

# HAND BOOK

OF

# QUALITATIVE CHEMICAL ANALYSIS.

SELECTED AND ARRANGED FOR THE

Students of the Agricultural College of Michigan,

BY

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## INORGANIC CHEMICAL ANALYSIS.

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THE object of Chemical Analysis is to ascertain the chemical composition of any given body. Inorganic chemical analysis is divided into Qualitative Analysis, and Quantitative Analysis. Qualitative Analysis is the separation and identification of the chemical components of any substance, either in a separate form or in some known state of chemical combination. It is also used to identify simple or elementary substances by bringing them into chemical combination with other substances whose chemical composition is already known. Qualitative Analysis teaches us to separate and identify the components of any substance with regard to their quality only, without regard to their quantity, and answers the question, "*What* does the substance contain?" Quantitative Analysis furnishes the methods of procedure by which we determine the relations of weight or volume which these elements bear to each other, and answers the question, "*How much* of its several given elements does the substance contain?"

The methods of Qualitative Analysis consist in bringing the substance under examination into contact with other bodies of known properties, and observing the phenomena which ensue. These phenomena consist in alterations, either in state of aggregation, form, or color, depending upon chemical change. By exhibiting the constituent parts of a substance of *unknown* composition, in forms of *known* composition, the constitution of the body examined, and the presence of its several component elements may be positively inferred. The separation and identification of substances are usually accompanied by physical changes. All bodies which we employ for the purpose of producing physical changes by chemical transformations are called *reagents*; and the resulting changes are called *reactions*. Acids, bases, salts, and elementary bodies are alike used as reagents. The reader will note a difference between *analysis* and *testing*: we test for any particular substance by eliciting some property peculiar to itself, such as a change of color (*e. g.*, the blood-red coloration formed by adding a sulphocyanide to a solution of ferric salt), or the production of a peculiar odor (*e. g.*, the garlic odor of the vapor of metallic arsenic).

By means of reagents the chemist interrogates the substance under examination, inquiring whether it contains this or that group of chemically similar elements, or only this or that member of such group. If the question be put correctly, that is, if all the conditions under which the reaction

expected can be produced by the reagent employed, be carefully observed, the answer is decisive as to the presence or absence of the element or group of elements sought. But if the properties and chemical relations of the bodies formed by the chemical changes which constitute the reaction, have been wholly or partially neglected, the answer is at least of doubtful accuracy, if not certainly erroneous.

Chemical substances act upon each other more certainly and speedily when they are in the *fluid state*, because the contact of the molecules is then more complete, and that interchange of particles which constitutes the reaction more easily effected. The fluid state may be secured either by *solution* or by *fusion*. Reagents, therefore, may be employed either in the *wet way* or in the *dry way*. In the wet way the reagent in solution is brought into contact with the substance to be analyzed, which is usually in the liquid form. In the dry way the substance to be analyzed and the reagent are brought together in the solid state and subjected to a heat sufficient to melt the reagent, or both the reagent and the assay. At a high temperature chemical reactions are secured similar to those obtained by solution: certain changes are also secured by the addition or abstraction of oxygen, according as we use the oxidizing or deoxidizing flame. The knowledge derived in the dry way by the use of the blowpipe, and by the behavior of bodies in the different flames which can be produced by it, is one of great importance in Qualitative Analysis. This method is largely employed in the preliminary examination, and the details of analysis in the dry way are described in connection with the preliminary examination.

Many reagents exhibit the same or similar behavior with a group of chemically similar elements, and with most of the compounds of these elements; and can therefore be used to divide the elements into groups of chemically similar substances. Such reagents are called *group reagents*. Others serve for the further distinction of the several members of such groups, and are termed *special reagents*. Their selection depends upon the knowledge of the behavior of such reagents to each single element of the group, or of each of its several compounds. The number of special reagents is much greater than that of the group reagents, their nature being as various as that of the substances which come under examination. Their selection depends on the solubility or insolubility, color, or other physical or chemical properties of the new compounds to which they give rise. Certain special reagents produce reactions which under given conditions are entirely characteristic of a given substance or compound. Such reagents and reactions are distinguished by being printed in **SMALL CAPS**.

It is the task of the analyst not only to establish that this or that body is present in a compound, but he is to prove that no other body is present beside those which he has actually found. Hence it is evident that he must not treat the substance under examination with reagents indiscrimi-

nately. He must follow a certain fixed order, a methodical system in the application of reagents. This systematic method consists in the employment of group reagents for the successive separation of groups of elements possessing certain common chemical properties, and finally, in the recognition of each member in such group by the use of special reagents which are characteristic.

The first thing to be done in the Qualitative Analysis of a solid body is to subject it to *Blowpipe Analysis, or analysis in the dry way*, whereby important information as to its composition may often be obtained. The substance is then dissolved and its constituents determined by analysis in the wet way. The course of Qualitative Analysis therefore embraces three parts :

- I. *Blowpipe Analysis;*
- II. *Solution, or conversion into the liquid form;*
- III. *Analysis of the solution in the wet way.*

# BLOWPIPE ANALYSIS.

## TABLE I.

### Preliminary Examination in Blowpipe Analysis.

The substance under examination is non-metallic, being neither a metal nor an alloy.

Reduce the substance to a fine powder in a porcelain mortar.

### FIRST STEP.

Place a few grains of the dry substance in a clean, dry test tube, and heat, at first gently, but if no change ensues, to a full red heat, and watch the changes.

Substance unaltered.	Indicates the absence of <ul style="list-style-type: none"> <li>organic matter ;</li> <li>volatile bodies ;</li> <li>fusible bodies ;</li> <li>salts containing water of crystallization ;</li> <li>salts containing interstitial water ;</li> <li>substance whose color is changed by heat.</li> </ul>
Changes color.	<ul style="list-style-type: none"> <li>Many metallic oxides ;</li> <li>White to yellow, h., to white, c., ZnO.</li> <li>White to yellowish brown, h., to dirty white, c., SnO<sub>2</sub>.</li> <li>Yellow to brownish red, h., to yellow, c., PbO.</li> <li>White to orange red, h., to yellow, c., Bi<sub>2</sub>O<sub>3</sub>.</li> <li>Red to black, h., to red, c., Fe<sub>2</sub>O<sub>3</sub>.</li> <li>Red to brown, h., red, c., or becoming red on rubbing, HgO.</li> <li>Brown to black, h., to red, c., Fe<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O.</li> <li>The red salts of Co., the pink salts of Mn., the blue and green salts of Cu., Fe. and Ni. lose water of hydration, and at high temperatures decompose, leaving blackish oxides of Co., Mn., Cu., Fe. or Ni.</li> </ul>
Aqueous vapors are expelled.	<ul style="list-style-type: none"> <li>Substances containing water of crystallization ;</li> <li>“ holding water mechanically enclosed (decrepitate) ;</li> <li>Decomposable hydrates ; (alum and borax intumesce.)</li> </ul>

TABLE I.—FIRST STEP, CONTINUED.

Sublimate forms.	<p>Gray tarnish or distinct globules easily united. Hg.  Substance melts, sublimes, giving crystalline sublimate white, c., probably <math>\text{HgCl}_2</math>.—with <math>\text{KHO}</math>. becomes yellow.</p> <p>Sublimes without melting, sublimate yellow, h., white, c., <math>\text{Hg}_2\text{Cl}_2</math>.—with <math>\text{KHO}</math>. becomes black.</p> <p>White sublimate without melting or changing color, when heated with <math>\text{Na}_2\text{CO}_3</math> evolving ammoniacal odor and the vapor changing red litmus to blue, salts of Ammonia.</p> <p>White sublimate without melting or changing color, octohedral crystals (use lens) <math>\text{As}_2\text{O}_3</math>;</p> <p>Substance melts, emits dense white vapors, forming crystalline sublimate which gives a strong acid reaction with blue litmus paper, <math>\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}</math>;</p> <p>Reddish-brown drops or yellow ring, S.</p> <p>Black sublimate, becoming red by rubbing with glass rod, <math>\text{HgS}</math>.</p> <p>Heavy fumes near the assay, crystalline needles, orange color with <math>\text{H}_2\text{S}</math>.—<math>\text{Sb}_2\text{O}_3</math>.</p> <p>Yellow needles, fusible to red drops, yellow on cooling, but becoming scarlet on standing, or speedily by rubbing—<math>\text{HgI}_2</math>.</p> <p>Yellow to red drops, becoming dark red or even black when hot—<math>\text{As}_2\text{S}_3</math>.</p>
Carbonization.	<p>Organic bodies;</p> <p>Cyanogen compounds.</p> <p>Blackening is not necessarily carbonization—usually a burnt odor and escape of combustible gases. Organic substances burn vividly when heated in test tube with <math>\text{KNO}_3</math>, with formation of <math>\text{K}_2\text{CO}_3</math>.</p>
Gases escape when strongly heated.	<p>O.—from Nitrates, Chlorates, Bromates, Iodates, and peroxides (ignites spark on splinter);</p> <p><math>\text{SO}_2</math>—from Sulphates, Sulphites, Hyposulphites, or oxidation of Sulphur or Sulphides, (odor of burning sulphur);</p> <p><math>\text{NO}_2</math>—from decomposition of the Nitrates of all metals except the alkalies (reddish brown fumes);</p> <p><math>\text{CO}_2</math>—from decomposition of carbonates (test by lime water);</p> <p><math>\text{CN}</math>—from decomposition of metallic Cyanides (odor and peach blossom flame);</p> <p><math>\text{H}_2\text{S}</math>—from Sulphides containing water (odor and lead paper);</p> <p><math>\text{NH}_3</math>—from salts of Ammonia and some Cyanogen compounds (odor and alkaline reaction with red litmus paper).</p>

## SECOND STEP.

A few grains of the substance are placed on charcoal and heated in the reducing flame.

Volatile without incrustation or the formation of metallic globule.	Salts of $\text{NH}_4$ ; $\text{As}_2\text{O}_3$ , (odor of garlic); Some compounds of U <sub>g</sub> .
Volatile (or partially volatile) with incrustation.	Incrustation yellow, c.— $\text{PbO}$ . Incrustation dark yellow, c.— $\text{Bi}_2\text{O}_3$ . Incrustation white, c.— $\text{Sb}_2\text{O}_3$ . Incrustation blue and yellow— $\text{MoO}_3$ . Incrustation reddish-brown, or a variegated tarnish— $\text{CdO}$ . Incrustation yellow, h. white, c.— $\text{ZnO}$ . Incrustation difficult to volatilize, yellowish, h. dirty white, c.— $\text{SnO}_2$ .
Non-volatile and infusible, no incrustation.	Assay darkens on heating; test for Fe. with the magnet. Platinum. Iridium.

NOTE.—Many substances which sublime in the test tube under *First Step*, will give an incrustation when treated on charcoal, but these incrustations should be disregarded, and the indications from the sublimation followed.

Fusible, non-volatile, absorbed by the coal or forms a bead.	Compounds of $\left\{ \begin{array}{l} \text{K.} \\ \text{Na.} \\ \text{Li.} \\ \text{Ba.} \\ \text{Sr.} \end{array} \right\}$ Some Salts of Ca. } Residue moistened and pressed on turmeric paper stains it brown—(alkaline.)
Infusible and color unchanged.	$\text{SiO}_2$ . $\text{Al}_2\text{O}_3$ . Some compounds of $\left\{ \begin{array}{l} \text{Ba.} \\ \text{Sr.} \\ \text{Ca.} \\ \text{Mg.} \end{array} \right\}$ Test for alkalinity by turmeric paper. Luminous when heated intensely.



## THIRD STEP.

A moistened Platinum wire is dipped into the powdered substance and strongly heated in the reducing flame. (Should the previous examination indicate the presence of any fusible metal, e. g., Pb, Sb, Bi., the experiment under this step should be omitted entirely, or a thread of asbestos used in place of the Platinum wire.) Moisten insoluble salt with HCl. Examine colored flames by the spectroscope.

Colors the flame	Yellow	{ Sodium. Molybdic trioxide—greenish yellow. Substances rich in carbon.
	Red	{ Lithium. Strontium (carmine.) Calcium (orange red.)
	Green	{ Thallium, emerald green. Copper (excepting $\text{CuCl}_2$ ) bright green. Barium, yellowish green. Molybdic acid, yellowish green. Boric acid, " " Phosphoric acid, bluish "
	Blue	{ Lead—azure blue. Arsenic—light blue in R. Fl. Chloride, Bromide and Iodide of Copper— blue, then green. Antimony (greenish blue.)
	Violet	{ Potassium (easily obscured), Rubidium and Cæsium. Cyanides (peach blossom.)

## FOURTH STEP.

Place some of the substance on charcoal and heat in Reducing flame, moisten with a drop of  $\text{Co}_2(\text{NO}_3)$ , then heat again intensely. (If the substance is dark colored the fourth step is usually unnecessary.)

	Blue glass	{	alkaline Phosphates. " Borates. " Silicates.
Colored Mass—(color best observed when assay is cold.)	Blue mass. (infusible).	{	$\text{Al}_2\text{O}_3$ . $\text{SiO}_2$ —(pale blue).
	Green	{	$\text{ZnO}$ . yellowish green c. $\text{SnO}_2$ . bluish green c. $\text{Sb}_2\text{O}_3$ dirty green c.
	Pink		$\text{MgO}$ .

## FIFTH STEP.

Mix some of the finely powdered substance with twice that amount of dry  $\text{Na}_2\text{CO}_3$ , place on charcoal and heat strongly in the Reducing flame, (a mixture,  $\text{KCy}$ . and  $\text{Na}_2\text{CO}_3$ . is a powerful reducing agent and should be used in treating compounds of Sn.) In testing the malleability of a globule, if it seems to flatten under the hammer (malleable), touch the flattened mass with a knife point; if it crumbles, it is brittle.

Metallic globule with incrustation.	<p>White incrustation. Globule easily formed and volatilized—brittle—Sb.            Slight white incrustation. Globule formed with difficulty, malleable, Sn.            Yellow incrustation. Globule easily formed—soft, very malleable. Pb.            Yellow incrustation. Globule easily formed, very fusible, brittle. Bi.</p>
Metallic globule without incrustation.	<p>Red globule or grains, Cu. }            Yellow globule, Au. } Malleable.            Silvery-white globule, Ag. }</p>
Metallic powder or grains without incrustation.	<p>Infusible and Magnetic, Fe.Ni.Co.            Infusible and non-Magnetic, Pt.Ir.W.            Metallic grains are found by scooping out the charcoal, grinding in porcelain mortar and washing away the coal in a stream of water.            The metallic substance may be revealed by <i>globules</i> remaining in the mortar, <i>metallic grains</i>, or by <i>metallic streak</i> on surface of the mortar.</p>
Incrustation without metallic grains or globule.	<p>White, very volatile, odor of garlic—As.            Yellow h. white c.—Zn.            Dark red, or variegated—Cd.</p>

TABLE II.

Beads on

Form a clear bead by fusing the flux on a loop of Pt. wire. The bead is  
ing flame and then in the reducing flame.

(In the following table h. signifies hot; c., cold; S.S., strongly saturated  
often varies with the temperature

Color of Beads.	WITH BORAX.	
	IN OXIDIZING FLAME.	IN REDUCING FLAME.
	With any amount which the bead will dissolve. { Silica Alumina Stannic oxide Oxide of Silver S.S. { Baryta Strontia Lime Magnesia } Opaque by flaming	With any amount which the bead will dissolve. { Silica. Alumina. Stannic oxide. S.S. { Baryta Strontia Lime Magnesia } Opaque by flaming Manganic oxide.
Colorless, h. and c.	N.S oxides of { Antimony Bismuth Cadmium Indium Lead Zinc.	N.S. oxides of { Antimony Bismuth Cadmium Lead Nickel Silver Zinc. (Gray at first from finely reduced metals, becoming clear as blast is continued.)
Gray and cloudy, c.		<i>On Charcoal.</i> Oxides of { Antimony Bismuth Cadmium Lead Silver Zinc Nickel.
Yellow, h.	S.S colorless, c. { Cadmium } Opaque by flaming Zinc S.S. colorless, c. { Antimony Bismuth Lead.	S.S. yellow to brown { Titanic acid. Enamel blue by flaming. Yellow to dark brown, c. { Tungstic acid.
	Feebly saturated, (more or less colorless, cold.) { Ferric oxide Uranic oxide Chromic oxide (yellowish green c.)	Brown to opaque c. { Molybdic acid.

TABLE II.

Platinum Wire.

then dipped into the finely powdered assay and heated, first in the oxidizing with the assay; N.S., not completely saturated. The color of the bead and the amount of assay used.)

## WITH MICROCOSMIC SALT.

## IN OXIDIZING FLAME.

Undissolved Silica (skeleton).\*  
Soluble with difficulty { Alumina.  
Stannic oxide.

S.S. { Baryta  
Strontia  
Lime  
Magnesia } Opaque by flaming.

N.S. oxid s of { Antimony  
Bismuth  
Cadmium  
Indium  
Lead  
Zinc.  
(Yellowish, h.,  
when S.S., or  
colorless, c.)

## IN REDUCING FLAME.

Undissolved Silica (skeleton).\*  
Soluble with difficulty. { Alumina.  
Stannic oxide.

S.S. { Baryta  
Strontia  
Lime  
Magnesia } Opaque by flaming.  
{ Manganic oxide.

S.S. oxide of { Antimony  
Bismuth  
Indium  
Cadmium  
Lead  
Silver  
Zinc.  
(Gray at first  
from finely re-  
duced metal,  
becomes clear  
as blast is con-  
tinued.)

*On Charcoal.*

As with borax.

S.S. oxides of { Antimony  
Bismuth  
Cadmium  
Lead  
Zinc.  
(colorless, c.)  
Yellowish opalescent, c., oxide Silver.  
Feebly saturated { Ferric oxide  
(S.S. red h., yellow c.)

Violet, c. { Titanic acid.  
Yellow to red h. } Ferric  
(on cooling, at } oxide.  
first greenish,  
then reddish.)  
Blood red c. { Titanic, and  
Tungstic acids  
containing iron.

\* In testing for Silica, the assay must not be powdered, only broken into small fragments to observe the skeleton.

TABLE II.—CONTINUED.

Color of Beads.	WITH BORAX.	
	IN OXIDIZING FLAME.	IN REDUCING FLAME.
Red to Brown, h	Yellow, c. { Ferric oxide Ceric oxide Uranic oxide. S.S. { Chromic oxide (yellowish green, c.) Oxide of Iron containing Manganese (yellowish red, c.)	
Violet, h	Red, c., { Manganic oxide Reddish brown, c { Oxide of Nickel	Becomes colorless. Becomes gray.
Blue, c.	h. and c. { Oxide Cobalt S.S. (green h.) { Oxide Copper	h. and c. { Oxide Cobalt Becomes red, c., in reducing flame.
Green, h.	Blue, c., Oxide of Copper. Ferric oxide, containing Cobalt or Copper, and oxide of Copper containing Iron or Nickel (the green color changes on cooling, according to the saturation, as well as the proportions in which the oxides are present, to light green, blue or yellow.)	S.S. (opaque red c.) CuO. Light to dark emerald green, according to saturation. { Chromic oxide h. and c. black by flaming Uranic Oxide
Green, c.	Yellow to red, h. { Chromic oxide	h. and c { Chromic oxide (emerald green)

TABLE II.—CONTINUED.

## WITH MICROCOSMIC SALT.

IN OXIDIZING FLAME.	IN REDUCING FLAME.
S.S. yellow c. { Ferric oxide { Ceric oxide. Reddish yellow, c., Nickel oxide. Emerald green, c., Chromic oxide.	
Manganic oxide	Titanic oxide, cold bead violet, hot bead yellowish.
h. and c. { Oxide Cobalt S.S. (green h ) { Oxide Copper	h. and c. { Oxide Cobalt Brownish h. { Tungstic acid.
Blue c. Oxide of Copper. Ferric oxide containing Cobalt or Copper, and oxide of Copper containing Iron or Nickel (the green color changes on cool- ing, according to the saturation, as well as the proportions in which the oxides are present, to light green, blue or green.) Yellowish green. Molybdic acid.	Uranic oxide.
Reddish h. { Chromic oxide { (emerald green) Yellowish h. { Uranic oxide { (yellowish green)	Yellowish green, h., Uranic oxide. Dirty green, h., Molybdic oxide. Reddish, h., Chromic oxide.

## TABLE III.

## Examination of Metallic Substances and Alloys.

<p>Heat on charcoal in the reducing flame.</p>	<p>Volatilized rapidly without fusing, forming white fumes, coloring the flame bluish, and giving the odor of garlic—As.</p> <p>Readily volatilized without fumes or distinct odor, and not coloring the flame—Hg.</p> <p>When strongly ignited burning with bluish-white blaze, forming incrustation on coal, yellow h. white c.—Zn.</p> <p>Readily fusible, very malleable, so soft that it can be cut by finger nail, burning with sky-blue flame, giving yellow incrustation c.—Pb.</p> <p>Rosy-white metal, very brittle, not coloring the flame, giving yellow incrustation c.—Bi.</p> <p>White, crystalline, very brittle metal, giving a greenish-blue flame, forming a white incrustation c.—Sb.</p> <p>White malleable metal, cannot be cut by finger nail, very fusible, not coloring flame, giving white incrustation difficult to volatilize—Sn.</p> <p>White malleable metal, not coloring flame, forming no incrustation on coal or only a slight red incrustation—Ag.</p> <p>Tinges oxidizing flame green, gives no incrustation and forms red malleable globule—Cu.</p> <p>Infusible, strongly magnetic—Fe.Co.Ni.</p> <p>Infusible, non-magnetic—Pt.Ir.W.</p>
<p>Heat some of the substance in a test tube to red heat.</p>	<p>Gray sublimate in cold part of the tube which may be united into silvery drops by rubbing with a glass rod—Hg.</p> <p>If there is no gray sublimate formed, absence of Hg.</p> <p>Dark Mirror on cooler part of the tube, becoming white and crystalline by repeated sublimation—As.</p> <p>Volatilizes at red heat and forms solid shining globules on cold part of the tube—Cd.</p>





TABLE IV.

Behavior of the Alkalies before the

	HEATED ON CHARCOAL.	COLORS FLAME.
Potash Compounds.	Fusible, non-volatile, absorbed by coal, or form a bead.	Violet, easily obscured by other salts. Use spectroscope.
Soda Compounds.	Fusible, non-volatile, absorbed by coal, or form a bead.	Yellow, very intense. Use spectroscope.
Ammonia Compounds.	Volatile and absorbed by the coal.	Faint green flame when strongly heated; best seen in darkened room.

TABLE V.

Behavior of Earths alone, and

	ALONE ON CHARCOAL AND IN THE FORCEPS.	WITH BORAX ON PLATINUM WIRE.
Alumina $\text{Al}_2\text{O}_3$ .	Unaltered.	Dissolves slowly to a clear bead, becoming opaque neither by flaming nor saturation. When much is added in fine powder the bead is cloudy, scarcely fusible, and shows a crystalline surface on cooling.
Silica $\text{SiO}_2$ .	Unaltered.	Dissolves slowly to a clear difficultly fusible bead, that cannot be made opaque by flaming.

## TABLE IV.

blowpipe with certain reagents.

## OTHER TESTS.

In presence of Soda compounds, Potash may be recognized by making a borax bead, adding a small quantity of boric acid, then adding Oxalate of Nickel to form a brown bead. Fusing any Potash compound with this bead will produce a fine blue bead best seen when cold.

In absence of Soda compounds the Nickel bead described above gives a brown color.

Any compound of Ammonia heated with  $\text{Na}_2\text{CO}_3$  in test tube evolves Ammonia, recognizable by odor, alkaline reaction, and white fumes with HCl.

## TABLE V.

with reagents before the blowpipe.

WITH MICROCOSMIC SALT ON PLATINUM WIRE.	WITH $\text{Na}_2\text{CO}_3$ ON CHARCOAL.	WITH SOLUTION OF $\text{Co}_2\text{NO}_3$ IN O.F.L.
Dissolves slowly to a clear bead, that is always clear. When much is added the undissolved portion becomes semi-transparent.	Swells a little, and forms an infusible compound, and the excess of soda goes into the coal.	After a <i>strong</i> blast assumes a fine blue color, the intensity of which is only properly apparent on cooling.
Dissolves only in very small quantity to a clear bead. The undissolved portion floats as a semi-transparent skeleton in the melted bead.	Dissolves with a lively effervescence to a clear bead.	With a little solution assumes a feeble bluish color, becoming a dark gray with more. The thinnest edges can be fused to a reddish blue glass in a <i>very</i> hot flame.

TABLE VI.

Behavior of alkaline earths, alone and

In this and the following table O.Fl. stands for oxidizing flame, and R.Fl. and sulphates, after treating with R.Fl. on charcoal, is detected by on turmeric paper, which becomes brown by the action of the alkaline

	ALONE ON THE CHARCOAL AND IN THE FORCEPS.	WITH BORAX ON A PLATINUM WIRE.
Baryta, BaO.	The hydrate fuses, boils, swells, becomes fixed on the surface and then sinks into the coal with violent ebullition. The carbonate fuses to a clear bead easily, and becomes enamel-white on cooling. On repeated fusing it becomes caustic (alkaline) and is absorbed. Colors the flame yellowish green.	The carbonate dissolves to a clear bead, with effervescence, and can be flamed enamel-white with a certain amount; with more it becomes enamel-white of itself on cooling.
Strontia, SrO.	The hydrate behaves like Baryta. The carbonate fuses only on the edges, ramifying like cauliflower; the projections are luminous, tinge the R.Fl. red, and have an alkaline reaction. In the forceps, colors the flame crimson.	Like Baryta.
Lime, CaO.	CaO. is unaltered. CaCO <sub>3</sub> becomes caustic, whiter, more luminous, then alkaline, and crumbles to a powder if moistened. In forceps, colors flame feebly red.	Dissolves easily. The clear bead can be flamed opaque. CaCO <sub>3</sub> dissolves with effervescence. With excess, the bead becomes cloudy and crystalline on cooling, but never so milk-white as with Baryta and Strontia.
Magnesia, MgO.	Magnesia is infusible, and unaltered. The carbonate is very luminous when heated, is decomposed and becomes strongly alkaline.	Like Lime but not so strongly crystalline.

TABLE VI.

with reagents before the blowpipe.

for reducing flame. The alkaline property of the earths, their carbonates removing the assay, moistening it with water, and pressing the substance

WITH MICROCOSMIC SALT OF A PLATINUM WIRE.	WITH $\text{Na}_2\text{CO}_3$ ON CHARCOAL.	SPECTRUM.
As with Borax.	Fuses with it and is absorbed by the charcoal.	Use spectroscope, and consult tables in Spectrum Analysis.
Like Baryta.	$\text{SrO}$ is insoluble. $\text{SrCO}_3$ fuses with any great amount of $\text{Na}_2\text{CO}_3$ to a clear bead, milk-white on cooling. More strongly heated, the bead boils and the caustic earth is absorbed. If more is added it does not dissolve, but becomes caustic and goes into the coal.	Use spectroscope.
Dissolves largely (the carbonate with effervescence) to a clear bead that can be flamed opaque when rather saturated. Perfectly saturated, the bead becomes milk-white on cooling.	Insoluble. The soda goes into the coal leaving the lime behind.	Use spectroscope.
		WITH SOLUTION OF $\text{Co}_2\text{NO}_3$ .
Like Lime.	Like Lime.	After long blowing, has a pale flesh color, only properly seen when quite cold. Phosphate and Arsenate fuse and become quite red.

## TABLE VII.

Behavior of the more important metallic oxides, alone and with In using BUNSEN'S FLAME METHOD the assay is supported on a carbonized less Bunsen gas flame: the reactions may consist in reduction of the filled with cold water and held so as to cut the portion of the flame celain; formation of colored flame; or of metallic globules (or grains)

## IN THE OXIDIZING AND

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Antimony.	O.Fl. Gives off dense fumes which form white coating on the charcoal. R.Fl. is reduced and volatilized, coating the coal with $Sb_2O_3$ ; tinges the flame greenish blue.	O.Fl. Dissolves largely to a clear bead, yellowish (h.), colorless (c.). On coal the dissolved oxide can be driven off.
Arsenic.	Volatilizes below a red heat, giving dense white fumes. Garlic odor.	o.
Bismuth.	It is easily reduced on coal in either O.Fl. or R.Fl. to a brittle metallic globule, volatilizable in either flame without coloring the flame, but forming a coating of yellow oxide (h.); beyond this coating is another thin one of white carbonate.	O.Fl. Dissolves easily to a clear yellow bead, colorless (c.), if a little oxide is used. With more oxide the bead is yellowish-red (h.), yellow on cooling and opalescent (c.).
Cadmium.	On charcoal in R.Fl. it shortly disappears giving off brown fumes, and coats the surrounding coal with reddish brown to dark yellow powder, the color of which is properly seen only when cold. Coating easily volatilized by either Blp. flame without coloring flame (distinction from Pb). The coal beyond the coating shows a variegated tarnish.	O.Fl. Dissolves very largely to a clear yellowish bead, almost colorless (c.). When strongly saturated, the bead becomes milk-white by flaming. R.Fl. The bead containing the oxide boils on coal: the Cadmium is reduced and immediately volatilized, coating the coal with dark yellow oxide.

TABLE VII.

reagents, on charcoal, in the gas flame, and before the blowpipe. match,\* or on a thread of Asbestos, and held in the upper part of the color-oxide to metallic vapor which may be condensed on a porcelain crucible charged with the metallic vapor, forming characteristic stains on the porcelain support.

## REDUCING FLAMES.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA.	AND OTHER REAGENTS.
Reduced to brittle globules, giving off greenish-blue flame: the vapor cut by cold porcelain surface gives black velvet coating of Sb. insoluble in NaClO.	Is reduced very easily on coal in either flame, but the metal volatilizes very rapidly, coating the coal with a white oxide of Antimony.	
Bluish flame with dense white smoke: vapor cut by cold porcelain surface gives lustrous brown coating, soluble in NaClO.	Is reduced on charcoal with evolution of arsenical fumes (odor of garlic).	
Easily reduced to brittle globules; does not color flame: vapor cut by cold porcelain surface deposits a grayish-brown lustrous coating.	On charcoal is reduced immediately to metallic Bismuth, giving a very fusible and brittle globule.	With KI+S. Any compound of Bismuth heated on coal, in O.Fl., with equal parts of KI and S. gives a scarlet coating on the coal, of BiSI. Use asbestos felt for support.
No globule; orange flame and reddish smoke: the vapor cut by cold porcelain surface gives a coating from brown to blue-black, according to depth of coating.	O.Fl. Insoluble. R.Fl. On coal immediately reduced and volatilized, coating coal with reddish brown to dark yellow oxide. The more remote portions of the coal assume a variegated tarnish.	

\* For metallic reductions, coat a splinter of wood with  $\text{Na}_2\text{CO}_3$ , carbonize the wood, and use this as support of assay in R.Fl.

TABLE VII.—CONTINUED.

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Chromium.	Unaltered in O.Fl. and R.Fl.	<p>O.Fl. Dissolves slowly but colors strongly. With little oxide the bead appears yellow (h.), but yellowish-green (c.). With more oxide it is a dark red (h.), but becomes yellow on cooling, and fine yellowish green (c.).</p> <p>R.Fl. The slightly saturated bead is green (h. and c.). With more it becomes emerald-green.</p>
Cobalt.	<p>O.Fl. Unchanged.</p> <p>R.Fl. Shrinks somewhat and is reduced without fusing to a metal (magnetic) and assumes a metallic lustre when rubbed in a mortar.</p>	<p>O.Fl. Colors very strongly; the bead is pure smalt-blue (h. and c.). The strongly saturated bead is so dark-blue as to appear black, but the blue color may be seen by melting the bead and drawing it out into a thread. R.Fl. As in O.Fl.</p>
Copper.	<p>O.Fl. Fuses to a black globule which soon spreads out and is reduced to metallic copper on the lower side.</p> <p>R.Fl. Reduced to copper, the reduced particles showing a copper lustre, but when the blast is stopped, oxidizing again on the surface. Strongly heated, it fuses to a globule of copper.</p>	<p>O.Fl. Colors rather strongly; a little causes a green bead (h.), blue (c.). With more it is a bark green to opaque (h.), greenish-blue (c.).</p> <p>R.Fl. Saturated to a certain degree the bead becomes colorless (h.), but red and opaque (c.), (cuprous oxide).</p>
Gold.	Is reduced on ignition in either flame, and can easily be melted to a globule.	<p>O.Fl. Reduced without dissolving. On coal can be fused to a button.</p> <p>R.Fl. The same.</p>



TABLE VII.—CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA.
O.	<p>O.Fl. On Pt. wire dissolves to a dark brownish-yellow bead, opaque yellow on cooling.</p> <p>R.Fl. The bead is opaque and green on cooling; cannot be reduced to a metal on charcoal but remains as green <math>\text{Cr}_2\text{O}_3</math> while the soda is absorbed by the coal.</p>
Infusible Magnetic powder.	<p>O.Fl. On Pt. wire, in very small quantity, dissolves to a transparent, feebly-red bead, gray when cold.</p> <p>R.Fl. On coal is reduced to a gray magnetic powder, assuming a metallic lustre by friction.</p>
<p>Green flame but no coating by condensed vapor; fuses to brown globules which show copper color by flattening and rubbing with a knife-blade on a slip of glass.</p>	<p>O.Fl. Dissolves on Pt. wire to a green bead (h.), losing color and becoming opaque on cooling.</p> <p>R.Fl. On coal is reduced very easily to a metal, which can be fused to one or more globules by sufficient heat.</p>
<p>Purple stain with small amount, but with larger amount yellow globules very malleable, insoluble in <math>\text{HNO}_3</math>.</p>	<p>As with Borax. The soda goes into the coal.</p>

TABLE VII.—CONTINUED.

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Iron.	O.Fl. Unchanged. R.Fl. Becomes black and magnetic ( $\text{Fe}_3\text{O}_4$ )=Magnetic oxide.	O.Fl. With little oxide the bead is yellow (h.), colorless (c.); with more it is red (h.), yellow (c.); with still more, dark-red (h.), and dark-yellow (c.). R.Fl. The bead becomes bottle-green.
Lead.	At a high temperature $\text{PbO}$ fuses to a yellow bead. On coal $\text{PbO}$ is reduced by either flame with effervescence, coating the coal with yellow oxide; beyond this is a thin coat of white carbonate. The coats disappear under the R.Fl., tinging the flame azure-blue.	O.Fl. Dissolves easily to a clear yellow bead, colorless (c.), and which with a larger quantity, becomes opaque by flaming; with still more it becomes opaque and enamel-yellow of itself on cooling.
Manganese.	O.Fl. Infusible. In a hot enough flame both the dioxide and sesquioxide are changed to proto-sesquioxide, yielding O., and turning brown-red. R.Fl. The same.	O.Fl. Colors very intensely. The hot bead is violet but on cooling is a violet red. An excess renders the bead quite black and opaque, the color being made visible by drawing the fused bead out into a thread. R.Fl. The bead becomes colorless (protoxide.)
Mercury.	Is instantly reduced and volatilized, giving a gray tarnish of Hg. on the coal some distance from the assay.	o.

TABLE VII.—CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA.	
Infusible magnetic grains.	O.Fl. Insoluble. R.Fl. It is reduced on coal, yielding a gray, magnetic, metallic powder, when the particles of coal are washed away.	
Colors flame sky-blue; forms metallic globules: vapor cut with cold porcelain surface gives a brown coating of the metal.	O.Fl. On Pt. wire it dissolves easily to a clear bead, becoming yellowish and opaque on cooling. R.Fl. Is immediately reduced on coal to a metal, which afterwards coats the coal with oxide.	With KI. heated on coal, a permanent yellow coating $PbI_2$ .
o.	O.Fl. On Pt. foil a very trifling quantity dissolves to a clear, transparent green mass (b.), becoming opaque and bluish-green (c.). R.Fl. Not reducible to a metal on coal. Any compound of Mn. fused with $KClO_3$ on Pt. foil gives a purple mass and makes a purple solution in water = $K_2Mn_2O_8$ .	
Volatilized easily, gives a gray stain to cold porcelain surface of Hg., which may be united into a globule.	Heated to redness in closed tube it is reduced and vaporized, the vapors condense on sides of tube as a gray film, which may be united into a globule by rubbing with a glass rod.	Heated with KI. and CaO in test tube, forms a scarlet sublimate, $HgI_2$ .

TABLE VII.—CONTINUED.

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Molybdic Oxide.	<p>O.Fl. Fuses, spreads out, volatilizes, and forms, at a certain distance, a yellow pulverulent coat, consisting of small crystals near the assay. The coat becomes white on cooling and the crystals colorless. Near the assay is a non-volatile film, <math>\text{MoO}_3</math>, dark copper-color (c) and of metallic lustre.</p> <p>R.Fl. The greater part sinks into the coal, and by a good flame can be reduced to a metal.</p>	<p>O.Fl. Dissolves easily and largely to a clear bead, yellow (h.), colorless (c.). A very large addition produces a bead dark yellow to dark red (h.), and opaline to a bluish-gray enamel (c.).</p> <p>R.Fl. The bead produced in O.Fl. becomes N.S. brown, and S.S. is opaque (<math>\text{MoO}_3</math>). In good flame black flocks of <math>\text{MoO}_3</math> separate and can be very distinctively seen in the yellowish bead when it is pinched out flat.</p>
Nickel.	<p>O.Fl. Unchanged.</p> <p>R.Fl. On coal is reduced to a metallic, coherent and infusible powder, which by friction in the mortar assumes a metallic lustre, and is decidedly magnetic.</p>	<p>O.Fl. Colors quite intensely; a little colors the hot bead violet, but a pale reddish brown (c.); with more the colors are darker.</p> <p>R.Fl. The bead becomes gray and cloudy, or quite opaque, owing to finely divided metallic Nickel. On continuing the blast the metallic particles collect together without fusing, and the bead becomes colorless.</p>
Silver.	<p>Reduced easily to metallic Silver in either flame; readily fuses to one or more globules.</p>	<p>O.Fl. Partly dissolved and partly reduced, the cold bead is opalescent or milk-white, according to the amount dissolved.</p> <p>R.Fl. On coal the bead is first grayish from reduced Silver, but after all the Silver is fused to a globule, the bead becomes clear and colorless.</p>

TABLE VII.—CONTINUED.

BUNSEN'S FLAME  
METHOD.

## WITH CARBONATE OF SODA.

Colors. flame greenish yellow; the vapor cut by cold porcelain surface gives a stain from purplish brown to deep blue.

O. Fl. On Pt. wire fuses with effervescence to a clear bead, milk white on cooling.

R. Fl. On coal fuses with effervescence at first, but afterwards the fused mass is absorbed by the coal, and the greater part of the acid is reduced to metallic Molybdenum, which can be obtained as a steel gray powder by washing away the particles of coal.

The change of color in Bp. flames is best seen when asbestos felt is used for support.

Magnetic grains.

O. Fl. Insoluble.

R. Fl. On coal is easily reduced to white metallic particles, which, after the coal is washed away, follow the magnet readily.

Easily reduced to white globules, very malleable.

Is instantly reduced to one or more globules of Silver, while the soda sinks into the coal.

TABLE VII—CONTINUED.

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Tin.	<p>O. Fl. The oxide becomes strongly luminous, and is yellow while hot, but dirty yellowish white when cold.</p> <p>R. Fl. Is reduced to a metal by a <i>continued and strong flame</i>; a trifling coating of <math>\text{SnO}_2</math> being generally formed near the assay.</p>	<p>O. Fl. Dissolves in trifling quantity, and very slowly to a clear bead, remaining colorless on cooling and not becoming opaque by flaming. A saturated and perfectly cold bead, when heated to low redness, becomes opaque, loses its spherical shape, and shows distinct crystallization.</p> <p>R. Fl. A not saturated bead is unchanged.</p>
Zinc.	<p>O. Fl. Becomes transiently yellow, is infusible, but strongly luminous when ignited.</p> <p>R. Fl. Gradually disappears, being reduced, volatilized, and again oxidized, and forms a new coating on another part of the coal, yellow (h.) white (c.).</p>	<p>O. Fl. Dissolves easily and largely to a clear bead, yellowish (h.) colorless (c.). With more oxide the bead becomes enamel-white by flaming; with still more the bead becomes enamel-white of itself on cooling.</p> <p>R. Fl. The saturated bead becomes cloudy and grayish by the first blast, but after longer blowing is clear again.</p>

TABLE VII--CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA.
<p>The Chlorides of Tin yield a vapor which deposits a brown metallic stain on cold porcelain, or a chalky coating of Stannic oxide.</p>	<p>O.Fl. On Pt. wire combines with the Soda with effervescence to a swollen infusible mass.  R.Fl. Reduced to Tin on coal.  By using <math>K_2CO_3</math>, the metal can be reduced more easily and effectually than with <math>Na_2CO_3</math>.</p>
<p>Zinc compounds strongly heated give a vapor which deposits a brown metallic stain on cold porcelain surface.</p>	<p>O.Fl. Insoluble.  R.Fl. On coal is reduced, volatilized and re-oxidized, giving a Zinc coating. With a good flame the Zinc flame may even be produced.</p>

## SOLUTION.

After the preliminary examination of a solid, the next step in analysis is to bring it into a liquid form, or dissolve it. In a complex body, a partial separation of its components may often be effected in the act of solution, and valuable hints in regard to the nature of a substance may be derived from its behavior with different solvents. Thus, one part of the substance may be soluble in water, while another is insoluble in water but soluble in acids, while another part is insoluble in water and acids. By dissolving in water and removing in this form, we may entirely separate this part of the substance from the rest; by treating the residue with acids, we may separate the two remaining classes of bodies in the substance. An important step in analysis may thus be secured in the act of solution.

**THE SUBSTANCE IS NOT METALLIC.** Non-metallic substances may be divided into three classes, according to their respective behavior with water and acids. These classes are:

1°. *Substances soluble in water.*

2°. *Substances insoluble (or sparingly soluble) in water, but soluble in Nitric, Hydrochloric, or Nitro-Hydrochloric acids.*

3°. *Substances insoluble in water and in any of these acids.*

Reduce the substance to a fine powder in a porcelain mortar; place half a gram of the powder in a test tube, add 20 c.c. of distilled water and heat to boiling.

1. *Soluble in water.* If the substance entirely dissolves it belongs to the first class. If it does not appear to dissolve even after protracted boiling, let the solid matter settle, pour off a little of the clear liquid and evaporate on a clean slip of Platinum foil or glass; if nothing remains, or only a very slight stain, the substance is practically insoluble in water; but if a distinct residue remains the substance is partially soluble in water; in which case, boil the undissolved residue with more water till no more will dissolve, and mix all the watery solutions for analysis. If the water will dissolve only a part of the substance, the original substance probably contains at least two bodies of different solubilities, which should be analyzed separately.

2. *Insoluble in water, but soluble in acids.* Treat the residue which water will not dissolve, with dilute HCl. If it does not dissolve, heat to boiling; if this fails to effect complete solution, decant the clear fluid into another test tube and boil the residue with concentrated HCl.; if it dissolves, add it to the fluid in the other test tube for analysis.



The reactions which may manifest themselves in this operation ought to be carefully watched; they may be:

- |                            |   |                                                                                                                                                                                                                                           |
|----------------------------|---|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Colorless gases escape. | { | Nearly odorless, effervescence— $\text{CO}_2$ from Carbonates.<br>Fetid odor, effervescence— $\text{H}_2\text{S}$ from Sulphides.<br>Odor of burning S.— $\text{SO}_2$ from Sulphites.<br>Odor of peach leaf— $\text{HCy}$ from Cyanides. |
| 2. Colored gases form.     | { | Pungent odor, yellow color— $\text{Cl}$ . and oxides of $\text{Cl}$ . from Peroxides, Chromates, Manganates, etc.<br>(View the tube lengthwise.)                                                                                          |

The student must bear in mind that  $\text{HCl}$ , when heated gives off a pungent odor, but it is colorless.

If the substance is not entirely dissolved (except separated Sulphur or gelatinous Silica) set aside this test tube with its contents, and treat some of the original substance with Nitric acid and heat to boiling; the escape of red fumes indicates an oxidizing process. If the substance does not dissolve (except Sulphur or Silica), mingle the contents of the test tubes in which the substance has been boiled in  $\text{HCl}$ . and  $\text{HNO}_3$ , and ascertain if the Nitro-Hydrochloric acid thus formed will dissolve it; if necessary, heat to boiling. The substance, or that portion of the substance which dissolves in acids, belong to the second class—*Substances insoluble in water, but soluble in acids.*

3. *Insoluble substances.* The substances which remain insoluble after this successive treatment with water and acids, belong to the third class—*Substances insoluble or very sparingly soluble in water and in acids.*

The bodies included in this class are Sulphates of Barium, Strontium, Calcium, and Lead; the Chlorides, Bromides, Iodides, Ferrocyanides, and Ferricyanides of Silver; the Ferrocyanides and Ferricyanides of several other metals; Silica and many Silicates; Native Alumina, Alumina which has been ignited, and many Aluminates; ignited Chromic oxide, and Chrome iron ore; ignited and native oxide of Tin; some Metaphosphates and some Arsenates; Fluoride of Calcium and a few other compounds of Fluorine; Sulphur and Carbon.

The preliminary examination by Table I. will give valuable information in regard to the composition of these insoluble compounds. If from such examination, it becomes probable that the substance belongs to any of the following classes, the special treatment of that class may be instituted at once. But if no indication of this nature appears, the finely powdered substance is intimately mixed with 4 parts of  $\text{Na}_2\text{CO}_3$  and converted into a soluble form by fusing on charcoal. The fused mass is boiled with ten volumes of distilled water, the watery solution (which will contain an excess of  $\text{Na}_2\text{CO}_3$ ) is filtered off and preserved for detecting the acid radical; the thoroughly washed residue is dissolved in  $\text{HCl}$ . or  $\text{HNO}_3$  and analyzed for the basic substance.

**SULPHATES** with  $\text{Na}_2\text{CO}_3$  upon charcoal in R.Fl. give a hepar, i. e., the moistened mass pressed upon Silver foil or Lead paper gives a brownish stain. Sulphate of Lead is blackened by  $\text{NH}_4\text{HS}$ ; with  $\text{Na}_2\text{CO}_3$  in R.Fl. on charcoal gives a metallic globule. Sulphate of Calcium is somewhat soluble in water, and its solubility is increased by  $\text{HCl}$ .

**SILICA AND SILICATES**, with *Microcosmic Salt*, give a skeleton of Silica. For this examination the assay should be in the form of splinters rather than in powder, to detect the skeleton. Fused with  $\text{Na}_2\text{CO}_3$ , the Silica becomes soluble in water; when treated with  $\text{HCl}$ , the Silica may separate as a gelatinous mass, or, if the watery solution is acidified and evaporated to dryness, the Silica is left as an insoluble powder.

**FLUORIDE OF CALCIUM AND INSOLUBLE FLOURIDES**, with concentrated  $\text{H}_2\text{SO}_4$  give off gaseous  $\text{HF}$ —which etches glass, and tarnishes a dry glass surface. For detecting  $\text{HF}$ . consult table for the analysis of acids.

**CHLORIDE, BROMIDE, AND IODIDE OF SILVER**. Blackened by  $\text{NH}_4\text{HS}$ . Boiled with  $\text{HCl}$ . and a fragment of  $\text{Zn}$ ., the Silver will deposit on the Zinc, and a chloride, bromide or iodide of Zinc will remain in solution. If fused with  $\text{Na}_2\text{CO}_3$ , the Silver is left in the form of carbonate, readily soluble in  $\text{HNO}_3$ . If any compound of Silver is treated with  $\text{Na}_2\text{CO}_3$  on charcoal in R.Fl. a globule of Silver is obtained.

**OXIDE OF TIN**. With  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ , on Charcoal in R.Fl. affords a metallic globule. After fusing with  $\text{Na}_2\text{CO}_3$  the oxide is soluble in  $\text{HCl}$ .

**ALUMINA AND ALUMINATES**. When moistened with a solution of  $\text{Co}_2\text{NO}_3$  and then ignited they give a blue infusible mass. They all are rendered soluble by fusing with four parts of  $\text{KHSO}_4$ ; then treated with water or dilute  $\text{HCl}$ .

**COMPOUNDS OF CHROMIUM**. With Borax these give a green bead both in O.Fl. and R.Fl. They are rendered soluble by fusing with  $\text{KHSO}_4$ , or  $\text{KNO}_3$ . Chrome iron ore requires successive treatment by both methods.

**CARBON** is usually black; is insoluble in water and in all acids; if treated with fused  $\text{KNO}_3$ , it burns vividly and  $\text{K}_2\text{CO}_3$  is formed; if placed on Platinum foil, and the foil is intensely heated by the blowpipe flame playing on the under side of the foil, the carbon is always burned away.

**INSOLUBLE FERROCYANIDES AND FERRICYANIDES** are easily decomposed by boiling for a few minutes in a solution of  $\text{Na}_2\text{CO}_3$ , when a soluble Ferrocyanide or Ferricyanide of Sodium is formed, and the base is left as a metallic oxide or carbonate—soluble in dilute acid.

Many other substances insoluble in water and acids, are decomposed by prolonged boiling with alkaline carbonates.

## SOLUTION OF SUBSTANCES WHICH ARE METALS OR ALLOYS.

The metals are classified according to their respective behavior with Nitric Acid.

I. Metals not acted on by  $\text{HNO}_3$ , Gold, Platinum, Iridium and Aluminum.

II. Metals which are oxidized by  $\text{HNO}_3$ , but whose oxides do not dissolve in an excess of this acid or in water: Antimony and Tin.

III. Metals which are converted into Nitrates, soluble in an excess of the acid or in water: All other metals.

Pour  $\text{HNO}_3$  over a small portion of the metal or alloy and apply heat.

1. Complete solution takes place speedily or upon the addition of water; absence of Gold, Platinum, Iridium, Aluminum, Antimony and Tin. Any metal whose Nitrate is soluble may be present.

2. A residue is left. If this is metallic, pour off the acid and test the solution to see if any part is soluble in  $\text{HNO}_3$ ; wash the residue and pour over it a little  $\text{HCl}$ ; if it dissolves with a brisk effervescence, probable presence of Aluminum; if  $\text{HCl}$  does not act on the substance, add  $\text{HNO}_3$  (thus forming Nitro-Hydrochloric Acid), dissolve the substance by application of a gentle heat, and examine the solution for Gold, Platinum and Iridium.

If the residue is not metallic but is a white pulverulent substance, it indicates the presence of Antimony or Tin. Pour off the Nitric Acid, wash the residue with water, dissolve it in  $\text{HCl}$ , and examine this solution for Antimony and Tin.

## METHOD OF ANALYSIS OF SUBSTANCES IN SOLUTION.

When we have a solution of unknown substances, the first step in its analysis is to separate it into *groups of chemically similar substances by means of the group reagents HCl, H<sub>2</sub>S., NH<sub>4</sub>HS., and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in the presence of NH<sub>4</sub>Cl.*

Suppose we have a solution containing members of all the groups; if we add to this HCl. to distinct acid reaction, all the Silver and Mercurous bases present will be precipitated as Chlorides, because they are insoluble in water and in HCl. If Lead is present in considerable quantity, the larger part will be precipitated because PbCl<sub>2</sub> is only sparingly soluble in cold water, but a small part will remain in solution because of this sparing solubility. By means of HCl. we thus remove all the Silver and Mercurous bases from the solution, and these bases need only be sought in the precipitate thrown down by HCl. If no precipitate form with HCl. these bases are entirely absent. But if HCl. is added in quantity insufficient to completely precipitate these bases, the subsequent addition of H<sub>2</sub>S. will precipitate them as Sulphides, and they will then appear among the members of the second group. The same fact is seen in nearly all the group-reagents; if any group-reagent is used in amount insufficient to produce complete precipitation, the addition of the next group-reagent will precipitate the members of the preceding groups.\* Hence the following rule: *Whenever any group-reagent produces a precipitate, continue to add it till no more precipitate forms.*

In using liquid reagents, it is not advisable to pour into the solution a large quantity of the reagent at once, because many reactions will escape notice. It is best to add the reagents drop by drop, and to observe closely any changes caused by the reagents in the solution for analysis.

Table VIII exhibits a scheme for separating unknown substances into groups of chemically similar substances preparatory to final analysis. The group-reagent is added till complete precipitation is secured, and then the entire contents of the test tube are thrown upon a filter to separate the solid part (*precipitate*) from the liquid part which runs through the filter (*filtrate*). The precipitate on the filter is washed with distilled water to remove any adhering portions of the liquid which may contain matters foreign to the precipitate, and this washed precipitate is then dissolved, and special reagents used for its analysis according to the Tables for analysis of the several groups.

\*The principal exception is that NH<sub>4</sub> HS will dissolve the Sulphides of As., Sb., Sn., Pt. and Au.

The *filtrate* (the clear liquid which passes through the filter) in each case is used for the separation of the succeeding group by use of the next group-reagent. In using the several group-reagents we need to attentively consider the character of the reactions which take place. For example: When we use HCl. for precipitating the members of Group I, we expect a white, rapidly-subsiding precipitate which does not disappear on adding more of the acid. If, however, we find a gelatinous precipitate, or a milky-white one that long remains in suspension, or the precipitate at first formed seems to diminish on adding more of the acid, we suspect the precipitate contains some substance not a member of Group I.

Especial care is required in the use of  $H_2S$ , because the solution of this gas, as ordinarily used, is a weak acid by reason of the sparing solubility of the gas. We can never be certain that we have secured the full action of this acid unless the solution smells distinctly of the acid, even after violent shaking of the test tube and its contents. Test the filtrate with a few drops of  $H_2S$ .

Whenever we have a solution containing an unknown number of unknown substances, the method of separation by group-reagents and the analysis of each group by itself is indispensable for accurate analysis. But if for any reason we know that we have only the members of one group present, the use of group-reagents is only necessary to identify the group, and instead of separating the group-precipitate and dissolving this for analysis, we may use the original solution at once for the application of the special reagents which serve to identify the members of that group. This method is specially applicable in laboratory practice where the student is set to analyze single salts. In the absence of such information it is best to follow the regular method, or at least to use the group-reagents in such way as to show the absence of other groups before using the original solution with the special reagents to identify the members of any group. Care and forethought may thus shorten many analytical processes without thereby impairing the accuracy of the results. In this study heedless haste and slovenly manipulation mature an early harvest of error and disappointment.

## TABLE VIII.

For classifying bases into groups by precipitation with the four GROUP the *Filtrate* (after separation of the precipitate) from each group

To the substance in solution add HCl. to acid reaction; if a precipitate precipitate which is GROUP I.

## GROUP I.

The precipitate by HCl. may contain:

AgCl. }  
PbCl<sub>2</sub>. } White.  
Hg<sub>2</sub>Cl<sub>2</sub>. }

Analyze by Table IX.

A precipitate of S. may form (milky white) from alkaline Poly-sulphides, insoluble in HCl.—of H<sub>2</sub>SiO<sub>3</sub>. (white and gelatinous) from Alkaline Silicates, insoluble in HCl. soluble in KHO.—of

BiOCl. }  
SbOCl. } White.

Soluble in excess of HCl. and therefore not members of this group.

To the filtrate from which HCl. will not form a precipitate after shaking thoroughly. The precipitate is

## GROUP II.

The precipitate by H<sub>2</sub>S. may contain:

PbS. }  
CuS. } Black.  
HgS. }  
Bi<sub>2</sub>S<sub>3</sub>. }

Au<sub>2</sub>S<sub>3</sub>. } Brown-  
PtS<sub>2</sub>. } black.

SnS—Brown.

CdS. }  
As<sub>2</sub>S<sub>3</sub>. } Yellow.

SnS<sub>2</sub>.—Dirty yellow.

Sb<sub>2</sub>S<sub>3</sub>. }  
Sb<sub>2</sub>S<sub>5</sub>. } Orange.

Analyze by Table X.

A precipitate of S. may form (milky white) from the presence of a Ferric Salt, or a Chromate.

To the filtrate from which and NH<sub>4</sub>HS. to complete

## GROUP III.

The precipitate by NH<sub>4</sub>HS. may contain:

FeS. }  
CoS. } Black.  
NiS. }

MnS. flesh-colored.

ZnS. dirty white.

Al<sub>2</sub>(HO)<sub>3</sub>. } Gelatinous  
white or gr'n-  
ish white in  
presence of  
trace of Iron  
Salts.

Cr<sub>2</sub>(HO)<sub>3</sub>. } Dirty green  
or peach blos-  
som.

Analyze by Table XI.

The precipitate may also contain:

Phosphates, } Al. } White,  
Arsenates } Ba. } soluble in  
or } Sr. } HCl. in-  
Oxalates } Ca. } soluble in  
of } Mg. } KHO.

H<sub>2</sub>SiO<sub>3</sub>, insoluble in HCl. but soluble in KHO.

## TABLE VIII.

REAGENTS, HCl, H<sub>2</sub>S, NH<sub>4</sub>HS, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, used in succession; being used for precipitating the succeeding group.

forms, continue to add HCl. till no more precipitate forms. Separate this

precipitate, add H<sub>2</sub>S. till the solution smells strongly of this acid, even GROUP II.

H<sub>2</sub>S. will not form a precipitate, add NH<sub>4</sub>Cl. NH<sub>4</sub>HO. to alkaline reaction, precipitation. The precipitate is GROUP III.

To the filtrate from which NH<sub>4</sub>HS. will not form a precipitate, add (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. to complete precipitation. The precipitate is GROUP IV.

## GROUP IV.

The precipitate by (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. may contain:

BaCO<sub>3</sub>. } White, soluble with  
SrCO<sub>3</sub>. } effervescence in Acetic  
CaCO<sub>3</sub>. } Acid.

Analyze by Table XII.

## GROUP V.

The filtrate from which (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. and NH<sub>4</sub>Cl. will not form a precipitate, may contain:

The Salts of { K.  
Na.  
Li.  
Mg.  
NH<sub>4</sub>.

in addition to the Salts of Ammonia added as reagents.

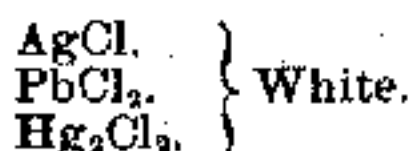
Analyze by Table XIII.

## TABLE IX.

## ANALYSIS OF GROUP I.

The white precipitate thrown down by HCl. and insoluble in excess of that acid.

This precipitate may contain:



Throw the precipitate on a filter and wash it with a *little cold water*.  $\text{PbCl}_2$  is sparingly soluble in cold water, but soluble in 30 volumes of boiling water; if too much water is used in washing the precipitate the whole of the Lead salt may be dissolved and washed away. Pour over the washed precipitate on the filter 30 volumes of boiling water, and reserve the filtrate for analysis for Lead. Then pour over the remaining precipitate  $\text{NH}_4\text{HO}$ , which will dissolve  $\text{AgCl}$ , but will not dissolve (but blacken)  $\text{Hg}_2\text{Cl}_2$ . Preserve the filtrate for analysis for Silver. Dissolve the blackened precipitate remaining on the filter in a little  $\text{HNO}_3$ , and use this solution for analysis for Mercury.

**LEAD.** *Analysis of the hot water filtrate.* If much lead is present the filtrate will deposit needle-shaped crystals of  $\text{PbCl}_2$  when it cools. To a test tube half full of solution of  $\text{H}_2\text{S}$ , add 3 or 4 drops of the filtrate; a **BLACK PRECIPITATE OR BROWN COLOR\*** of  $\text{PbS}$  will be formed. To a test tube half full of the filtrate add a few drops of  $\text{H}_2\text{SO}_4$ , a **WHITE INSOLUBLE PRECIPITATE** indicates Lead. To another part of the filtrate add a few drops of  $\text{HNO}_3$ , then a few drops of  $\text{K}_2\text{Cr}_2\text{O}_7$ , a **YELLOW PRECIPITATE** (subsiding after a time if the solution is dilute) indicates Lead.

A few drops of solution of  $\text{KI}$  added to solution of any Lead salt will form a **YELLOW PRECIPITATE** of  $\text{PbI}_2$ . Any soluble salt of Lead will precipitate  $\text{Pb(OH)}_2 \cdot 2\text{PbCO}_3$  (white lead) by action of  $\text{Na}_2\text{CO}_3$ . If  $\text{PbCO}_3$  be reduced with the blowpipe on charcoal, a malleable globule of Lead will be obtained, and a yellow incrustation on the coal. Lead colors the blowpipe flame sky-blue.

Solution of a Lead salt is precipitated by  $\text{KHO}$  as a white hydrate,  $\text{Pb(OH)}_2$ ; soluble in excess of  $\text{KHO}$  as Potassic Plumbite ( $\text{K}_2\text{PbO}_3$ ).

Metallic Zinc precipitates Lead crystals (*Arbor Saturni*) from solution of Lead salts.

\* One part of lead in 100,000 parts of water will exhibit this brown coloration upon the addition of  $\text{H}_2\text{S}$ . Any salt of Lead will be blackened by action of  $\text{H}_2\text{S}$ .



The insoluble salts of Pb. are readily decomposed and the Pb. secured in metallic form by adding to such Lead salt Conc. HCl. and a slip of Zn. If PbS. is thus treated, Pb. is rapidly set free and H<sub>2</sub>S. escapes. With PbSO<sub>4</sub>, the reaction is slower but the results the same. If PbCrO<sub>4</sub> is treated with HCl. and Zn., Cl. escapes, Cr<sub>2</sub>Cl<sub>6</sub>. (green) is formed and Pb. finally set free.

**SILVER.** *Analysis of the ammonia solution.* To a small portion of this solution add HNO<sub>3</sub> to acid reaction: a WHITE PRECIPITATE INSOLUBLE IN HNO<sub>3</sub> indicates Silver. AgCl. spread on paper and exposed for 10 minutes to direct sunlight becomes PURPLE TO BLACK by reduction of the Silver salt.

If the ammonia solution contains Silver, drop a small slip of Zinc into the solution and heat gently till the Silver is all deposited in a mossy coating (gray to dark brown in color) on the Zinc; pour off the water, wash thoroughly with water, remove the Zinc and Silver, pull off the mossy incrustation of Silver and dissolve it in a small quantity of HNO<sub>3</sub>. filter from any residue, neutralize the excess of acid with Na<sub>2</sub>CO<sub>3</sub>. and apply to this solution the special tests for Silver.

If a portion of the silver precipitate be burnished, a silvery lustre will appear.

A solution of a silver salt will be precipitated CURDY WHITE (AgCl.) by HCl.; insoluble in HNO<sub>3</sub>., but soluble in NH<sub>4</sub>HO.

Na<sub>2</sub>CO<sub>3</sub>. will precipitate silver salts as grayish-white Ag<sub>2</sub>CO<sub>3</sub>., soluble in NH<sub>4</sub>HO.

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. precipitates a brick-red Ag<sub>2</sub>CrO<sub>4</sub>., soluble in HNO<sub>3</sub>. and in NH<sub>4</sub>HO.; decomposed by HCl. or a chloride into white AgCl.

Na<sub>2</sub>HPO<sub>4</sub>. gives a yellow precipitate, Ag<sub>3</sub>PO<sub>4</sub>.

KI. precipitates yellow AgI. insoluble in HNO<sub>3</sub> and in NH<sub>4</sub>HO.; soluble in excess of KI.

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. precipitates white Ag<sub>2</sub>S<sub>2</sub>O<sub>3</sub>., soluble in excess.

A slip of Zinc or Copper will reduce Silver solutions to the metallic state (*Arbor Diance*).

The insoluble salts of Silver are decomposed by Zn. in the presence of HCl.; the Silver is separated in metallic form, while the acid element usually remains in combination as a salt of Zn.

The salts of Silver are readily blackened by H<sub>2</sub>S.

Any compound of Silver treated with Na<sub>2</sub>CO<sub>3</sub> in the reducing flame on charcoal will form white globule of Silver. Any salt of Silver held on a carbonized match in the reducing Bunsen flame will form white malleable globules of Silver.

**MERCURY.** *Analysis of the black residue remaining on the filter after the precipitate was treated with NH<sub>4</sub>HO.* The black residue is NH<sub>2</sub>Hg<sub>2</sub>Cl. Dissolve this in HNO<sub>3</sub> (and a few drops of HCl.) by aid of heat, by which

means the Mercury is changed to  $\text{HgCl}_2$ , which is soluble, and will now give the reactions for *Mercuric* instead of *Mercurous* base. The fact that the original material was precipitated by  $\text{HCl}$  proves that it was *Mercurous* salt, because the *Mercuric* compounds are not precipitated by  $\text{HCl}$ . The special tests for *Mercurous* salts must be secured by use of the *original solution before precipitation by HCl*.

If a drop of the solution of the black residue be placed on a clean slip of Copper, after remaining a few minutes, washed off, and the spot rubbed with a cloth, a BRIGHT SILVERY SPOT, READILY VOLATILIZING BELOW A RED BRAT, is proof of the presence of Mercury.

A few drops of the original solution, acidified by  $\text{HNO}_3$ , placed on Copper will form a silvery spot if  $\text{Hg}$  is present.

Any dry compound of Mercury heated with  $\text{Na}_2\text{CO}_3$  to a high temperature in a test tube will deposit GLOBULES OF MERCURY on the cold part of the tube. Any dry compound of Mercury heated red hot with a mixture of air-slacked lime, Carbonate of Sodium and Iodide of Potassium, in a test tube, will form a SUBLIMATE, SCARLET TO YELLOW, on the cold part of the tube.

*Special reactions for Mercurous salts.* The Caustic Alkalies gives a black precipitate  $\text{Hg}_2\text{O}$ ;  $\text{H}_2\text{S}$  an immediate black precipitate,  $\text{Hg}_2\text{S}$ ;  $\text{KI}$  gives a greenish-yellow precipitate,  $\text{Hg}_2\text{I}_2$ ;  $\text{K}_2\text{Cr}_2\text{O}_7$  gives an orange precipitate,  $\text{Hg}_2\text{CrO}_4$ , reddish in presence of  $\text{HNO}_3$ .

## TABLE X.

## ANALYSIS OF GROUP II.

Substances not precipitated by HCl., but completely precipitated in presence of HCl. by  $H_2S$ . in form of Sulphides.

To the solution from which HCl. will not throw down a precipitate, add HCl. to acid reaction, and then  $H_2S$ . till the solution smells strongly of this acid, even after shaking thoroughly, and the filtrate will form no more precipitate with  $H_2S$ . The precipitate is Group II. Filter and wash the precipitate for analysis.

The group is divided into two divisions to facilitate analysis.

DIVISION A.—*Sulphides soluble in KHO. and in  $NH_4HS$ .* This division may contain :

$As_2S_3$ —Bright yellow ;	soluble in $(NH_4)_2CO_3$ ;	insoluble in HCl.
$SnS$ —Brown ;		
$SnS_2$ —Dirty yellow ;	} Soluble in Conc. HCl.	Insoluble in $(NH_4)_2CO_3$ .
$Sb_2S_3$ } Orange ;		
$Sb_2S_5$ }		
$Au_2S_3$ } Brown-black ;	insoluble in HCl. and in $HNO_3$ .	
$PtS_2$ }	Soluble in aqua regia.	

DIVISION B.—*Sulphides insoluble in KHO. and in  $NH_4HS$ .* This division may contain :

$HgS$ —Black ;	insoluble in boiling $HNO_3$ . in absence of HCl.
$CuS$ }	} Soluble in boiling $HNO_3$ .
$Bi_2S_3$ } Black ;	
$PbS^*$ —Brown-black ;	
$CdS$ —Yellow ;	

Some hints concerning the kind of substances present may be derived from the color of the precipitated Sulphides. If it is a bright yellow, Arsenic or Cadmium is probably present : if a dirty yellow, Stannic Sulphide : if orange, Antimony : if brown, Stannous Sulphide. If the precipitate is light colored, Lead, Copper, Mercury and Bismuth are all absent, because the Sulphides of all these metals are black. The lighter color of the Sulphides of the other metals may be entirely concealed by any of these black Sulphides. While it is useless to search for metals of the Lead and Copper class in a light colored precipitate in the Second Group, the student is not to infer that the Arsenic and Tin bases must be absent from the black precipitates, but must determine their presence or absence by special investigation.

\* $PbS$ . may appear in this group because of the sparing solubility of  $PbCl_2$ , of the first group.

First wash the precipitate by  $H_2S$ , to remove any members of subsequent Groups. *If the precipitate is light colored*, it can contain only the members of the first subdivision (Sulphides soluble in  $KHO$ ), and Cadmium. Boil a small quantity of the yellowish precipitate in a little solution of  $KHO$ : if a bright yellow precipitate remains undissolved, Cadmium is present; but if the precipitate dissolves, in part or in whole, a Sulphide of Antimony, Arsenic or Tin is present.

*If the precipitate is black*, mix a small quantity with  $KHO$ . and heat gently: filter, and to the filtrate add a few drops of  $HCl$ : if a yellow or orange precipitate forms (to be carefully distinguished from separated  $S$ .) the original precipitate contains both *the first and second subdivisions of Group II.*, and the whole of the black precipitate must be boiled with  $KHO$ ., filtered, and from the filtrate the members of the first subdivision separated by the action of  $HCl$ .

The separation of the first and second subdivision may be readily effected as follows: treat the black precipitate with solution of  $(NH_4)_2CO_3$ . and filter off the ammoniacal solution, which may contain the Sulphides of Arsenic; wash the residual black precipitate and boil it in solution of  $KHO$ . which will dissolve all the Sulphides of Antimony and Tin. Filter and wash the precipitate still remaining, which will contain the second subdivision of Group II., while the filtrates secured by the Ammoniacal and Potassic Solutions will contain the first subdivision, and these members may be recovered from the solutions by the action of  $HCl$ . which will precipitate them as Sulphides.

## ANALYSIS OF DIVISION A. OF GROUP II.

Sulphides soluble in KHO. and in  $\text{NH}_4\text{HS}$ . but insoluble in dilute HCl.

[ The Salts of Gold and Platinum belong in this Group and Subdivision, but they are seldom found in ordinary analysis, and are more readily identified by special methods than by systematic precipitation by Group Reagents. They will not be embraced in Group work, but the special tests for these bases will be given in their appropriate place.]

The members of Division A. of Group II. are:

$\text{As}_2\text{S}_3$ —Bright yellow	} Soluble in $(\text{NH}_4)_2\text{CO}_3$ , Insoluble in HCl.	} All soluble in a boiling solution of KHO.
$\text{SnS}$ —Brown		
$\text{SnS}_2$ —Dirty yellow	} Soluble in Conc. HCl. Insoluble in $(\text{NH}_4)_2\text{CO}_3$ .	
$\text{Sb}_2\text{S}_3$ } Orange		
$\text{Sb}_2\text{S}_5$ }		

Separation of As., Sb. and Sn. from their mixed Sulphides in Division A. of Group II.

1. Boil the mixed sulphides in  $(\text{NH}_4)_2\text{CO}_3$ ; if solution is complete, absence of Sb. and Sn. and presence of As. To the clear ammonical solution or filtrate from insoluble sulphides add HCl. to acid reaction, and separate the yellow  $\text{As}_4\text{S}_6$  for further treatment.

2. If an insoluble residue is left from  $(\text{NH}_4)_2\text{CO}_3$ . dissolve in Conc. HCl. and filter from any residue. Place in the clear solution clean iron wire and boil. Sb. will be deposited on the iron, and  $\text{SnCl}_4$  will be reduced to  $\text{SnCl}_2$ . Remove the iron wire and Sb. and test the clear liquid for  $\text{SnCl}_2$  by  $\text{HgCl}_2$ . Wash the iron wire, remove the Sb. deposited on it, or left as black grains in the liquid; dissolve in aqua regia and test for  $\text{SbCl}_3$ .

3. Instead of the reduction by iron wire, use Zn. HCl., testing the escaping H. for  $\text{SbH}_3$ ; remove the Zn. and Sn. deposited on it, wash the Sn. and dissolve in boiling Conc. HCl. and test for stannous salts. The black grains of Sb. left in the solution, insoluble in HCl., dissolve in aqua regia and test for salts of Sb.

Arsenic may be found in two degrees of oxidation, as  $\text{As}_2\text{O}_3$ . (arsenious) and  $\text{As}_2\text{O}_5$  (arsenic), and the reactions of their salts will vary in some degree according to the degree of oxidation. By the prolonged action of  $\text{H}_2\text{S}$ . in presence of HCl. the arsenic salts are reduced to arsenious sulphide and give reactions of the arsenious class.

The degree of oxidation must be determined in the original solution before the use of reducing agents, such as  $\text{H}_2\text{S}$ . Many of the special tests give best results with the original solution or substance dissolved in  $\text{H}_2\text{O}$ . or in HCl.

**ARSENIC.** To the Solution of Sulphide of Arsenic in  $(NH_4)_2CO_3$ , add *HCl.* to the complete precipitation of  $As_2S_3$ . Separate and wash the yellow precipitate. Dry the precipitate and mix it with  $Na_2CO_3$ , and powdered charcoal, place the mixture in a dry test tube and heat the salts to red heat. The  $As_2$  will volatilize and condense upon the cold part of the tube in a black SHINING MIRROR OF METALLIC  $As_2$ , and a GARLIC ODOR MAY BE DETECTED AT THE MOUTH OF THE TUBE.

**ARSENIOUS OXIDE.** Solution of  $As_2O_3$ , in presence of *HCl.*, gives a BRIGHT YELLOW PRECIPITATE OF  $As_2S_3$ . INSOLUBLE IN *HCl.* BUT READILY SOLUBLE IN  $(NH_4)_2CO_3$ . This is one of the most delicate and characteristic tests for Arsenic, since one part of the Sulphide requires nearly 1,000,000 parts of water to dissolve it when *HCl.* is present. The only Sulphides that could be mistaken for  $As_2S_3$ , are  $CdS$ ,  $SnS_2$ , and  $Sb_2S_3$ .—but these are all insoluble in  $(NH_4)_2CO_3$ , in which  $As_2S_3$  is soluble.

A solution of Arsenious trioxide in water gives a green precipitate of  $CuHAsO_3$ , (Scheele's Green) with Ammonio-Sulphate of Copper—soluble in *HCl.* and  $NH_4HO$ .

A watery solution of the trioxide will give a yellow precipitate ( $Ag_3AsO_3$ ) with Ammonio-Nitrate of Silver, easily soluble in  $HNO_3$ , and in  $NH_4HO$ . Ammonia water will dissolve many Arsenites, and the presence of Arsenical salts may easily be shown in this way. If wall papers containing the green Arsenite of Copper be moistened with a few drops of Ammonia water, and this be squeezed out upon a white plate, and a crystal of  $AgNO_3$  be dropped into the solution, a yellow precipitate around the crystal will show the presence of Arsenic.

**ARSENIC PENTOXIDE.** Solution of  $As_2O_5$  is not immediately precipitated by  $H_2S$  in presence of *HCl.*, but by the prolonged action of  $H_2S$  the pentoxide is reduced to trioxide and precipitated as  $As_2S_3$ . By boiling the Arsenic Acid or Arsenate with  $Na_2S_2O_3$ , the reduction to Arsenious condition is speedily effected, when addition of  $H_2S$  and *HCl.* will cause the immediate precipitation of  $As_2S_3$ ; this is sometimes obscured by separated Sulphur, in which case the  $As_2S_3$  may be dissolved by  $(NH_4)_2CO_3$ , filtered from insoluble materials, and the Arsenious Sulphide precipitated from the filtrate by *HCl.*

Ammonio-Nitrate of Silver forms a BRICK-RED PRECIPITATE  $Ag_3AsO_4$ .—easily soluble in  $HNO_3$ , and in  $NH_4HO$ . If the Arsenic Acid contains an excess of  $HNO_3$ , e.g. when the Sulphide has been oxidized and dissolved by  $HNO_3$ , add  $AgNO_3$  to the clear solution and drop into this a crystal of Acetate of Sodium, when the characteristic brick-red  $Ag_3AsO_4$  will form in the fluid surrounding the crystal.

Ammonio-Sulphate of Copper precipitates light greenish-blue Arsenate of Copper ( $Cu_22AsO_4$ ) easily distinguished from Scheele's Green.

$MgSO_4$ , in presence of  $NH_4HO$ , and  $NH_4Cl$ , precipitates Arsenic Acid as a white crystalline salt  $MgNH_4AsO_4$ . This salt closely resembles the corresponding Phosphate, but the Arsenate can readily be distinguished from the Phosphate by the method of reduction by boiling with the Hyposulphite of Sodium and precipitation of  $As_2S_3$  by  $H_2S$  and  $HCl$ , already pointed out—reactions not given by a Phosphate. If solution of Molybdate of Ammonia in excess be added to a solution of an Arsenate and the liquid warmed, a bright yellow precipitate of Arsenio-Molybdate of Ammonium will form, very similar to Phospho-Molybdate of Ammonium.

The Arsenites are much more common and important salts than the Arsenates. All the soluble or vaporous compounds of Arsenic are very poisonous.

**REDUCTION TEST.** If any dry compound of Arsenic be mixed with twenty times its volume of dry  $K_2F_3Cy_6$ , or a mixture of charcoal and  $KCy$ , and then heated in a closed glass tube a MIRROR OF METALLIC ARSENIC WILL FORM IN THE TUBE, AND A GARLIC ODOR MAY BE OBSERVED AT THE OPEN END OF THE TUBE. If this metallic mirror is gently heated while a current of air traverses the tube, the Arsenic will OXIDIZE TO  $As_2O_3$  AND DEPOSIT WHITE OCTOHEDRAL CRYSTALS ON THE COOL PART OF THE TUBE. [Use magnifying glass]. The  $As_2O_3$  may be dissolved in water, and the usual tests applied.

**REINSCH'S TEST.** In mixtures containing organic matter, the soluble compounds of Arsenic may most easily be separated by boiling the liquid with one-tenth its volume of  $HCl$  for a short time, to remove Nitrates, etc., then placing a slip of clean and bright Copper in the liquid and continuing the boiling for a few minutes. If any soluble compound of Arsenic is present, the metal will be precipitated on the surface of the Copper as a GRAY DEPOSIT OF ARSENIDE OF COPPER— $Cu_3As$ . If the Copper slip (or the gray scales, if much Arsenic was present) be withdrawn, washed, dried placed in a dry test tube and heated red-hot, a part of the Arsenic will oxidize to  $As_2O_3$  and form WHITE OCTOHEDRAL CRYSTALS on the cool part of the tube.

Under like conditions the compounds of Antimony and Mercury may form metalline deposits on Copper; but the Antimony does not readily volatilize by heat, or form octohedral crystals at some distance from the Copper, and the Mercury when heated forms a film or drops of Mercury on the glass tube.

For detecting small traces of As. an iron-copper couple is prepared by twisting a fine and bright wire of copper around a small rod of iron, e. g., a nail, and the couple placed in a  $HCl$  solution of As. A gray film is deposited on the copper in presence of one part of As. in 10,000.

**MARSH'S TEST.** Any soluble compound of Arsenic in presence of nascent Hydrogen will form Arsenetted Hydrogen— $AsH_3$ . In order to be assured

of the purity of our materials and the absence of every trace of Arsenic from the chemicals employed it is desirable to perform a *blank experiment* by forming Hydrogen with the Zinc and Sulphuric acid, and testing the gas to see if it affords any indication of Arsenic; if Arsenical compounds are entirely absent, the liquid to be tested is then added to the Hydrogen generator, and the escaping gas tested for  $AsH_3$ .

In this investigation the student will bear in mind that Hydrogen mixed in certain proportions with air becomes dangerously explosive in the presence of flame. Before heating the tube which conveys the escaping gas, or igniting the gas as it escapes, he will wait till the Hydrogen has expelled the most of the air from the generator. He will also bear in mind that  $AsH_3$  is poisonous, and if breathed in large amount often causes fatal results.

A convenient generator for laboratory use may be made out of a wide-mouthed pint bottle with a tight-fitting cork having two perforations; through one a safety tube passes nearly to the bottom of the bottle, through which liquids may be poured into the bottle without removing the cork; through the other opening a tube of infusible glass passes through the cork, is bent above the cork at right angles so as to pass horizontally and the end is drawn down to a small jet. A half ounce of pure mossy zinc is placed in the bottle, four ounces of water and half ounce of C.P.,  $H_2SO_4$  are poured in, and the cork with its tubes inserted. If Hydrogen forms rapidly the air will be expelled from the bottle in two to five minutes, when the gas may safely be tested. Heat a part of the horizontal glass tube red-hot and see if any metallic deposit forms in the tube near the flame; at the same time light the Hydrogen escaping at the jet, and cut the flame with a cold surface of porcelain, and see if any brown spot forms on the porcelain. If no Arsenical deposits appear, pour into the bottle through the safety tube the liquid to be tested; heat the tube and cut the flame as before and watch results.

If a BROWN TO STEEL GRAY RING IS DEPOSITED WITHIN THE GLASS TUBE AND BEYOND THE FLAME, which is easily vaporized by heat, and in a current of air oxidized by heat to  $As_2O_3$ ; and if the flame cut by a cold porcelain surface forms BROWN, LUSTROUS SPOTS, READILY SOLUBLE IN SOLUTION OF  $NaClO$ , then Arsenic is present.

As Antimonetted Hydrogen,  $SbH_3$ , may be formed under like conditions, and comports itself in many respects like  $AsH_3$ , it is important to carefully distinguish between them. The following reactions will serve to distinguish these metals from each other.



<p><i>Arsenic deposit in tube.</i> Deposit BEYOND the flame. Easily vaporized by heat; does not melt.</p>	<p><i>Antimony deposit in tube.</i> Deposit BEFORE OR ON BOTH SIDES of the flame. Melts to small globules; vaporized at red heat.</p>
<p><i>Arsenic spots.</i> Lustrous brown gray to black. SOLUBLE IN NaClO. Dissolved by drops of HNO<sub>3</sub> when warmed. This solution with AgNO<sub>3</sub> and a little Ammonia gives a brick red precipitate.</p>	<p><i>Antimony spots.</i> Velvety brown to black. INSOLUBLE IN NaClO. Whitens but does not dissolve in HNO<sub>3</sub>. Treated with AgNO<sub>3</sub> and a little Ammonia gives no color, but blackens when heated.</p>

The color of the spots, their solubility or insolubility in NaClO, the position of the deposit in heated glass tube, the difference in volatility, taken together serve to distinguish Arsenic from Antimony.

**BETTENDORFF'S METHOD, MODIFIED.** If any compound of Arsenic free from Sulphur, be placed in a concentrated solution of SnCl<sub>2</sub> to which half its volume of Conc., H<sub>2</sub>SO<sub>4</sub> has been added (to set free fuming HCl.) and the whole heated to boiling, the Arsenic will be reduced to a metallic state FORMING A DEEP BROWN COLORATION, if the quantity is small, or a BROWNISH-BLACK PRECIPITATE if much Arsenic is present.

This reaction is very delicate, but requires the presence of *fuming HCl*. The compounds of Antimony do not give this reaction. This process will serve to distinguish between Arsenic and Antimony, or to detect Arsenic in the presence of a large amount of Antimony.

The following reactions, *taken together*, distinguish Arsenic from all other substances:

1. Formation of a black, shining sublimate by reduction.
2. Conversion of this sublimate into As<sub>2</sub>O<sub>3</sub> by heating in a current of air.
3. Solution of this crystalline sublimate in dilute HCl. gives a yellow precipitate with H<sub>2</sub>S. soluble in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>.
4. Formation of AsH<sub>3</sub>. with deposit in heated glass tube, and lustrous brown spot on cold porcelain surface when its flame is cut, the spot soluble in NaClO.
5. Garlic odor when sublimate (1.) is heated in a small amount of air, or when the white sublimate (2.) is heated with reducing agents.
6. Production of brownish-black precipitate by boiling Conc. solution of SnCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. (Bettendorff's Method).

**ANTIMONY AND TIN.**—From the Potassic solution of Sulphides, precipitate the Sulphides completely by HCl, wash the precipitate and dissolve in Conc. HCl. by aid of heat; if solution is milky from separated S., filter. If the precipitate from the Potassic solution by HCl. is orange color, Sb<sub>2</sub>S<sub>3</sub> is present; if brown, SnS; if a dingy yellow, SnS<sub>2</sub>. These colors are not

conclusive of the absence of Sulphides of a different color because a small amount of such Sulphides may be concealed by the color of associated Sulphides.

If the chlorides (of Antimony and Tin) formed by dissolving the Sulphides in Conc. HCl, be poured into a Hydrogen generator, the Tin will be deposited on the Zinc as a spongy metallic mass, with some of the Antimony, while a part of the Antimony will be converted into gaseous  $SbH_3$ , and if the flame of escaping gas be cut by a cold porcelain surface, a LUSTRELESS BLACK SPOT, INSOLUBLE IN  $NaClO$  is proof of the presence of Antimony. Remove the metals deposited on Zinc, wash them and heat with Conc. HCl. The Tin will dissolve and may be tested by  $HgCl_2$ ; the Antimony will remain as black flakes or powder; wash and dissolve in Conc. HCl. with a small crystal of  $KClO_3$ , and apply special tests.

**SPECIAL TESTS FOR ANTIMONY.** The salts of Antimony in presence of HCl. are precipitated by  $H_2S$ . as an ORANGE-COLORED SULPHIDE,  $Sb_2S_3$ , insoluble in dilute HCl., soluble in solution of KHO. If any acid salt of Antimony is boiled with  $Na_2S_2O_8$ , the Sulphide of Antimony is speedily deposited as a dark-red powder.

If any solution of Antimony acidified with HCl. be placed on a slip of Platinum foil and a rod of Zinc touch the foil through the solution, the FOIL WILL BE STAINED BLACK BY DEPOSITION OF METALLIC ANTIMONY, insoluble in HCl. Under similar treatment Tin will be deposited on the Zinc in the form of a loosely adherent, dull gray powder, readily soluble in HCl.

For detecting minute traces of Sb. the solution is acidified with HCl. and a small rod of iron with fine platinum wire wound around it to form a small Fe. and Pt. couple, is placed in the solution, a black stain is deposited on Pt. wire if a trace of Sb. is present.

If Chloride of Antimony be poured into a large volume of water, a white precipitate will form,  $SbCl_3 + H_2O = SbOCl + 2HCl$ . This oxychloride of Antimony is readily soluble in Tartaric Acid (distinction from  $BiOCl$ .)

When a small quantity of any compound of Antimony is supported on a thread of asbestos and held in the upper reduction cone of a Bunsen burner, the flame becomes tinged bluish-white; if the flame is cut with a cold porcelain surface, a brownish-black spot of metallic Antimony is formed on the porcelain, insoluble in  $NaClO$ . If any compound of Antimony is heated on a carbonized match, brittle metallic globules will form on the match.

If any compound of Antimony be treated with  $Na_2CO_3$  on charcoal before RFl. white, brittle globules of Antimony will be obtained, and a white coating on the coal.

KHO precipitates Antimonious Salts as  $Sb(OH)_3$ , soluble in excess of KHO.— $Na_2CO_3$ , forms a similar hydrate, soluble in excess on heating.

**TIN.** Tin forms two classes of salts—Stannous and Stannic—which have very different reactions with many reagents. Many chemicals will change the salts from one class to the other. For example, the Stannous Sulphide is soluble in  $\text{NH}_4\text{HS}$ , but when precipitated from this solution by  $\text{HCl}$ , it is found in the form of Stannic Sulphide. When either Chloride of Tin is treated with metallic Zinc, the Tin is precipitated in the metallic form, and when the metal is dissolved in  $\text{HCl}$ , only  $\text{SnCl}_2$  is formed. The degree of oxidation of the compounds of Tin must be determined in the original solution.

**STANNOUS SALTS.** In normal and not too acid solutions of Stannous Salts,  $\text{H}_2\text{S}$  precipitates BROWN STANNOUS SULPHIDE,  $\text{SnS}$ , insoluble in  $(\text{NH}_4)_2\text{CO}_3$ ; soluble in Conc.  $\text{HCl}$ , in  $\text{NH}_4\text{HS}$ , and in  $\text{KHO}$ .

Stannous chloride PRECIPITATES  $\text{HgCl}_2$  AS  $\text{Hg}_2\text{Cl}_2$ .  $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + \text{Hg}_2\text{Cl}_2$ . In excess of  $\text{SnCl}_2$ , the  $\text{Hg}_2\text{Cl}_2$  is reduced to METALLIC MERCURY, FORMING A GRAY PRECIPITATE WHICH MAY BE GATHERED INTO A GLOBULE by boiling with  $\text{HCl}$ . By rubbing the grayish powder on bright surface of  $\text{Cu}$ , the SILVERY COLOR OF  $\text{Hg}$ , AMALGAM may be formed.

These reactions with  $\text{H}_2\text{S}$  and  $\text{HgCl}_2$  are distinctive of Stannous Chloride.

If a drop of solution of  $\text{SnCl}_2$  be placed on white filter paper and a drop of dilute solution of  $\text{AuCl}_3$  be placed on this, a purple stain of finely divided gold will form in consequence of the reducing action of  $\text{SnCl}_2$ .

$\text{SnCl}_2$  boiled with excess of Oxalic Acid forms  $\text{SnC}_2\text{O}_4$ , insoluble in strong solution of  $\text{H}_2\text{C}_2\text{O}_4$ .

$\text{KHO}$  precipitates  $\text{SnCl}_2$  as white  $\text{SnHOCl}$ , soluble in  $\text{HCl}$ , and in excess of  $\text{KHO}$  forming  $\text{K}_2\text{SnO}_2$ .

**STANNIC SALTS.** Solution of Stannic salts in presence of  $\text{HCl}$  forms a DINGY YELLOW PRECIPITATE with  $\text{H}_2\text{S}$  of  $\text{SnS}_2$ , insoluble in  $(\text{NH}_4)_2\text{CO}_3$ , but readily soluble in  $\text{KHO}$ , and soluble by aid of heat in Conc.  $\text{HCl}$ .

Stannic Chloride does not precipitate  $\text{HgCl}_2$  or  $\text{AuCl}_3$ , nor reduce Ferric Salts to Ferrous state.

$\text{SnCl}_4$  in presence of  $\text{HCl}$  and metallic Iron is reduced to  $\text{SnCl}_2$ , which may be detected by  $\text{HgCl}_2$ .

Both  $\text{SnCl}_2$  and  $\text{SnCl}_4$  in presence of  $\text{HCl}$  will be reduced to metallic state by a slip of  $\text{Zn}$ , forming the TIN TREE.

## ANALYSIS OF DIVISION B. OF GROUP II.

Sulphides insoluble in  $\text{NH}_4\text{HS}$ . and in  $\text{KHO}$ .

The members of Division B. of Group II. are :

HgS—black :	insoluble in $\text{HNO}_3$ .
CuS—black :	} Soluble in $\text{HNO}_3$ .
$\text{Bi}_2\text{S}_3$ —black :	
CdS.—yellow :	
(PbS—black):	

Boil the Sulphides in dilute  $\text{HNO}_3$ . If there is a black insoluble residue it is probably HgS. Filter from any insoluble residue. The solution may contain  $\text{Cu}_2\text{NO}_3$ ,  $\text{Bi}_3\text{NO}_3$ ,  $\text{Cd}_2\text{NO}_3$  and  $\text{Pb}_2\text{NO}_3$ . To a few drops of the solution add a drop of dilute  $\text{H}_2\text{SO}_4$ ; if a white precipitate forms, add dilute  $\text{H}_2\text{SO}_4$  to the whole solution and filter out  $\text{PbSO}_4$  and apply to this the special tests for Lead given in Table IX. To the filtrate or the solution from which  $\text{H}_2\text{SO}_4$  does not form a precipitate, add  $\text{NH}_4\text{HO}$  to alkaline reaction; a white precipitate indicates Bismuth; filter; a blue filtrate indicates Copper, but it may also contain Cadmium, which by itself forms a colorless solution.

**BISMUTH.** Dissolve the white precipitate thrown down by  $\text{NH}_4\text{HO}$  in a small quantity of  $\text{HNO}_3$ , and expel any excess of acid by boiling. Fill a test tube half full of water containing some  $\text{NH}_4\text{Cl}$ , and drop into this a few drops of the Nitrate of Bismuth; a **WHITE PRECIPITATE ( $\text{BiOCl}$ ) INSOLUBLE IN TARTARIC ACID** shows the presence of Bismuth: (distinction from  $\text{SbOCl}$ )

$\text{K}_2\text{Cr}_2\text{O}_7$  added to Salts of Bismuth precipitates a yellow basic chromate of Bismuth, soluble in  $\text{HNO}_3$  (distinction from Lead).

$\text{H}_2\text{S}$ , produces a black precipitate of  $\text{Bi}_2\text{S}_3$ , insoluble in dilute  $\text{HCl}$ , and in  $\text{NH}_4\text{HS}$  but dissolved by  $\text{HNO}_3$ .

$\text{KI}$ , precipitates brown  $\text{BiI}_3$ , soluble in excess of  $\text{KI}$ , and in  $\text{HCl}$ .

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ , precipitates white  $\text{Bi}_2(\text{C}_2\text{O}_4)_3$ , insoluble in dilute acids.

$\text{Na}_2\text{HPO}_4$ , precipitates white  $\text{BiPO}_4$ , soluble in  $\text{HCl}$ .

If  $\text{SnCl}_2$ , is dissolved in excess of  $\text{KHO}$  (aided by heat), and to the clear solution a drop of any Salt of Bismuth is added and the mixture boiled, **AN INTENSELY BLACK PRECIPITATE WILL FORM,  $\text{Bi}_2\text{O}_3$ .** Very delicate test.

Any compound of Bi, heated on charcoal with  $\text{KI}$ ,\* and  $\text{S}$ , will form a **SCARLET COATING  $\text{BiSI}$ , ON THE COAL.**

If a mixture of  $\text{KI}$ ,  $\text{S}$ , and charcoal dust be ground up with a Bi. compound and heated strongly in an open glass tube, **A SCARLET SUBLIMATE WILL FORM,  $\text{BiSI}$  on cool part of the tube.**

\*  $\text{KI} + \text{S}$ , liable to deliquesce if exposed to the air for a long time. A mixture of  $\text{Cu}_2\text{I}_2$ , and  $\text{S}$ , is far superior, and is permanent.

Any compound of Bismuth heated on an asbestos thread in upper reduction flame of Bunsen burner, forms a brown or black deposit upon a cold porcelain surface cutting the flame; this coating of metallic Bismuth is only slowly dissolved by cold dilute  $\text{HNO}_3$ . On a carbonized match, brittle globules of metallic Bismuth, which will break under the hammer.

All compounds of Bismuth are easily reduced to metallic state by heating in R.Fl. with  $\text{Na}_2\text{CO}_3$  on charcoal, with a yellow coating on the coal, forming a very fusible and brittle globule. If the globule seems to flatten under the hammer, its brittle nature is shown by its crumbling when touched by the point of a knife.

Solution of Bi. salts reduced to metal by a slip of zinc suspended in the solution.

**COPPER.** If the ammoniacal solution from precipitation of Bismuth is blue, it contains Copper. To confirm this, expel the ammonia by boiling, acidify with  $\text{HCl}$ , to a portion add  $\text{K}_2\text{FeCy}_6$ . A REDDISH BROWN PRECIPITATE,  $\text{Cu}_2\text{FeCy}_6$  INSOLUBLE IN  $\text{HCl}$  BUT SOLUBLE IN  $\text{NH}_4\text{HO}$  is proof of Copper.

$\text{KHO}$ . added to saturation to solution of salts of Cu. precipitates blue hydrate  $\text{Cu}(\text{OH})_2$ —insoluble in excess: when boiled it becomes black,  $\text{CuO}$ .

$\text{Na}_2\text{CO}_3$  precipitates greenish blue basic carbonate  $\text{CuCO}_3\text{Cu}(\text{OH})_2$ : on boiling, black  $\text{CuO}$ .

$\text{NH}_4\text{HO}$ . short of saturation precipitates pale-blue basic salts: saturated, blue hydrate,  $\text{Cu}(\text{OH})_2$ : supersaturated, deep blue solution, "celestial water."

$\text{H}_2\text{S}$ . precipitates from Salts of Copper the brownish black  $\text{CuS}$ .

The Chloride of Copper colors flame first *blue*, then *green*: all other salts of Copper color the flame green.

Any compound of Copper on a Carbonized Match will yield red globules of Copper by Bunsen's flame method, the copper easily seen when the assay is rubbed with a knife blade on a glass slip. The green flame is seen during the reduction.

Any compound of Copper is easily reduced to metallic state by treating with  $\text{Na}_2\text{CO}_3$  on charcoal in R.Fl. The metal is melted into a globule only by a strong blast. The grains of Cu. may be seen by rubbing the assay in a porcelain mortar and washing away the charcoal in a stream of water, as flattened grains, or metallic streaks.

If a slip of bright metallic iron be placed in an acid solution of Cu., the Cu. will be deposited on the iron in METALLIC FORM.

If any salt of Cu. containing no free  $\text{HNO}_3$  be acidulated with  $\text{HCl}$ . and a solution of equal parts of  $\text{NH}_4\text{Cys}$ . and  $\text{NH}_4\text{HSO}_5$  be added to the Cu. solution: on boiling the Cu. WILL BE COMPLETELY PRECIPITATED AS

**WHITE CuCyS.** This process separates Cu. from every other metal in a mixed solution.

To detect very minute traces of Cu. place a zinc-platinum couple (made by twisting a fine Pt. wire around a small slip of Zn.) in the acid solution: if much Cu. is present the Pt. wire becomes speedily covered with black deposit of Cu.: if very minute traces only, leave the couple for several hours, remove the Pt. wire, wash with water, and expose the wet wire to vapors of HBr, (by heating KBr. and  $H_2SO_4$ ); the deposit on the wire becomes deep purple in presence of Cu.

**CADMIUM.** If the solution (from separation of Bismuth) is colorless it may contain Cadmium. Add HCl. to acid reaction, and then  $H_2S$ . a **BRIGHT YELLOW PRECIPITATE, INSOLUBLE IN  $NH_4HO$ .**, but soluble in hot  $H_2SO_4$ . is decisive of the presence of Cadmium.

*Separation of Cd. and Cu.* If the solution from which Bi. has been separated by  $NH_4HO$ . is blue from presence of Cu., acidify by HCl., add  $Na_2S_2O_3$  and boil till the precipitate becomes a dark brown (not black) and the liquid colorless and transparent; filter and neutralize the filtrate with  $NH_4HO$ . and add  $NH_4HS$ . The **YELLOW PRECIPITATE** of CdS. is proof decisive.

If  $Na_2HPO_4$  is added to a salt of Cd., then  $NH_4Cl$ . and  $NH_4HO$ . and the mixture boiled, pearly white plates of  $CdNH_4PO_4$  will form and rapidly precipitate as the liquid cools.

Cadmium salts do not color the flame.

**MERCURY.** The black insoluble residue remaining after heating the sulphides of this subdivision with  $HNO_3$  is probably HgS. Dissolve in hot Conc. HCl. with addition of a small crystal of  $KClO_3$ . Boil to expel excess of acid, filter if necessary, and to a portion of the liquid add  $SnCl_2$ , a **WHITE PRECIPITATE BECOMING BLACKISH-GRAY IN EXCESS OF  $SnCl_2$** , is proof of Mercury. This gray precipitate may be gathered into a globule by boiling with HCl. If the grayish powder does not readily unite into globules, rub the powder on a bright copper surface, when a silvery spot will form if Hg. is present.

Place a few drops of the solution on a clean slip of Copper, after a few minutes wash the Copper and rub the spot with a wet cloth; a **BRIGHT SILVERY SPOT, volatilizable by heat**, is proof of Mercury.

The action of  $H_2S$ . on a Mercuric salt is characteristic; a small amount may form a white precipitate, but increasing amounts of  $H_2S$ . **CHANGES THE COLOR TO YELLOW, ORANGE, RED, AND FINALLY TO BLACK.**

Solution of KI. precipitates Mercuric salts, **AT FIRST SALMON COLOR, SPEEDILY BECOMING SCARLET.** The precipitate is soluble in excess of either the Mercuric salt or the Iodide.

In solution of a Mercuric salt  $NH_4HO$  forms a white precipitate  $NH_2HgCl$ . soluble in HCl.

KHO. short of saturation produces reddish-brown basic salts; saturated, HgO., soluble in 200,000 of water.  $K_2Cr_2O_7$  precipitates orange,  $HgCrO_4$ , soluble in  $HNO_3$ .

If any dry compound of Mercury be ground in a mortar with its own volume of Potassium Iodide, Sodium Carbonate, and ten volumes of air-slacked lime, and the mixture be strongly heated in a dry test tube, a sublimate of  $HgI_2$ ,—yellow to scarlet in color—will form on the cold part of the tube.

If any compound of Mercury be treated in the same way with omission of the Iodide, a gray tarnish of Mercury will form in the tube, visible as globules by magnifying glass, and may be united into larger globules by rubbing with a glass rod.

#### SPECIAL TESTS FOR GOLD AND PLATINUM.

Gold and Platinum are insoluble in  $HNO_3$  and in  $HCl$ , but soluble in a mixture of these Acids=Aqua Regia. They are precipitated in the form of brownish-black sulphides by  $H_2S$ .—soluble in alkaline sulphides—soluble in Aqua Regia. Gold and Platinum are usually found in the metallic state (native) but Gold is often found in smaller quantity associated with metallic Sulphides. If these Sulphides are roasted to burn off the Sulphur, the Gold may then be dissolved by heating with Aqua Regia, and the solution tested for the metal.

**GOLD.** Solution of a salt of Gold is precipitated by solution of  $FeSO_4$  in the FORM OF FINELY DIVIDED METALLIC GOLD. If the quantity of Gold is small the precipitate may remain suspended in the water for hours: appears brown by reflected light, and blackish blue by transmitted light.

If any solution of Gold be dropped on white paper and a drop of  $SuCl_2$  dropped on the moistened spot, a rich purple color of finely divided Gold (Purple of Cassius) will appear.

If any solution of gold moisten a piece of white paper (unglazed), this be dried and then burned so as to consume the carbon of the paper (or burn it white) a PURPLE COLORATION will appear whereon the salt of Gold was applied. This is the most delicate test for Gold, and easiest of application.

The Chloride of Gold, even in dilute solutions, stains the skin a lasting purple color.

Any compound of Gold heated on a carbonized match in Bunsen's flame will form yellow malleable globules of metallic Gold. Heated with  $Na_2CO_3$  on charcoal will give yellow globules of gold.

If a solution of Gold is boiled with Oxalic acid the Gold is slowly but completely precipitated in metallic form (distinction from Platinum).

**PLATINUM.** Platinic salts are precipitated as a YELLOW CRYSTALLINE PRECIPITATE (octohedral crystals) by  $KCl$ : ( $PtCl_4 \cdot 2KCl$ ) sparingly soluble in water; insoluble in alcohol.  $NH_4Cl$  forms a similar precipitate.

$\text{SnCl}_2$  imparts an *intensely dark brownish red color to Platinic salts from reduction to  $\text{PtCl}_2$ .*

Any salt of Platinum heated on charcoal in R.Fl. yields a GRAY INFUSIBLE, NON-MAGNETIC POWDER, only soluble in Nitro Hydrochloric acid.

Treated with a carbonized match in the Bunsen reduction flame the same result is secured.



## TABLE XI.

## ANALYSIS OF GROUP III.

Substances whose salts are not precipitated by  $H_2S$  in presence of  $HCl$ , but are completely precipitated by  $NH_4HS$  in presence of  $NH_4Cl$  and  $NH_4HO$ , as sulphides or as hydrated oxides.

The precipitate may contain:

$CoS$ . } Black, insoluble in dilute  $HCl$ .

$NiS$ . }

$FeS$ . Black.

$MnS$ . Flesh-color.

$ZnS$ . Dingy-white.

$Al_2(OH)_6$ . Dirty white and gelatinous.

$Cr_2(OH)_6$ . Bluish or grayish green.

Phosphates, Borates and Oxalates of Ba. Sr. Ca. Mg—white.

} All  
Soluble in  
dilute  $HCl$ .

The color of the precipitate may afford valuable hints in regard to its composition. If it is white it may contain Zinc and Alumina, (Phosphates, Borates and Oxalates of alkaline earths); if pure flesh-color, Manganese; if light-colored, Iron, Nickel and Cobalt are all absent; but if it is black, all the members of the Group may be present, since the strong color of the black Sulphides will conceal the light-colored Sulphides and Hydroxides.

For convenience in analysis, Group III is divided into two divisions, based upon the solubility or insolubility of their hydroxides in solution of  $NH_4Cl$  in presence of  $NH_4HO$ .

**DIVISION A.** *Substances whose hydroxides are insoluble in solution of  $NH_4Cl$  in presence of  $NH_4HO$ .*

Division A. contains {  $Al_2(OH)_6$ .—dirty white, gelatinous.  
 $Cr_2(OH)_6$ .—bluish or grayish green.  
 $Fe_2(OH)_6$ .—yellow to brown.

(Phosphates and Oxalates of Alkaline Earths—white.)

**DIVISION B.** *Substances whose hydroxides are soluble in excess of solution of  $NH_4Cl$  in presence of  $NH_4HO$ , but their sulphides insoluble.*

Division B. contains {  $CoS$ . } black; insoluble in dilute  $HCl$ ,  
 $NiS$ . }  
 $MnS$ .—flesh color } Soluble in dilute  $HCl$ .  
 $ZnS$ .—dingy-white }

**DIVISION A.** Boil the filtrate from which  $H_2S$  will form no precipitate to expel all traces of  $H_2S$ , add a few drops of  $HNO_3$  and boil for a moment; then add  $NH_4Cl$  in excess, and  $NH_4HO$  to complete saturation. If a precipitate forms, filter and wash the precipitate; perforate the point of the filter and wash the precipitate into a test tube by a little solution of  $KHO$ : boil, filter, and to the clear filtrate add  $NH_4Cl$  in excess and boil: a precipitate of  $Al_2(OH)_6$  is conclusive evidence of  $Al$ .

Test the precipitate insoluble in KHO, with borax bead: an EMERALD-GREEN BEAD IN R.F.L. AND O.F.L. IS EVIDENCE OF Cr.

Dissolve the residue insoluble in KHO, in HCl, and add  $\text{NH}_4\text{CyS}$ : a BLOOD-RED COLORATION AND NO PRECIPITATE IS EVIDENCE OF Fe.

SPECIAL OPERATIONS REQUIRED WHEN PHOSPHORIC, ARSENIC, AND OXALIC ACIDS ARE PRESENT.

When Phosphates, Arsenates, etc., of Aluminum, Iron, Barium, Strontium, Calcium or Magnesium are present they will be precipitated by  $\text{NH}_4\text{HO}$ ., because these salts are insoluble in an alkaline fluid, even in the presence of  $\text{NH}_4\text{Cl}$ .

Dissolve the washed precipitate in  $\text{HNO}_3$  and boil; add  $\text{Hg}_2\text{2NO}_3$ ; a white precipitate indicates an Oxalate. The Oxalates may be decomposed by igniting on Platinum foil, when the bases will be left in the form of Carbonates.

Add two drops of the Nitric solution to 20 drops of Molybdate of Ammonia and heat gently: an intense yellow color or yellow precipitate shows presence of Phosphoric or Arsenic Acid. In such case add Ferric Chloride and Sodium Acetate to the solution, boil and filter while hot. The precipitate will contain the Phosphoric Acid, etc., in insoluble combination with the Iron, while the Alkaline earths will appear in the filtrate in the form of Acetates.

IRON. The Salts of Iron may exist in two states of oxidation—Ferrous and Ferric—exhibiting very different reactions with reagents according as they are in one or other state of oxidation. These salts are readily changed by reagents from one to the other state.

The Salts of Iron are not precipitated by  $\text{H}_2\text{S}$  in the presence of HCl., but may be more or less completely precipitated when combined with a weak acid, e. g., a basic Acetate.

In presence of HCl.  $\text{H}_2\text{S}$ . will reduce ferric salts to ferrous, milky-white S., being separated. For example,  $\text{Fe}_3\text{Cl}_6 + \text{H}_2\text{S} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$ . In like manner  $\text{NH}_4\text{HS}$  precipitates ferric salts as  $\text{FeS}$ ., some S. being precipitated at the same time. The Iron Salts are thus precipitated as *ferrous sulphides*, irrespective of the degree of oxidation in the original solution. The original condition of the salt can only be determined by *tests applied to the original solution*.

*Ferric Salts* are precipitated as brown Hydroxides by KHO. and by  $\text{NH}_4\text{HO}$ .

With  $\text{K}_4\text{FeCy}_6$  they form a DEEP BLUE PRECIPITATE  $\text{Fe}_4(\text{FeCy}_6)_3$  or Prussian Blue, insoluble in HCl.

With  $\text{NH}_4\text{CyS}$  they give a BLOOD-RED COLOR, but no precipitate.

With  $\text{K}_2\text{FeCy}_6$  they give a greenish-brown color, but no precipitate.

With  $\text{NH}_4\text{HS}$  they form a black precipitate of  $\text{FeS}$ .

*Ferrous Salts* tend to oxidize into the Ferric condition, and are with difficulty preserved in the Ferrous state.

With alkaline hydroxides they form Ferrous hydroxide,  $\text{Fe}(\text{HO})_2$ ,—white, but rapidly becoming green, then rusty-red, by oxidation, — $\text{Fe}_2(\text{OH})_6$ .

With  $\text{K}_4\text{FeCy}_6$  they form a white precipitate, rapidly becoming blue, by oxidation.

With  $\text{K}_3\text{FeCy}_6$  a DEEP BLUE PRECIPITATE,  $\text{Fe}_3(\text{FeCy}_6)_2$ , insoluble in  $\text{HCl}$ .

With  $\text{NH}_4\text{CyS}$  Ferrous Salts do not form a precipitate or red color.

Any salt of Iron treated with  $\text{Na}_2\text{CO}_3$  on charcoal by R.Fl. gives infusible magnetic grains of metallic Iron.

The distinctive characteristics of Ferric and Ferrous Salts are that with  $\text{K}_3\text{FeCy}_6$  the Ferrous Salts form a deep blue precipitate—none with Ferric Salts; that  $\text{NH}_4\text{CyS}$  forms a red color with Ferric Salts—none with Ferrous.

*Separation of Iron and Manganese.* To a solution of  $\text{Fe}_2\text{Cl}_6$  and  $\text{MnCl}_2$  add so much Tartaric Acid that no precipitate will form on adding  $\text{NH}_4\text{HO}$  in excess: add  $\text{K}_4\text{FeCy}_6$  and boil, when  $\text{Mn}_2\text{FeCy}_6$  (pinkish) will precipitate and Iron remain in solution. If Salts of Ni., Co. or Zn. are present, they will be precipitated as Ferrocyanides by the foregoing treatment.

**ALUMINUM.** In the absence of Chromium compounds, the hydroxide of Aluminum is best precipitated by boiling the neutral or slightly acid solution with excess of  $\text{Na}_2\text{S}_2\text{O}_3$ , when all the Aluminum is thrown down as  $\text{Al}_2(\text{HO})_6$  in form of a granular powder, rapidly subsiding, easily washed and entirely free from Zinc. This is the easiest and best way of separating Aluminum from all associated metals except Chromium.

Aluminum hydroxide is readily soluble in  $\text{KHO}$ . Addition of  $\text{NH}_4\text{Cl}$  in excess and heating to boiling WILL CAUSE PRECIPITATE of  $\text{Al}_2(\text{OH})_6$ .

The presence of organic acids and of some neutral compounds retards or prevents the precipitation of  $\text{Al}_2(\text{OH})_6$  by alkaline reagents.

$\text{NH}_4\text{HS}$ . precipitates salts of Al. as  $\text{Al}_2(\text{OH})_6$  and  $\text{H}_2\text{S}$ . is liberated.

$\text{Na}_2\text{CO}_3$  precipitates  $\text{Al}_2(\text{OH})_6$  and  $\text{CO}_2$  escapes.

$\text{Na}_2\text{HPO}_4$  precipitates  $\text{Al}_2(\text{PO}_4)_2$  insoluble in Acetic Acid.

If any compound of Aluminum (except Silicate) is intensely heated before the blow-pipe, moistened with Cobalt solution and again ignited, an INFUSIBLE MASS OF SKY-BLUE COLOR is produced. Decisive only with infusible bodies.

**CHROMIUM.** The salts of which Chromium is the base are precipitated in the form of  $\text{Cr}_2(\text{HO})_6$ —dingy violet green—by  $\text{NH}_4\text{HS}$ , and by  $\text{KHO}$ . soluble in excess of the latter FORMING A GREEN SOLUTION, precipitable by long boiling. The solution of Chromic-hydroxide in  $\text{KHO}$ . is speedily precipitated by boiling with  $\text{Na}_2\text{S}_2\text{O}_3$ .

Any compound of Chromium boiled in  $\text{HNO}_3$  with a few grains of  $\text{KClO}_3$  is soon oxidized to  $\text{H}_2\text{CrO}_4$ , and the color of the solution changes to

orange: if the acid be nearly neutralized with  $\text{NH}_4\text{HO}$ . and a few drops of solution of  $\text{PbNO}_3$  added, a YELLOW PRECIPITATE  $\text{PbCrO}_4$  will be thrown down.

If the solution be nearly neutralized by  $\text{NH}_4\text{HO}$ . and then acidified with Acetic Acid and solution of  $\text{BaCl}_2$  be added;  $\text{BaCrO}_4$ , yellow, insoluble in Acetic Acid, will be formed and subside after standing some time.

If any compound of Cr. is completely fused with  $\text{KNO}_3$  on Pt. foil, dissolved in water and neutralized with Acetic Acid, the addition of  $\text{AgNO}_3$  will form dark red  $\text{Ag}_2\text{CrO}_4$ . Soluble chlorides decompose  $\text{Ag}_2\text{CrO}_4$ , forming  $2\text{AgCl}$ . and  $\text{H}_2\text{CrO}_4$ .

Chromic salts give an EMERALD GREEN BEAD IN BOTH FLAMES with borax bead.

The acids of Chromium, in the presence of  $\text{HCl}$ ., are reduced to basic condition by  $\text{H}_2\text{S}$ . In the analysis of Chromates, the Chromium is usually reduced and detected as a basic substance. The salts in which Chromium is the base are usually violet or green in color, but the salts in which it acts as an acid are usually yellow or red. The great variety of colors gives the name Chromium—the color metal.

**DIVISION B.** Add to the filtrate from Division A.  $\text{NH}_4\text{HS}$ ., which will precipitate the remaining members of Group III as sulphides.

Division B. contains	{	$\text{CoS}$ .	}	black, insoluble in dilute $\text{HCl}$ .
		$\text{NiS}$ .		
		$\text{MnS}$ .—flesh-color,	}	Soluble in dilute $\text{HCl}$ .
		$\text{ZnS}$ .—dingy-white,		

Wash the precipitate on the filter with water, and then pour on it cold dilute  $\text{HCl}$ . and save the filtrate to test for Mn. and Zn. A black residue on the filter reserve for testing for Co. and Ni.

Digest the filtrate (or the clear solution if no black sulphides remain undissolved) with  $\text{KHO}$ . in excess; if a white precipitate (becoming brown by exposure to air), presence of Mn. Filter and dissolve the precipitate in  $\text{HCl}$ ., neutralize with  $\text{NH}_4\text{HO}$ ., and add  $\text{H}_2\text{S}$ . A FLESH-COLORED PRECIPITATE SHOWS Mn.

To the filtrate from  $\text{KHO}$ . add  $\text{H}_2\text{S}$ . or a few drops of  $\text{NH}_4\text{HS}$ . A WHITISH PRECIPITATE INSOLUBLE IN ACETIC ACID IS  $\text{ZnS}$ .

**MANGANESE.** The most characteristic reaction for Manganese is the FORMATION OF THE FLESH-COLORED  $\text{MnS}$ . by  $\text{NH}_4\text{HS}$ . or by  $\text{H}_2\text{S}$ . in an ammoniacal solution. The least trace of Salts of Iron, Nickel or Cobalt will conceal the color by the formation of Black Sulphides.

$\text{KHO}$ . precipitates  $\text{Mn}(\text{HO})_2$ —white, becoming brown by oxidation.

$\text{Na}_2\text{CO}_3$  precipitates white  $\text{MnCO}_3$ , becoming brown by oxidation.

$\text{K}_4\text{FeCy}_6$  precipitates pinkish  $\text{Mn}_2\text{FeCy}_6$ . Soluble in  $\text{HCl}$ .

If  $\text{Na}_2\text{HPO}_4$  and  $\text{NH}_4\text{HO}$  be added to a solution of a salt of Mn. and the mixture boiled, white, insoluble  $\text{MnNH}_4\text{PO}_4$  precipitates.

Any compound of Manganese, free from Chlorides, fused with  $\text{PbO}_2$  and  $\text{HNO}_3$  gives a PURPLE COLORED SOLUTION of Permanganic Acid, —  $\text{H}_2\text{Mn}_2\text{O}_8$ .

Any compound of Manganese fused with  $\text{KNO}_3$  and  $\text{Na}_2\text{CO}_3$  on Platinum foil forms a GREEN MASS (h.) and BLUISH GREEN (c.) of  $\text{K}_2\text{MnO}_4$ . Very delicate reaction, and but little of Manganese should be used.

Any compound of Mn. fused with  $\text{KHO}$ . and  $\text{KClO}_3$  on Pt. foil will give a purple mass of  $\text{K}_2\text{Mn}_2\text{O}_8$ . When this is dissolved in water it forms a purple solution.

Fused with a borax bead in O.Fl., Manganese gives a violet-colored bead; best observed when only a little Manganese is used.

ZINC. The salts of Zinc are precipitated as hydroxide by  $\text{NH}_4\text{HO}$ . readily soluble in excess. From this solution  $\text{H}_2\text{S}$ . PRECIPITATES THE DINGY WHITE  $\text{ZnS}$ ., insoluble in Acetic acid, soluble in  $\text{HCl}$ .

*Zinc is the only metal that forms a white sulphide.*

From neutral and from Acetic acid solutions of Zinc,  $\text{H}_2\text{S}$ . precipitates whitish  $\text{ZnS}$ .

From acid and alkaline salts alike  $\text{NH}_4\text{HS}$  precipitates white  $\text{ZnS}$ . completely.

$\text{Na}_2\text{CO}_3$  precipitates a white basic carbonate.

$\text{Na}_2\text{HPO}_4$  precipitates white  $\text{Zn}_3(\text{PO}_4)_2$ : soluble in  $\text{KHO}$ . and in  $\text{NH}_4\text{HO}$ . and in strong acids.

$\text{K}_4\text{FeCy}_6$  precipitates from solution of Zinc salts, white  $\text{Zn}_2\text{FeCy}_6$ ., insoluble in water and nearly insoluble in cold  $\text{HCl}$ .

If any compound of Zinc is treated with  $\text{Na}_2\text{CO}_3$  on charcoal in R.Fl. the charcoal will be COATED WITH INCRUSTATION, YELLOW (h.) WHITE (c.), without the formation of a metallic globule.

If  $\text{ZnO}$  is moistened with Cobalt solution and heated in O.Fl. A GREEN COLOR IS PRODUCED.

*Black Sulphides insoluble in dilute HCl.*—Examine some of the black sulphides insoluble in  $\text{HCl}$ . with a borax bead in blowpipe flame. A BLUE BEAD IN BOTH FLAMES shows the presence of Cobalt: A REDDISH BEAD IN O.Fl. BECOMING GRAY AND CLOUDED in R.Fl. shows presence of Nickel. The strong coloring property of Cobalt with borax may conceal the presence of Nickel.

Puncture the bottom of the filter with a glass rod and wash the black sulphides into a test tube. Add conc.  $\text{HCl}$ . and a small amount of  $\text{KClO}_3$  and dissolve with aid of heat; filter if necessary.

*Separation of Co. and Ni. when present as Chlorides.*—Add  $\text{Na}_2\text{HPO}_4$  in excess to the mixed Chlorides, then  $\text{HCl}$ . and boil for a few minutes: while still near boiling temperature, add  $\text{NH}_4\text{HO}$ . cautiously, till the precipitate at first thrown down is redissolved: then stir vigorously to promote

crystallization when  $\text{CoNH}_4\text{PO}_4$ , as fine purple crystals, will separate. The Ni. remaining in solution gives a blue color more or less intense according to the amount of Ni. present.

The Ni. can be separated as  $\text{NiS}$ . by adding  $\text{NH}_4\text{HS}$ .

**NICKEL.** Salts of Nickel have usually a fine green color. They are precipitated as  $\text{NiS}$ —black—by  $\text{NH}_4\text{HS}$ . the precipitate very sparingly soluble in  $\text{NH}_4\text{HS}$  *imparting a brown color to the filtrate.* They are precipitated as bluish green hydroxide  $\text{Ni(OH)}_2$  by  $\text{NH}_4\text{HO}$ . very soluble in excess and forming a violet blue solution.

Organic Acids, Sugar, etc., interfere with precipitation by alkalies.

$\text{K}_4\text{FeCy}_6$  precipitates greenish-white  $\text{Ni}_2\text{FeCy}_6$ , insoluble in  $\text{HCl}$ ., soluble in  $\text{NH}_4\text{HO}$ .

$(\text{NH}_4)_2\text{C}_2\text{O}_4$  precipitates very slowly, but almost completely in 24 hours, the green  $\text{NiC}_2\text{O}_4$ .

Salts of Ni. are precipitated by  $\text{KCy}$ ,  $\text{Ni(Cy)}_2$ , soluble in excess of  $\text{KCy}$ . When this solution is boiled with  $\text{NaClO}$ . a BLACK PRECIPITATE forms,  $\text{Ni(OH)}_2$ . Delicate and decisive reaction.

$\text{KHO}$ . precipitates light-green  $\text{Ni(OH)}_2$  insoluble in excess; very soluble in  $\text{NH}_4\text{HO}$ . (In presence of salts of ammonia,  $\text{KHO}$ . readily sets free  $\text{NH}_4\text{HO}$ .)

$\text{Na}_2\text{HPO}_4$  precipitates greenish-white  $\text{Ni}_3(\text{PO}_4)_2$ , soluble in  $\text{HCl}$ . and  $\text{NH}_4\text{HO}$ .

**COBALT.** The hydrated salts of Co. are usually rose colored; the anhydrous salts, blue.

$\text{KHO}$  precipitates blue basic salt, and in excess  $\text{Co(OH)}_2$ , insoluble in excess of  $\text{KHO}$ ., but soluble in  $\text{NH}_4\text{HO}$ .

$\text{NH}_4\text{HS}$ . precipitates black  $\text{NiS}$ . insoluble in dilute  $\text{HCl}$ ., but readily soluble in aqua regia.

$\text{Na}_2\text{HPO}_4$  precipitates rose colored  $\text{CoHPO}_4$ , soluble in  $\text{NH}_4\text{HO}$ . and in  $\text{HCl}$ .

From concentrated solutions  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . precipitates pinkish  $\text{CoC}_2\text{O}_4$ , soluble in  $\text{NH}_4\text{HO}$ . and in acids.

$\text{K}_4\text{FeCy}_6$  precipitates greenish  $\text{Co}_2\text{FeCy}_6$  insoluble in  $\text{HCl}$ . To  $\text{Co(NO}_3)_2$  add Tartaric Acid, then  $\text{NH}_4\text{HO}$ . in excess, then a few drops of  $\text{K}_3\text{FeCy}_6$ , a deep red color will appear.

Bead of Borax with any compound of Cobalt GIVES A BLUE BEAD IN BOTH BLOWPIPE FLAMES. This is the most characteristic test of Co. and most easily applied. If much Co. is used, the color is best seen by drawing the bead out into a thread.

## TABLE XII.

## ANALYSIS OF GROUP IV.

Substances not precipitated by  $\text{NH}_4\text{HS}$ , but completely precipitated by  $(\text{NH}_4)_2\text{CO}_3$  in the presence of  $\text{NH}_4\text{Cl}$ .

Boil the filtrate from  $\text{NH}_4\text{HS}$ . to decompose that salt, and to the clear solution add  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HO}$ , and  $(\text{NH}_4)_2\text{CO}_3$ . to complete precipitation of the members of Group IV.

The precipitate may contain :

$\left. \begin{array}{l} \text{BaCO}_3. \\ \text{SrCO}_3. \\ \text{CaCO}_3. \end{array} \right\}$	White, soluble with effervescence in Acetic Acid.
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Wash the precipitate and dissolve in Acetic Acid.

To a small portion of this solution add a few drops of  $\text{K}_2\text{Cr}_2\text{O}_7$ ; if a **YELLOW PRECIPITATE FORMS** it shows the presence of Barium. In such case filter off  $\text{BaCrO}_4$ . and divide the filtrate into two parts: to one add its own volume of solution of  $\text{CaSO}_4$ . and shake the mixture thoroughly and repeatedly to promote precipitation.

If no precipitate forms set the tube aside for ten minutes: a **WHITE PRECIPITATE** shows presence of Strontium. If no precipitate forms at the end of ten minutes, **ABSENCE OF STRONTIUM**.

If Strontium is absent, add to the other portion of the solution  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ : a **WHITE PRECIPITATE** insoluble in Acetic acid but soluble in  $\text{HCl}$ . shows presence of Calcium. But if Strontium is present, first add  $\text{K}_2\text{SO}_4$  to the other part of the filtrate, boil for a few minutes, filter, and add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . to the clear filtrate; if a precipitate now forms, Calcium is present; if no precipitate, Calcium is absent.

**BARIUM.** From Salts of Barium  $\text{H}_2\text{SO}_4$  and soluble sulphates **THROW DOWN A WHITE, HEAVY PRECIPITATE INSOLUBLE IN WATER AND IN  $\text{HCl}$ ;**  $\text{BaSO}_4$ .

From  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ . precipitates  $\text{BaCrO}_4$ . **YELLOW SALT INSOLUBLE IN  $\text{HC}_2\text{H}_3\text{O}_2$ .**

$\text{H}_2\text{SiF}_6$ . precipitates  $\text{BaSiF}_6$ . as a **WHITE CRYSTALLINE PRECIPITATE** (distinction from Strontium and Calcium).

Solution of  $\text{CaSO}_4$  precipitates the salts of Barium *instantly*—of Strontium *only after an interval*—and of Calcium *not at all*.

$\text{BaCl}_2$  **COLORES THE GAS-FRAME YELLOW GREEN.\***

**STRONTIUM.** Concentrated solution of a salt of Strontium is precipitated by  $\text{H}_2\text{SO}_4$ ,  $\text{SrSO}_4$ —white—soluble in 5,000 parts of water. Solution of  $\text{CaSO}_4$  **GIVES A TARDY PRECIPITATE** with salts of Strontium.

\* Use the spectroscope to distinguish these several colored flames.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$  forms a white precipitate insoluble in Acetic Acid.

The Nitrate and Chloride of Strontium COLOR THE GAS FLAME DEEP RED: VIEWED THROUGH BLUE GLASS THE COLOR IS ROSE-RED.\*

$\text{H}_2\text{SiF}_6$  does not precipitate Sr.— $\text{K}_2\text{Cr}_2\text{O}_7$  does not precipitate Sr. These two tests distinguish Ba. from Sr. and Ca.

**CALCIUM.** In concentrated solutions of salts of Calcium,  $\text{H}_2\text{SO}_4$  and alkaline Sulphates precipitate  $\text{CaSO}_4$ , soluble in 400 parts of water. Solution of  $\text{CaSO}_4$  of course will give no precipitate with salts of Calcium.

In absence of salts of Barium and Strontium, the most delicate test for salts of Calcium is  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , which throws down a WHITE PRECIPITATE, INSOLUBLE IN ACETIC BUT SOLUBLE IN HYDROCHLORIC ACID. This Oxalate of Calcium requires 200,000 parts of water to dissolve it.

Nitrate and Chloride of Calcium COLOR THE GAS FLAME ORANGE-RED\*—often mistaken for the crimson color of Strontium, but when viewed through blue glass the color is faint green-gray.

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\* Use the spectroscope to distinguish these several colored flames.



## TABLE XIII.

## ANALYSIS OF GROUP V.

Substances not Precipitated by Group Reagents.

This group includes

Potassium.	} Alkali Metals.
Sodium.	
Ammonium.	
Magnesium.	

Divide the filtrate from which  $(\text{NH}_4)_2\text{CO}_3$  will not produce a precipitate, into two parts: to one add  $\text{Na}_2\text{HPO}_4$  and shake thoroughly. If no precipitate forms, rub the inside of the test tube with a glass rod and set aside the test tube for a few hours. A WHITE CRYSTALLINE PRECIPITATE SHOWS THE PRESENCE OF MAGNESIUM. In very dilute solutions the precipitate forms only after the lapse of several hours.

Evaporate the other part of the filtrate to dryness and heat red hot on Platinum foil to expel all salts of Ammonium. If a solid residue, dissolve in a few drops of water, moisten a clean Platinum wire in this solution and place it in the gas flame: A PURPLE COLOR OF THE FLAME INDICATES POTASSIUM: A BRILLIANT YELLOW, SODIUM. Use the spectroscope to distinguish these colored flames.

**MAGNESIUM.** The salts of Magnesium do not color the flame.

The WHITE CRYSTALLINE PRECIPITATE formed by  $\text{Na}_2\text{HPO}_4$  in presence of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$  is most characteristic of Magnesium.

The Sulphate of Magnesium is very soluble in water, which distinguishes this metal from those of the Alkaline Earths.

If any compound of Magnesium be heated to redness on charcoal, then moistened with solution of Cobalt, and again heated, at first gently, and then intensely in O.Fl. A PINKISH MASS IS OBTAINED. Alkalies and Alkaline Earths prevent this reaction.

$\text{KHO}$  precipitates Magnesium hydroxide,  $\text{Mg}(\text{HO})_2$  from salts of Magnesium.  $\text{NH}_4\text{Cl}$  prevents this reaction.

Alkaline Carbonates precipitate basic Carbonates in absence of  $\text{NH}_4\text{Cl}$ .

**POTASSIUM.** The most characteristic test of Potassium is the VIOLET COLORED FLAME—best seen with the Chloride. If Sodium is present the intense color of this yellow flame obscures the feebler color of the Potassium flame, but by the use of the blue Cobalt glass the yellow rays are intercepted, and then the characteristic color of the Potassium flame can be observed.

Tartaric Acid added in excess to a concentrated Potassium salt will form a WHITE CRYSTALLINE PRECIPITATE— $\text{KHC}_4\text{H}_4\text{O}_6$ . Ammonium forms a similar salt.  $\text{PtCl}_4$  added to  $\text{KCl}$  forms a A YELLOW CRYSTALLINE PRECIPITATE  $\text{K}_2\text{PtCl}_6$ . The crystals under the microscope are seen to be octohedrons, or 8 faced crystals.

To secure this reaction place a drop of the condensed solution on a glass slide, acidify with a drop of Conc.  $\text{HCl}$ ., add a drop of  $\text{PtCl}_4$ ., and stir the mixture with a glass rod, rubbing the glass surface to make lines. The  $\text{K}_2\text{PtCl}_6$  will form in crystals along these lines if  $\text{K}$ . is present. Insoluble in alcohol.

Ammonia forms a similar precipitate with Platinic Chloride.

The tests by precipitation for Potassium, therefore, are decisive only after all the compounds of Ammonium have been expelled by heating the residue red hot.

**SODIUM.** There is no satisfactory precipitant for salts of Sodium. The BRILLIANT YELLOW FLAME REACTION is most satisfactory, and is relied on for the detection of the compounds of Sodium.

**AMMONIUM.** The Salts of Ammonium having been freely used as reagents in the separation of the Groups, and the salts thus employed all appearing in the successive filtrates, their presence in the final filtrate is no proof that they existed in the original solution. For these reasons *the original solution must be tested for this substance.*

Any salt of Ammonium boiled with  $\text{KHO}$  WILL GIVE OFF GASEOUS AMMONIA,  $\text{NH}_3$ . *readily recognized by its odor, by its alkaline action on red litmus paper, and by forming white fumes when a rod moistened with Conc.  $\text{HCl}$ . is held near the escaping gas.*

If any salt of Ammonium (in the absence of Sulphides and Cyanides) be added to Nessler's Test,\* A BROWN PRECIPITATE,  $\text{NH}_2\text{HgCl}$ ., will form, or if the quantity is very small, a brown coloration in the liquid. Very sensitive test.

If  $\text{NH}_4\text{HO}$ . or  $(\text{NH}_4)_2\text{CO}_3$  is added to solution of  $\text{HgCl}_2$ . "WHITE PRECIPITATE" of  $\text{NH}_2\text{HgCl}$ . will form (Bohlig's Test). This test is extremely delicate, and will often serve to detect the presence of Ammonia in rain water and other natural waters.

If Ammonium is in too small amount to be detected by these tests, it may yet be found by distilling the water with  $\text{KHO}$ . and testing the distillate.

Nessler's Test is prepared as follows :

To a solution of  $\text{HgCl}_2$ . add solution of  $\text{KI}$ . till the scarlet precipitate— $\text{HgI}_2$ .—at first formed, is *nearly* all redissolved ; then add  $\text{KHO}$ : let the

\* As the preparation of this test requires care and time, the student will not prepare it for himself, but will find it ready for use among the select reagents. Only a few drops are necessary to test for Ammonium, and excess of the reagent will not produce better results.

mixture stand till all sediment subsides, then pour off the clear liquid for Nessler's Test.

In using the Nessler Test, the *original solution*, or the material to which no ammonia compound has been added as reagent, must be employed. Since the Test is very strongly alkaline the student must be on his guard against precipitation of colored oxides such as  $\text{Fe}_2(\text{OH})_6$ . It is a good practice to add a few drops of  $\text{KHO}$ . and then apply the Nessler Test to the clear liquid to detect ammonia.

TABLE XIV.—SOLUBILITIES

A=soluble in water; a=sparingly soluble in water; B=insoluble in water; C=insoluble in water and acids; BC=soluble in part, but precipitated by a large quantity of water, precipitation prevented by acids; C=insoluble in water and acids; BC=soluble in part, but

SALTS.	ACIDS.	K <sub>2</sub> O.	NH <sub>3</sub> O.	(NH <sub>4</sub> ) <sub>2</sub> O.	BaO.	SiO.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub>	MnO.	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	CuO.	CoO.
Hydrate.....	H(HO).	A	A	A	A	a	a	B	B	B	B	B	B	B
Sulphide.....	H <sub>2</sub> S.	A	A	A	A	A	A	aB		B	B		B	B
Chloride.....	HCl.	A	A	A	A	A	A	A	A	A	A	A	A	A
Iodide.....	HI.	A	A	A	A	A	A	A	A	A	A	A	A	A
Bromide.....	HBr.	A	A	A	A	A	A	A	A	A	A	A	A	A
Cyanide.....	HCy.	A	A	A	a	A	A	A		B	A		B	B
Ferrocyanide.....	H <sub>4</sub> FeCy <sub>6</sub> .	A	A	A	a	A	A	A	B	B	C	C	C	BC
Ferricyanide.....	H <sub>3</sub> FeCy <sub>6</sub> .	A	A	A	A		A	A		C	C	A	C	C
Fluoride.....	HF.	A	A	A	B	B	B	B	B	B			B	a
Silicate.....	H <sub>2</sub> SiO <sub>3</sub> .	A	A		BC	BC	BC	C	B	B	B	B	B	
Fluo Silicate.....	H <sub>2</sub> SiF <sub>6</sub> .	a	A		C	A	aB	A		A	A	A		aB
Sulphate.....	H <sub>2</sub> SO <sub>4</sub> .	A	A	A	C	C	aC	A	A	A	A	A	A	A
Sulphite.....	H <sub>2</sub> SO <sub>3</sub> .	A	A	A	B	aB	aB	aB	A	a	A	A	A	B
Nitrate.....	HNO <sub>3</sub> .	A	A	A	A	A	A	A	A	A	A	A	A	A
Chlorate.....	HClO <sub>3</sub> .	A	A	A	A	A	A	A	A	A	A	A	A	A
Phosphate.....	H <sub>3</sub> PO <sub>4</sub> .	A	A	A	B	B	B	B	B	B	B	B	B	B
Arsenite.....	H <sub>3</sub> AsO <sub>3</sub> .	A	A	A	a	a	B	B		B	B	B	B	B
Arseniate.....	H <sub>3</sub> AsO <sub>5</sub> .	A	A	A	B	B	B	B	B	B	B	B	B	B
Chromate.....	H <sub>2</sub> CrO <sub>4</sub> .	A	A	A	B	a	a	A		A		A	A	B
Acetate.....	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .	A	A	A	A	A	A	A	A	A	A	A	A	A
Tartrate.....	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .	A	A	A	B	B	B	a	A	aB		AB	B	A
Oxalate.....	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	A	A	A	B	B	B	a	B	a	B	B	B	B
Borate.....	H <sub>3</sub> BO <sub>3</sub> .	A	A	A	B	B	B	a	B	B	B	B	B	B
Carbonate.....	H <sub>2</sub> CO <sub>3</sub> .	A	A	A	B	B	B	B		B	B		B	B

## OF NORMAL SALTS.

water—soluble in acids; AB—soluble in small amount of water, but presence of free acid; aB—sparingly soluble in water—solubility increased not completely by acids.

NiO.	ZnO.	CdO.	PbO.	Ag <sub>2</sub> O.	Hg <sub>2</sub> O.	HgO.	ZnO.	SnO <sub>2</sub> .	Bi <sub>2</sub> O <sub>3</sub> .	PtO <sub>2</sub> .	Sb <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	SALTS.	ACIDS.
B	B	B	B	B	B	B	B	BC	B	B	B	BC	Hydrate.....	H(HO).
B	B	B	B	B	B	B	B	B	B	B	B	...	Sulphide.....	H <sub>2</sub> S.
A	A	A	a	C	B	A	A	A	AB	A	A	A	Chloride.....	HCl.
A	A	A	B	C	B	B	A	A	A	A	AB	A	Iodide.....	HI.
A	A	A	C	C	B	A	A	A	AB	A	AB	A	Bromide.....	HBr.
B	B	aB	B	B	..	A	..	..	..	A	..	B	Cyanide.....	HCy.
C	C	B	B	C	C	B	C	C	C	..	..	..	Ferrocyanide....	H <sub>4</sub> FeCy <sub>6</sub> .
C	B	B	a	C	..	..	C	..	..	..	..	..	Ferricyanide....	H <sub>3</sub> FeCy <sub>6</sub> .
a	a	a	aB	A	B	aB	A	A	A	..	A	A	Fluoride.....	HF.
..	B	B	B	..	..	..	..	..	..	..	..	..	Silicate.....	H <sub>2</sub> SiO <sub>3</sub> .
A	A	A	A	A	B	A	..	A	..	..	..	..	Fluo Silicate....	H <sub>2</sub> SiF <sub>6</sub> .
A	A	A	C	a	a	A	A	..	A	..	..	A	Sulphate.....	H <sub>2</sub> SO <sub>4</sub> .
B	a	aB	B	a	..	A	A	..	B	A	a	a	Sulphite.....	H <sub>2</sub> SO <sub>3</sub> .
A	A	A	A	A	AB	A	..	A	AB	A	AB	A	Nitrate.....	HNO <sub>3</sub> .
A	A	A	A	A	A	B	A	A	A	A	A	A	Chlorate.....	HClO <sub>3</sub> .
B	B	B	B	B	B	B	B	B	B	..	a	B	Phosphate.....	H <sub>3</sub> PO <sub>4</sub> .
B	..	..	B	B	B	B	..	..	..	..	B	..	Arsenite.....	H <sub>3</sub> AsO <sub>3</sub> .
B	B	..	B	B	B	a	..	B	B	..	B	B	Arseniate.....	H <sub>3</sub> AsO <sub>4</sub> .
B	A	B	B	B	B	A	B	..	B	..	B	B	Chromate.....	H <sub>2</sub> CrO <sub>4</sub> .
A	A	A	A	A	A	B	A	A	A	..	..	A	Acetate.....	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .
B	B	a	B	B	B	B	a	..	B	..	..	A	Tartrate.....	H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .
B	B	B	B	B	B	B	B	A	B	..	B	A	Oxalate.....	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .
B	B	a	B	B	..	..	B	..	B	..	..	B	Borate.....	H <sub>3</sub> BO <sub>3</sub> .
B	B	B	B	B	B	B	..	..	B	..	..	..	Carbonate.....	H <sub>2</sub> CO <sub>3</sub> .

## ANALYSIS OF ACIDS.

After the bases have been identified, the next step in analysis is to identify the acids. In this investigation great assistance may be derived in regard to the probable presence or absence of many of the acids by consulting Table XIV of Solubilities. For example, if we have found Barium in a soluble compound, or a compound soluble in HCl., there is no need of seeking for  $H_2SO_4$ , because  $BaSO_4$  is insoluble in water and acids. In a solution of Silver there is no use of seeking for HCl, HBr, HI,  $H_2S$ ,  $H_4FeCy_6$ , or  $H_3FeCy_5$ , because the Silver salts with these Acids are all insoluble. On the other hand, the Nitrate and Acetate of Silver are soluble, and Silver may therefore be present in the form of Nitrate or Acetate.

Again, if a lime salt is but sparingly soluble in water, and its solubility sensibly increased by HCl. the Table shows this is characteristic of the Sulphate.

The Acid combinations of Arsenic, Antimony, Manganese and Chromium will have been detected in the examination for bases; the acid combinations of these metals will not, on this account, be fully treated in speaking of the Analysis of Acids.

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## PRELIMINARY EXAMINATION OF THE SOLID SUBSTANCE FOR ACIDS.

### Successive Steps in Preliminary Examination.

1st. Heat some of the dry substance red hot on Platinum foil: Chars and forms combustible vapors, organic substance. The organic acids present may be Acetic, Tartaric, Citric, etc., Hydroferrocyanic, Hydroferricyanic, (and Cyanides of heavy metals).

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2d. Place some of the substance on charcoal and heat in O.Fl:

Deflagration ensues; presence of Chlorates, Chromates, Manganates, Nitrates, or Permanganates. Should this reaction (deflagration) take place, the treatment under 4th step must be omitted to avoid explosions likely to occur with chlorates.

3d. Place some of the substance in a test tube, overflow it with twice its volume of dilute  $H_2SO_4$ , and if no change ensue, heat to boiling.

Effervescence liberating,	}	Carbonic.— $CO_2$ —Odorless—turns lime water turbid, forming $CaCO_3$ .
		Sulphurous.— $SO_2$ —Odor of burning sulphur, bleaches litmus paper.
		Hyposulphurous. $SO_2$ and $H_2S$ } Odor of burning sulphur and rotten eggs, bleaches litmus paper; Sulphur separates in solution.
		Hydrosulphuric.— $H_2S$ .—Odor of rotten eggs. } Blackens lead paper.

No change taking place in the cold, the tube is heated to boiling and any volatile acid expelled.

These acids may be,	}	Hydrocyanic.—Detected by characteristic odor of a bruised peach leaf.
		Acetic.—Detected by odor of vinegar.
		Hydrochloric. } Detected by white fumes, formed Nitric. } by holding glass rod moistened Hydriodic. } with $NH_4HO$ at the mouth of the Hydrobromic. } tube. (The first two fume strongly, the last two slightly.)

4th. The finely powdered substance is mixed with half its volume of  $MnO_2$ , placed in a test tube, overflowed with Conc.  $H_2SO_4$  and heated to a temperature less than the boiling point of the Sulphuric Acid.

Hydrobromic: brown vapor of Bromine.

Hydriodic: violet vapor of Iodine.

Hydrochloric: yellow-green gas, Chlorine. This gas poured into another tube containing water, agitated—a drop of  $AgNO_3$  produces curdy white precipitate,  $AgCl$ .—bleaches solution of Indigo.

Hypochlorous: yellowish gas,  $Cl_2O$ ; bleaches Indigo solution.

Hydrofluoric: white fumes; etches glass; does not precipitate  $AgNO_3$ .

Nitric. } Orange-red fumes evolved.  
Nitrous. }

Oxalic: colorless gas escapes ( $CO_2$ ) with effervescence. Test with lime water.

If, in this preliminary examination, evidence is obtained of the presence of certain acids, the special tests for these acids (given in the succeeding pages) may be at once applied, without resorting to the use of Group-Reagents for the classification of acids. But in the absence of any such special indications, the Group-Reagents must be employed for the separation and identification of the acids.

## SEPARATION AND CLASSIFICATION OF ACIDS.

The substance for analysis being in solution (thus preventing the use of the preliminary examination for acids), or the preliminary examination failing to show any indications of the acids present, the analysis for acids is commenced by a separation into groups, in a manner similar to the separation of bases.

In the analysis of the bases, certain acids and salts have been used as Group Reagents, and their presence in the final filtrate from the fifth group of bases would be no proof that they existed in the original substance or solution. In the analysis of acids, therefore, *the original substance must be employed*. It is also apparent that where HCl, HNO<sub>3</sub>, etc., have been used to dissolve the substance for analysis, their presence must be borne in mind in testing for the acids.

The acids cannot be separated into groups with the precision with which we separate bases; yet the detection and identification of acids are greatly facilitated by proper grouping. The presence of bases of the I., II., III. and IV. Groups may interfere with the reactions of the Acid Group Reagents. It is often desirable to separate these bases before making analysis of the acids, especially if several acids are present. These bases may be separated by boiling the solution with Na<sub>2</sub>CO<sub>3</sub> in excess, filtering off the separated bases, and adding to the filtrate just enough HNO<sub>3</sub> to make it neutral, and boiling the solution to expel CO<sub>2</sub>; the acids will then be present in the form of Salts of Sodium.

It must be borne in mind that by this method of treatment CO<sub>2</sub> has been removed and HNO<sub>3</sub> has been added. *The original substance*, therefore, must be tested for the presence of these acids and not the solutions prepared as indicated in the preceding paragraph.

## CLASSIFICATION OF ACIDS.

In the analysis of Acids we employ *Group-Reagents* (as with bases) to classify them, and *Special Reagents* to identify the individual acids. The Group-Reagents are BaCl<sub>2</sub>, CaCl<sub>2</sub>, AgNO<sub>3</sub>, and Fe<sub>2</sub>Cl<sub>6</sub>.

## GROUP A.

Add to the neutral Solution BaCl<sub>2</sub> to complete precipitation: if no precipitate forms, all the following acids are absent; if a precipitate forms, any of the following acids may be present:

## Precipitate.

a.	}	Chromate of Barium—yellow	} Soluble in HCl.
		Carbonate " " —white	
		Phosphate " " "	
		Sulphite " " "	
		Oxalate " " "	
b.	}	Sulphate of Barium—white	} Insoluble in HCl.
		Fluosilicate " " "	



In the absence of salts of Ammonium, the precipitate may be :

Arsenate Arsenite Borate Tartrate	}	of Barium—white. Soluble in HCl.
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If a precipitate forms, add HCl. If it does not all dissolve, filter. The insoluble precipitate shows the presence of Sulphuric or Fluosilicic acid. Add to the filtrate  $\text{NH}_4\text{HO}$  to alkalinity, if a precipitate forms, any or all the acids in subdivision a. may be present. Should the precipitate when treated with  $\text{HNO}_3$ , effervesce, the escaping gas odorless, the presence of Carbonic acid would be indicated.

### GROUP B.

Add to the original (neutral) solution  $\text{CaCl}_2$  to complete precipitation. White precipitate, shows presence of

a.	{	Sulphate Sulphite Carbonate Phosphate Oxalate Fluoride Silicate	}	Insoluble in $\text{NH}_4\text{Cl}$ .
b.	{	Borate Tartrate	}	Soluble in $\text{NH}_4\text{Cl}$ .

If a precipitate forms add  $\text{NH}_4\text{Cl}$ ; if it does not all dissolve, filter, and add to insoluble residue (a.) Acetic acid :

*Dissolved.*

Carbonate (effervescence).  
 Phosphate.  
 Sulphite.

*Undissolved.*

Sulphate } White and pulverulent.  
 Oxalate }  
 Fluoride, gelatinous.

### GROUP C.

Add to the original solution  $\text{AgNO}_3$ .

If no precipitate forms, all the following salts are absent; if precipitate forms, the color may give a useful hint:

Precipitate WHITE:	{	Bromide. Chloride. Cyanide. Carbonate. Sulphocyanide. Oxalate. Acid Borates. Iodide (yellowish white). Ferrocyanide (yellowish white).
Precipitate YELLOW:	{	Phosphate. Arsenite.
Precipitate RED:	{	Chromate. Arsenate. Ferricyanide—brown.
Precipitate BLACK:	{	Sulphide. Sulphite (dirty brown).

Neutral Borates, brown; blackens on heating.

If the precipitate is white or yellowish white, boil it with dilute  $\text{HNO}_3$ . A residue will show the presence of a Chloride, Bromide, Iodide, Cyanide or Sulphocyanide. Allow the residue to subside, pour off the  $\text{HNO}_3$ , and add  $\text{NH}_4\text{HO}$  to the residue. The Chloride and Cyanide will dissolve readily; the Bromide, Sulphocyanide and Ferrocyanide will dissolve with difficulty; and the Iodide almost entirely insoluble.

If the precipitate is yellowish white, and changed to brown by boiling in  $\text{HNO}_3$ , the brown salt soluble in  $\text{NH}_4\text{HO}$ , a Ferrocyanide is present (changed to Ferricyanide by boiling with  $\text{HNO}_3$ ).

#### GROUP D.

Add to the original solution  $\text{Fe}_2\text{Cl}_6$ .

Precipitate deep blue, Ferrocyanide.

Precipitate yellowish white, insoluble in Acetic Acid, Phosphate.

Brown coloration, no precipitate, Ferricyanide.

Blood-red coloration not changed by  $\text{HCl}$ , bleached at once by  $\text{HgCl}_2$ , Sulphocyanide.

Blood-red coloration, disappearing rapidly on addition of  $\text{HCl}$  and boiling—Sulphite.

Brownish-red color, quickly destroyed by  $\text{HCl}$ , Acetate.

It will be observed that many acids appear in the precipitates of two or more groups, and it would at first seem to be impossible to separate out and recognize the various acids under these circumstances. But if the analyst will carefully compare the precipitates obtained by the four operations under Groups A, B, C and D, he will, at the end of such comparative study, have a reasonable clue by which he may proceed to apply Special Reagents for the various precipitable Acids.

Consult also Table XIV, under the headings  $\text{BaO}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Ag}_2\text{O}$ , for useful hints in regard to acids probably present.

## SPECIAL REACTIONS WITH THE ACIDS PRECIPITATED By $\text{BaCl}_2$ and by $\text{CaCl}_2$ .

### GROUPS A. AND B. OF ACIDS.

**ARSENIOUS AND ARSENIC:** These acids are separated and identified in analysis of the bases.

**ARSENIOUS ACID,  $\text{H}_3\text{AsO}_3$ :** Precipitates  $\text{Ca}(\text{OH})_2$  as white  $\text{Ca}_3(\text{AsO}_3)_2$ , soluble in  $\text{NH}_4\text{Cl}$  and in  $\text{HCl}$ . Precipitates *yellow*  $\text{Ag}_3\text{AsO}_3$ , soluble in  $\text{NH}_4\text{HO}$  and in  $\text{HNO}_3$ . This precipitate is best secured by using \*Ammonio-Nitrate of Silver. \*Precipitates from Ammonio-Sulphate of Copper *green*,  $\text{CuHAsO}_3$ . "Scheele's Green."—Soluble in  $\text{NH}_4\text{HO}$  and in  $\text{HNO}_3$ .

**ARSENIC ACID,  $\text{H}_3\text{AsO}_4$ :** Precipitates *brick-red*  $\text{Ag}_3\text{AsO}_4$  from Ammonio-Nitrate of Silver. Soluble in  $\text{NH}_4\text{HO}$  and in  $\text{HNO}_3$ . Precipitates *greenish-blue*,  $\text{CuHAsO}_4$ , from the Ammonio-Sulphate of Copper. Soluble in  $\text{NH}_4\text{HO}$  and in  $\text{HNO}_3$ . Forms a *yellow precipitate* with excess of Molybdate of Ammonia dissolved in  $\text{HNO}_3$ . Insoluble in  $\text{HNO}_3$ ; soluble in  $\text{NH}_4\text{HO}$ .

**BORIC:** If  $\text{HCl}$  is added to a Borate and Turmeric paper be moistened with this solution, THE PAPER ON DRYING IS STAINED BROWNISH-RED. If conc.  $\text{H}_2\text{SO}_4$  is added to a Borate, alcohol poured on this in a watch glass and the mixture ignited, the flame is tinged yellowish green. Addition of  $\text{CaF}_2$ , so as to form the volatile  $\text{BF}_3$ , will increase the intensity of color of flame. Mix a Borate with  $\text{CaF}_2$  and moisten with conc.  $\text{H}_2\text{SO}_4$ . On a loop of Pt. wire place a little of this in colorless gas flame and look for *green flame*. Acid Borates form a *white* precipitate of  $\text{Ag}_2\text{BO}_3$  with  $\text{AgNO}_3$ . Neutral Borates form *brown* oxide of Silver, becoming black on boiling.

**CHROMIC ACID,  $\text{H}_2\text{CrO}_4$ :** Chromic acid is often reduced to an oxide and separated as a base in analysis, because reducing agents, e. g.,  $\text{H}_2\text{S}$ , and  $\text{NH}_4\text{HS}$ , reduce Chromic acid to Chromic oxide. The normal Chromates are yellow, and the acid Chromates are red. The Bichromate of Potassium in the solid form has the composition  $\text{K}_2\text{Cr}_2\text{O}_7$ , or  $\text{K}_2\text{CrO}_4 + \text{CrO}_3$ . In the solution it may be considered as combining with  $\text{H}_2\text{O}$  and forming  $\text{KHCrO}_4$ . Thus  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{KHCrO}_4$ . The reactions are most easily written out with this formula for acid Chromates. Chromates precipitate *yellow*  $\text{PbCrO}_4$  from lead salts.

\*Ammonio-Nitrate of Silver is prepared by precipitating  $\text{AgNO}_3$  by a little  $\text{NH}_4\text{HO}$ , and continuously adding  $\text{NH}_4\text{HO}$ , till the precipitate of  $\text{Ag}_2\text{O}$  nearly dissolves. The solution is the reagent desired. The Ammonio-Sulphate of Copper is prepared in the same way with  $\text{CuSO}_4$ .

The precipitation is promoted by  $\text{HNO}_3$ . With  $\text{Hg}_2(\text{NO}_3)_2$  Chromates precipitate *dark red*  $\text{Hg}_2\text{CrO}_4$ .  $\text{K}_2\text{Cr}_2\text{O}_7$  precipitates  $\text{BaCl}_2$  as *yellow*  $\text{BaCrO}_4$ . If any Chromate is boiled with conc.  $\text{HCl}$ . and Alcohol,  $\text{Cr}_2\text{Cl}_6$  will be formed, coloring the solution intense green. Any Chromate heated with conc.  $\text{H}_2\text{SO}_4$  and  $\text{NaCl}$ . in a test tube evolves red vapor of Chromyl Chloride,  $\text{CrO}_2\text{Cl}_2$ .

**CARBONIC,  $\text{H}_2\text{CO}_3$ :** Carbonates are decomposed by dilute  $\text{HCl}$ . the decomposition attended by a **BRISK EFFERVESCENCE** of  $\text{CO}_2$ , colorless and odorless. When this gas is poured into a clean test tube, a little Lime water added and shaken up, a white precipitate forms,  $\text{CaCO}_3$ —. Solutions of Carbonates precipitate  $\text{CaCl}_2$  forming  $\text{CaCO}_3$ , readily soluble in dilute  $\text{HCl}$ . with effervescence.

**HYDROFLUORIC,  $\text{HF}$ :** The most characteristic reaction of this acid is its power to etch glass. If a finely powdered Fluoride is made into a paste with conc.  $\text{H}_2\text{SO}_4$  in a lead crucible, the crucible covered with a piece of glass coated with beeswax, in which lines have been traced with a sharp point of wood, laying bare portions of the glass surface, and the crucible gently warmed for an hour, upon removing the wax by scraping and washing with turpentine, the exposed lines will be found **ETCHED INTO THE GLASS**. If the quantity of Fluoride was small the etching may be invisible, but will appear by breathing on the glass. If a powdered Fluoride mixed with powdered Silica be placed in a dry test tube, overflowed with conc.  $\text{H}_2\text{SO}_4$  and gently heated, dense white fumes of Hydrofluosilic acid will escape into the air.

**OXALIC ACID,  $\text{H}_2\text{C}_2\text{O}_4$ :** Precipitates  $\text{CaCl}_2$  as *white*  $\text{CaC}_2\text{O}_4$ , insoluble in Acetic Acid, soluble in  $\text{HCl}$ . Precipitates  $\text{AgNO}_3$  as white  $\text{Ag}_2\text{C}_2\text{O}_4$ , insoluble in dilute  $\text{HNO}_3$ , soluble in  $\text{NH}_4\text{HO}$ . The dry salt explodes when heated,  $\text{Ag}_2\text{C}_2\text{O}_4 = 2\text{Ag} + 2\text{CO}_2$ . Heated with  $\text{MnO}_2$  and dilute  $\text{H}_2\text{SO}_4$ , a brisk effervescence from escape of  $\text{CO}_2$ . Oxalates of the alkalies and alkaline earths are converted into carbonates on ignition.

**PHOSPHORIC ACID,  $\text{H}_3\text{PO}_4$ :** Precipitates *yellow*  $\text{Ag}_3\text{PO}_4$ . (distinction from  $\text{H}_2\text{AsO}_4$ , brick-red). Precipitates  $\text{Ca}_3(\text{PO}_4)_2$ , soluble in Acetic Acid when freshly precipitated. Precipitates  $\text{Mg}$ . in presence of  $\text{NH}_4\text{Cl} + \text{NH}_4\text{HO}$ . as  $\text{MgNH}_4\text{PO}_4$ , a white crystalline precipitate; in very dilute solutions, only after a time, promoted by shaking and stirring.  $\text{Fe}_2\text{Cl}_6$  added to an alkaline Phosphate forms *yellowish-white* flocculent precipitate  $\text{Fe}_2(\text{PO}_4)_2$ , insoluble in Acetic Acid. A few drops of dilute solution of Phosphate in  $\text{HNO}_3$ . added to 20 drops of  $(\text{NH}_4)_2\text{MoO}_4$ . in excess of  $\text{HNO}_3$ . will form an intense yellow precipitate of Phospho-Molybdate of Ammonia, insoluble in  $\text{HNC}_2$ , soluble in  $\text{NH}_4\text{HO}$ . The solution of Phosphate must not be too strong, as the yellow precipitate is soluble in excess.

**SILICIC,  $H_2SiO_3$ .** : Only the alkaline Silicates are soluble. If to a (not too dilute) solution of an alkaline Silicate  $NH_4Cl$  is added the Silica will be precipitated because an alkaline chloride is formed, and Silica does not enter into combination with  $NH_4HO$ , set free by the reaction. If  $HCl$  is added to a concentrated solution of an alkaline Silicate, the solution sets into a jelly-like mass from formation of Hydrate of Silica. But if  $HCl$  in excess is added at once to a not too concentrated solution of a Silicate, the Silicic Acid remains in solution; if this solution is evaporated to dryness, the white powder insoluble in  $HCl$  is Silica. The Silica is soluble in a boiling solution of  $KHO$ . In the solid state Silica is best recognized by bead with Microcosmic salt, forming skeleton of Silica.

**SULPHURIC,  $H_2SO_4$ .** : The reaction with  $BaCl_2$ , giving a white precipitate insoluble in  $HCl$  is very characteristic of Sulphuric acid and Sulphates. A similar precipitate is formed by Selenic and by Fluosilicic Acid; but these acids are so rare that the above reaction with Barium Chloride is usually accepted as proof of the presence of Sulphuric Acid.

**SULPHUROUS ACID,  $H_2SO_3$ .** Only the alkaline Sulphites are soluble in water. The Sulphites of  $Ba$ ,  $Sr$  and  $Ca$ , are insoluble as normal salts, but become soluble as Bisulphites in excess of  $H_2SO_3$ , but these salts are again precipitated on boiling from escape of  $SO_2$ . If  $HCl$  is added to a Sulphite, the stifling odor of  $SO_2$  may be recognized. This gas will first redden and then bleach blue litmus paper. Sulphites precipitate  $AgNO_3$ , as white  $Ag_2SO_3$ . On heating it blackens and decomposes into metallic Silver and Sulphuric Acid.  $Ag_2SO_3 + H_2O = 2Ag + H_2SO_4$ . With  $Hg_2(NO_3)_2$ —a gray precipitate of  $Hg$ .  $Hg_2SO_3 + H_2O = 2Hg + H_2SO_4$ . With  $Fe_2Cl_6$ —a red color, destroyed by heating with  $HCl$ . A sulphite added to  $Zn + HCl$  forms  $H_2S$ , at once.  $H_2SO_3 + 3H_2 = H_2S + 3H_2O$ . In presence of  $HCl$  Sulphites reduce many salts, e. g.,  $Fe_2Cl_6$  to  $FeCl_2$ .— $K_2Mn_2O_8$  to  $KCl$  and  $MnCl_2$ .— $K_2CrO_4$  to  $KCl$  and  $Cr_2Cl_6$ .

### GROUP C.: ACIDS PRECIPITATED BY $AgNO_3$ .

[The reactions of Iron Salts with the Ferrocyanogen compounds are so characteristic and easily secured that their identification is referred to Group D.]

**HYDROBROMIC ACID,  $HBr$ .** : Solution of  $HBr$  and soluble Bromides produce a yellowish-white precipitate of  $AgBr$ , with  $AgNO_3$ .—insoluble in  $HNO_3$  and difficult to dissolve in  $NH_4HO$ . If Chlorine water is

added to a solution of a Bromide, a *yellow to reddish* color is produced, which becomes manifest when the liquid is shaken up with a few drops of  $\text{CS}_2$  to dissolve Br. If any Bromide be mixed with  $\text{MnO}_2 + \text{H}_2\text{SO}_4$ , and heated *brownish-red* vapors of Br. appear, best seen by looking lengthwise through the test tube. Br. colors solution of starch *yellow*.

**HYDROCYANIC, HCN:** HCN. gas has the odor of bruised peach leaves. HCN. and soluble Cyanides precipitate  $\text{AgNO}_3$  as  $\text{AgCN}$ ., white, not blackened by sunlight (distinction from  $\text{AgCl}$ .), soluble in boiling  $\text{HNO}_3$ . If a Cyanide is warmed with  $\text{KHO}$ . and three or four drops of  $\text{FeSO}_4$  solution and two of  $\text{Fe}_2\text{Cl}_6$  for a short time, and then slightly acidulated with  $\text{HCl}$ . to dissolve the hydroxides, Prussian blue will appear. If a drop of  $\text{NH}_4\text{HS}$  is added to a Cyanide in solution and heated gently, then acidified with  $\text{HCl}$ . a drop of  $\text{Fe}_2\text{Cl}_6$  will produce a *blood-red color*.

**HYDROCHLORIC ACID, HCl:** Precipitates  $\text{AgNO}_3$  as a *curdy white* precipitate,  $\text{AgCl}$ ., insoluble in  $\text{HNO}_3$ , readily soluble in  $\text{NH}_4\text{HO}$ . By prolonged exposure to sunlight it becomes violet and finally black. Gaseous  $\text{HCl}$ . forms white fumes of  $\text{NH}_4\text{Cl}$ . with  $\text{NH}_3$ . Mercurous Nitrate forms a white precipitate,  $\text{Hg}_2\text{Cl}_2$ , with  $\text{HCl}$ . or soluble Chlorides, insoluble in  $\text{HNO}_3$  or  $\text{NH}_4\text{HO}$ . but blackened by the latter. Any Chloride heated with  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  evolves *Chlorine gas*—recognized by odor, color and bleaching properties. If the gas is poured into a tube containing a little water, the tube agitated and a drop of  $\text{AgNO}_3$  added, a curdy precipitate of  $\text{AgCl}$ . will be formed.

**HYDRIODIC, HI:** With  $\text{HI}$  or soluble Iodides,  $\text{AgNO}_3$  precipitates  $\text{AgI}$  *yellowish white*, insoluble in both  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$ . A mixture of  $\text{CuSO}_4$  and  $\text{FeSO}_4$  precipitates from solutions of Iodide, Cuprous Iodide in form of *dirty white* precipitate. Chlorides and Bromides are not thus precipitated. If clear starch paste is added to a solution of an Iodide in the cold, the Chlorine water added drop by drop, a *blue color will form from formation of Iodide of Starch*. Heat and an excess of Chlorine water removes the coloring. Any Iodide heated with conc.  $\text{H}_2\text{SO}_4$  and  $\text{MnO}_2$  liberates Iodine in the free form, giving beautiful violet vapors, which condense in dark brownish scales on the cooler portions of the tube. Solution of Mercuric Chloride added to an Iodide in solution, gives a *salmon colored precipitate, rapidly becoming scarlet*,  $\text{HgI}_2$ . Nitrate of Lead with solution of Iodide gives beautiful yellow precipitate, slightly soluble in boiling water, but precipitated as the water cools, in form of glistening yellow scales of  $\text{PbI}_2$ .

**HYDROSULPHURIC,  $\text{H}_2\text{S}$ :** Recognized easily by its characteristic odor. The acid and any of its soluble salts precipitate Lead salts from solution in the form of brownish black  $\text{PbS}$ . Paper moistened with

$Pb(NO_3)_2$  when held in the gas or moistened with the solution of the gas is *stained brown*.  $AgNO_3$  produces a black precipitate of  $Ag_2S$ , insoluble in  $NH_4HO$ , oxidized (into Silver Sulphate) by  $HNO_3$ , and dissolved. The sulphur radical in many insoluble sulphides can rapidly and easily be separated and identified by the reducing influence of metallic Zinc in presence of  $HCl$ . The metals forming insoluble sulphides are mostly found in the I. and II. Groups. With the exception of Arsenic (a semi metal) all the sulphides of these metals may be decomposed, the metal secured in metallic form and the sulphur eliminated as  $H_2S$ , capable of easy detection and identification. Place the powdered Sulphide in a test tube, pour on it a quantity of conc.  $HCl$  and insert a slip or rod of Zn. *Test the escaping gas by its odor and reaction with Lead paper for  $H_2S$* . After a time the metal will be found precipitated on the Zn. and may be removed, washed and identified. In the case of Mercury and Antimony, better results are secured by wrapping a slip of clean Copper around the Zinc to form a Zn.Cu. couple. The Hg. will form an amalgam with the Copper.

#### GROUP D.: ACIDS IDENTIFIED BY FERRIC CHLORIDE.

While some of these Acids are precipitable by Nitrate of Silver, they are most easily identified by Salts of Iron.

**HYDROFERROCYANIC,  $H_4FeCy_3$ .**: In solution of Ferrocyanides, Ferric Chloride gives a *deep blue precipitate* insoluble in  $HCl$ .—Prussian Blue  $Fe_4(FeCy_6)_3$ . Solution of Copper Sulphate gives a *chocolate brown precipitate*— $Cu_3FeCy_6$ .—insoluble in  $HCl$ , soluble in  $NH_4HO$ .

**HYDROFERRICYANIC,  $H_3FeCy_6$ .**: In solution of Ferricyanides, Ferric Chloride gives a brownish green coloration, but no precipitate. With *Ferrous salts a deep blue precipitate*,  $Fe_3(FeCy_6)_2$ —Turnbull's Blue, insoluble in  $HCl$ . The addition of  $SnCl_2$  to a mixture of Ferric Chloride and Ferricyanide, gives instantly a blue precipitate from the reduction of Ferric to Ferrous Chloride.

**TANNIC**: With solution of Ferric Chloride forms a bluish-black (ink) precipitate. Precipitates solution of gelatine.

**GALLIC**: Forms a precipitate similar to that of the Tannic Acid. Does not precipitate solution of gelatine.

**SULPHOCYANIC**: With solution of Ferric Chloride, *an intense blood-red coloration*, but no precipitate. THE COLOR IS NOT CHANGED BY  $HCl$  EVEN WHEN BOILED, BUT QUICKLY DISCHARGED BY  $HgCl_2$ .

**SULPHUROUS:** With Ferric Chloride forms a *red color rapidly destroyed by boiling with HCl.*

**ACETIC:** Acetates form a brownish-red color destroyed by HCl in the cold.

**PHOSPHORIC:** With Ferric Chloride a yellowish-white precipitate, insoluble in Acetic Acid.

## SUBSTANCES THAT DECOLORIZE SULPHATE OF INDIGO.

- |                                     |                                                                                                                                           |
|-------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| 1. Without addition of an acid :    | { Chlorine.<br>Hypochlorous Acid.<br>Chlorous Acid.<br>Hypochlorites.<br>Bromine.<br>Nitric Acid (not too dilute).<br>Alkaline Sulphides. |
| 2. On addition of HCl and heating : | { Chlorates.<br>Nitrates.<br>Iodates.<br>Bromates.<br>Manganates.<br>Manganic Oxide.<br>Plumbic Oxide.                                    |

In applying this test, enough of the Indigo solution is placed in water to give a blue color, and the substance is then dropped into the solution and the changes observed, which occur speedily if at all.

## ACIDS NOT PRECIPITATED BY GROUP REAGENTS.

Crystals of Nitrates, Chlorates, Bromates, Permanganates and Iodates deflagrate on red-hot charcoal.

**NITRIC:** All normal nitrates are soluble; a few basic Nitrates (of Hg and Bi) are insoluble in water.

If a Nitrate is added to Sulphuric Acid and Copper, and the mixture heated, *nitric oxide is evolved and the air in the test tube becomes orange-colored;* best seen by looking lengthwise through the test tube.

If a Nitrate is added to conc. Sulphuric Acid, and a strong solution of Ferrous Sulphate carefully poured over the Acid without mixing the solutions, a *brown ring* will form between the two layers of liquid, best seen by reflected light. The color disappears on boiling, the NO. being expelled by heat.

If Brucine dissolved in  $H_2SO_4$  be poured on a solid containing even a very small amount of a Nitrate, a blood-red color will form.



If solution of Sulphate of Indigo is added to a Nitrate with HCl, the color does not disappear, but the color is discharged by boiling the mixture.

**CHLORIC:** Chlorates when heated red-hot give off Oxygen and are reduced to Chlorides, and then give reactions for Hydrochloric Acid.

When Chlorates are heated with conc. HCl, a yellow gas is given off, which bleaches Indigo very powerfully.

**BROMIC AND IODIC:** When Bromates and Iodates are heated red-hot they give off Oxygen and are reduced to Bromides and Iodides, and then give reactions for Hydrobromic and Hydriodic acids respectively.

**PERMANGANATES:** Are all soluble in water, the solution having a deep purple color. Permanganic Acid ( $H_2Mn_2O_7$ ) is readily reduced a Manganous salt ( $MnCl_2$ ) by the action of Oxalic Acid in presence of HCl, the purple color being rapidly destroyed. The Mn. is then readily detected by the tests used for this base.

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**ORGANIC ACIDS; EVOLVE COMBUSTIBLE GASES AND BLACKEN (BY SEPARATION OF CARBON) WHEN HEATED STRONGLY ON PLATINUM FOIL.**

Cyanogen compounds of the heavy metals will exhibit the same reactions.

**ACETIC:** The normal Acetates are all soluble in water: a few basic Acetates are insoluble. Acetic Acid has the characteristic odor of vinegar. If Sulphuric Acid is added to an Acetate and warmed, the odor of Acetic Acid is evolved. If equal volumes of Sulphuric Acid and Alcohol are added to an Acetate and heated, the fragrant odor of Acetic Ether is obtained. If an Acetate is added to neutral Ferric Chloride, a brownish red color appears from formation of Ferric Acetate. The color disappears at once when HCl. is added (distinction from Sulphocyanides and Sulphites).

**TARTARIC:** Chloride of Calcium from neutral solutions of the Tartarates throws down a white chrySTALLINE precipitate of Tartrate of Calcium, soluble in Acetic (distinction from Oxalates). Tartaric Acid added in excess to KHO precipitates "Cream Tartar" —  $KHC_4H_4O_6$ , white, crystalline, soluble in 180 parts of water. Thorough shaking promotes the formation of the precipitate.  $AgNO_3$  precipitates white  $Ag_2C_4H_4O_6$ , soluble in  $NH_4HO$ . If this ammonia solution be boiled in a test tube, the liquid becomes black from precipitated Silver, and a Silver coating will form on the inside of the test tube.

## LIST OF THE ELEMENTS, SYMBOLS, ATOMICITIES, AND COMBINING WEIGHTS.

NAME.	SYMBOL.	ATOMICITY.	COMBINING WEIGHTS.
Aluminum	Al.	III	27.
Antimony	Sb.	III and V	120.
Arsenic	As.	III and V	75.
Barium	Ba.	II	137.
Beryllium	Be.	II	9.
Bismuth	Bi.	III and V	210.
Boron	B.	III	11.
Bromine	Br.	I	80.
Cadmium	Cd.	II	112.
Cæsium	Cs.	I	133.
Calcium	Ca.	II	40.
Carbon	C.	IV	12.
Chlorine	Cl.	I	35.5
Cerium	Ce.	IV	93
Chromium	Cr.	III	52.5
Cobalt	Co.	II	58.8
Copper	Cu.	II	63.
Didymium	D.	II	95.
Erbium	E.	II	112.6
Fluorine	F.	I	19.
Gallium	Ga.	III	69.8
Gold	Au.	III	197.
Hydrogen	H.	I	1.
Indium	In.	III	113.4
Iodine	I.	I	127.
Iridium	Ir.	II	198.
Iron	Fe.	II and VI	56.
Lanthanum	La.	II	93.6
Lead	Pb.	II	207.
Lithium	Li.	I	7.
Magnesium	Mg.	II	24.4
Manganese	Mn.	II	55.
Mercury	Hg.	II	200.
Molybdenum	Mo.	III	96.
Nickel	Ni.	II	58.8
Niobium	Nb.	V	94.
Nitrogen	N.	III and V	14.
Osmium	Os.	VI	199.2
Oxygen	O.	II	16.
Palladium	Pd.	II	106.
Phosphorus	P.	III and V	31.
Platinum	Pt.	II	197.5
Potassium	K.	I	39.1
Rhodium	Rh.	II	104.4
Rubidium	Rb.	I	85.4
Ruthenium	Ru.	VI	104.4
Selenium	Se.	VI	79.5

## LIST OF THE ELEMENTS, SYMBOLS, ETC.—CONTINUED.

NAME.	SYMBOL.	ATOMICITY.	COMBINING WEIGHTS.
Silver	Ag.	I	108.
Silicon	Si.	IV	28.
Sodium	Na.	I	23
Strontium	Sr.	II	87.5
Sulphur	S.	VI	32.
Tantalum	Ta.	V	182.
Tellurium	Te.	VI	128.
Thallium	Tl.	III	204.
Thorium	Th.	II	231.5
Tin	Sn.	II and IV	118.
Titanium	Ti.	IV	50.
Tungsten	W.	VI	184.
Uranium	U.	II	120.
Vanadium	V.	V	51.2
Yttrium	Y.	III	88.
Zinc	Zn.	II	65.
Zirconium	Zr.	IV	90

## REAGENTS.

## ACIDS.

- Conc.  $H_2SO_4$ .—C. P. Acid.  
 Dilute  $H_2SO_4$ .—C. P. Acid 1:5 pure water.  
 Conc.  $HNO_3$ .—C. P. Acid.  
 Dilute  $HNO_3$ .—C. P. Acid 1:3.  
 Conc.  $HCl$ .—C. P. Acid.  
 Dilute  $HCl$ .—C. P. Acid 1:3.  
 Aqua Regia— $HNO_3$ , 1;  $HCl$ , 3. Prepared only as required for use; does not keep long.  
 Acetic Acid—Sp. gr. 1.04, 1:1.  
 Tartaric Acid—Crystals 1:4.  
 Hydrofluosilicic Acid—Saturated solution.  
 Hydrosulphuric Acid—Saturated solution of  $H_2S$  in water, acidulated with  $HCl$ .

## BASES AND BASIC SALTS.

- $KHO$ .—Fused sticks 1:10. Dissolve the sticks in water, decant clear solution from any solid impurities.  
 $NH_4HO$ .—Conc. Ammonia Water 1:5.  
 $NH_4HS$ .—Yellow Ammonic Sulphide and  $NH_4HO$ . equal parts; water five parts.

$(NH_4)_2CO_3$ . { Dissolve one part of commercial Carbonate of Ammonia  
 in five parts of water containing one part of  $NH_4HO$ .

$Na_2CO_3$ .— $Na_2CO_3$ . (dry) 1:5.

$Ca(OH)_2$ . { Saturate cold water with slaked lime, and decant the  
 clear solution of "Lime Water."

## SALTS.

$BaCl_2$ .—1:15.

$CaCl_2$ .—1:10.

$CaSO_4$ .—Saturated solution.

$MgSO_4$ .—1:10.

$(NH_4)_2C_2O_4$ .—1:25. Dissolve in hot water.

$NH_4Cl$ .—1:10 { Sal-ammoniac usually contains Iron. Add to the  
 solution of  $NH_4Cl$ . a little  $NH_4HO$ .; decant from any  
 precipitate and neutralize with  $HCl$ .

$KI$ .—1:60.

$K_2Cr_2O_7$ .—1:10. Use warm water.

$K_4FeCy_6$ .—1:15.

$K_3FeCy_6$ .—1:15. Does not keep long.

$NH_4CyS$ .—1:20.

$\text{AgNO}_3$ .—1:20.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .—1:10.

$\text{Hg}_2(\text{NO}_3)_2$ .—1:20 + two  $\text{HNO}_3$ .

$\text{HgCl}_2$ .—1:20.

$\text{FeSO}_4$ . { Dissolve 12 parts  $\text{FeSO}_4$  and 6 parts  $(\text{NH}_4)_2\text{SO}_4$  in 100 water,  
and add 2 parts  $\text{H}_2\text{SO}_4$ .\*

$\text{Fe}_2\text{Cl}_6$ .—1:10.

$\text{Na}_2\text{HPO}_4$ .—1:15.

$\text{SnCl}_2$ . { Boil granulated Sn. with  $\text{HCl}$  till the acid is saturated; dilute  
with 4 parts of water made acid with  $\text{HCl}$ .

$(\text{NH}_4)_2\text{MoO}_4$ . { Dissolve 1 part in five  $\text{NH}_4\text{HO}$ ., and pour this into 20  
parts dilute  $\text{HNO}_3$ .

$\text{Co}(\text{NO}_2)_2$ .—1:15.

$\text{NaClO}$ . { Shake 1 part "Chloride of Lime" with 10 of water; add  
 $\text{Na}_2\text{CO}_3$  in solution as long as precipitate forms, and decant  
the clear solution.

In preparing any of these reagents, if a precipitate forms it should be removed by filtering or other means, and *only the clear solution used as a reagent.*

#### METALS AND OXIDES.

IRON in form of clean wire—wire nails.

COPPER, as sheet copper, or fine wire.

ZINC (free from As.) granulated, strips of sheet zinc or small sticks.

LEAD DIOXIDE,  $\text{PbO}_2$ , by boiling "Red Lead" in dilute  $\text{HNO}_3$ , washing the brown oxide to remove  $\text{Pb}(\text{NO}_3)_2$ , and drying the  $\text{PbO}_2$  for use.

MANGANESE DIOXIDE. Powdered "Black Oxide of Manganese" of commerce.

#### TEST PAPERS.

*Litmus.* Reduce litmus cubes to a coarse powder; boil this for ten minutes in thirty volumes of alcohol; pour off the alcohol and boil again with fresh alcohol; pour off all the alcohol, and pour on the purified litmus 100 volumes of cold distilled water and let it stand for two days: pour off the clear liquid and preserve this test solution in a bottle without a stopper. The residual litmus can be treated three or four times in succession with cold water to prepare a test solution. The solution is reddened by acids and blued by alkalis. Carbonic acid gives a wine-red, which may be removed by boiling or by prolonged stirring.

\* Ammonio-Ferrous Sulphate dissolved in water acidulated with  $\text{H}_2\text{SO}_4$  answers the purpose satisfactorily.

make *Blue Litmus* paper, add  $\text{KHO}$  to the Litmus solution until a drop of the solution on white paper leaves a blue stain. Dip strips of printing paper in the solution and dry for use.

to prepare *Red Litmus*, add dilute  $\text{HCl}$  till the solution is permanently acid; then dip white paper in the solution and dry for use.

*Turmeric Paper.* Digest the coarsely powdered root repeatedly in small quantities of water to remove objectionable coloring matter, and then in alcohol. Pour off the alcoholic solution and dip into this strips of printing paper; dry these and keep them in the dark. Alkalies turn turmeric paper brown. Turmeric paper is a very sensitive test for Alkalies and Alkaline Earths.

All these papers should be kept in a bottle and away from the light.

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