}\right)_3$. $\operatorname{Fe_2O_3}$. (This ppt. when boiled with ammonia, gives ammonium succinate, which may be identified by the BaCl₂ test as above.)

PROTEIDS.

Approximate composition, C, H,118 N,18 O,28 S.

General characters:

Amorphous. Solutions lavorotatory.

Diffuse with very great difficulty (except peptones, which are highly diffusible).

General tests:

- Millon's reagent* gives a precipitate which turns red on heating. The liquid also turns red. With minute quantities a red solution only is produced.
- 2. Strong nitric acid produces a yellow colour, changed to orange by ammonia.
- Heated with caustic potash and a few drops of cupric sulphate a violet solution is obtained. (Peptones give a red colour, if very little copper salt be added.)

^{*} Prepared by dissolving mercury in an equal weight of strong nitric acid at a gentle heat, diluting with twice its bulk of water, and allowing it to settle.

PROTEIDS (continued).

Egg-Albumin.

Soluble in water.

Silver nitrate, mercuric chloride, and lead acetate, precipitate it from its solution. Strong alcohol first precipitates, afterwards coagulates it.

Strong acids, especially nitric, coagulate it.

Heated to about 70°C. it is coagulated. If however a dilute acid or an alkali be first added, no coagulation occurs on heating, and the solutions contain "acidalbumin" and "alkali-albumin" respectively, which are precipitated on neutralizing the liquid.

Egg-albumin differs from serum-albumin in some respects, e.g. in being coagulated by ether, and in its coagulated form being nearly insoluble in strong nitric acid.

Casein.

Insoluble in water, and in neutral saline solutions.

Soluble in dilute acids and in alkalies, reprecipitated on neutralization. If an alkaline phosphate be present, however, it is not reprecipitated on neutralizing its alkaline solution.

Casein very closely resembles alkali albumin in properties; according to some authors it is identical with potassium albuminate.

Fibrin

Has a filamentous structure, and possesses great elasticity.

Insoluble in water. Very sparingly soluble, and with change, in dilute alkalies, and in strong neutral solutions of sodium chloride, potassium nitrate, &c.

Fibrin has the property of readily decomposing hydrogen dioxide, oxygen being evolved. If fibrin be treated with tincture of guaiacum, and hydrogen dioxide added, a blue colour is obtained.

GELATIN or GLUTIN.

Amorphous. Percentage composition differs but slightly from that of the proteids. Easily soluble in water on heating, gelatinises on cooling. Aqueous solution is lavorotatory, and is not diffusible.

Tannic acid throws down a yellowish precipitate, even from very dilute solutions.

Mercuric chloride also precipitates it.

CAMBRIDGE: PRINTED BY J. & C. F. CLAY, AT THE UNIVERSITY PRESS.



