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ELEMENTARY

QUANTITATIVE ANALYSIS.

BY

ALEXANDER CLASSEN,

PROFESSOR IN THE ROYAL POLYTECHNIC SCHOOL, AIX-LA-CHAPELLE.

TRANSLATED, WITH ADDITIONS,

BY

EDGAR F. SMITH, A.M., Ph.D.,

ASSISTANT IN ANALYTICAL CHEMISTRY IN THE TOWNE SCIENTIFIC
SCHOOL, UNIVERSITY OF PENNSYLVANIA.

With Thirty-six Illustrations.

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PREFACE.

THIS translation of Classen's work has been made with a view of presenting to the American student of Chemistry a compact and thoroughly useful manual of quantitative analysis.

The aim of the author has been to teach this subject by means of examples—commencing with simple determinations followed by separations, including quite a number of important alloys, and then advancing to the analysis of minerals and such products as are met with in the many departments of applied chemistry. The methods employed in the various determinations and separations are such as can be used at all times—care having been taken to exclude all that have but a very limited use, and such as have proved on trial to be devoid of practical merit.

This work has been adopted as a text-book in the laboratories of almost all the prominent German universities and polytechnic schools, and has taken rank by the side of the older and larger works on the same subject. Among practical chemists, too, it has quite an extensive circulation. In France, Russia, and Poland, where translations have appeared, it has been no less favorably received; and in this country, with those who have employed the work in the original as a guide in laboratory instruction, it has become quite popular and been very highly commended.

Here and there throughout the work the translator has taken the liberty of making additions; these are distinguished from the original text by being inclosed in brackets.

To all who kindly furnished suggestions and methods in reply to letters and specimen sheets issued more than a year ago, the translator would return his sincere thanks.

Laboratory of the University of Pennsylvania,
August, 1878.

CONTENTS.

QUANTITATIVE ANALYSIS.

Calcium Carbonate.

CALCITE—MARBLE—$CaCO_3$.

MERELY the estimation of the calcium will be here required.* For this purpose 0.3–0.4 grm. of the pulverized substance, previously dried at 100° C., are placed in a beaker of about 200 C. C. capacity, and solution effected by the addition of dilute hydrochloric acid. The acid solution is largely diluted with water, and to this ammonium hydrate is added until the liquid yields an alkaline reaction. The calcium is now precipitated as oxalate. To the warm solution is added ammonium oxalate in moderate excess, and the beaker then put in a warm place until the precipitate has fully subsided, which will require at least twelve hours. After filtering off the calcium oxalate wash it perfectly with hot water, and, when dry, convert it either into carbonate or oxide. To estimate the calcium as carbonate heat the bottom of the crucible containing the oxalate to faint redness for about five minutes. After cooling weigh, and then moisten the residue with a few drops of ammonium carbonate to convert into carbonate any caustic lime that may have been produced. This operation must be repeated until a con-

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* The determination of carbon dioxide in carbonates will be discussed on p. 33.

stant weight is obtained. For the conversion of the calcium carbonate into oxide ignition over a blast lamp is all that is necessary. Constant weight, however, must be obtained. Ignite at first but ten minutes, then notice whether upon continued heating the weight diminishes.

$CaCO_3 : Ca :: \text{wt. } CaCO_3 : x$ or

$CaO : Ca :: \text{wt. } CaO : x$.

Copper Sulphate.

$CuSO_4 + 5H_2O$.

Copper Determination.—First method. Dissolve about 1 grm. of the above salt in water, and bring the solution to boiling in a porcelain dish. Sodium or potassium carbonate is now added in slight excess, and the ebullition continued for some time. When the precipitate has subsided the clear supernatant liquid is decanted, and hot water poured over the precipitate and this again boiled. This operation is repeated until almost all the alkali present has been removed, and the precipitate then transferred to a filter and washed with boiling water. Continue the latter operation until a drop of the filtrate evaporated upon platinum foil no longer leaves a residue. After drying the cupric oxide thus obtained separate it carefully from the filter and place it in a porcelain crucible. The filter itself is incinerated upon the crucible lid. The crucible with its contents is ignited over an ordinary Bunsen lamp until the weight remains constant.

[Second method. After dissolving the salt in water pass hydrogen sulphide gas through the acidulated solution. The copper is precipitated as sulphide, and, after standing a short time, may be transferred to a filter and slightly washed. The dry precipitate is placed in a platinum crucible, the filter ash added, and then upon this are placed a few drops of concentrated sulphuric acid, an equal amount of water and a small portion of strong nitric acid.

The crucible is gradually heated upon a hot iron plate and the excess of acid evaporated, leaving finally pure copper sulphate, which may be weighed as such; or, the crucible is heated strongly over a Bunsen burner and cupric oxide formed. The crucible should be covered during the operation, and the salt stirred from time to time with a platinum wire. The method was proposed by Dr. Genth, and affords accurate results. The amount of copper in cupric oxide is readily calculated from the formula—

$$\mathrm{CuO} : \mathrm{Cu} :: \mathrm{wt.\ CuO} : x.]$$

Sulphuric Acid Determination.—This is based upon the insolubility of barium sulphate in hot water and strongly diluted acids. The acid in this compound is estimated by dissolving about .5 grm. of the salt in water, acidulating the solution with a few drops of hydrochloric acid and boiling. Barium chloride is added as long as a precipitate of barium sulphate is formed, and the solution boiled and stirred for some time after complete precipitation has been effected. Proceed as above described, when the barium sulphate has settled, washing the precipitate upon the filter with hot water until silver nitrate produces no turbidity in the washings. The dried precipitate is treated the same as the cupric oxide. The barium sulphate obtained in this manner generally contains weighable quantities of barium chloride—which were not removed by washing; therefore digest the weighed precipitate with dilute hydrochloric acid, filter through a small filter, and again wash the precipitate perfectly with hot water, by decantation, ignite and weigh.

The barium sulphate that adheres to the filter will be reduced upon ignition to barium sulphide, and render the results too low. This may be avoided if the precipitate, before weighing, be evaporated to dryness with a few drops of sulphuric acid.

Water Determination.—Copper sulphate, heated some time in an air-bath at 120° C., loses only four molecules of its water of crystallization. To expel the fifth it is necessary to increase the temperature to 250° C. To prevent the anhydrous salt from attracting moisture, it is advisable to employ a well-closed glass tube in weighing the substance. The difference in the two weighings expresses the amount of water of crystallization.

Magnesium Sulphate.

$MgSO_4 + 7H_2O$.

For the estimation of the magnesium dissolve 1–1.5 grms. of the air-dried salt in water, and add sufficient ammonium chloride so that upon the addition of ammonium hydrate magnesium hydrate may not be thrown down; add now to this solution sodium-ammonium phosphate,* and a white crystalline precipitate of magnesium-ammonium phosphate will be produced.

When the supernatant liquid has become clear, filter and wash the precipitate with a mixture of 1 part ammonium hydrate (.96 sp. gr.) and 3 parts water, until the addition of nitric acid and silver nitrate to the filtrate does not produce a precipitate of silver chloride, then dry.

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* If we have employed sodium phosphate for the precipitation, the liquid should stand at least twelve hours, so that the precipitate may separate perfectly.

Place the dried precipitate in a porcelain crucible.* First the filter should be carefully removed and reduced to ash upon the crucible lid. Heat the crucible gently and gradually increase the temperature over a Bunsen lamp until constant weight is obtained. If the color of the precipitate after ignition is not pure white, moisten it with a drop of nitric acid, and again ignite. The residue is magnesium pyrophosphate. The amount of magnesium is determined from the equation—

$$Mg_2P_2O_7 : 2Mg : : \text{wt. } Mg_2P_2O_7 : x.$$

To estimate the sulphuric acid proceed as directed under Copper Sulphate. The amount of water is ascertained by drying a weighed portion of the substance at 210° C. until the weight is constant.

Barium Chloride.

$BaCl_2 + 2H_2O$.

The barium is determined as carbonate. Dissolve 0.5 grm. substance in water, add ammonium carbonate in slight excess, and digest gently for some hours upon a sand-bath. Wash the precipitate with water containing ammonium hydrate, dry, and ignite gently over a Bunsen lamp.

The barium can also be determined as sulphate by precipitating the solution acidified with hydrochloric acid with sulphuric acid. (See the determination of sulphuric acid in Copper Sulphate.)

Chlorine Determination.—Add silver nitrate to the warm solution of the substance (previously acidified with

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* It is not advisable to employ a platinum crucible, because, by an incomplete incineration of the filter, phosphoric acid will be reduced, and probably cause an injury to the crucible.

nitric acid),* stir the liquid continually with a glass rod, which aids in uniting the particles of silver chloride, and the supernatant liquid will become clear much sooner. Filter and wash the precipitate with hot water by decantation (until no silver reaction is produced in the filtrate); finally, bring the same with aid of a feather upon the filter. After drying separate the precipitate as well as possible from the filter, and place it in a porcelain crucible. The filter should be ignited alone upon the inverted cover of the crucible. The particles of silver chloride adhering to the filter are readily reduced in this operation to the metallic state, and should be again converted into silver chloride. To this end moisten the ash when cool with a few drops of nitric acid, warm gently, and add a drop of hydrochloric acid. Evaporate the liquid carefully, place the inverted cover on the crucible, and apply heat until the contents of the latter begin to fuse. Instead of fusing the silver chloride, it can be placed on a filter dried at 120° C., and then dried at the same temperature until the weight remains constant. As silver chloride is readily decomposed by direct sunlight, it is advisable to exclude this as much as possible during the precipitation, etc.

$$AgCl : Cl :: \text{wt. } AgCl : x.$$

The amount of water in the salt is easily determined by glowing a weighed portion of the barium chloride.

Zinc Sulphate.

$ZnSO_4 + 7H_2O$.

Determination of the Zinc as Oxide.—The aqueous solution of the substance (about 1 grm.) is brought to

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* Never acidify the hot aqueous solution first with nitric acid and then add silver nitrate, because hydrochloric acid will always be volatilized.

ebullition in a porcelain dish,* and sodium carbonate added gradually in excess. Continue boiling some time and then filter off the clear liquid. Pour hot water upon the residue and again boil. Repeat this operation until a drop of the filtrate leaves no residue on platinum foil when evaporated to dryness. Dry the zinc carbonate, and, having incinerated the filter upon a porcelain lid, convert the carbonate into the oxide by heating the porcelain crucible containing it over an ordinary lamp.†

Determination as Zinc Sulphide.—Add ammonium nitrate‡ to the diluted liquid, then a few drops of ammonium hydrate, and precipitate the zinc from its solution while warm with ammonium sulphide. The supernatant liquid should not be filtered off until the zinc sulphide has fully subsided, which will be hastened by standing in a warm place. Wash the precipitate by decantation with water containing a few drops of ammonium sulphide and ammonium nitrate. To weigh the zinc sulphide as such it must be ignited in a stream of hydrogen gas. The apparatus shown in Fig. 1 is employed for the purpose.

The hydrogen gas streaming from the spherical apparatus is dried by passing first through calcium chloride and then through sulphuric acid. To prevent explosions a small glass tube is placed between the crucible and sulphuric acid; it contains fine wire pressed in cotton (Fresenius). The dried precipitate (the filter having been

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* If the precipitation occurs in glass vessels, or a porcelain dish of poor quality, the zinc carbonate will invariably contain silicic acid and alumina. These will remain behind when the precipitate is dissolved in hydrochloric acid, and the liquid supersaturated with ammonium hydrate.

† Always examine the zinc oxide for alumina and silicic acid, and deduct the same.

‡ The addition of ammonium nitrate hastens the precipitation of the zinc sulphide.

incinerated on a platinum wire) is placed in an unglazed porcelain crucible (Rose's crucible), mixed with powdered sulphur, and covered with a perforated porcelain lid,* through which a narrow tube passes, conducting hydrogen gas into the crucible during the ignition over an ordinary lamp. Heat of course must not be applied until all the air has been expelled from the apparatus and crucible.

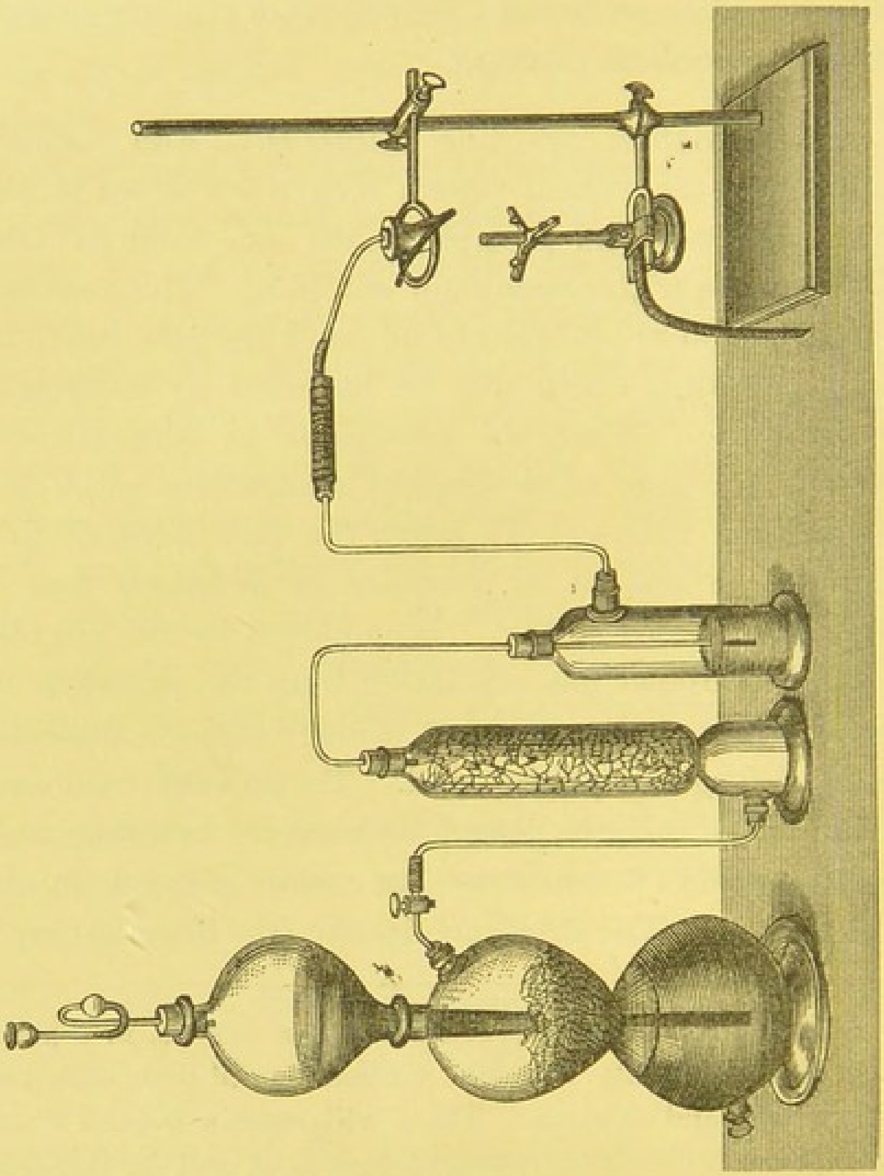

Fig. 1.

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* Rose suggests a platinum cover. This is not to be recommended, because the hydrogen gas generally employed in this operation contains hydrogen arsenide, which would in a very short period attack the platinum and render it useless.

After ignition for 5–10 minutes, allow the crucible to cool in a stream of hydrogen gas.

For the determination of the water of crystallization, heat a weighed portion of zinc sulphate at 220° C. until the weight remains constant.

The sulphuric acid is determined as directed on p. 15.

Manganous Chloride.

$MnCl_2 + 4H_2O$.

Determination of the Manganese as Protosesquioxide.—Precipitate the hot aqueous solution of the salt (1 grm.) contained in a porcelain or platinum dish with an excess of sodium carbonate, and treat the precipitate of manganese carbonate in a manner similar to that described above in the determination of zinc. The filtrate invariably holds in solution minute traces of manganese carbonate. For the separation of these, evaporate the solution to dryness in either a platinum or porcelain dish. Boil the residue with water, and bring the slight precipitate of manganese protosesquioxide upon a separate filter. Both precipitates when dried are placed into a platinum crucible and ignited with free access of air, whereby the manganous carbonate is converted into manganese protosesquioxide. As free alkali almost invariably adheres to the first, it is well to wash the ignited residue with hot water. The aqueous solution is passed through a small filter, which is dried and incinerated, and added to the portion contained in the crucible.

Determination as Manganese Sulphide.—The precipitation like that of zinc is effected by ammonium sulphide. Instead of adding ammonium nitrate to the solution, we can use the chloride, and wash the manganese sulphide with water containing ammonium chloride and ammonium sulphide. The manganese sulphide mixed with sulphur must be ignited over a blast lamp in a stream of hydrogen gas, as it retains some of the sulphur very readily. It is also absolutely necessary to allow the manganese sulphide to cool in a stream of hydrogen gas, because, if exposed to the air while warm, it will be readily oxidized.

To estimate the chlorine present, precipitate a solution of the salt (0.5–1 grm.) with a solution of silver nitrate, and proceed as directed above under Barium Chloride, etc.

Estimate the water by drying a weighed portion of the substance at 150° C. until the weight becomes constant.

Cobaltous Chloride.

$CoCl_2 + 2H_2O$.

Determination of the Cobalt as Metal.—The aqueous solution of the salt (1 grm.) is placed either in a porcelain* or platinum dish, and brought to boiling. Add sodium hydrate in slight excess, and continue boiling until the hydrate of cobalt has assumed a brownish-black color. When the precipitate has fully subsided, filter off the clear fluid, and wash by decantation with hot water until the presence of alkali can no longer be detected in the filtrate.

The cobalt oxide is converted into metallic cobalt by ignition in a stream of hydrogen gas. (See p. 20.)

The last traces of alkali that may adhere to it are removed by washing with hot water. The residue is again ignited in a stream of hydrogen gas.

Determination as the Nitrite of the Sesquioxide of Cobalt and Potassium.—Mix the concentrated solution of the salt with an excess of sodium or potassium hydrate;

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* A glass vessel must not be used here.

add sufficient acetic acid to redissolve the precipitate that may be at first produced by these reagents, and then mix in a concentrated solution of potassium nitrite acidified with acetic acid, and allow the whole to stand at least twenty-four hours. The nitrite of cobalt and potassium is washed with a solution of one part potassium acetate in nine parts of water, to which some potassium nitrite has been added. Finally dissolve the precipitate in hydrochloric acid, and precipitate the cobalt from this solution with potassium hydrate, and proceed as directed above.

The chlorine is determined as mentioned under Barium Chloride, and the water estimated by drying the salt at 150° C.

Nickel Sulphate.

$NiSO_4 + 7H_2O$.

For the determination of the nickel proceed as directed above in the estimation of cobalt. The nickel hydrate is washed by decantation with hot water, and, after drying, ignited in a stream of hydrogen gas, and then weighed. The nickel thus obtained must be examined for alkali, and finally repeatedly washed with hot water (see Cobalt Chloride, p. 22). The sulphuric acid is determined as sulphate of barium.

Nickel sulphate dried at 103° C. loses six molecules of water, but the seventh escapes first at a temperature of 280° C.

Ferrous Sulphate.

$FeSO_4 + 7H_2O$.

Determination of the Ferrous Oxide.—By boiling the aqueous solution of the air-dried salt (1 grm.) with nitric acid, the ferrous will be changed to ferric oxide, and the conversion indicated by the yellow color of the liquid; add ammonium hydrate in slight excess, and allow the precipitate of ferric hydrated oxide to subside. Filter, wash with hot water by decantation, dry, and ignite in a platinum or porcelain crucible, placed over an ordinary lamp. The filter should have previously been removed as well as possible from the precipitate, and incinerated upon a platinum wire.

Sulphuric Acid Determination.—This is determined in the filtrate from the ferric hydrate, by acidifying the solution with hydrochloric acid, and precipitating the boiling liquid with barium chloride. The barium sulphate is treated as described in the analysis of Copper Sulphate.

Water Determination.—The water of crystallization contained in ferrous sulphate cannot be estimated by heating a weighed portion in a crucible at a fixed temperature, because the ferrous salt gradually passes into the ferric state. The drying, therefore, must be effected with exclusion of air. For this purpose, take a small flask of difficultly fusible glass (this flask may be readily made by blowing a bulb on the end of a piece of difficultly fusible glass-tubing), introduce the substance (0.5 grm.) and weigh. The neck of the flask, about 2. cm. from the bulb, is drawn out and bent so as to make the whole represent a small retort. Now apply heat to the vessel to expel the water from its neck (ferrous sulphate loses its water of crystallization at 280° C.). When aqueous vapors are no longer produced, and the retort still hot, seal the tube, and allow the apparatus to cool. After cooling, the point of the tube is broken off, and it together with the retort again weighed.*

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* For the direct method of determining the water, see p. 36.

Sodium Phosphate.

$Na_2HPO_4 + 12H_2O$.

Determination of the Phosphoric Acid as Magnesium Pyrophosphate. I. Direct Estimation.—Dissolve 0.5 grm. of the crystallized, air-dried salt in about 100 C. C. of water, mixing with it 10 C. C. of magnesium chloride solution, which contains in a litre 101.5 grms. crystallized magnesium chloride, 200 grms. ammonium chloride, and 400 grms. ammonium hydrate (0.96 sp. gr.).* After the solution has stood from three to four hours,† filter off the precipitate of ammonium-magnesium phosphate,‡ and wash it with a mixture of one part ammonium hydrate (0.96 sp. gr.) and three parts water. Continue washing until the addition of nitric acid and silver nitrate produces no cloudiness. Dry and transfer the precipitate, carefully separated from the filter, to a porcelain crucible. The filter should be incinerated upon the inverted crucible lid. The heating of the crucible should at first be gentle, increasing gradually.

II. Indirect Determination.—Mix the solution of the substance (0.2 grm.) in about 50 C. C. of water, with about 10 C. C. molybdenum solution;§ and to render the preci-

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* 1000 C.C. of this solution precipitates 35.5 grms. phosphoric acid.

† If the phosphoric acid solution is more dilute, and there is less than .01 grm. phosphoric acid in 100 C.C., a much longer period than this is required for the complete separation of the precipitate.

‡ The precipitate is not totally insoluble in water containing ammonium hydrate. Instead of washing a long time, use an exhaust-pump in filtering.

§ The molybdenum solution is prepared by dissolving 150 grms. ammonium molybdate in 1 litre of water. This solution pitation of the phosphoric acid complete, digest the whole from four to six hours at a temperature of 50° C. After cooling, the precipitate of ammonium-molybdenum phosphate is filtered and washed, either with a molybdenum solution (1 : 3) or with ammonium nitrate solution, acidified with nitric acid (15 grms. salt in 100 C.C. water), and dissolved upon the filter in the least possible quantity of ammonium hydrate (1 part ammonium hydrate to 3 parts water). Now, mix hydrochloric acid with the ammoniacal solution until the precipitate that was produced is gradually redissolved—the liquid is, however, alkaline,—and after cooling, precipitate with magnesium chloride. The ammonium-magnesium phosphate, as thus obtained, very frequently has molybdic acid adhering to it; to remove this, redissolve and reprecipitate the magnesium.

Sodium Determination.—To estimate the sodium directly, the phosphoric acid must first be removed. Mix the aqueous solution of the salt (about 0.5 grm.) with lead acetate, as long as a precipitate of lead phosphate is produced. Filter off the precipitate and wash it with water. The excess of lead can be thrown down by hydrogen sulphide. The filtrate from the lead sulphide should be evaporated to dryness with hydrochloric acid, the residue will contain all the sodium as chloride of sodium. Use a porcelain dish for the evaporation. Dissolve the residue in a small quantity of water, bring it into a platinum crucible, and again evaporate. The chloride of sodium remaining should be ignited very gently, in a small, well-closed

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is poured into 1 litre of pure nitric acid, of commercial concentration. 100 C. C. of the latter solution correspond to 0.1 grm. phosphoric acid. The concentration of the phosphoric acid solution is so arranged that 0.1–0.2 grm. are contained in 50–100 C.C. of the liquid.

crucible. Before ignition the salt should be dried in an air-bath, at about 110° C., preventing thus any loss by decrepitation.

As sodium chloride is volatilized by a strong red heat, care should be taken to regulate the temperature so that the bottom of the crucible is only of a faint red color.

Water Determination.—Drying the salt at 300° C., it loses 12 molecules of water. If the residue is ignited, it will be converted into sodium pyrophosphate.

Separation of Barium from Calcium.

For analysis a mixture of the carbonates may be employed.

[*First Method.*—Dr. Frerichs proposes the following course, and I have found it to yield very satisfactory results.

A mixture of the neutral salts is treated with sodium acetate and acetic acid, and to this is added a neutral solution of potassium chromate, until the liquid above the precipitate appears yellow. After several hours' standing, collect the precipitate upon a filter, wash with acetic acid and dry. The dried barium chromate is separated very carefully from the filter, placed in a porcelain crucible, the ash added, and then heated, either upon a warm iron plate or over a small gas flame.

In the filtrate, from the barium chromate the calcium may be precipitated with an excess of ammonium hydrate and ammonium carbonate. The calcium carbonate, after being thoroughly washed, is dried and ignited, together with the filter, in a platinum crucible. By ignition it is converted into oxide.]

Second Method.—The separation according to this method is based upon the decomposition of calcium sulphate by ammonium carbonate. The hydrochloric acid solution of the bases is evaporated to dryness with addition of sulphuric acid (avoid an excess). Expel all the free acid by ignition, and digest the residue with a concentrated solution of ammonium carbonate containing ammonium hydrate.

After four or five hours' treatment, the calcium sulphate will have been converted into the carbonate (the decomposition is hastened by frequent stirring of the liquid), while the barium remains unaffected. Filter, wash the precipitate with a solution of ammonium carbonate, and then with water, until the presence of sulphuric acid can no longer be detected. Dissolve the calcium carbonate in dilute hydrochloric acid, and precipitate the calcium from this solution as oxalate (p. 13). Weigh the insoluble barium sulphate as such. (See Sulphuric Acid Determination, p. 15.)

Separation of Strontium from Calcium.

The separation of these bases is founded upon the different deportment of their nitrates with absolute alcohol. Evaporate their hydrochloric acid solution, with addition of nitric acid, to dryness upon a water-bath. Digest the residue with nitric acid and again evaporate to expel all the hydrochloric acid. Pour absolute alcohol (or better, a mixture of equal parts alcohol and ether) over the nitrates, and shake repeatedly. Calcium nitrate is dissolved. Filter off the strontium nitrate, convert it into the sulphate by evaporation with dilute sulphuric acid, and weigh as such. Remove the alcohol and ether from the solution containing the calcium and determine the latter as oxalate.

Separation of Barium, Strontium, Calcium, and Magnesium.

The magnesium is separated from the alkaline earths by evaporating their solution to dryness and digesting the residue with strong alcohol, adding sulphuric acid drop by drop in slight excess. The sulphates of barium, strontium, and calcium will be precipitated, while magnesium sulphate remains in solution. After the precipitate has subsided, filter and wash, at first with absolute alcohol, and then with alcohol of 30 to 40 per cent., to remove traces of magnesium sulphate that may have been precipitated together with the others. The filtrate from the insoluble sulphates is boiled to expel the alcohol, and, after adding ammonium hydrate in excess, the magnesium is precipitated as ammonium-magnesium phosphate (see p. 16). The separation of the alkaline earths depends upon their different deportment with ammonium carbonate. The sulphates of strontium and calcium are converted into carbonates, while the barium sulphate remains undecomposed.

Pour over the mixed sulphates a concentrated solution of ammonium carbonate containing ammonium hydrate, and stir the same frequently. After standing six hours, filter and wash the precipitate with a dilute solution of ammonium carbonate and water. Treat the precipitate with hydrochloric acid, weigh the insoluble residue of barium sulphate as such, and separate the chlorides of calcium and strontium as directed, p. 28.

Lead Chromate.

$PbCrO_4$.

Pulverize the substance (0.5 grm.) and dry at 100° C.; then digest with strong fuming hydrochloric acid until perfect decomposition has taken place, after which the excess of acid should be evaporated. We thus have the lead converted into the chloride and the chromic acid reduced to chromium chloride. Alcohol should be added to the cold solution to render the precipitation of the lead chloride complete, after which it is brought upon a weighed filter and dried at 100° C. The washing should be with alcohol, and the precipitate dried at 100° C. until constant weight is obtained.

In the filtrate from the lead chloride determine the chromium as the hydrated oxide. Bring the solution* in a platinum dish to boiling to expel the alcohol, then add ammonium hydrate in slight excess. Chromic hydrate is soluble to a slight extent (with a red coloration) in an excess of ammonium hydrate, therefore continue boiling until the supernatant liquid becomes perfectly colorless. The precipitate is thoroughly washed by decantation with hot water. Dry and ignite, together with the filter, in a platinum crucible.

Lead and chromium may be separated by precipitating the former as sulphide from an hydrochloric acid solution. Add a sufficient quantity of hot water to the solution of the substance to redissolve all the lead chloride that may have separated out, and then conduct a stream of hydrogen sulphide gas into the solution.† Filter off the precipitate and wash it with water containing hydrogen sulphide gas.

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[*] According to the investigations of Souchay, this precipitation should not occur in glass vessels, as the ammonium hydrate attacks the latter, and consequently constituents of the glass are invariably contained in the precipitate.

[†] Lead is only completely precipitated as sulphide from a hydrochloric acid solution when the latter is very dilute and the passage of hydrogen sulphide through the liquid has been continued for some time.

Ignite (after adding flowers of sulphur) in a stream of hydrogen gas, and weigh* (see p. 20).

Determine the chromium in the filtrate from the lead as above directed.

Potassium Bichromate.

$K_2Cr_2O_7$.

Heat the salt gently until it begins to melt, and then dissolve about 0.5 grm. of the same in water. Add hydrochloric acid and alcohol, and boil until the liquid assumes an intense green color. The solution contains the chlorides of potassium and chromium. Precipitate the chromium from this solution with ammonium hydrate. Evaporate the bulk of the liquid in a porcelain dish, then transfer it to a platinum crucible and volatilize the ammonium chloride. Ignite the residue of potassium chloride in a well-covered crucible. The bottom of the crucible only should glow faintly.

Dolomite.

Composition.—Carbonates of magnesium and calcium, with generally small quantities of ferrous carbonate, aluminum, and silicic acid.

Pulverize the substance and dry it at 100° C. Determine the oxides by dissolving 1–1.5 grms. of the substance in hydrochloric acid in a porcelain dish. Boil the solution to expel the carbon dioxide, then evaporate the liquid to

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* Strong ignition will cause the volatilization of lead sulphide. Care must be taken not to allow the bottom of the crucible to have more than a faint red glow. (See *Journal für prakt. Chemie*, 96, 257.)

dryness on a water-bath. Heat the residue for some time in an air-bath at 120° C. to effect perfect separation of the silicic acid and undecomposed material that may be present. After cooling moisten with hydrochloric acid, heat the dish gently upon a sand-bath, and dilute with water. The silicic acid that may have separated out is filtered off, washed with hot water, dried, and weighed. The filtrate from the silicic acid is boiled with a few drops of nitric acid to convert the ferrous into ferric compounds, which is easily noticed by the deep yellow color imparted to the liquid, ammonium hydrate added in slight excess, and the solution stirred. Filter off the precipitate consisting of the oxides of iron and aluminum, excluding the air as much as possible. The precipitate, after washing with hot water and dissolving in warm dilute hydrochloric acid, is again precipitated with ammonium hydrate.* The ammonium hydrate precipitate is generally so small that the oxides are dried, ignited, and weighed together. For their separation proceed as described under Chromite.

The calcium in the filtrate from the above precipitate is thrown down as oxalate, and this then converted either into the corresponding carbonate or oxide (see p. 13). As some magnesium oxalate is invariably precipitated along with the calcium, the precipitate in all accurate analyses should be redissolved and the precipitation repeated. To this end add ammonium hydrate in slight excess to the solution, and also a small quantity of ammonium oxalate. Unite the filtrates, and when necessary concentrate the liquid by evaporation—precipitating the magnesium from the cold solution by adding ammonium-sodium phosphate. The further treatment of this precipitate has been already described (p. 17).

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* A second precipitation is necessary because the first precipitate always contains calcium and magnesium.

[Another method, proposed and recommended by Dr. Genth for the separation of calcium and magnesium from the other constituents of dolomite and limestones, is the following:—

A weighed portion of the powdered and dried substance is placed in a platinum crucible and then very strongly ignited. The cooled mass, consisting of calcium and magnesium, together with the other oxides, is digested for some time with a small quantity of a rather concentrated ammonium chloride solution. The calcium and magnesium oxides are dissolved, and may be separated in the usual manner in the filtrate. The insoluble residue is treated with hydrochloric acid and the above course pursued.]

Carbon Dioxide Determination (Direct).—The estimation is effected by the method originally described by Kolbe, but more recently modified by Fresenius, viz., by the increase in weight of a tube filled with soda-lime. The apparatus described by Fresenius is composed of the following parts (see Fig. 2):—

The flask *K*, of from 200 to 300 C.C. capacity, serving for the decomposition of the substance, is closed by a doubly perforated caoutchouc cork. The one perforation holds the safety-tube *a*, the other the bulb-tube *b*. The safety-tube is divided at *a*, and connected by means of a gum tube to the funnel *c*. By the aid of the pinch-cock *o*, we can not only regulate the acid supply, but also, after finishing the experiment, connect the tube with the soda-lime tube *d*, and the small flask *e*, containing potassium hydrate. The bulb-tube *b*, serving for the condensation of steam mechanically carried over, is cut obliquely at the lower end. To free the carbon dioxide from steam and hydrochloric acid, three U-tubes, about 17 cm. long and 16 mm. wide, are placed before the generating flask. Of these the first tube, *f*, is filled only at the bend, while *g* is perfectly filled with pieces of calcium chloride. The tube

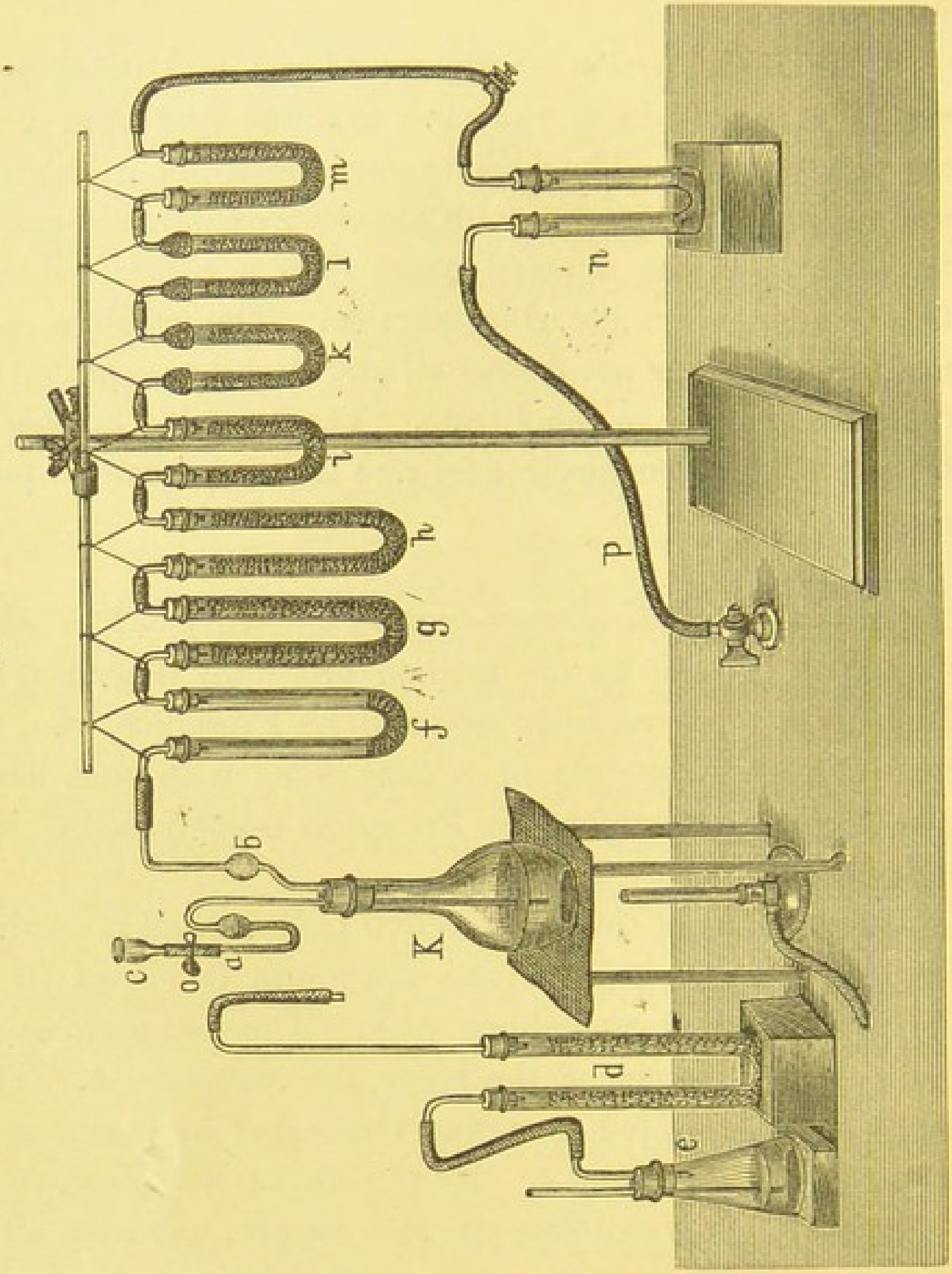

Fig. 2.

h serves solely for the absorption of hydrochloric acid carried over during the operation, and is filled with pieces of pumice stone, previously boiled with copper sulphate and then dried at 250°–300° C. in an air-bath. Connected with *h* there is also the tube *i*, filled with calcium chloride; and joined to the latter are two tubes, *k* and *l*, 11 cm. long and 12 mm. wide respectively, which are filled $\frac{5}{6}$ of their length with coarse soda-lime, and the extreme end with calcium chloride. To prevent the entrance of carbon dioxide and steam from without, thus altering the weight of these tubes, there is attached to them the tube *m*, which has the same dimensions as the absorption-tubes, and is filled in the limb adjoining these tubes with calcium chloride, while the outer limb contains soda-lime.

To enable the operator to have better control over the course of the decomposition, it is advisable to add the tube *n*, both limbs of which are partly filled with water.

The calcium chloride should be previously tested, because it is capable of absorbing carbon dioxide when not pure.

Having weighed both absorption-tubes, *k* and *l*, and brought the weighed substance (2–3 grms.) into the flask *K*, be satisfied, first of all, that the connections of the entire apparatus are tight. Unite all the parts, close the pinch-cock *o*, and, with the aid of an aspirator or air-pump, rarefy the air in the apparatus by sucking upon the gum tube *p*. When all the parts fit closely and properly, the passage of air through *n* continues but a short time. Open the pinch-cock *o*, pour water in the flask, close *o* again, and fill the upper funnel tube with dilute hydrochloric acid, allowing, by partly opening the pinch-cock, the acid to gradually enter the flask. When the action of the acid upon the substance ceases, remove the funnel *c*, join the funnel-tube *a* with the tube *d* and the flask *e*, and draw a slow current of air through the apparatus. In the mean time, bring the contents of the flask to boiling, which will expel the carbon dioxide, and the latter will be carried by the current of air into the absorption apparatus. When cool, weigh the tubes *k* and *l*:

their increase in weight expresses the amount of carbon dioxide present.

$$\text{Orig. sub.} : CO_2 \text{ found} :: 100 : x.$$

Should the dolomite dried at 100° C. lose more water at an increased temperature, this cannot be estimated by igniting a weighed quantity of substance gently and considering the difference in weight as representing the water. The carbon dioxide present would also be expelled, and, further, the ferrous oxide that existed in the mineral would pass into the ferric state. Under these circumstances, the water is best determined by direct weighing. Take a tube of difficultly fusible glass about 30 cm. long and 12 mm. wide, and seal the one end. Into this introduce, to $\frac{1}{3}$ its length, gently ignited lead carbonate, then the mixture of the latter substance with the dolomite, and finally, more lead carbonate. The tube should be tapped upon a table to produce a channel, and the open end then closed with either a dry perforated gum or ordinary cork, into which has been fitted a weighed calcium chloride tube. The tube containing the mixture of lead and dolomite is placed upon a combustion-oven and heated its entire length, commencing with the layer of lead carbonate, and gradually advancing to the end.

Should any water collect in that portion of the tube extending beyond the oven, it can readily be driven into the calcium chloride tube with the aid of a small lamp. When the substance has been completely decomposed, the calcium chloride tube is reweighed.

Alum.

Composition: Aluminum, potassium, ammonium,* sulphuric acid and water.

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* Commercial potash alum contains it.

Determination of the Aluminum and Potassium.—About 1.5 grms. of the salt are dissolved in water in a platinum or porcelain dish, then ammonium chloride and hydrate added—the latter in slight excess. Boil the liquid until the odor of ammonia is only slightly perceptible, allow the precipitate produced to subside, filter and wash by decantation with hot water. Owing to the gelatinous character of aluminum hydrate, it is washed very slowly, and therefore it is advisable in filtering to use a Bunsen pump, or allow the imperfectly washed precipitate to dry, and then renew the washing. The precipitate, when dried, is placed in a platinum crucible, and the filter incinerated apart from it. Finally, the well-closed crucible is heated, at first gently, and then gradually increasing the temperature to a red glow.

In the presence of sulphuric acid, aluminum sulphate is frequently precipitated with the hydrate, and for this reason the ignition of the precipitate should finally be continued over the blast lamp.

The filtrate from the aluminum hydrate is placed in a platinum or porcelain dish and evaporated to dryness, to estimate the potassium as sulphate. The residue is ignited to expel all ammoniacal salts; what remains is a mixture of neutral and acid potassium sulphates. To convert the latter into the corresponding neutral salt (glowing merely effects a partial change), ignite the mass gently, and add from time to time small pieces of pure ammonium carbonate. Continue this for some time, and if the weight of the crucible remains the same after a second ignition with ammonium carbonate, the residue consists entirely of neutral potassium sulphate.

The ammonia may be estimated by boiling a portion of the salt with potassium or sodium hydrate. The apparatus shown in Fig. 3 is designed for this purpose.

The tubulated retort *r* contains a concentrated solution of sodium or potassium hydrate. Both receivers V and V′ are partly filled with dilute hydrochloric acid. The liberated ammonia passes through the cooler K. As an ordinary or even gum cork will absorb ammonia very readily, care should be taken that this gas does not come in immediate contact with these substances. When the apparatus has been completely connected, introduce the substance, placed in a small tube, into the tubulure of the retort, and distil off about one-third of the contents. The ammonium

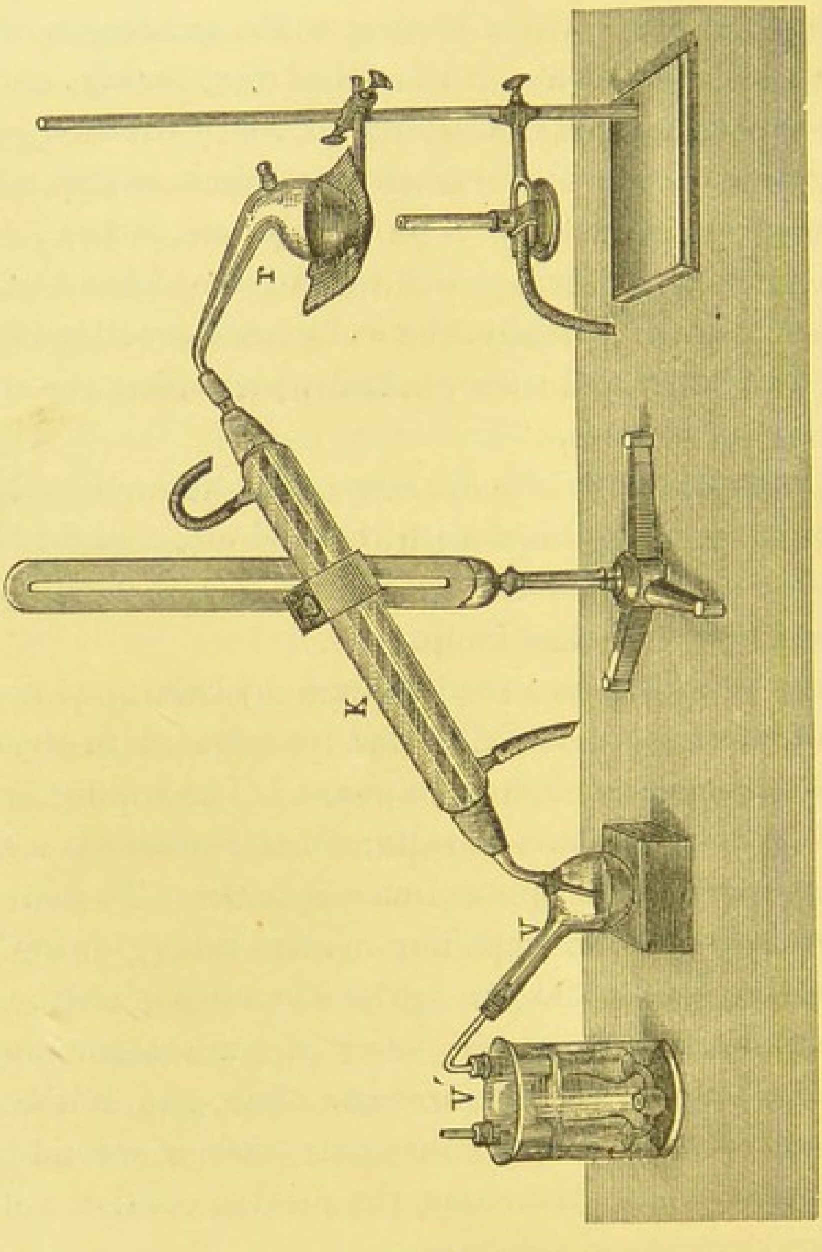

Fig. 3.

chloride formed is estimated by mixing with the liquid in the receivers an excess of platinic chloride, and evaporating almost to dryness at as low a temperature as possible. Pour alcohol (80 per cent.) over the cold residue, stir well, and filter after the precipitate has subsided. The precipitate of ammonio-platinic chloride is brought upon a weighed filter that has been dried at 130° C. Wash with alcohol, finally with a mixture of equal parts of alcohol and ether. Dry at 130° C., until constant weight is obtained.

If the quantity of the precipitate is small, instead of filtering and drying upon a weighed filter, it can be converted into metallic platinum by ignition in a porcelain crucible, and from this the ammonia that was present be ascertained by calculation. To prevent any loss in this operation begin heating the precipitate gradually.

Instead of converting the ammonium chloride into the double salt with platinum, the weight of the former can be directly taken. In this case the liquid contained in the receivers is evaporated to dryness in a platinum dish placed on a water-bath, and the residue then dried in an air-bath at 100° C., until a constant weight is obtained. This method, however, affords less accurate results, as there is invariably some ammonium chloride volatilized.

Finally, the ammonia may be determined in the following manner: conduct the gas into a measured quantity of acid (hydrochloric, sulphuric, or oxalic) of known strength, and titrate the unneutralized portion of the acid with a standard alkaline solution. For the particulars of this operation see "Analysis of Guano."

When alum contains oxide of iron in large quantities, which is seldom the case, it may be best determined volumetrically. The found percentage must then be deducted from the aluminum precipitate.

Determine the sulphuric acid as barium sulphate.

The water in alum cannot be estimated by loss in weight by ignition, because not only it but also sulphuric acid and ammonia are volatilized. When ammonia is absent, the water may be determined as described in the analysis of dolomite. This method is not applicable in the presence of ammonia, because the latter, upon glowing with lead carbonate, is expelled and absorbed by the calcium chloride. This being the case, connect with the tube containing the alum and lead carbonate two V-shaped tubes filled with pumice-stone saturated with sulphuric acid. The increase in weight of the tubes will indicate the amount of water plus the ammonia, and from this subtract the amount of the latter directly determined.

Heavy Spar.

BARITES.

Composition: Barium sulphate, with frequently small quantities of strontium sulphate.

The finely powdered and dried (100° C.) substance, (1 grm.) is thoroughly mixed in a platinum crucible with 4–5 times its weight of sodium carbonate, and fused over a blast lamp. (A good Bunsen burner will generally suffice.) The ignition should be continued until the contents become liquid, and then pour the same into a platinum dish. If the latter is sufficiently large the crucible can be placed in the same, water added, and the whole digested on a water-bath until, upon stirring with a glass rod, no hard, undecomposed particles can be detected. If it is not desired to pour out the liquid contents of the crucible, allow the latter to cool, and then boil with water. The latter procedure requires considerable time. The aqueous solution contains, together with the undecomposed sodium carbonate, all the sulphuric acid in the form of sodium sulphate. The residue consists of the carbonates of strontium and barium. After freeing the crucible from the adhering precipitate, and rinsing with water, the insoluble residue is filtered off and washed until a drop of filtrate does not indicate a sulphuric acid reaction. The weight of the gently ignited precipitate will represent the sum of the strontium and barium carbonates. Dissolve the mixture in acetic acid, and separate the bases just as barium is separated from calcium. (See p. 27.)

To determine the sulphuric acid in the aqueous extract of the fused mass, acidify the liquid carefully with hydrochloric acid; then heat to expel all the carbon dioxide, and finally precipitate with barium chloride (p. 15).

When the heavy spar contains silica it will be found in the aqueous solution, together with the sodium sulphate, and should be removed before precipitating the sulphuric acid. Evaporate the solution to which hydrochloric acid has been added to dryness, and heat the residue for some time at 120° C. When cool, moisten with hydrochloric acid, and add water. (See DOLOMITE, p. 31.) The filtrate from the silicic acid can now be employed for the sulphuric acid determination. The silicic acid is strongly ignited in a platinum crucible and weighed.

If calcium sulphate be present in the heavy spar, the three sulphates can be separated by treatment with ammonium carbonate (p. 29).

Separation of Potassium from Sodium.

A mixture of equal parts of the chlorides is employed in the analysis.

The separation of these alkalies is based upon the precipitation of the potassium as potassium-platinum chloride, while the corresponding sodium compound remains dissolved. The chlorides (about 0.5 grm.), dried at 100° C., are dissolved in the least possible quantity of water, and then mixed with a concentrated neutral solution of platinic chloride,* and evaporated almost to dryness upon a water-bath. The temperature should not be too high. Pour alcohol (80 per cent.) over the cold residue, and treat the potassium-platinum chloride just as the ammonium compound. (See p. 39.)

If the solution employed for washing consists of a mixture of 2 vols. alcohol and 1 vol. ether, not any potassium-platinum chloride will be dissolved. However, the filtrate should be tested for traces of it. For this purpose evaporate it again to dryness with addition of more platinic chloride, and treat the residue again with alcohol. Calculate the amount of potassium chloride in the double salt

$$K_2PtCl_6 : 2KCl :: \text{wt. } K_2PtCl_6 : x.$$

The amount of sodium chloride is found by difference.

[Instead of weighing the double salt upon a weighed filter, which is at the best tedious and inconvenient, it may after washing with alcohol be rinsed with water into a small beaker, and to the aqueous solution a little dilute hydrochloric acid and a piece of pure zinc added. The application of heat aids the reduction. When the zinc is completely dissolved, the liquid is diluted and filtered. The residual platinum is thoroughly washed with hot water, dried, ignited, and weighed. One equivalent of platinum represents one equivalent of potassium.]

Instead of separating the potassium chloride as a double

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* Enough platinic chloride must be added to convert both the potassium and sodium into double salts with it, otherwise sodium chloride will invariably be mixed with the potassium-platinum chloride, and cannot be removed by washing with alcohol.

salt, we can determine the amount of chlorine in a mixture and from this calculate the quantity of potassium and sodium chlorides present.*

To determine the chlorine the solution of the substance is mixed with silver nitrate and the silver chloride obtained weighed. (See Barium Chloride, p. 17.)

If S represents the sum of potassium and sodium chlorides,
C the found amount of chlorine,
x the unknown amount of potassium chloride,
y the unknown amount of sodium chloride,
then $a + y = S$ (1).

The molecular weight of potassium chloride is 74.57; it contains in one part by weight $\frac{35.46}{74.57} = 0.47552$ chlorine: the molecular weight of sodium chloride is 58.46; the amount of chlorine in it is $\frac{35.46}{58.46} = 0.60657$.

Then $0.47552x + 0.60657y = C$ (2),

and $x = \frac{(0.60657\,S) - C}{0.13105}$

and $y = S - x$.

Instead of determining the silver gravimetrically as silver chloride, it may be estimated volumetrically much more rapidly and with just as great accuracy. This method of estimation depends upon the deportment of a silver nitrate solution of known strength with a solution of an alkaline chloride in the presence of chromic acid. When silver nitrate is added to a solution of an alkaline chloride containing potassium chromate, all the chlorine will at first be precipitated as silver chloride, after which the

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* This indirect method of determining the potassium and sodium is only accurate when the quantity of potassium chloride with the sodium chloride is not too small.

silver acts upon the chromic acid of the chromate, forming silver chromate. The formation of the latter compound, which is characterized by an intense blood-red color, serves as a means of recognizing the close of the reaction.

For the execution of this method of determining chlorine allow silver nitrate to drop from a burette into the chloride solution containing potassium chromate until the white precipitate of silver chloride is colored distinctly red by the silver chromate.* The solution should be continually stirred. The amount of chlorine present is calculated from the number of C. C. of the silver nitrate solution that has been used.

There is required :—

1. *A Neutral Solution of Silver Nitrate.*—The solution is made $\frac{1}{10}$ normal, *i. e.*, 10.8 grms. metallic silver or 17 grms. silver nitrate are dissolved and diluted to 1 litre. If 1000 C. C. of this solution contain exactly 10.8 grms. silver, these correspond to 3.546 grms. chlorine, 3.646 grms. hydrochloric acid, or 5.846 grms. sodium chloride, etc. In order, however, to be satisfied as to the correct strength of the solution, prepare

2. *A Solution of Sodium Chloride.*—This is done by dissolving 5.846 grms. chemically pure and dry sodium chloride in 1 litre of water.

To standardize the silver nitrate solution allow about 10 C. C. of the sodium chloride solution to flow out the burette, mix in a few drops of potassium chromate, and add from the burette, while stirring, silver nitrate until the final reaction appears. When the silver nitrate solution is $\frac{1}{10}$ normal, then 10 C. C. of the sodium chloride solution will exactly correspond to 10 C. C. of the silver solution.

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* As silver chromate is soluble in acids, both the liquid to be treated and the silver nitrate solution must be perfectly neutral.

Mixture of Potassium Chloride, Sodium Chloride, and Magnesium Sulphate.

The separation of magnesium from the alkalies according to the following method, must be preceded by the removal of the sulphuric acid. For this purpose, acidify the boiling solution of the substance with a few drops of hydrochloric acid, and add barium chloride. Filter off the barium sulphate and evaporate the filtrate to dryness, in a platinum dish, having first added an excess (about four times the amount) of pure oxalic acid for the conversion of the alkalies and the magnesium into oxalates. By igniting the residue, we have the alkaline carbonates and magnesia produced. Treat the residue with small quantities of hot water, dissolving by this means the alkalies and separating them from the magnesia (and barium carbonate), then evaporate to dryness with dilute hydrochloric acid, converting the alkalies into chlorides which may then be separated in the manner already described (p. 41).

The weighed alkaline chlorides should always be examined for traces of magnesia, and the amount deducted from the others. (See p. 16.)

$$(Mg_2P_2O_7 : 2MgCl_2 : : \text{wt. } Mg_2P_2O_8 : x.)$$

The magnesia may be separated from the barium carbonate by dissolving the residue in dilute hydrochloric acid, precipitating the barium with dilute sulphuric acid, and determining the magnesium in the filtrate in the usual manner.

Another method employed in separating magnesium from the alkalies is based upon the precipitation of the magnesium as magnesium-ammonium carbonate.

It is immaterial whether the magnesium and alkalies exist as chlorides, sulphates, or nitrates. To the very concentrated solution of the substance add, in excess, a concentrated solution of ammonium carbonate* and hydrate, and allow the same to stand twenty-four hours. The precipitate after filtering should be washed with a similar solution of ammonium carbonate, dried, and by strong ignition converted into magnesia. It is to be remarked that in this separation the magnesia almost invariably retains potassium carbonate mixed with it. (The sodium carbonate is perfectly dissolved.) It is, therefore, of the utmost importance that the ignited magnesia be treated with small quantities of water and again ignited. The washings should be added to the liquid containing the alkalies. The alkalies are most readily determined as sulphates.

The filtrate from the magnesia precipitate should be brought into a platinum or porcelain dish, covered and heated on a water-bath to expel the ammonia and produce a partial decomposition of the ammonium carbonate. When carbon dioxide is no longer liberated, add dilute sulphuric acid drop by drop to the cold liquid and evaporate to dryness. If the evaporation has taken place in a porcelain dish, bring the residue into a weighed platinum crucible and ignite to expel the ammoniacal salts. The residue contains not only the alkaline sulphates, but also their hydrosulphates; therefore, continued ignition with repeated addition of ammonium carbonate is necessary to obtain a constant weight. (See Potassium Determination in ALUM, p. 37.) Examine the alkalies for magnesium.

When sodium and potassium are present together, in-

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* According to Schaffgotsch, a solution of this kind is best prepared by dissolving 230 grms. ammonium carbonate in 180 grms. ammonium hydrate (specific gravity 0.92) and diluting to 1 litre.

stead of separating the potassium with platinic chloride,* the sulphuric acid in their sulphates may be determined, and the quantity of sodium and potassium calculated from this.

If S represents the weight of sodium and potassium sulphates, and s the found quantity of sulphuric acid, then

$$x = \frac{s - 0.45919\,S}{0.10419}.$$

$$y = S - x.$$

Alloy of Copper and Silver.

SILVER COINS.

The solution of the coin (about 0.5 grm.) is effected by bringing it in contact with dilute nitric acid in a porcelain dish, which is well covered with a watch-glass and heated upon a water-bath. Finally, evaporate the solution to dryness, dissolve the residue in hot water, rinsing the solution into a beaker, and precipitate the silver by the addition of dilute hydrochloric acid.

By the application of heat and frequent stirring, the precipitate may readily be balled together, and filtered after standing a short time. The subsequent treatment of the precipitate has already been described in the analysis of barium chloride (p. 17).

The copper in the filtrate from the silver chloride may

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* When the alkalies are present as sulphates, to determine the potassium as potassium-platinum chloride, it is necessary to first convert the sulphates into chlorides. This is effected by adding to the solution barium chloride and removing the excess of the latter with ammonium carbonate, or by repeatedly igniting the sulphates with ammonium chloride until constant weight is obtained.

be precipitated as sulphide by conducting hydrogen sulphide into the solution. The precipitant should be added until the odor of hydrogen sulphide is strongly perceptible, and the precipitate then rapidly filtered, with exclusion of air. Cover the beaker and funnel with glass plates. After washing the precipitate with water containing hydrogen sulphide, dry and ignite it strongly—with addition of sulphur—in a stream of hydrogen gas (see p. 20). The residue is cuprous sulphide (Cu_2S). As copper sulphide oxidizes exceedingly readily, the filtration and washing should not be interrupted. When oxidation has occurred (recognized by the cloudiness of the filtrate), the precipitate upon the filter is completely washed with water containing hydrogen sulphide, and the filtrate treated a second time with hydrogen sulphide gas. The small quantity of copper sulphide produced is brought upon a separate filter.

If the copper is precipitated from a hot solution, a sulphide of a more compact nature is obtained, which may be washed very readily.

$$Cu_2S \ : \ Cu_2 \ : : \ \text{wt. } Cu_2S \ : \ x.$$

[As a control, get the copper in the form of sulphate and determine it by electrolysis. The platinum crucible containing the solution of the copper salt serves as negative pole of a weak Bunsen battery consisting of one or two cells. A stout platinum wire will answer as positive electrode, and is allowed to dip into the copper solution. The wire should not be allowed to touch the sides of the crucible. Care must be taken to regulate the current so that the copper will be deposited upon the walls of the crucible as a compact, bright coating. The time necessary to effect complete precipitation varies from one to three hours. Whether the copper has been completely removed or not may be ascertained by placing a drop of the solution on a porcelain plate and adding a little hydrogen sulphide. After precipitation wash the copper with distilled water, dry carefully, and weigh with the crucible.

When the copper is thrown out of the solution in spongy masses, it not only oxidizes very readily, but it is also difficult to free it of impurities mixed with it.]

Alloy of Copper and Zinc.

BRASS.

Dissolve the alloy in dilute nitric acid, and proceed precisely as described in the preceding analysis. When the brass, as is generally the case, contains lead, the nitric acid solution is evaporated to dryness, with addition of sulphuric acid, upon a water-bath, until all the nitric acid has been expelled and the lead completely converted into sulphate. Pour cold water over the residue, stir the liquid with a glass rod until all the lead sulphate that has separated out appears perfectly white, then add one-third volume alcohol.* Wash the filtered precipitate with dilute alcohol (until the addition of barium chloride to the washings produces no cloudiness), dry, and then ignite in a porcelain crucible. It should be borne in mind that, upon incinerating the filter, the lead sulphate adhering to the latter will be reduced to metallic lead; therefore adopt the course pursued in the determination of chlorine (p. 18), incinerate the filter upon the inverted crucible lid, dissolve the metallic lead in a few drops of nitric acid, evaporating

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* If more alcohol than this is added, copper sulphate will very likely separate out, but may be redissolved by the addition of more water.

this solution to dryness with addition of dilute sulphuric acid.

$$PbSO_4 : Pb :: \text{wt. } PbSO_4 : x.$$

After thus removing the lead, heat the liquid that remains upon a water-bath to expel the alcohol present, and then effect the separation of the copper and zinc by conducting hydrogen sulphide into the solution. Since in this method some sulphide of zinc is very apt to be precipitated together with copper sulphide, the liquid should be made strongly acid* by the addition of hydrochloric acid, and the copper sulphide filtered immediately after the precipitation. As regards the filtration of the copper sulphide, what has already been mentioned (precipitation of copper in silver coins) should be borne in mind. Notwithstanding all this, however, the copper sulphide is not absolutely free from zinc sulphide, and, if the separation is to be very perfect, the precipitation must be repeated. In this case transfer the precipitate to a porcelain dish, dry the filter, and after its incineration add the ash to the precipitate and dissolve the latter in *aqua regia*. Evaporate this solution to dryness upon the water-bath, dissolving the residue in water, and, after the addition of hydrochloric acid, reprecipitate the copper as sulphide. The copper sulphide obtained is ignited in a hydrogen stream and determined as Cu_2S.

The filtrates from the copper sulphide are united, and the zinc then precipitated as sulphide. To this end heat the liquid to incipient ebullition, then add ammonium in excess and some ammonium sulphide.† The precipitate is washed with water containing ammonium sulphide and

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* According to Grundmann's experiments, 10 C. C. hydrochloric acid are required for 0.2 grm. cupric oxide.

† The sulphide of zinc precipitated from a hot solution is more compact and much more readily filtered.

ammonium nitrate, then dried and ignited, mixed with sulphur, in a stream of hydrogen (see p. 20).

$$ZnS : Zn :: \text{wt. } ZnS : x.$$

When lead is not present in the brass, the nitric acid solution may be evaporated to dryness without the addition of sulphuric acid. The residue is then dissolved in water, hydrochloric acid added, and precipitation produced by hydrogen sulphide.

Another method for the separation of copper and zinc is based upon the deportment of the former with sodium hyposulphite. If the solution of a copper salt is mixed with sodium hyposulphite, a precipitate of copper hyposulphite is produced, which decomposes very readily upon boiling into copper sulphide and sulphuric acid.

Zinc salts are not precipitated by this reagent. To effect the separation of these two metals by means of this method, their nitric acid solution should be evaporated to dryness with sulphuric acid, the residue dissolved in water, and sodium hyposulphite added to the boiling solution until the addition no longer produces a precipitate of cuprous sulphide, Cu_2S. This cuprous sulphide possesses entirely different properties from that obtained by precipitation with hydrogen sulphide. It does not oxidize on exposure to the air, and may be easily washed with hot water not containing any hydrogen sulphide. It should also be ignited in a stream of hydrogen.

In order that the zinc may be estimated in the filtrate from the cuprous sulphide, the excess of sodium hyposulphite must be previously removed. Add nitric acid to the solution, then evaporate it to dryness upon the water-bath, dissolving the residue in water, filtering off the sulphur that may have separated out, and finally precipitate the zinc with sodium carbonate (see p. 18). As regards the purity of the zinc oxide, see remark I., p. 19.

Alloy of Antimony and Lead.

TYPE METAL.

The alloy is divided as finely as possible, and about 0.5 grm. of it then transferred to a porcelain dish containing equal parts of nitric acid and concentrated tartaric acid, and the whole heated upon a water-bath. To the solution is now added an excess of ammonium hydrate, until the liquid imparts an alkaline reaction, then an excess of ammonium sulphide. By this means we have the antimony dissolved as antimony-ammonium sulphide ($Sb(SNH_4)_3$), whilst the lead remains insoluble.

Digest the precipitate for some time upon the water-bath, filter without bringing the precipitate on the filter, and then digest it again with small quantities of ammonium sulphide, and finally determine the lead sulphide by *gentle* ignition in a stream of hydrogen (p. 20). The antimony in the filtrate from the lead sulphide separates out upon the addition of hydrochloric acid. Carefully mix the solution contained in a covered beaker with dilute hydrochloric acid, until its addition is no longer followed by the precipitation of antimony sulphide; then apply heat upon the water-bath until the odor of hydrogen sulphide is no longer perceptible.* The precipitate, which consists of sulphur and antimony sulphide, is brought upon a weighed filter, dried at 100° C., washed with water containing hydrogen sulphide, and dried again at 100° C., until the weight becomes constant. To estimate the quantity of antimony sulphide present, weigh off a portion of the dried precipitate, place it in a porcelain boat, and insert this into a glass tube, through which a

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* This may be hastened by conducting carbon dioxide into the hot solution.

slow current of dry carbon dioxide is transmitted, and the contents of the boat cautiously ignited, until no more sulphur escapes and the antimony sulphide has become black.

$$Sb_2S_3 : 2Sb :: \text{wt. } Sb_2S_3 : x.$$

As a control for the analysis, a second portion of the weighed precipitate may be converted into the antimoniate of the teroxide of antimony. This is effected by moistening a weighed portion of the precipitate, placed in a porcelain crucible, with a few drops of nitric acid (sp. gr. 1.42), then adding a somewhat larger quantity (about 8 to 10 times the quantity) of fuming nitric acid. Cover the crucible with a watch-glass or a concave porcelain cover, and carefully apply heat upon the water-bath until all action ceases, finally allowing the acid to evaporate. The residual mass consists of a mixture of antimonic acid and sulphuric acid. For the conversion of the former into teroxide and the expulsion of the sulphuric acid, gradually ignite the contents of the crucible to intense glowing.

$$SbO_2 : Sb :: \text{wt. } SbO_2 : x.$$

The lead sulphide as above obtained invariably has antimony sulphide adhering to it. The separation is more complete if the greater portion of the lead is first removed from its nitric acid solution by the addition of sulphuric acid (without alcohol), and determined as such. The lead still remaining in the filtrate may be separated from the antimony by the addition of ammonium hydrate and ammonium sulphide. If pure nitric acid replaces nitric acid and tartaric acid in the decomposition of the alloy, antimonic acid will separate out, and the separation of the two metals will be very imperfect, even if the treatment with ammonium sulphide be repeated.

Alloy of Tin and Lead.

Soft Solder.

Warm the alloy with nitric acid until all action ceases, then evaporate the solution to dryness upon a water-bath. After moistening the residue with a few drops of nitric acid, pour water over it, and remove the stannic oxide by filtration. The precipitate is washed with water, dried, and ignited strongly in a porcelain crucible placed over a blast-lamp.

The incineration of the filter is best performed upon the inverted lid of the crucible, and the ash carefully heated with a few drops of nitric acid, to oxidize the reduced tin.

The filtrate from the oxide of tin is mixed with dilute sulphuric acid, and evaporated on the water-bath, until all the nitric acid has been expelled; the residue, after cooling, treated with alcohol, and the lead sulphate filtered off. The precipitate should be washed with alcohol, and treated as described on page 49.

Weighable quantities of lead always adhere to the tin oxide as above obtained by oxidation with nitric acid; these, however, may be estimated by mixing the weighed precipitate with four to five times its quantity of equal parts of sodium carbonate and flowers of sulphur, and fusing (over an ordinary burner) in a porcelain crucible. The residue is treated with water, and the tin dissolved as sodium-sulphostannate (Na_2SnS_3), while the lead oxide that adhered to the stannic oxide will remain as insoluble lead sulphide. Remove the latter by filtration, wash with water containing hydrogen sulphide, and weigh as such.

From the found amount of lead sulphide calculate the lead oxide, and subtract this from the stannic oxide, thus obtaining the correct amount of the latter.

Tin and lead may be separated in a manner similar to that employed in the separation of antimony and lead—by means of ammonium sulphide. Evaporate the nitric acid solution to dryness, mix the residue with ammonium hydrate and sulphide, and proceed as above. The lead sulphide, after being dried, is mixed with four to five times its weight of equal parts of sodium carbonate and sulphur, then fused. The aqueous extract from the fused mass, after filtering off the lead sulphide, is added to the ammonium sulphide solution, and the tin precipitated by the addition of hydrochloric acid to the liquid contained in a covered beaker. After the precipitate has fully separated, warm upon a water-bath.

As soon as the liquid ceases to impart the odor of hydrogen sulphide, filter off the mixture of tin sulphide and sulphur; wash the precipitate perfectly with a solution of ammonium acetate, containing a few drops of acetic acid. Place the dried precipitate in a weighed porcelain crucible, heating it gradually with access of air to expel the sulphur. Finally, ignite over a blast-lamp.

The final traces of sulphuric acid that may remain are expelled by placing a small piece of ammonium carbonate in the crucible, and again igniting. The filter should be burned upon the inverted crucible lid. The ignited residue is SnO_2.

Alloy of Lead and Bismuth.

The nitric acid solution of the alloy is evaporated upon a water-bath until it attains a syrupy consistence, a little water is then added, the liquid stirred with a glass rod and again evaporated. This operation should be repeated three or four times (the residue should then contain no more nitric acid), when the cooled mass is finally mixed with a cold solution of 1 part ammonium nitrate in 500 parts water, and then allowed to stand a short time. Filter and wash the bismuth nitrate with a solution of ammonium nitrate having the above concentration; dry and ignite in a porcelain crucible. The filter should be burned upon the inverted crucible lid. The ignited residue is oxide of bismuth, Bi_2O_3.

The oxide first obtained may be converted into metallic bismuth, if ignited in a current of hydrogen gas.

In the filtrate from the bismuth nitrate determine the lead as sulphide, precipitating it either with hydrogen or ammonium sulphide. (See p. 52.)

The insolubility of lead sulphate affords another method for the separation of these two metals. The solution is freed from nitric acid by evaporation—sufficient hydrochloric acid, however, being added to dissolve all the bismuth.* To ascertain when a sufficient amount of acid has been added, pour a small portion of acidified liquid upon a watch-glass and add a few drops of water. If an immediate turbidity forms, enough acid has not been added. Rinse the liquid upon the watch-glass with alcohol. For the precipitation of the lead, add dilute sulphuric acid to the liquid, and if any lead chloride has separated out, allow the acid to act upon it, before the addition of alcohol (sp. gr. 0.8). Wash the lead sulphate first with alcohol, mixed with a small quantity of hydrochloric acid, finally with pure alcohol. The precipitate is ignited as described, p. 49, and then weighed.

The filtrate is at once mixed with a large quantity of water and the bismuth precipitated as oxychloride (BiOCl —bismuth basic chloride). If no further precipitation is produced upon the addition of more water, filter off the precipitate, and by fusing it with KCy convert it

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* If much lead has gone in solution, crystalline lead chloride will separate.

into metallic bismuth.* For this purpose the bismuth oxychloride, placed in a porcelain crucible, is mixed with five times its quantity of potassium cyanide and fused over an ordinary lamp. By protracted fusion the small particles of bismuth may be collected to one large globule. After cooling, digest the fused residue with cold water, filter the bismuth upon a dried and weighed filter, washing it at first with dilute and finally with absolute alcohol. Dry at 100° C. and weigh.

In the process of fusion the porcelain crucible is generally more or less attacked, and the bismuth consequently rendered impure by loosened particles of the crucible. To avoid the error thus occasioned, dissolve the bismuth in dilute nitric acid and weigh the residue.

Alloy of Lead and Zinc.

Add sulphuric acid to the nitric acid solution and evaporate the latter upon the water-bath until nitric acid vapors no longer escape, then pour water upon the cooled residue and add one-third volume of alcohol. Filter the separated lead sulphate, wash with aqueous alcohol, dry, ignite, and weigh (p. 49).

After the expulsion of the alcohol from the filtrate, the zinc in the latter is determined either as sulphide or oxide (p. 18).

Hydrogen sulphide may be employed for the separation of these two metals. Evaporate the nitric acid solution to dryness, take up the residue with a large quantity of water, adding a few drops of hydrochloric acid, and precipitate the lead with the above reagent (p. 30).

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* In this case the BiOCl cannot be directly weighed, because in the presence of sulphuric or phosphoric acids the precipitate will consist of compounds of bismuth with these acids.

Precipitate the zinc in the filtrate as sulphide or carbonate.

Alloy of Bismuth and Copper.

The nitric acid solution of the alloy is evaporated upon a water-bath, the residue mixed with a few drops of hydrochloric acid and a large quantity of water added. When the bismuth oxychloride formed has subsided, and the liquid remains clear upon the further addition of water, transfer the precipitate to a weighed filter, wash it with water slightly acidulated with hydrochloric acid, then dry it at 100° C. until constant weight is obtained.

$$BiOCl : Bi : : \text{wt. } BiOCl : x.$$

The copper in the filtrate may be separated either as oxide (p. 14), sulphide (p. 15), or as metallic copper.

For the execution of the latter mode of estimation, concentrate the filtrate, placed in a weighed platinum dish,* by evaporation, and throw into the liquid a small piece of zinc or cadmium.† When necessary add drop by drop sufficient hydrochloric acid to produce a moderate evolution of hydrogen gas, and cover the dish with a watch-glass. When the reduction is complete (ascertained by the addition of ammonium hydrate to a portion of the clear liquid) and all the zinc is dissolved, pour off the fluid (when necessary through a small filter), wash the copper by decantation with boiling water, until the liquid ceases to give a hydrochloric acid reaction. The last traces of water are removed by rinsing out the dish with absolute alcohol. Dry the copper at 100° C. and weigh.

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* A porcelain dish may be used; the reduction, however, will then be much slower.

† Cadmium is preferable to zinc, because the latter generally leaves a residue when dissolved in acids.

As cadmium is not so greatly acted upon by dilute acids as zinc, the same piece may be repeatedly employed for reduction. (Classen, *Journal f. prakt. Chemie*, 96, 257.)

Alloy of Copper and Tin.

BRONZE.

Bring the alloy into a porcelain dish provided with a cover, and pour over it nitric acid of sp. gr. 1.3, and, when the first action ceases, and there is no longer any visible decomposition occurring, apply heat. After all the tin has been converted into stannic oxide, evaporate the solution upon the water-bath. Care should be taken to expel the nitric acid perfectly, and the cold residue is then moistened with a few drops of nitric acid, and this diluted with water. After the stannic oxide has perfectly separated, filter the clear supernatant liquid and wash the precipitate with water, until the washings no longer give an acid reaction with blue litmus paper. The stannic oxide is ignited and weighed. (See p. 54.)

To remove the cupric oxide invariably adhering to the stannic oxide, mix the latter with four to five times its quantity of equal parts of sodium carbonate and sulphur; then fuse in a porcelain crucible. (See p. 54.)

The copper sulphide obtained by lixiviating the fused residue is ignited in a current of hydrogen gas, then estimated, and the amount of cupric oxide calculated from the found sulphide is deducted from the first weight of stannic oxide.

In the filtrate from the tin, the copper is determined as given above.

When the bronze contains lead, its precipitation precedes that of the copper. This is effected by adding dilute sulphuric acid to the solution, and then evaporating. (See BRASS, p. 49.)

A second method for separating copper from tin is based upon the precipitation of the latter with dilute sulphuric acid. The residue obtained by the evaporation of the nitric acid solution is moistened with strong hydrochloric acid, and after standing some time (about half an hour), mixed with water and heated until all the stannic oxide has been dissolved. From this solution of stannic chloride the tin is precipitated by dilute sulphuric acid. When the stannic oxide has fully settled, it is filtered and washed with water until nitrate of silver causes no cloudiness when added to the washings. If more hydrochloric acid was added to the liquid than was required to dissolve the stannic oxide, it must be diluted with a large excess of water, so that the stannic oxide will separate out perfectly. The liquid should then be first filtered, after having stood from twelve to twenty-four hours. The dried precipitate is repeatedly ignited with the addition of a small piece of ammonium carbonate.

The copper in the filtrate can be estimated after one of the methods already described.

Alloy of Nickel and Copper.

NICKEL COINS.

The residue obtained by the evaporation of the nitric acid solution is dissolved in water; this solution strongly acidified with hydrochloric acid, and the copper precipitated by hydrogen sulphide. The copper sulphide is filtered, ignited, and weighed; the precautions mentioned on p. 48 being closely observed.

The filtrate is boiled to expel the hydrogen sulphide, and the nickel precipitated by the addition of sodium hydrate. (See p. 23.)

Besides the two metals just disposed of, nickel coins frequently contain weighable quantities of iron and cobalt, which would be precipitated as hydrated oxides together with the nickel. This being the case, dissolve the metallic nickel that has been obtained in nitric acid, and very nearly neutralize the solution with ammonium hydrate; then add ammonium carbonate in excess. After the solution has been digested some time, the precipitate of ferric oxide is filtered and dissolved upon the filter in hydrochloric acid, and the precipitation with ammonium carbonate repeated. By ignition in a stream of hydrogen gas, ferric oxide is converted into metallic iron. To estimate the cobalt evaporate the filtrate from the ferric hydrated oxide to dryness, expel all ammoniacal salts by gently igniting the residue; then dissolve the latter in hydrochloric acid, with addition of a few drops of nitric acid, and precipitate the cobalt as potassium-cobaltic nitrite, just as given on page 22.

The found percentages of metallic iron and cobalt are deducted from the nickel.

The iron may also be separated from the nickel and cobalt by neutralizing the acid solution with ammonium hydrate, then adding acetate of sodium or ammonium, and finally precipitating with a neutral alkaline succinate at a gentle heat, and filtering the succinate of iron from the solution which contains the rest of the metals. The precipitate of iron is washed with cold water, then with warm ammonium hydrate, and by ignition converted into ferric oxide.

Alloy of Copper, Zinc and Nickel.

The residual mass remaining after the evaporation of the nitric acid is taken up with water, the solution acidified with hydrochloric acid, and hydrogen sulphide added to throw down the copper. (See p. 48.) The filtered copper sulphide should be dissolved and the precipitation repeated. (See BRASS, p. 50.)

Boil the filtrate to fully expel the hydrogen sulphide (finally adding a few drops of nitric acid), and mix with it so much sodium carbonate that merely the slightest trace of free acid exists in the solution. We can very readily hit this point if we add sodium carbonate, drop by drop, until a precipitate is just produced, and this then dissolved in a drop of hydrochloric acid. Conduct hydrogen sulphide into this (cold) solution as long as zinc sulphide is precipitated, then add a few drops of a dilute sodium acetate solution and more hydrogen sulphide, until the liquid is fully saturated with the gas. After standing twelve hours, the zinc sulphide is filtered, washed and weighed (p. 20).

If this mode of procedure is closely pursued, the zinc sulphide that is obtained is perfectly free from nickel. It is advisable to redissolve the precipitate and repeat the precipitation.

After boiling off the hydrogen sulphide in the filtrate, the nickel is precipitated and determined as given on page 23.

When cobalt and iron are present, the nickel is to be separated from these. (See p. 61.)

Another method of separation for these metals depends upon the deportment of a solution of the cyanides of the bases in potassium cyanide with potassium sulphide. The concentrated solution (free from hydrogen sulphide) of the two metals is mixed with an excess of sodium hydrate, and the precipitate formed dissolved in potassium cyanide, and upon the addition of potassium sulphide only zinc sulphide will be precipitated.

The filtrate from the zinc sulphide is boiled, and a drop of *aqua regia* added to decompose the potassium-nickel cyanide. The ebullition is continued until the odor of hydrocyanic acid is no longer perceptible, and the nickel then precipitated in the usual manner with sodium hydrate.

As the zinc sulphide precipitated by potassium sulphide readily retains some of the precipitant, it should not be directly weighed, but be again dissolved in hydrochloric acid, and after the removal of the hydrogen sulphide the zinc is precipitated with sodium carbonate (p. 18).

Alloy of Tin, Copper, Lead and Zinc.

If the alloy can be pulverized, mix a weighed portion of the same (about 1 grm.) in a porcelain crucible with 6 to 7 times its quantity of equal parts of sodium carbonate and sulphur, then fuse. The aqueous extract of the fused mass contains the sodium-tin sulphide, while the residue consists of the sulphides of the other three metals. The latter are filtered with exclusion of air, and washed with water containing hydrogen sulphide. From the sodium sulphide solution the tin is thrown down and estimated as in the analysis of SOFT SOLDER (p. 55).

Dissolve the sulphides of copper, lead and zinc in *aqua regia*, and evaporate the solution to dryness. The methods may here be employed which have already been given in the analysis of BRASS (p. 49).

If the alloy cannot be cut into small pieces, it must be oxidized with nitric acid. The method of procedure then is analogous to that employed in analyzing SOFT SOLDER (p. 54). The residual stannic oxide, however, always contains weighable quantities of copper and lead, and must, therefore, be fused with soda and sulphur and the tin determined in the aqueous extract from the fused mass (p. 54).

The remaining metallic sulphides are dissolved in nitric acid, and this then added to the original solution. For the rest, follow the method given on page 49.

Alloy of Tin, Lead, Bismuth and Cadmium.

WOOD'S METAL.

The residue that remains after evaporating the nitric acid is moistened with a little of the same acid, and the stannic oxide that has separated from the aqueous solution is filtered off. (See BRONZE, p. 59.) To free the latter from the adhering metallic oxides (contains besides lead a tolerably large quantity of bismuthic oxide) fuse the washed precipitate with sodium carbonate and sulphur, and precipitate the tin as sulphide, according to page 55, from the aqueous solution of the fused mass.

The insoluble sulphides remaining after the treatment with water are dissolved in nitric acid, and this solution added to the original.

After expelling as much acid as possible from the solution, precipitate first the lead as sulphate, and then the bismuth as oxychloride, proceeding in these operations as directed on page 56.

The filtrate from the latter precipitate is concentrated by evaporation, and the cadmium thrown down by hydrogen sulphide gas as cadmium sulphide. The precipitate is collected upon a filter, dried at 100° C., and weighed, and then washed first with water containing hydrogen sulphide, to which has been added some hydrochloric acid, and finally pure water is employed. The cadmium sulphide is dried at 100° C., until constant weight is obtained, and from this is then estimated the metallic cadmium present—

$$CdS : Cd = 144 : 112.$$

Instead of estimating the cadmium as sulphide it may be separated as carbonate, and this converted by ignition into oxide. The method of procedure in this instance is then perfectly similar to that described in the estimation of zinc as oxide (p. 18). In igniting the precipitate, care should be taken to have previously removed it perfectly from the filter. However, to avoid the reduction or volatilization of any adherent cadmium carbonate while burning the filter, moisten the latter with a solution of ammonium nitrate, dry, and then incinerate it upon a crucible lid.

$$CdO : Cd = 128 : 112.$$

Alloy of Tin, Lead, Bismuth and Mercury.

The course of analysis is similar to that employed in the preceding example. In the filtrate from the bismuth oxychloride precipitate the mercury as sulphide by hydrogen sulphide. The precipitate is collected as soon as possible upon a weighed filter, washed with water, dried at 100° C., and weighed.

$$HgS : Hg = 232 : 200.$$

To separate the bismuth from mercury according to the above directions, it is required that the latter be present in the solution as a mercuric compound. To be certain that all the mercurous nitrate has been converted into mercuric nitrate, the digestion of the alloy with an excess of nitric acid is continued for some time.

Alloy of Antimony and Tin.

A weighed quantity of the finely divided alloy placed in a covered porcelain dish is oxidized by the gradual addition of strong nitric acid (1.4 sp. gr.), and heat then applied, after the first action has ceased, until the residue appears perfectly white. After evaporation the residue is brought into a silver crucible, the last particles of oxide adhering to the dish being rinsed into the crucible with sodium hydrate, this then evaporated and the residue mixed with eight times its bulk of solid sodium hydrate, and fused for some time at a red heat over an ordinary burner. To dissolve out the sodium stannate that has been formed, pour a large quantity of hot water upon the cooled mass, stir well, and when the liquid has become cool add one-third vol. alcohol of 0.833 sp. gr. After the sodium antimoniate remaining insoluble has subsided, filter, washing the residue first with a mixture of equal volumes of water and alcohol of the above strength, and finally with three volumes alcohol and one volume water.

To the alcoholic filtrate add hydrochloric acid to acid reaction,* and precipitate the tin by hydrogen sulphide as tin sulphide. This is finally estimated as oxide. (See p. 55.)

To estimate the antimony dissolve the sodium antimoniate upon the filter with a mixture of equal parts of hydrochloric and tartaric acids. The solution is diluted with water and the antimony precipitated as sulphide. (See p. 52.)

Alloy of Arsenic, Antimony and Tin.

In commencing the analysis treat the finely divided alloy precisely as in the foregoing example. Besides the sodium stannate the alcoholic filtrate from the sodium antimoniate† contains also the arsenic as sodium arseniate.

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* In case a white precipitate of sodium stannate separates out on the addition of the acid, it is not necessary to add enough of the latter to redissolve the former, but it may be converted into sulphide by leading hydrogen sulphide into the solution.

† For the estimation of the antimony the sodium antimoniate is treated as heretofore.

The liquid is again mixed with hydrochloric acid, and hydrogen sulphide conducted into it. As the arsenic acid is but slowly precipitated* as arsenic tersulphide, hydrogen sulphide should be allowed to stream through the solution heated to about 70° C., for some time. When the precipitation is complete, allow the solution to stand several hours in a warm place, and expel the excess of hydrogen sulphide by passing carbon dioxide through the liquid. The sulphides are collected upon a weighed filter, and dried at 100° C., until constant weight has been obtained.†

To estimate the arsenic and tin in this mixture of arsenic sulphide, tin sulphide and sulphur, introduce a weighed portion of the precipitate into a bulb-tube,‡ connecting the one limb of the latter with a hydrogen sulphide apparatus, while the other bending downwards dips into a solution of ammonium hydrate.

To guard against any loss of arsenic sulphide a second absorption apparatus partly filled with ammonium hydrate is placed before the receiver.

When the entire apparatus is filled with hydrogen sulphide, commence heating the contents of the tube at first gently, but gradually intensifying the heat, as long as a coating of arsenic sulphide is produced.

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* Upon first passing hydrogen sulphide through an acid solution containing arsenic acid, there is no precipitation, because the H_2S has a reducing effect upon the acid: $H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O$.

† In regard to the filtration of the tin sulphide, attention should be paid to what has already been said (p. 55).

‡ It is very difficult to fill the weighed substance into the tube without suffering some loss, and it is therefore advisable to first dry the tube at 100° C., and determine its weight, then bring an indefinite amount of substance into it, dry at the same temperature, and reweigh the tube.

After the apparatus has cooled cut off the bent limb of the tube immediately behind the bulb, and dissolve out the sublimate contained in it with warm dilute potassium hydrate. Finally, the potassium hydrate and the contents of the bulb are brought in a porcelain dish and evaporated to dryness upon a water-bath. The residue is carefully oxidized with fuming nitric acid. Or hydrochloric acid may be poured directly upon the contents of the bulb, a little potassium chlorate added, and heat applied until all

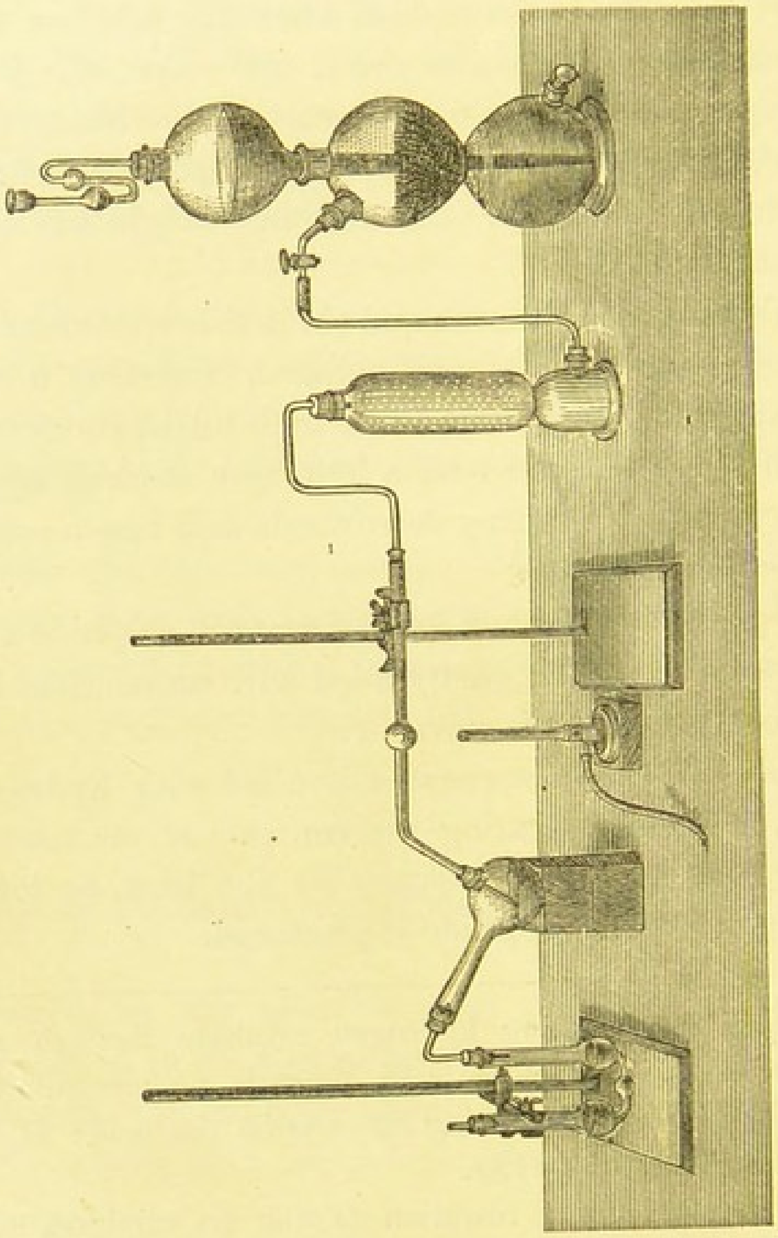

Fig. 4.

the suspended arsenic sulphide has been dissolved—the arsenic existing in the solution as arsenic acid.

In both instances the unoxidized sulphur that remains behind should be filtered off, and after the addition in excess of ammonium hydrate to the filtrate, throw down the arsenic as ammon-magnesium arseniate. The precipitation and washing of the precipitate is executed as given in the determination of phosphoric acid. (See Sodium Phosphate —direct determination of the phosphoric acid, p. 25.) The precipitate may be either dried at 105°–110° C. upon a weighed filter, and then weighed, or by gradual heating it may be converted into magnesium arseniate. pyro

In the latter case the precipitate is transferred to a porcelain crucible, the filter, after being moistened with ammonium nitrate, incinerated upon a platinum wire, and the whole then heated at first in an air-bath to 130° C., the temperature being gradually increased to 400° C. After continuing this several hours until all the ammonia has been volatilized, the contents of the crucible are gradually more strongly ignited, finally to intense redness.

The precipitate dried at 100° C. has the composition

$$MgNH_4AsO_4 + H_2O;$$

the ignited precipitate is

$$Mg_2As_2O_7.$$

The tin sulphide remaining in the tube after the decomposition is converted into oxide* by emptying it into a porcelain crucible, moistening with a few drops of nitric acid, and then applying heat, at first gently, then gradually raising it to a bright redness (p. 55).

If a bulb-tube of difficultly fusible glass has been employed in the operation, the tin sulphide may be converted

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* The tin sulphide contains variable quantities of sulphur, and therefore cannot be determined in this form.

into oxide by igniting the former strongly, and passing a current of air over it.

Another method of separation for these three metals is based upon the fact that from a potassium sulphide solution of their sulphides, sulphurous acid will precipitate the antimony and tin as sulphides, while the arsenic will remain in the solution as potassium arsenite. The alloy is previously oxidized with nitric acid, then evaporated to dryness, and the residue digested with potassium sulphide until perfect solution has been effected. The solution is now mixed with a large excess of aqueous sulphurous acid, and the whole digested for some time upon the water-bath, and finally boiled to expel all the sulphurous acid, and the liquid reduced to one-third its original volume.

The sulphides of antimony and tin are filtered off, and separated as directed on page 65.

The filtrate is acidified with hydrochloric acid, and the arsenic precipitated by means of hydrogen sulphide. The arsenic tersulphide is filtered and dissolved in hydrochloric acid upon the addition of potassium chlorate, and determined as ammon-magnesium arseniate as already above described.

Cassiterite.

TIN STONE.

Composition.—Stannic oxide together with small quantities of ferric oxide.

The method of analysis to be employed here readily follows from what has already been given. As the mineral is not attacked by acids, a weighed portion of it should be dried at 100° C., then fused in a porcelain crucible with eight times its quantity of sodium carbonate and sulphur. The fused mass after becoming cool is treated with water, and the tin which has passed into solution in the form of sodium-tin sulphide may be precipitated and determined as heretofore directed. Generally, after the treatment of the fused mass with water, there remains a slight black residue of iron sulphide, which is filtered, washed with water containing hydrogen sulphide, and then dissolved in hydrochloric acid with addition of some nitric acid. Upon the addition of ammonium hydrate to this solution the iron is precipitated as hydrated oxide of iron. (See p. 24.)

Siderite.

Composition.—Ferrous carbonate together with manganous, calcium and magnesium carbonates.

Estimation of the Iron, Manganese, Calcium and Magnesium.—A weighed portion of substance* (1.5–2 grms.), dried at 100° C., is placed in a well-covered porcelain dish and dissolved by the addition of hydrochloric acid. When insoluble gangue remains the solution is diluted with water and filtered, and the weight of the gangue determined by ignition in a platinum crucible.

To separate iron from manganese and the alkaline earths, after either of the subjoined methods, it is required that the iron exist in the ferric state, whilst the manganese should be present in the form of protoxide. The conver-

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* In the analysis of ores and furnace products it is necessary to first obtain a good average sample. The ores, etc., are reduced to small pieces the size of a pea in an iron mortar, and the sample then uniformly spread out. A small portion of the rather finely divided substance is removed with a spatula or spoon, placed in an iron mortar and rubbed to a fine powder. With this sample proceed as is generally done, grinding it in an agate mortar until no hard pieces are any longer noticed with the pestle.

sion of the ferrous chloride in the solution into ferric chloride may be effected by the addition of a sufficient quantity of concentrated nitric acid to the liquid, and heating until the latter has assumed a pure yellow color. Pulverized potassium chlorate may be substituted for nitric acid in the oxidation. To the perfectly cool and strongly diluted liquid* add first an excess of ammonium chloride, then neutralize the greater portion of the free acid with ammonium hydrate, finally with a dilute solution of ammonium carbonate. The precipitate produced by this last reagent disappears at first promptly when the liquid is stirred, but gradually more slowly, then add ammonium carbonate, drop by drop, until the liquid, after some standing, becomes somewhat turbid. If, however, too much ammonium carbonate has been added, and the precipitate produced remains, mix in acetic acid, drop by drop, and allow it sufficient time to act, so that the precipitate may be dissolved by the least possible quantity of acetic acid.

The solution is now brought to boiling and continued in ebullition until the carbon dioxide has been completely expelled. The separated precipitate of basic ferric oxide subsides very rapidly, and may be very quickly washed by decantation with hot water. At the close of the operation add a few drops of ammonium hydrate to the wash-water.

If the liquid had not been exactly neutralized, or if too much acetic acid had been employed to effect the solution of the precipitate produced by ammonium carbonate, a portion of the ferric oxide may remain in solution, which would be indicated by the yellow coloration of the supernatant liquid. This being the case, add ammonium hy-

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* The separation from manganese is only a success when the quantity of iron dissolved in a litre is at the highest 3.4 grms.

drate, drop by drop, to slight alkaline reaction,* stir well, and allow the precipitate to subside.

The precipitate of ferric oxide must be washed until the addition of silver nitrate to the filtrate causes no cloudiness, then dried, ignited, and weighed (p. 24).

Another and much better method for the separation of iron from manganese is based upon the precipitation of a dissolved ferric salt as basic ferric acetate. The solution of the ferric salt is neutralized with sodium carbonate, proceeding just as in the neutralization with ammonium carbonate, and then adding sodium or ammonium acetate in somewhat of an excess. The solution is heated to boiling, causing the iron to be precipitated as basic ferric acetate, whilst the manganese (and the alkaline earths) remain dissolved. The rest is the same as in the preceding method.

The filtrate from the iron should be acidified with hydrochloric acid,† then concentrated by evaporation and the manganese precipitated as sulphide. The liquid is placed in a flask of about 200 C. C. capacity, mixed with ammonium hydrate to alkaline reaction, and then ammonium sulphide in slight excess added.‡

Fill the flask almost full with water (best boiled) and

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* An excess of ammonium hydrate should be avoided, since, if allowed to stand a while, manganic hydrated oxide is apt to separate.

† Hydrochloric acid is merely added to prevent the separation of manganic hydrate.

‡ For precipitation employ yellow ammonium sulphide free of dissolved sulphur, or some that has not been decomposed by the action of the air. When the solution of the manganese salt that is to be precipitated contains a proportionately large quantity of ammonium hydrate, the precipitation of the manganese can be totally prevented if ammonium sulphide containing polysulphides is employed.

allow twelve hours for the manganese sulphide to settle. It is then filtered and washed with water containing ammonium chloride and sulphide (then proceed as directed on page 22), ignited and weighed.

The filtrate from the manganese sulphide is acidified with hydrochloric acid, warmed until the liquid becomes clear, and the separated sulphur then filtered off. Saturate the solution with ammonium hydrate and precipitate the calcium as oxalate (p. 13), and the magnesium in the filtrate throw down as magnesium-ammonium phosphate (p. 16).

[Or, instead of precipitating the manganese as sulphide, it may be removed from the solution by adding bromine water to the rather dilute acetate solution. The manganese present will fall down as binoxide. The solution should be heated after adding the bromine, and the liquid then allowed to stand some hours before filtering. Wash, first by decantation, then upon the filter. It may now be directly ignited or redissolved and precipitated by sodium carbonate and determined as protosesquioxide. In the filtrate determine the calcium and magnesium as above directed.]

When rather large quantities of calcium are present in the siderite, it is not advisable to first precipitate the manganese by ammonium sulphide, because the alkaline solution readily absorbs carbon dioxide and calcium carbonate will be admixed with the manganese sulphide. The precipitation of the calcium as oxalate, therefore, here precedes that of the manganese. The filtrate from the ferric oxide, concentrated by evaporation, is mixed with ammonium hydrate to alkaline reaction, then rendered *slightly* acid by acetic acid, and ammonium oxalate added. In the filtrate from the calcium oxalate precipitate first the manganese, and, after destroying the ammonium sulphide with hydrochloric acid, remove the magnesium, as above directed.

The carbon dioxide is determined after the method given at page 33, and the water according to page 36. For both analyses the substance should have been dried at 100° C.

Instead of estimating the iron from the ferric oxide obtained,* it is preferable, particularly when the ascertainment of the amount of iron is solely regarded, to employ the volumetric method of determination, which is excellent, both on account of its rapid as well as sure execution.

This method depends upon the following principle: If potassium permanganate is added to the acid solution of a ferrous salt, the latter will be converted into ferric oxide, and the color of the permanganate will disappear as long as ferrous oxide remains in the liquid.

$$10FeO + Mn_2O_7 = 2MnO + 5Fe_2O_3, \text{ or}$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

As soon as the oxidation is complete, the first drop of permanganate in excess will produce a distinct rose-red coloration.

The estimation of the iron after this method is so executed that, to the liquid containing it in the ferrous condition, permanganate is added from a burette until a permanent, slight red coloration is imparted to the solution.

Since, in this process, the permanganic acid is reduced to manganous oxide, the iron solution must always contain a certain amount of free acid, to retain in solution the manganous oxide. As a permanganate solution, a liquid is employed which contains approximately 5.65 grms.

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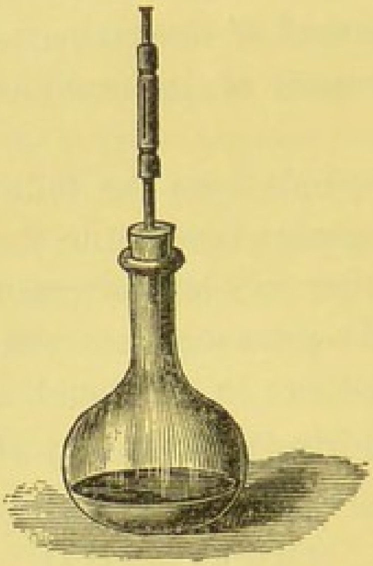
* The direct gravimetric estimation of the obtained ferric oxide only affords a correct result when alumina and phosphoric acid are not at the same time present, as they would also be mixed with the precipitate.

crystallized permanganate, dissolved in 1 litre of water. 1 C. C. of this solution about corresponds to 0.01 grm. of metallic iron. As the solution is not absolutely stable, no definite strength is assigned it. This is ascertained immediately before being employed.

Fig. 5.



Standardizing the Potassium Permanganate.—Weigh off about 0.2 grm. thin, clean, piano wire, dissolving it, placed in a flask of about 200–300 C. C., in dilute sulphuric acid, with application of heat. To prevent the oxidation of any of the ferrous salt produced during the operation, there is secured upon the neck of the flask a caoutchouc valve, which permits the exit of vapors, but prevents their entrance. Or, while the solution is being effected, a stream of carbon dioxide is conducted through the liquid to hinder the oxidation of the ferrous salt. When the solution is finished, dilute the liquid with water (boiled water is best), adding afterwards dilute sulphuric acid. The permanganate solution is now passed in from a burette, until its color begins to disappear rather slowly, when it is added drop by drop, until the liquid has acquired a light rose-red coloration. To better perceive this, place a piece of white paper beneath the flask.

Read off upon the burette the number of C. C. permanganate that have been used. If a equals the weighed amount of iron wire, t the C. C. permanganate used, then 1 C. C. of the latter will correspond to $\frac{a}{t}$ grm. iron.

As the piano wire is not absolutely chemically pure, containing upon an average about 0.4 per cent. carbon, therefore the weighed quantity of it must be multiplied by 0.996, to ascertain the actual amount of iron present. 0.2 grm. piano wire, therefore, contains 0.1992 grm. pure iron.

In place of the iron, in standardizing the permanganate, ferrous-ammonium sulphate may be employed. As the iron in this salt is exactly $\frac{1}{7}$ of its weight, in this case 1 C. C. of permanganate would $= \frac{a}{7t}$ grm. iron.

For the determination of the amount of iron in siderite proceed first as was done in standardizing the solution. The requirement is, that all iron be present in the ferrous state. Further, that the liquid to be titrated contains neither free hydrochloric nor nitric acid.*

Dissolve 0.2–0.4 grm. (depending upon the amount of iron in the mineral) in hydrochloric acid, and evaporate the solution to dryness on a water-bath. The residue is saturated with an excess of dilute sulphuric acid, heated and then diluted with a large quantity of water. When a large amount of insoluble silicic acid is present, it should be first filtered, in order that the final reaction may be better observed. As a portion of the ferrous oxide is con-

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* Hydrochloric acid has a direct decomposing effect upon potassium permanganate:—

$$KMnO_4 + 8HCl = HCl + MnCl_2 + 5Cl + 4H_2O.$$

It is obvious that neither oxidizing compounds nor organic substances decomposing permanganate should be present.

verted into ferric oxide while effecting solution and the evaporation of the liquid (siderite may also contain ferric compounds), the latter must be again reduced to the ferrous state. To this end throw small pieces of zinc into the warm solution; they will be dissolved with liberation of hydrogen gas.

During the process of the reduction of the ferric to ferrous oxide the yellow color of the solution gradually disappears, and eventually it becomes colorless. The reduction may be hastened by a continual, gentle heating of the liquid. When the disengagement of the gas has grown weaker, add more dilute sulphuric acid.

Just as soon as the liquid has become colorless and all the zinc has passed into solution, without cooling the latter add potassium permanganate until the final reaction is observed.

By throwing a piece of platinum wire or foil into the liquid simultaneously with the zinc, the reduction is more rapid than with pure zinc.

Potassium permanganate may also be employed for the estimation of ferrous oxide in the presence of ferric oxide. Dissolve a weighed portion of the substance with exclusion of air (either in the above-figured apparatus supplied with a Bunsen valve or by allowing a current of carbon dioxide to stream over it), and the liquid may then be directly employed in estimating the amount of ferrous oxide.

A second portion of the dissolved mineral is reduced with zinc and the entire amount of iron then estimated with permanganate. From the amount of permanganate used in both experiments the quantity of ferrous and ferric oxides may be readily calculated.

If hydrochloric acid is required for the decomposition of the substance, the greater portion of it should afterwards be expelled, and during this operation a current of carbon dioxide should be allowed to pass over the liquid.

The titration should then occur in a cold solution, strongly diluted with water.

Another method for the oxidation of ferrous oxide, allowing the use of hydrochloric acid solutions, consists in oxidizing the ferrous oxide with chromic acid.

With ferrous salts, chromates are so decomposed that ferric compounds are formed, and the chromic acid is reduced to oxide.

$$2H_2CrO_4 + 6FeO = Cr_2O_3 + 3Fe_2O_3 + 2H_2O.$$

A liquid containing 4.919 grms. dry potassium chromate, dissolved in 1 litre of water, is employed as a normal solution. For standardizing the solution, an indefinite amount of iron or ferrous-ammonium sulphate is weighed off, this dissolved in hydrochloric acid, and to it added a solution of potassium bichromate, until all the ferrous oxide has been converted into ferric oxide. Ferricyanide of potassium serves as an indicator. The final reaction is ascertained by placing a drop of the liquid upon a porcelain plate, and adding to it a drop of ferricyanide of potassium. As long as a blue precipitate, or blue coloration, is produced, ferrous salts are still present. The chromate solution is added until the coloration no longer occurs.

Hematite.

The pure mineral consists of ferric oxide, water, and gangue, insoluble in acids, and besides weighable quantities of manganic oxide, alumina, calcium, magnesium, phosphoric and sulphuric acids are some of its general constituents.*

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* Is there, which is seldom the case, a determinable amount of copper present, it is precipitated as sulphide from the hydrochloric acid solution (p. 47). In the first precipitation it gene-

When the hematite contains merely the first-mentioned constituents, all that is necessary to estimate the ferric oxide, is to dissolve in fuming hydrochloric acid from 0.2 to 0.3 grm. substance, finely pulverized and dried at 100° C., and determine the iron, after previous reduction to protoxide, after the method given in the analysis of Siderite.

Another volumetric method for the determination of iron, which can only be employed provided the solution contains the iron in the ferric state, depends upon the reduction of the ferric oxide by a stannous chloride solution of known strength.

Stannous chloride decomposes ferric chloride to ferrous chloride and stannic chloride :—

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + (FeCl_2)_2.$$

The excess of stannous chloride added is determined by a solution of iodine in potassium iodide.

$$2SnCl_2 + 2I = SnCl_4 + SnI_2.$$

If starch paste has previously been added to the liquid, the end of the reaction, when all the stannous chloride has been converted into stannic chloride and iodide, will be indicated by the appearance of starch iodide, which will impart a distinct blue coloration to the liquid.

For the execution of this method there is required :—

1. A solution of ferric chloride of known strength. This may be prepared by dissolving 10.04 grms. thin piano-forte wire (see the standardizing of the permanganate solution) in hydrochloric acid, and gradually adding pulverized potassium chlorate for the conversion of ferrous to ferric oxide. Finally the solution is boiled to expel all the chlorine present, and after cooling diluted to 1 litre.

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rally contains iron, and should, therefore, be dissolved and reprecipitated.

2. A stannous chloride solution, which may be prepared by dissolving about 15 grms. of tin in hydrochloric acid.

3. A solution of iodine in potassium iodide. This may be made by dissolving about 5 grms. iodine in potassium iodide, and diluting to 1 litre.

The ratio of the stannous chloride solution to the iodine solution may now be determined by measuring off about 2 C. C. stannous chloride, adding a few drops of thin starch paste, and allowing an iodine solution to pass in drop by drop from a burette, until the liquid becomes blue. The number of C. C. required is noted.

To fix the ratio of the stannous chloride to that of the ferric chloride, measure off about 10 C. C. of the latter in a small flask, and to the boiling liquid add from a burette stannous chloride, until the yellow liquid has become perfectly colorless. After the solution is cool, mix starch paste with it and determine the excess of stannous chloride by means of iodine.

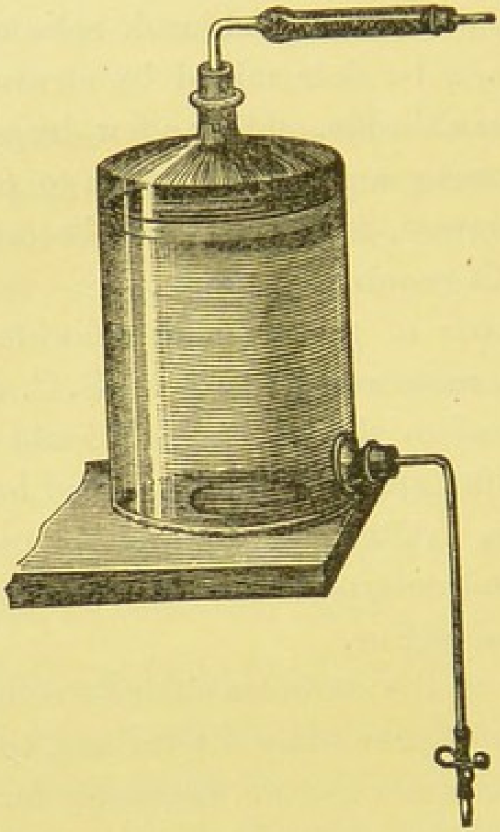
As the ratio of the stannous chloride solution to that of the iodine has been previously determined, the actually used C. C. of the stannous chloride necessary for the reduction of the ferric solution can be easily calculated, by deducting from the used stannous chloride that calculated from the iodine solution that had been added. As stannous chloride gradually oxidizes upon preservation, its strength must be ascertained upon every occasion when it is used. In order to avoid this oxidation Mohr proposed to preserve it under a petroleum layer (about 10 mm. deep). The most practical arrangement of a flask serving for this purpose is pictured in Fig. 6.

The determination of ferric oxide in hematite is executed exactly as in the standardizing of the solution.

The gangue or matrix in hematite, which is insoluble in hydrochloric acid, should be ignited in a platinum crucible and weighed.

If the portion of substance dried at 100° C. continues to lose water upon stronger ignition, this may be readily estimated by glowing gently.

Fig. 6



If the mineral contains the above-mentioned admixtures, the silicic acid, manganese, calcium and magnesium may be estimated as directed in the analysis of Siderite (p. 71).

The ferric oxide separated from manganese contains also some silicic acid, together with all the alumina and phosphoric acid.

The silicic acid and alumina in the ignited and weighed precipitate may be estimated by fusing the latter in a platinum crucible with 5–6 times its quantity of potassium hydrosulphate (acid sulphate of potassium), increasing the heat gradually to a strong red glow, and then extracting the cooled fused mass with water. The residual silicic acid is filtered off, and weighed after ignition.

The quantity of alumina is found when the rest of the silicic acid, the phosphoric acid, and the directly determined (volumetrically) iron have been subtracted from the weighed precipitate of ferric oxide.

The estimation of the phosphoric acid is best executed in another portion (5–10 grms.) of the dried substance. The finely pulverized substance is digested with nitric acid* to perfect decomposition, evaporated to dryness, and the residue warmed with dilute nitric acid. After dilution with water, filter off the silica and precipitate the phosphoric acid by ammonium molybdate (see p. 25).

When the mineral cannot be perfectly decomposed by nitric acid, mix it with six times its quantity of a mixture of 6 parts sodium carbonate and 1½ parts silica; then fuse in a platinum crucible for about one-half hour—not allowing the temperature to become too great. The aqueous extraction of the fused mass contains all the phosphoric acid. When manganese is present in large quantities, potassium manganate will be dissolved, and the solution have a green coloration imparted to it; now add a few drops of alcohol, and warm; filter the colorless liquid, and wash the residue with water containing some sodium carbonate.

Hydrochloric acid is gradually added to acid reaction to the alkaline solution, and the whole heated until the carbon dioxide has been expelled, and the liquid then evaporated to dryness to cause the separation of the silicic acid. Dissolve the residue in water, filter, and precipitate the phosphoric acid by the addition of ammonium molybdate (p. 25).

Determine the sulphuric acid by fusing a weighed portion of the mineral with an equal quantity of sodium car-

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* The liquid from which the phosphoric acid is to be precipitated should not contain any hydrochloric acid.

bonate, dissolving the fused mass with water, and, after separating out the silicic acid (see above), precipitate the filtrate with barium chloride.

The determination of the sulphuric acid in the hydrochloric or nitric acid solution affords less accurate results, because, upon the one hand, the barium sulphate invariably contains iron, while, upon the other, it is more or less soluble in ferric chloride.

In estimating the water in hematite containing the alkaline carbonates, care must be taken not to determine it by loss, but it should be directly estimated (p. 36).

Limonite.

Composition.—Hydrated ferric oxide, with manganic oxide, alumina (calcium oxide, magnesia), phosphoric acid, silicic acid, sulphuric acid, and gangue insoluble in acids.

For the estimation of the manganese, alumina, calcium oxide, magnesia, silicic acid, and gangue, dissolve the pulverized and dried (at 100° C.) mineral in fuming hydrochloric acid; and to separate the silicic acid evaporate the solution to dryness. Moisten the residue with hydrochloric acid, warm gently, then dilute with water and filter off the silicic acid and gangue.

The oxides in solution are determined as directed under Siderite.

When it is particularly desirable to determine the quantity of silica found together with the gangue, boil the residue obtained above for some time in a platinum dish with sodium carbonate, transferring the insoluble residual gangue to a filter, weigh, and dry at 100° C. The gangue should at first be washed with boiling water, then with water acidulated with hydrochloric acid, and, finally, with pure water. Dry the residue at 100° C., until the weight becomes constant.

The silicic acid, dissolved by the sodium carbonate, is determined by acidifying the solution with hydrochloric acid, and evaporating it to dryness. Moisten the perfectly dry residue with hydrochloric acid, dilute with water, and filter off the remaining insoluble silica. After washing with hot water, ignite it strongly in a platinum crucible, and weigh.

In determining the iron, proceed after page 75 or page 80.

Phosphoric and sulphuric acids are determined as in Hematite.

The water is ascertained either by ignition or after page 36, in the presence of alkaline carbonates.

Clay Iron Ore.

Composition.—Ferric oxide, alumina, and water.

When this mineral is completely soluble in hydrochloric acid, *i. e.*, when the argillaceous residue after digestion with hydrochloric acid is free from ferric oxide, the latter may be best determined volumetrically according to page 80. The insoluble residue is then filtered off, washed, ignited, and weighed.

Should it happen that the iron cannot be perfectly extracted by digestion with hydrochloric acid, the mineral must then be decomposed by fusion. The finely pulverized substance is mixed with 4–5 times its quantity of sodium carbonate (or a mixture of 5 parts sod. carbonate and 7 parts potassium carbonate), then fused. After cooling, dissolve the residue in hydrochloric acid, determining the iron volumetrically.

When calcium and magnesium are present in the mineral, they are estimated as directed on page 71.

The water is determined by loss, the air-dried substance being ignited.

Magnetite.

MAGNETIC IRON.

Composition.—Ferrous and ferric oxides. The analysis may be variously executed.

First Method.—Dissolve a weighed amount of the exceedingly finely pulverized substance in hydrochloric acid, in a current of carbon dioxide gas, and then determine the ferric oxide with stannous chloride.

A second portion of the substance is dissolved in hydrochloric acid with the addition of potassium chlorate, and the entire amount of iron then determined as hydrated ferric oxide with ammonium hydrate (p. 23).

Second Method.—In a weighed portion of the substance, treated as directed in the first paragraph of the first method, the ferrous oxide may be determined with potassium permanganate, and then in the same liquid, the entire amount of ferric oxide can be estimated with stannous chloride. Or, after the determination of the ferrous oxide with permanganate, reduce the liquid with zinc, and again estimate all the iron with potassium permanganate.

Or, determine in one weighed portion the ferrous oxide with permanganate, while in another the amount of sesquioxide is ascertained by means of stannous chloride.

With respect to the estimation of the admixtures occurring in magnetite the analyses of Siderite and Hematite may be referred to.

Bog Iron Ore.

Composition.—Mixtures of ferric hydrated oxide with silicates of ferrous and ferric oxides, manganic oxide, alumina (cupric oxide), calcium oxide, magnesia, sulphuric, phosphoric and arsenic acids, and organic substances and sand.

The oxides are determined as directed in the respective analyses of Siderite and Hematite. When arsenic acid and cupric oxide are present, the course of the analysis must be somewhat modified. After effecting the separation of the silicic acid and gangue (see p. 84), heat the hydrochloric acid solution, and while doing this pass in hydrogen sulphide gas, allowing the saturated solution to stand some time in a warm place; then filter off the mixture of copper sulphide and arsenic tersulphide.

As sulphur invariably separates out when hydrogen sulphide is conducted into solutions of ferric oxide, and as this obstructs the filtration and washing, it is advisable to first reduce the ferric to ferrous oxide, by heating the liquid with sulphurous acid or sodium hydrosulphite. The excess of sulphurous acid is removed by ebullition, and hydrogen sulphide then added.

The filtrate is boiled to expel completely the hydrogen sulphide, oxidized with nitric acid or potassium chlorate, and then employed for the estimation of the remaining oxides.

The separation of the sulphides of arsenic and copper is effected by digesting the mixture on a water-bath with a solution of sodium or potassium sulphide, and filtering off the insoluble copper sulphide (p. 48).

The addition of dilute hydrochloric or sulphuric acid to the filtrate will precipitate the arsenic sulphide, which is filtered, washed and dissolved in hydrochloric acid containing potassium chlorate (p. 68). From this solution, after neutralization with ammonium, the arsenic acid may be thrown down, as magnesium-ammonium arseniate (p. 69).

As the copper sulphide that remains invariably contains iron, it must be dissolved in concentrated nitric acid, and after the evaporation of the latter, it is reprecipitated by hydrogen sulphide.

The iron contained in bog iron ore may be best estimated volumetrically in a separate portion of substance. If stannous chloride is then employed, the ferrous oxide present must first be converted into ferric oxide by warming the solution with potassium chlorate.

For the estimation of ferrous in presence of ferric oxide, see Siderite (p. 71), and Magnetite (p. 86).

The phosphoric and sulphuric acids are determined as directed on page 83.

Owing to the presence of organic substances, the amount of water cannot be estimated by ignition, nor even by absorption, because upon igniting with lead oxide, the hydrogen of the organic compounds will be oxidized to water.

Dry a portion of the substance in an obliquely inclined platinum crucible, and apply heat—at first gently, but gradually increasing it. By this means we will be able to ascertain the percentage of water plus the organic material.

Chromite.

CHROMIC IRON.

Composition.—Chromic oxide, ferrous oxide (ferric oxide), alumina, magnesia; sometimes, as impurities, manganous oxide, calcium oxide, and silicic acid.

The analysis of this mineral has long presented great difficulties, because the chromite is neither attacked by acids (with the exception of concentrated sulphuric acid; see below), nor by fusion with alkaline carbonates.

The decomposition may, however, be very easily effected, if potassium fluoride dissolved in hydrofluoric acid be made use of, as proposed by Gibbs.

The finely powdered mineral is evaporated with a concentrated solution of potassium fluoride in hydrofluoric acid, and the platinum crucible heated to faint redness for about one-half of an hour. After the decomposition the fused mass in the platinum crucible is warmed with hydrochloric acid, until hydrofluoric acid no longer escapes. Should there, after this, remain an insoluble green colored residue, filter it off, and repeat the ignition with potassium fluoride. Generally, however, in most cases one fusion is sufficient to cause a perfect decomposition of the mineral.

The chromium oxide is separated from the other oxides present by diluting the solution largely with water, mixing in with this sodium carbonate in slight excess, and then adding sufficient bromine water* to oxidize the chromic oxide to chromic acid. The liquid should be constantly stirred, and heated to 80° or 90° C., and the insoluble oxides finally separated by filtration from the sodium chromate.

The chromium may now be estimated, either as barium chromate or chromium oxide.

For the execution of the first method acidify the alkaline chromate solution slightly with acetic acid; then heat to boiling, and add barium acetate, and after the solution has cooled mix with it some alcohol. When the barium chromate has perfectly subsided, it is filtered off, and

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* The bromine water at the same time converts ferrous and manganous to ferric and manganic oxides.

washed with water containing $\frac{1}{12}$ vol. alcohol, dried and gently ignited.

To avoid a reduction of the precipitate adhering to the filter, moisten the latter with a few drops of ammonium nitrate, dry and incinerate upon a platinum wire.

$$2BaCrO_4 : Cr_2O_3 :: \text{wt. } BaCrO_4 : x.$$

To estimate the chromium as oxide, add sulphurous acid or alcohol to the solution acidified with hydrochloric acid; then boil. Precipitate the chromium in a platinum or porcelain dish, with ammonium hydrate. When alcohol has been employed it should be expelled by boiling prior to the precipitation.

The insoluble oxides (ferric oxide, alumina, manganic oxide, calcium oxide, and magnesia), which, after treat ment with bromine water, were precipitated with sodium carbonate, are dissolved in hydrochloric acid, and separated according to page 71.

The iron precipitate produced by boiling the solution with ammonium carbonate or sodium acetate contains all the aluminum, which may be either determined by difference or directly.

In determining the aluminum by difference, the yet moist iron precipitate is dissolved in hydrochloric acid, and the solution reduced to a definite volume (about 200 C.C.). In the one half the entire amount of alumina and ferric oxide is found by precipitation with ammonium hydrate (p. 23 and p. 37), whilst in the other measured portion of the liquid the iron is volumetrically estimated.

The direct determination of aluminum in the presence of ferric oxide is based on the principle that the former is not precipitated by ammonium and ammonium sulphide in the presence of tartaric acid. Mix the hydrochloric acid solution with an excess of tartaric acid, add ammonium hydrate and sulphide, and filter off the iron sulphide, the air being excluded, and wash with water containing ammonium sulphide.

The filtrate in a platinum dish, after the addition of sodium carbonate, is evaporated to dryness and ignited, until all the carbon has been burned. In the hydrochloric acid solution of the residue the aluminum is thrown down by ammonium hydrate.

This method has not the least advantage over the preceding, and, besides, is much more detailed and less accurate.

For the estimation of ferrous oxide contained in chromite, introduce about 0.5 grm. of the finely pulverized mineral into a glass tube closed at one end, and drawn out at the other. Pour over the substance about 10 C.C. of sulphuric acid of 1.34 sp. gr. The tube is now sealed above, and heated in a paraffin-bath at 250°–300° C. for ten hours. When the mineral is completely decomposed, break off the point of the glass tube, pour its contents into water, rinse out the tube with water, and determine the ferrous oxide with potassium permanganate (p. 75).

If the chromite contains silicic acid it cannot, of course, be determined in the portion decomposed by potassium fluoride. For this purpose a separate portion (or in the direct determination of the ferrous oxide, the same portion) should be decomposed with sulphuric acid as above described. All the silicic acid will remain behind upon diluting with water.

[Another method for decomposing chromite, proposed by Dr. Genth, and which is very satisfactory, is the following:—

Take 0.5 grm. of the impalpable powder, and fuse in a capacious platinum crucible with 6 grms. of potassium bisulphate for fifteen minutes, at a temperature scarcely above the fusing point of the latter; then raise the heat somewhat, so that the bottom of the crucible may just appear red, and keep it so for fifteen or twenty minutes. The fusing mass should not rise higher than half way up the crucible. The mass begins to fuse quietly, and abundant fumes of sulphuric acid escape. At the expiration of twenty minutes the heat is increased as much as necessary to drive out the second equivalent of sulphuric acid, and even to decompose partially the sulphate of iron and chromium. To the fused mass now add 3 grms. pure sodium carbonate, heat to fusion, and add in small portions from time to time during an hour 3 grms. nitre, maintaining a gentle red heat all the while ; then heat for fifteen minutes to bright redness. Treat the cold mass with boiling water, filter hot, wash the residue with hot water, then digest in the heat with hydrochloric acid. If anything remains undissolved, it is a portion of the ore undecomposed, and must be subjected to the above operation. To weigh such a residue, and deduct it from the ore first taken, is not good, as it never possesses the composition of the original substance. The alkaline solution, which often contains, besides the chromic acid, also some silicic, titanic, and manganic acids, and alumina is evaporated with excess of ammonium nitrate on a water-bath nearly to dryness, and till all free ammonia is expelled. On addition of water, the silicic acid, alumina, titanic acid, and manganese sesquioxide remain undissolved, while the chromic acid passes into solution, and can be determined as above.]

Pyrolusite.

MANGANESE ORES.

The naturally occurring pyrolusite consists generally of a mixture of manganese superoxide with hydrated oxide of manganese, ferrous or ferric oxide, quartz, clay, calcite, etc.

The commercial value of the ore depends upon the amount of manganese superoxide it contains.

Estimation of the Water.—Dry a weighed portion of the substance at 120° C. until constant weight is obtained. The drying may be greatly accelerated by heating the substance in a thick metallic dish, and stirring with a thermometer, until the latter has reached the temperature 110° C. (Mohr.) As the dried substance absorbs moisture from the air tolerably rapidly, it should be transferred while yet hot to a small glass tube, that can be well closed, and then allowed to cool. The dried mineral is employed for analysis.

As regards the estimation of the manganese superoxide, various methods have been proposed, from which I cite only those in most frequent use.

Method of Fresenius and Will.

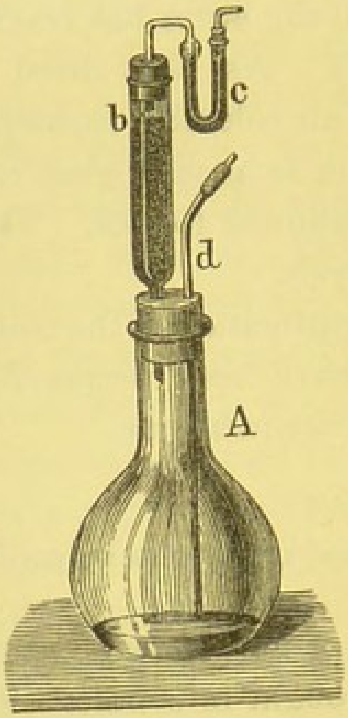
In the presence of an excess of sulphuric acid, manganese superoxide brought in contact with oxalic acid is so decomposed that manganous sulphate, carbon dioxide and water are produced :—

$$MnO_2 + C_2H_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

From the above we have one molecule manganese superoxide corresponding to two molecules of carbon dioxide, or 87 parts MnO_2 by weight = 88 parts CO_2. To ascertain the amount of manganese superoxide in a definitely weighed quantity, it is only necessary to multiply the found amount of carbon dioxide by $\frac{87}{88}$, or 0.98863. If a multiple of 0.98863 of black oxide of manganese, *e. g.* 3. 0.98863 = 2.9659 grms., be weighed off, it is afterwards only necessary to divide the found centigrammes of carbon dioxide by three, to ascertain directly the percentage of manganese superoxide in an ore.

According to the quality of the ore, we employ for each estimation from 2.9659 to 4.9431 grms. The weighing is best performed in a tared porcelain or platinum boat. This operation must be rapidly executed.*

Fig. 7.



The apparatus pictured in Fig. 7 is designed for the decomposition of the manganese ore.

A is a small flask of about 150 C. C. capacity; *b*, a glass tube filled with pieces of pumice-stone; *c*, tube containing calcium chloride. The tube *d* extends almost to the bottom of the flask, and is closed above by a small glass rod.

After transferring the manganese ore to *A*, add to it about 50 C. C. water, and, after the insertion of the tube *b*, mix in 4–5 C. C. concentrated sulphuric acid. When

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* A slight error cannot be avoided, because the sample will invariably attract some moisture. If this is not allowable, the weighing of a definite quantity of the ore must be dispensed with, and a closed glass-tube be used in the operation.

alkaline carbonates are contained in the ore, they will be decomposed by the acid. The carbon dioxide may be removed by sucking on the tube *d*, closing it again with the glass rod, and reweighing the apparatus. (Mohr.)

As regards the quantity of oxalic acid necessary for the decomposition of the ore, we know from the above reaction that, for one molecule $MnO_2 = 87$, one molecule of crystallized oxalic acid $= 126$ is required. Granted that the ore is chemically pure, 2.9659 grms. of it would, therefore, decompose 4.29 grms. oxalic acid.

When the apparatus has been weighed, bring the weighed amount of oxalic acid rapidly into the flask *A*, and immediately close it. The liberated carbon dioxide will be perfectly dried by the pieces of pumice-stone moistened with sulphuric acid, and also by the calcium chloride. When the evolution of carbon dioxide commences to diminish, heat the flask until the liberation of the gas can no longer be observed. After the apparatus has cooled remove the glass stopper from the tube *d*, and dislodge the carbon dioxide that may remain in the apparatus by suction upon the calcium chloride tube *c*, then reweigh the apparatus.

Method of Bunsen.

When manganese dioxide is heated with hydrochloric acid, there are produced manganese chloride and chlorine gas:—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

If the evolved chlorine be conducted into a solution of potassium iodide, a quantity of iodine equal to that of the chlorine will separate out, and this may be estimated either by means of sulphurous acid (Bunsen), or, what is preferable, by sodium hyposulphite (Schwarz).

When a solution of iodine in potassium iodide is mixed with sodium hyposulphite, the hyposulphurous acid will be converted into tetrathionic acid :—

$$2H_2S_2O_3 + 2I = H_2S_4O_6 + 2HI \text{ or}$$
$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$

On adding a starch solution to the iodine solution, the blue coloration of the liquid (starch iodide) will disappear the moment the iodine has become converted into hydriodic acid and sodium iodide.

For the execution of this method a sodium hyposulphite solution of known strength is required. This may be prepared by dissolving 24.8 grms. of pure crystallized sodium hyposulphite in 1 litre of water. As the solution, when exposed for some time to the air, oxidizes, and accordingly loses its standard, it is well to add 5 grms. of ammonium carbonate to prevent as much as possible the occurrence of this alteration. (Mohr.) However, in all cases, it is advisable to determine accurately the actual strength of the solution before using it.

For this purpose dissolve 0.1–0.2 grm. pure iodine* in potassium iodide (should not contain any iodic acid), dilute the solution with water, and add from a burette the hyposulphite solution to be examined until the iodine solution bears a faint reddish-brown color. Bring into this a few C. C. of starch solution,† and again add sodium

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* For the production of pure iodine, mix the latter with one-sixth its weight of potassium iodide, dry in a watch-glass until iodine vapors arise, then cover it with a second watch-glass which will closely fit the first. By a constant gentle application of heat the iodine is volatilized, condenses on the upper watch-crystal, and, after the completion of the sublimation, may be collected, and preserved in a glass vessel provided with a well-fitting cork.

† The starch solution is prepared by gradually mixing finely pulverized starch with cold water (1 part starch to 100 parts water), and heating the solution to boiling.

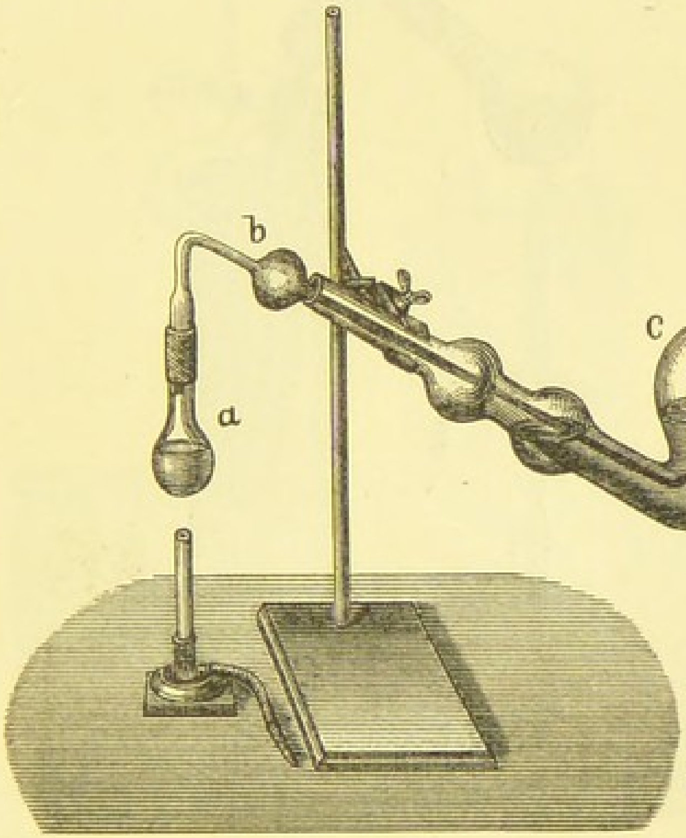
hyposulphite drop by drop until the blue solution is just decolorized. If x represents the required C. C. of sodium hyposulphite solution, a the amount of iodine taken, we have:—

$$I : Na_2S_2O_3 + 5H_2O = a : x.$$

x C. C. sodium hyposulphite contain therefore $\frac{248a}{127}$ grms. pure hyposulphite.

The apparatus (Fig. 8) of Bunsen (modified by Fresenius) is commonly employed for the decomposition of manganese dioxide by means of hydrochloric acid.

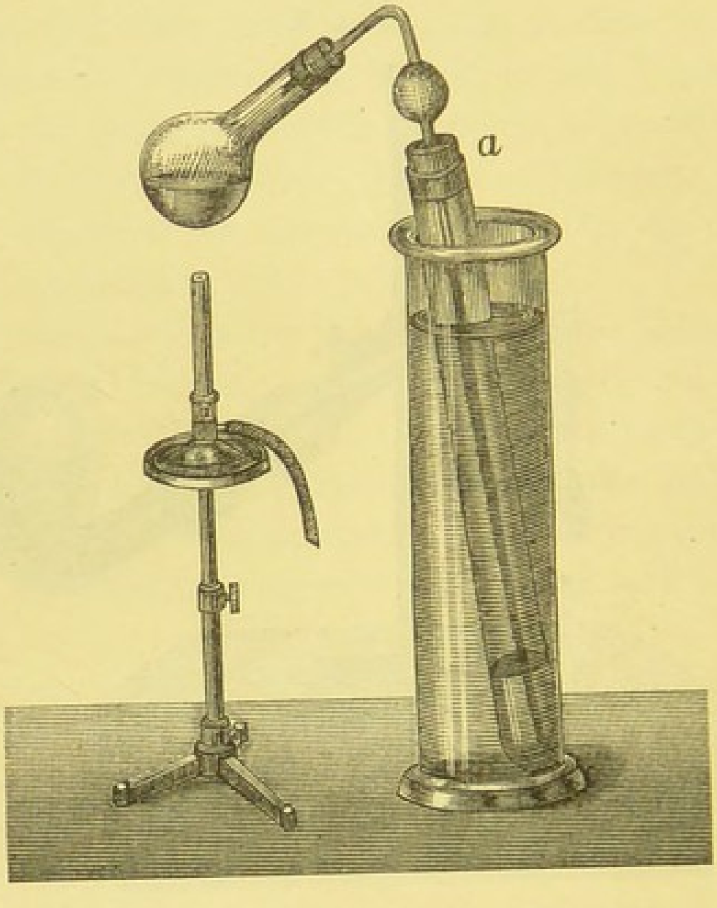
Fig. 8.



a is a small flask of about 50 C. C capacity, which is connected by means of a caoutchouc tubing with the pipette-shaped tube b. The latter at one end is drawn out to a point and bent upwards. The retort c is filled one-third with a solution of potassium iodide (1 part potassium iodide in 10 parts water).

Introduce the weighed quantity of the pulverized manganese dioxide (0.1–0.2 grm.) into the flask *a*, fill this then to two-thirds its capacity with fuming hydrochloric acid, connect *a* and *b* as soon as possible, pushing the latter into the retort. Upon the application of heat to the flask the liberation of chlorine commences, and after from two to three minutes' continued ebullition, during which time about one-third of the liquid will have been distilled off, the chlorine will be perfectly expelled. Grasp the tube at *b* with the left hand and remove it from the liquid, continually applying heat with the right hand to the flask *a*.

Fig. 9.

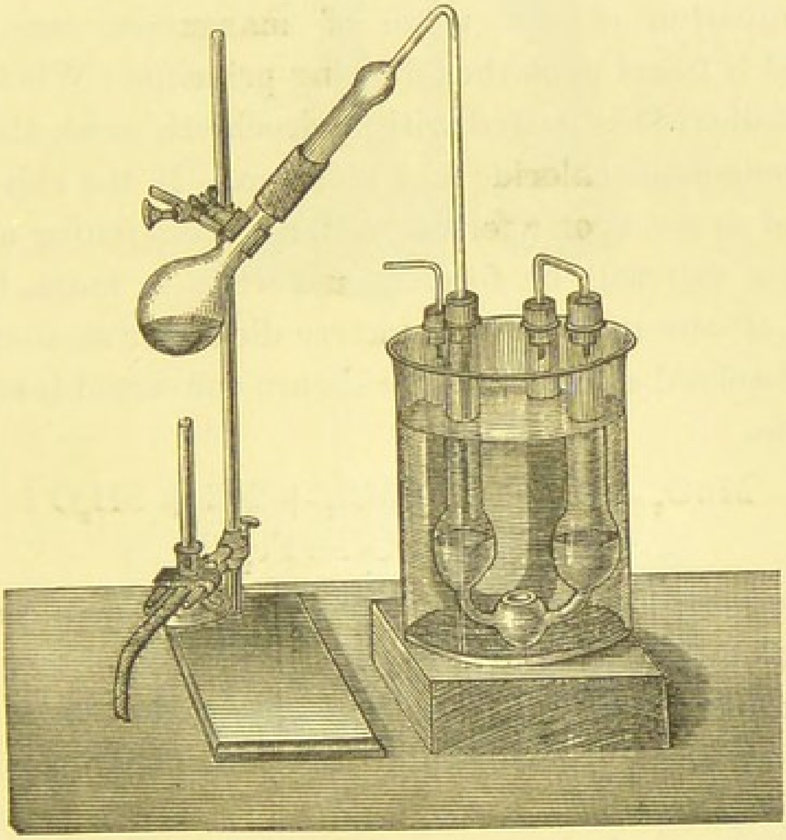


When the contents of the retort become cold, which may be greatly hastened by sinking it in cold water, rinse the solution carefully into a beaker, proceeding then as directed in the standardization of the solution.

The potassium iodide solution may be prevented from passing back into the flask *a*, if at the moment we place the manganese dioxide in the flask a piece of magnesite be also added, which will during the decomposition afford a continuous stream of carbon dioxide.

For the chlorine distillation, Mohr makes use of the apparatus represented by Fig. 9.

Fig. 10.



The tube conducting the gas is sunk into a glass tube of 320–340 Mm. length and 25–30 Mm. width, partly filled with potassium iodide, and this then introduced into a larger glass cylinder containing water. The cork *a* is loosely inserted in the tube containing the potassium iodide. When the distillation is finished, grasp the tube at *a*, and rapidly remove it from the liquid.

The construction of a third piece of apparatus, proposed by Fresenius, is shown in Fig. 10. This form is superior to the preceding two, from the fact that it is impossible for the potassium iodide solution to recede.

In regard to the calculation of the analysis, it must be borne in mind that 1 molecule of found iodine (I_2) corresponds to 1 molecule chlorine (Cl_2), and therefore to 1 molecule manganese dioxide (MnO_2).

Third Method.—The following method, generally known as the "Iron test," is used principally in England for the determination of the value of manganese ores. The method is based upon the following principle: When manganese dioxide is heated with hydrochloric acid, there result manganous chloride and chlorine. If the chlorine is allowed to act upon a ferrous salt, a corresponding amount of ferric salt will be formed, and what is more, by the action of one molecule manganese dioxide, two molecules iron dissolved as ferrous chloride are converted into ferric chloride.

$$MnO_2 + 4HCl = MnCl_2 + 2Cl + 2H_2O\,;$$
$$2FeCl_2 + 2Cl = Fe_2Cl_6.$$

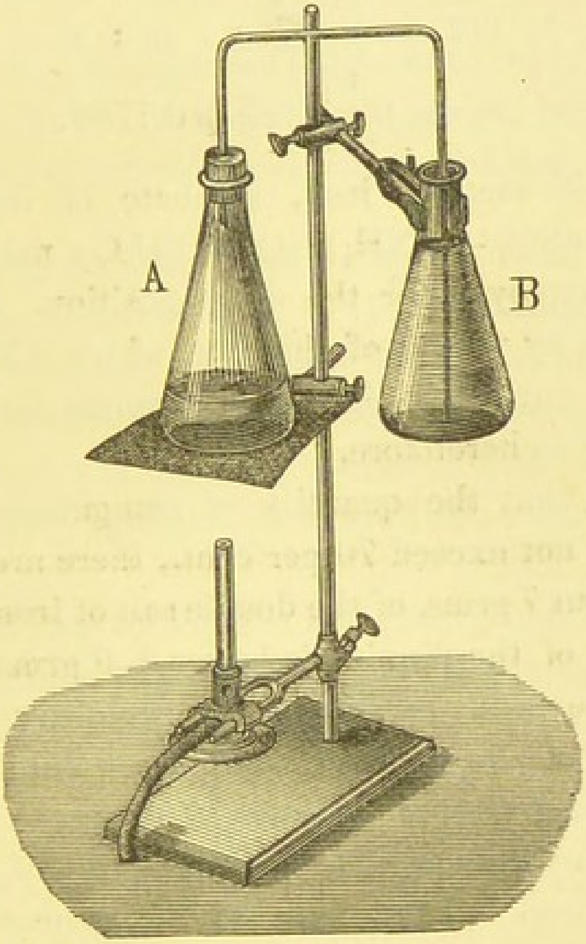
When definite amounts of iron and manganese ore have been taken for the decomposition, it is only necessary, in order to ascertain the quantity of manganese dioxide the latter contains, to determine the unoxidized portion of the ferrous salt.

The apparatus shown in Fig. 11 is employed in the execution of this process.

A and B are two small flasks connected with each other by means of a glass tube bent twice at right angles. B is filled with water, the glass tubing in it extending to the bottom. A contains the weighed quantity of iron—about 1 grm. piano-forte wire (equalling about 0.996 grm.

iron; see p. 77), and the black oxide of manganese. After adding hydrochloric acid, connect A and B, and apply heat. When complete solution has been effected, remove the lamp, and in a short time the water in B will flow back into A, cooling its contents, and preparing it for immediate titration with potassium permanganate.

Fig. 11.



It should be remembered here, that in the presence of hydrochloric acid potassium permanganate may be decomposed (p. 78). To prevent this a large dilution with water is absolutely necessary.

Representing the number of C. C. of permanganate required for the oxidation of the iron employed in the experiment by *m*, and by *n* the C. C. permanganate used upon the addition of the manganese ore after the decomposition, the difference of these two numbers, $m - n = p$, would represent the quantity of iron converted by the manganese dioxide into ferric chloride. As 2 atoms of Fe are converted by 1 mol. MnO_2 from the ferrous to the ferric state, the quantity of MnO_2 in the weighed portion of the manganese ore is ascertained from the following proportion :—

$$2Fe : MnO_2 :: p : x$$

$$112 : 87 :: p : x$$

$$x = p\frac{87}{112} = p0.7768.$$

Instead of metallic iron, sulphate of iron and ammonium ($FeSO_4 + (NH_4)_2SO_4 + 6H_2O$) may be advantageously employed for the decomposition. 2 molecules = 784 parts by weight of this salt, which will decompose 1 mol. = 87 parts by weight of manganese dioxide. Proceed exactly as heretofore.

Provided that the quantity of manganese dioxide in the ore does not exceed 70 per cent., there are used for 1 grm. ore about 7 grms. of the double salt of iron, and where the quantity of the dioxide is larger 8–9 grms. are taken.

If m = the C. C. permanganate necessary for the decomposition of the weighed quantity of the double sulphate of iron and ammonium, and n the C. C. permanganate which were used after the reduction of the ore, the quantity of iron oxidized by the manganese dioxide is again the difference between m and $n = p$; $p\frac{87}{184} = p. 0.11095$, corresponding to the quantity of manganese dioxide in the ore.

As already mentioned (p. 77), solutions of ferrous salts containing hydrochloric acid are not suitable for titration with potassium permanganate. In this case the ferrous oxide may be more accurately estimated with potassium chromate (p. 79). If the normal solution contains exactly 4.919 grms. potassium bichromate in a litre, each C. C. will be equivalent to 0.004357 grm. MnO_2. When 0.4357 grm. manganese are taken, the C.C. of potassium bichromate employed represent the percentage of manganese dioxide.

Psilomelane.

Composition.—Manganous oxide, oxygen, cupric oxide, ferric oxide, oxides of nickel and cobalt, barium oxide, calcium oxide (magnesia), potassium, lithium, and water.

Estimation of the Manganese, Copper, Iron, Nickel, Cobalt, Barium, Calcium, and Magnesium.—About 1.5–2 grms. of the mineral, dried over sulphuric acid, are dissolved in hydrochloric acid, and this solution, after being evaporated almost to dryness, is diluted with water. The insoluble residue (gangue) is filtered off, washed, ignited, and weighed.

Heat the filtrate to boiling, and precipitate the barium with dilute sulphuric acid (p. 15), wash the precipitate of barium sulphate perfectly with boiling water, and in the filtrate determine the copper as sulphide by precipitation with hydrogen sulphide (p. 48).

After the expulsion of the hydrogen sulphide from the filtrate of the copper sulphide, convert the ferrous into ferric oxide, and separate the latter from the remaining oxides by neutralizing the solution with ammonium hydrate and ammonium carbonate. (See p. 71.)

As the psilomelane generally contains but a slight quantity of ferric oxide, and its separation being tolerably difficult, it appears advisable, after the filtration and washing of the precipitate, to redissolve the same in hydrochloric acid, and repeat the precipitation by saturating the solution with ammonium hydrate.

The filtrate from the ferric oxide should be concentrated by evaporation and placed in a flask, and after neutralization with ammonium hydrate, yellow ammonium sulphide is added in slight excess. When the precipitate produced has fully subsided, filter the sulphides of manganese, nickel, and cobalt, excluding air contact as much as possible. Wash the mixture with water containing $(NH_4)_2S$. Remove the beaker containing the filtrate, replacing it by a porcelain dish, into which the precipitate is washed after breaking the filter. To avoid the loss of the particles adhering to the latter, dry the filter, and after incineration, add the ash to the principal portion.

To effect the separation of manganese sulphide from the sulphides of cobalt and nickel, treat them with a mixture of 11 parts hydrochloric acid of 1.12 sp. gr. and 6 parts hydrogen sulphide, and after digestion for a short time upon the water-bath, filter as rapidly as possible, and wash the residue with hydrogen sulphide, containing a few drops of hydrochloric acid. All the manganese sulphide will be dissolved, and after filtration it may be precipitated and estimated according to page 21.

The sulphides of nickel and cobalt remaining undissolved by hydrochloric acid are, after the incineration of the filter, ignited with free access of air and weighed as oxides.

The quantity of nickel is usually too small to determine it separately. The separation of the two metals may, however, be effected by means of potassium nitrite.

[The separation is as follows :—

Precipitate the cobalt and nickel from the solution with potassium hydrate; filter, wash perfectly and then dissolve in hydrochloric acid. Evaporate this solution to dryness in a dish placed on a water-bath. Dissolve the residue in a small quantity of water. Add to the concentrated liquid a concentrated solution of potassium nitrite, which is rendered slightly acid by the addition of rather dilute acetic acid. Allow the whole to stand for at least twenty-four hours in a moderately warm place. The yellow colored double salt of cobalt separates slowly. When the precipitation is complete, the yellow supernatant liquid is filtered, and after the salt has been thoroughly washed with sodium acetate, rinse it from off the filter into a beaker glass and boil for some time with dilute sodium hydrate. The cobalt will separate out as black hydrated oxide, and is easily washed.

Determine the nickel in the first filtrate from the cobalt salt.]

To determine the calcium and magnesium, acidify the filtrate from the sulphides with hydrochloric acid, and boil to expel the hydrogen sulphide. Filter the liquid when sulphur has separated; precipitate the calcium as oxalate (p. 13), and subsequently the magnesium as ammon-magnesium phosphate (p. 16).

To determine the magnesium accurately it is necessary to have previously evaporated the filtrate from the calcium oxalate to dryness and expelled the ammoniacal salts by gentle ignition. The magnesium is then estimated in the hydrochloric acid solution of the residue.

Determination of the Alkalies.—This is best executed with a separate portion of substance. Neutralize the hydrochloric acid solution with ammonium hydrate, and mix in ammonium carbonate as long as a precipitate is produced, then add ammonium sulphide in slight excess. The liquid is heated for some time upon the water-bath, and filtered, after the precipitate has fully subsided.

The filtrate contains the alkalies together with magnesium and some calcium. First, destroy the ammonium sulphide with some hydrochloric acid, neutralize the filtrate with ammonium hydrate, and add in excess oxalic acid or ammonium oxalate, and evaporate the solution to dryness in a platinum dish.*

By igniting the residue gently the oxalates of the alkalies are converted into carbonates and the magnesium oxalate is altered to magnesia. (See p. 45.) By treating the residue with small quantities of hot water the alkalies are dissolved, and after filtering from the magnesia, the solution should be acidified with hydrochloric acid and evaporated to dryness in a small porcelain dish. Rinse the residue with absolute alcohol into a small flask and add an equal volume of anhydrous ether. The flask is well corked and allowed to stand twenty-four hours with frequent shaking of its contents.

Pour off the solution of lithium chloride in ethereal alcohol from the potassium chloride, washing the latter with a similar mixture and allowing the solution to evaporate in the air. The lithium chloride as thus obtained invariably contains some potassium chloride, which remains undissolved by repeated extraction with ethereal alcohol. (See the analysis of Mineral Water.)

Add a few drops of concentrated sulphuric acid to the lithium chloride remaining after the evaporation of the ethereal alcohol, and determine it as sulphate. (Determination as potassium sulphate, p. 37.)

By gently igniting the potassium chloride in a closed platinum crucible, it may be weighed as such (p. 31). The lithium sulphate and potassium chloride should both be examined for magnesia.

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* The liquid freed from the separated sulphur can under certain conditions contain sulphuric acid (from the ammonium sulphide used). This should be removed with barium chloride, before evaporating with oxalic acid. The ignited residue will contain magnesia and barium carbonate. (See p. 45.)

Determination of the Oxygen.—The psilomelane very probably contains the manganese as dioxide together with manganous and manganic oxides, which, however, cannot be determined by analysis. All the manganese, therefore, present, is calculated as manganous oxide, and the amount of oxygen, corresponding to the oxide or dioxide, ascertained in a separate portion.

The estimation is most accurately executed according to the method suggested by Bunsen (p. 95). The quantity of iodine separated by the chlorine in the decomposition is in proportion to the sought amount of oxygen as 254 : 16 or = 1 : 0.06299. 1 part iodine, therefore, corresponds to 0.06292 part oxygen.

Water Determination.—Best determined according to the method described on page 36. A tube of porcelain should be substituted for glass in this instance, as psilomelane only loses its water of crystallization at a high temperature.

Sphalerite.

ZINC-BLENDE.

The zinc-blende contains throughout together with zinc sulphide determinable quantities of lead, copper, iron, manganese, cadmium, and silicic acid.

In the following lines the complete analysis of the mineral will be first described, and then the separate estimation of the zinc.

Powder the mineral finely and dry it at 100° C. Dissolve about 1 grm., placed in a porcelain dish covered with a watch-glass, either in fuming nitric acid, or *aqua regia*, for which purpose, first moisten the portion intended for analysis with water, and add nitric acid drop by drop between the watch-glass and the dish. When the acid has acted for some time in the cold, apply heat either upon a water-bath or sand-bath, until red colored vapors no longer appear, then evaporate to dryness. Moisten the residue with hydrochloric acid, warm gently and add a large quantity of water. Should any crystalline lead chloride remain undissolved together with the gangue (only occurs when the blende is rich in lead), pour the liquid through a filter and dissolve out the lead chloride from the residue with boiling water.

The insoluble gangue remaining after the washing is ignited and weighed.

To determine the lead, evaporate the hydrochloric acid solution with sulphuric acid, until the former acid has been perfectly expelled, and weigh the lead as sulphate (p. 49).

After the evaporation of the alcohol, precipitate the copper and cadmium as sulphides with hydrogen sulphide. Wash with water containing hydrogen sulphide. If the sulphides are digested with dilute sulphuric acid (1 part sulphuric acid to 5 parts water), the cadmium will be dissolved, and may again be precipitated from the filtrate as sulphide, and determined as such (p. 64). The copper sulphide, insoluble in sulphuric acid, is also estimated as such (p. 48).

Boil the filtrate from the sulphides until the hydrogen sulphide is perfectly expelled, then mix with it sufficient nitric acid or bromine water to oxidize all the ferrous to ferric oxide. The iron is separated from the zinc and manganese by means of ammonium and ammonium carbonate (p. 71), or, better, with sodium acetate. It is well, however, to remember that the precipitate of ferric oxide invariably contains perceptible quantities of zinc oxide; therefore, redissolve the filtered and imperfectly washed precipitate in hydrochloric acid, reprecipitating the iron by saturating the solution with ammonium hy drate. This is finally, as described at page 24, ignited and weighed.

For the separation of the zinc and manganese, strongly acidify the liquid with acetic acid and conduct hydrogen sulphide gas through the hot solution. Ignite the zinc sulphide in a stream of hydrogen, and weigh (p. 20).

To the filtrate from the zinc sulphide add ammonium hydrate, and precipitate the manganese with ammonium sulphide (p. 21).

If, in the analysis of zinc blende, the estimation of the zinc is all that is required, proceed in the following manner:—

The solution of the mineral is precipitated with hydrogen sulphide gas, and, after boiling off the latter, oxidize the liquid with nitric acid or bromine water. Remove the iron by the addition of ammonium hydrate, and to simultaneously precipitate the manganese add a few drops of potassium permanganate, or, what is less ~~preferable~~ desirable, a solution of microcosmic salt (am. sod. phosphate). As the precipitate of manganese and iron produced by ammonium hydrate retains zinc (dependent upon the quantity of iron), it should, after filtering and washing with hot water, be redissolved in hydrochloric acid, and the precipitation, as heretofore, repeated.

The zinc is either directly determined by ammonium sulphide, or, what is better,* it is precipitated from an acetic acid solution by hydrogen sulphide, and determined as sulphide (p. 19).

When it is desirable to determine the zinc, not as sulphide, but as oxide, in which case the precipitation with sodium carbonate should only be performed in platinum

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* Sulphide of zinc precipitated from a hot acetic acid solution is more readily filtered than that produced by ammonium sulphide.

vessels, or very excellent porcelain dishes, the removal of the iron is accomplished by neutralizing the solution with sodium carbonate and boiling with sodium acetate (p. 73).

Instead of determining the zinc gravimetrically, it is frequently estimated volumetrically,* which is to be particularly recommended when several determinations are to be made at the same time. Of the methods proposed for this purpose, only the most practical, and those affording the most accurate results, are described.

The addition of a solution of sodium sulphide to an ammoniacal solution of zinc, causes, as is known, a white precipitate of zinc sulphide to be formed. The end-reaction is ascertained by means of lead paper. For this purpose take the best glazed paper, that generally used in the manufacture of visiting cards, and known in trade as polka-paper. For the production of the final reaction, a glass tube, rounded at both ends, of about 25 Cm. length and 7 Mm. diameter, may be taken. Stir the liquid well with this, and, by placing the finger upon the upper end, take out a portion of the solution. Place the tube upon a piece of lead paper, and allow the liquid to pass drop by drop from the tube into the glass. As soon as a slight excess of sodium sulphide is present, a brown ring upon the lead-paper is perceptible, which necessarily grows more intense in proportion to the excess of sodium sulphide present in the liquid.

If the liquid to be titrated contains a large excess of ammonium hydrate, a replacement between the suspended zinc sulphide and the lead salt occurs, whereupon a black ring of lead sulphide is produced before the zinc is precipitated. It is, therefore, enjoined, that the ammonium hydrate be almost entirely expelled by boiling before the titration takes place.

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* The ammoniacal filtrate from the iron and manganese may be employed for this purpose.

Cobalt-paper may be substituted for lead-paper. It is obtained by saturating Swedish filter-paper with a solution of cobaltic chloride (0.35 grm. in 100 C. C.). When an excess of sodium sulphide is present, there is produced, after the absorption of a drop of the liquid to be tested, a sharply defined dark coloration.

That the results of this process may be accordant, it is necessary always to obtain an equally strong reaction, both in the standardization of the sodium sulphide solution and when using the latter. The degree of dilution of the solution to be titrated comes here into consideration, and, therefore, care should be had that this be approximately the same both in the standardization of the solution and the actual titration.

The crystallized sodium sulphide (Na_2S+9H_2O) serves for the experiment. Its aqueous solution is diluted with water until 1 C. C. of the same is equivalent to 0.005 grm. zinc.

The strength of the solution is ascertained with chemically pure zinc. Dissolve the zinc in nitric acid in an inclined beaker glass, add ammonium hydrate, until the precipitate produced by the latter has been redissolved, and, after diluting with water, titrate with sodium sulphide.

As already indicated, exactly the same conditions must be observed in the standardization of the solution as in the actual analysis. For instance, if, in the solution of an ore, about 50 per cent. zinc has been found, there must have been in standardizing the sodium sulphide solution, supposing that 1 grm. zinc-blende was taken for the estimation, 0.49–0.50 grm. pure zinc dissolved, and the liquid mixed with ammonium hydrate diluted with the same quantity of water as in the titration of the sample of ore.

Sulphur Determination. — Zinc-blende may be very readily oxidized by fuming nitric acid, if the precaution is only observed, to allow the acid to act at first for some time in the cold. The most practicable method of procedure is, after having moistened the ore with water, and placed in a well-covered porcelain dish, to add fuming nitric acid drop by drop, until, upon further addition, no action is any longer perceptible. After allowing the solution to stand several hours, it should be gently warmed upon a sand- or water-bath. This should be continued as long as red vapors are formed. Add hydrochloric acid drop by drop, apply heat, and evaporate the solution to dryness. The residue is moistened with hydrochloric acid and dissolved in water. The sulphuric acid contained in the filtrate from the gangue is precipitated as barium sulphate.

Calamine and Smithsonite.

Composition.—Zinc, cadmium, copper, lead, iron, manganese, calcium, magnesia, carbon dioxide, silicic acid, and water.

The analysis may be executed precisely as that of zinc blende. To determine the silicic acid in the presence of sand and gangue, boil the insoluble residue with sodium carbonate (p. 84).

In the filtrate from the manganese sulphide, determine the calcium oxide and magnesia (p. 74).

When the calcium is present in a rather large quantity, it is rather better to precipitate it first as oxalate, and determine the manganese and magnesia in the filtrate (p. 74).

When weighable quantities of antimony and arsenic are present in the calamine, the course of the analysis must be somewhat altered. The precipitate produced by hydrogen sulphide, containing beside the copper and cadmium also the arsenic and antimony as sulphides, is digested with sodium sulphide, whereupon the latter sulphides are dissolved, and can be, after filtering, reprecipitated as sulphides by the addition of dilute hydrochloric or sulphuric acid to the filtrate. Treat the dried precipitate with carbon disulphide to remove the sulphur mixed with it, and, after drying, again oxidize the precipitate in a porcelain crucible with fuming nitric acid.

Proceed with the residue as directed at page 65 (Alloy of Antimony and Tin), dissolving the sodium antimoniate in hydrochloric acid, and determining the antimony as sulphide. Precipitate the arsenic acid in the filtrate as magnesium-ammonium arseniate (p. 69).

As smithsonite loses its carbon dioxide perfectly upon ignition, it is not necessary to pursue the method given upon page 33. The water and carbon dioxide may be determined simultaneously. Weigh off into a porcelain boat from 1 to 2 grms of the mineral, and introduce this into a tube of difficultly fusible glass, connecting it with a previously weighed calcium chloride tube, to which is also attached a U-shaped tube filled with soda-lime. After having strongly ignited the substance, reweigh the tubes, and from the increase in weight calculate the amount of water and carbon dioxide.

Phosphorite.

Composition.—Calcium phosphate, with calcium chloride and fluoride; also small quantities of ferric oxide, alumina (magnesia), alkalies, and water.

Estimation of the Oxides.—First Method: 1–1.5 grms. finely-powdered, air-dried phosphorite are placed in a porcelain dish, concentrated hydrochloric acid added, and the whole digested for an hour upon a water-bath. When the solution is complete, evaporate the liquid to dryness upon the water-bath, moisten the residue with hydrochloric acid, and, after warming, dilute with water. The silica remaining insoluble is filtered off, washed, ignited, and weighed.

Determine the calcium by evaporating the filtrate from the silica, and adding sulphuric acid and alcohol (avoid an excess of the former). For calcium sulphate see p. 29.

The filtrate contains, besides the oxides of aluminum and iron, all the phosphoric acid. The separation of the latter is readily facilitated by adding lead acetate to the alcoholic solution as long as a precipitate forms, filtering, and washing perfectly the mixture of lead phosphate, sulphate, and chloride with alcohol; after the expulsion of the alcohol precipitate the excess of lead in the filtrate with hydrogen sulphide. It is not well to undertake the estimation of the phosphoric acid in the precipitate caused by lead acetate, but it is necessary to determine it in a separate portion (see below). Boil the filtrate from the lead sulphide to expel the hydrogen sulphide, add ammonium chloride, and then nitric acid to cause oxidation, and precipitate the iron and aluminum with ammonium (p. 37). These are separated as directed on page 90.

The filtrate contains the magnesium and alkalies; these are separated according to page 45.

The preceding method is more particularly intended for the estimation of calcium in the presence of phosphoric acid than the separation of the latter from ferric oxide, alumina, etc., because, on the addition of an excess of sulphuric acid, a larger or smaller precipitate of lead sulphate (lead phosphate and chloride) is produced, the filtering and washing of which require too much time. If the determination of the calcium is all that is desired, we can obtain very good results with the following method:

Mix the filtrate from the silicic acid with ammonium or sodium hydrate to alkaline reaction, and add a slight excess of acetic acid. When ferric oxide or alumina is present, the precipitate produced by ammonium or sodium hydrate does not fully disappear, and there remains undissolved iron or aluminum phosphate.

After allowing the precipitate to stand twelve hours, filter, and in the filtrate determine the calcium as oxalate (p. 13). If a large excess of acetic acid was required to effect the solution of the ammonium-hydrate precipitate, it would be well before precipitating the calcium to almost neutralize (the liquid must react acid) the solution with ammonium hydrate, and then mix with it ammonium oxalate.

Second Method.—The solution of the phosphorite, after filtering off the silicic acid and expelling the hydrochloric acid by evaporation, is mixed with an excess of metallic tin* and fuming nitric acid, and heat applied upon a water-bath until all the metal has been oxidized. Thus, the phosphoric acid will be converted into stannic phosphate, which is insoluble in nitric acid. Allow the precipitate of stannic phosphate and oxide to settle, filter the clear liquid, wash the precipitate perfectly by decantation with water containing nitric acid, and determine in the filtrate the oxides, as above directed.

The precipitate of zinc phosphate and oxide may also be used for the estimation of the phosphoric acid. (See Analysis of Plant Ashes.)

Fluorine Determination.—Its direct determination when existing together with phosphoric acid, in compounds in-

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* The tin should be 6–8 times the quantity of phosphoric acid present.

soluble in water, is accompanied with some difficulties, for which reason the calcium fluoride present is frequently calculated from the difference, as the phosphoric and hydrochloric acids are united with the calcium, and the remainder of the latter regarded as calcium fluoride.

A direct method for the determination of the fluorine is the following:—

The finely pulverized mineral is mixed with fine silica (use the silicic acid separated from silicates) and potassium carbonate, then fuse at a gentle red heat.*

The aqueous extraction of the fused mass contains all the fluorine as potassium fluoride as well as potassium phosphate and silicate.

The phosphoric acid in this solution is thrown down with silver nitrate. Filter the silver phosphate, washing it with the least possible quantity of water, and precipitating the excess of silver in the filtrate with sodium chloride.

To separate the silicic acid contained in the filtrate from the fluorine, mix the solution with ammonium carbonate, digest for some time upon a water-bath, and evaporate the filtrate from the silicic acid to dryness. The hot aqueous solution of the residue contains not only potassium fluoride, but also always small quantities of silicic acid, which may be removed by adding to the solution sodium carbonate, and a solution of zinc oxide in ammonium hydrate in slight excess, and then evaporating upon a water-bath until the liquid no longer imparts the odor of ammonia. Filter off the zinc silicate, wash it with water, and determine the fluorine in the filtrate as calcium fluoride. For this purpose pour the liquid into a platinum or porcelain dish, bring it to ebullition, and after adding calcium

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* The application of a too intense heat should be avoided on account of the volatility of the fluorides.

chloride, continue boiling for some time. The solution should not be filtered until it appears perfectly clear. Wash the precipitate by decantation with hot water. Pour water over the precipitate, bring it to boiling, filter off the clear solution, and repeat this operation until the precipitate is perfectly washed, then rinse it on to a filter.

The precipitate formed by calcium chloride is a mixture of calcium fluoride and carbonate (produced by the action of the sodium carbonate upon the calcium chloride). To separate the latter from the calcium fluoride, ignite the dried precipitate in a platinum crucible, and treat it, after cooling, with acetic acid. When the calcium carbonate is fully dissolved, evaporate the solution for the expulsion of the acetic acid to dryness upon a water-bath, and remove the calcium acetate by washing with water. The now remaining pure calcium fluoride is again ignited and weighed.

Chlorine Determination.—Dissolve about five grms. phosphorite in nitric acid and determine the chlorine as silver chloride. It must be remembered that while warming with nitric acid too strong an application of heat will cause the volatilization of hydrochloric acid.

Phosphoric Acid Determination.—Take about 0.2–0.3 grm. substance and dissolve by digesting with fuming hydrochloric acid.*

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* In estimating the phosphoric acid in phosphorites containing considerable quantities of iron or aluminum, it is recommended, where it is desired to determine the phosphoric acid volumetrically, to employ 5 per cent. sulphuric acid for the decomposition of the mineral. The residue, consisting of gypsum, silica, ferric oxide, etc., is washed with water, and the filtrate, after being made alkaline with ammonium or sodium hydrate, is mixed with acetic acid to acid reaction.

When the decomposition is complete, the solution is evaporated upon the water-bath, moistened with nitric acid, again evaporated, and the residue, after the addition of nitric acid, warmed and dissolved in water.

In this necessarily previously filtered liquid precipitate the phosphoric acid with ammonium molybdate and determine as magnesium pyrophosphate as directed on page 25.

Phosphoric acid may be volumetrically determined with very great accuracy. The following method is universally employed in practical work. It is based upon the precipitation of the phosphate in an acetic acid solution with acetate of uranium. The moment that all the phosphoric acid has become uranium phosphate, is indicated by the addition of potassium ferrocyanide. With the latter compound, uranium salts produce a reddish-brown precipitate of uranium ferrocyanide. The following solutions serve for the execution of this method:—

1. An aqueous solution of uranium acetate—not nitrate. Dissolve about 38 grms. crystallized uranium acetate in water, adding about 5 C. C. concentrated acetic acid to this, and diluting the whole to about 1 litre.

1 C. C. of this solution is approximately equivalent to 0.005 grm. phosphoric acid. As basic salts separate out from the solution upon standing, it should be first filtered, after having stood some time, and the standardization then made.

2. A solution of sodium acetate: obtained by dissolving 100 grms. sodium acetate in 900 C. C. water, and adding 100 C. C. acetic acid, of 1.04 sp. gr.

3. A solution of neutral calcium phosphate ($Ca_3P_2O_8$), serving for the standardization of the uranium solution. Formerly a solution of sodium phosphate* was used for

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* This solution contained 10.087 grms. crystallized sodium phosphate to the litre.

this purpose.* More recent experiments have, however, proved that if the uranium solution be taken for the determination of the phosphoric acid combined with calcium, a calcium salt must also be used in the standardizing of the solution, because the quantity of phosphoric acid in solutions of calcium phosphate was in all cases too low, where sodium phosphate had been employed as a basis in determining the strength of the uranium solution. This occurrence is readily explained by the fact that uranium phosphate always precipitated with it small traces of calcium phosphate.

To obtain a solution of calcium phosphate, dissolve about 5.5 grms. dried, neutral calcium phosphate in the smallest quantity of nitric acid possible (finally evaporating the excess), and dilute the liquid with water to 1 litre.

The actual amount of phosphoric acid in this solution may be ascertained by the precipitation of 50 C. C. of the same with a molybdic solution, or more readily by evaporating an equal quantity in a platinum dish, with the addition of some ammonium, igniting the residue, and weighing. The phosphoric acid may be calculated from the $Ca_3P_2O_8$ thus obtained.

In determining the strength of the uranium solution, mix 50 C. C. of the above calcium phosphate solution with 10 C. C. of sodium acetate, and allow the uranium solution to drop from a burette into the cold liquid, until almost all the phosphoric acid has been converted into uranium phosphate.† The solution is boiled, and a drop of the same placed on a porcelain plate, together with some finely pulverized potassium ferrocyanide (or a freshly prepared solution of this salt). The slightest excess of

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* Abesser, Märker and Jani On the Methods of Determining Phosphoric Acid. Zeitschrift für Analytische Chemie, xii. 239.

† The amount necessary for this is determined by a previous experiment.

the uranium solution will be indicated by the reddish-brown coloration of the powder, or the potassium ferrocyanide solution. When the reaction is complete, read off the number of C. C. used, and from this calculate the strength of the liquid.

In using this method for the determination of phosphoric acid in phosphates, it is necessary that the test be executed under the same conditions (dilution of the phosphoric acid solution, etc.) as in the standardization of the solution.

The phosphorite is either dissolved in fuming hydrochloric or 5 per cent. sulphuric acid, and in case the former has been used, the excess of acid is removed by evaporation, so that upon the subsequent addition of water the liquid will not be rendered turbid. The hydrochloric acid that remains is neutralized with ammonium hydrate (by all means avoid an excess), and the precipitate produced by the latter dissolved in acetic acid. Finally, add 10 C. C. sodium acetate, and dilute the liquid with water to the same volume as in the standardizing of the solution, proceeding then exactly as directed in that case.

Boronatrocalcite.

Composition.—Calcium, sodium, boracic acid, and water; frequently also potassium and sodium chlorides, and sodium sulphate.

Determination of the Oxides.—First of all it is necessary to volatilize the boracic acid. Pour hydrofluoric acid over a weighed portion of the substance, and digest for some time upon a water-bath. After the mass has cooled, concentrated sulphuric acid is carefully added drop by drop, and heat gradually applied until the excess of sulphuric acid has been entirely expelled. By this process we volatilize all the boracic acid as boron fluoride, whilst the bases are converted into their corresponding sulphates.

Ammonium fluoride may be substituted for hydrofluoric acid. The substance should be thoroughly mixed with it, and, after the addition of concentrated sulphuric acid, heated gradually.

The sulphates are dissolved in hydrochloric acid, and, after neutralizing the solution with ammonium hydrate, the calcium is thrown down as oxalate (p. 13).

The alkalies are estimated by evaporating to dryness the filtrate from the calcium oxalate, and determining the residue—consisting of sodium and potassium sulphates. In connection with this it is well to bear in mind, that upon final ignition the addition of ammonium carbonate is required to convert any hydrosulphates into the corresponding neutral salts (p. 37).

When potassium and sodium are present together, they are determined as given on page 46.

The hydrochloric and sulphuric acids in the nitric acid solution are estimated as usual as silver chloride (p. 17) and barium sulphate (p. 15).

Determination of the Boracic Acid as Potassium Borofluoride.—Neutralize the hydrochloric acid solution of the mineral with ammonium hydrate, and to the warmed liquid add ammonium carbonate in some excess. After the calcium carbonate has fully subsided, filter and wash the same with water. To the filtrate add potassium hydrate ($1\frac{1}{2}$ part potassium hydrate for 1 part borate) and concentrate it by evaporation, mixing then with the solution so much hydrofluoric acid that upon the application of heat vapors of the acid are expelled, finally evaporating to dryness in an air-bath. By extracting the residue with a solution of potassium acetate, which contains 20 per cent. of the latter, all the potassium borofluoride will remain undissolved. This is then transferred to a weighed filter, dried at 100° C., washed first with a ~~sodium~~ potassium acetate solution, until the addition of calcium chloride to the filtrate produces no cloudiness; then continue the washing, replacing, however, the potassium acetate with strong alcohol.

The potassium borofluoride is dried at 100° C., until the weight becomes constant.

$$2KBFl_4 : B_2O_3 :: \text{wt } KBFl_4 : x.$$

The water in boronatrocalcite is best determined by mixing a weighed portion of the substance with a weighed quantity of newly ignited lead oxide, and then heating.

Boracite.

Composition.—It contains magnesium borate together with magnesium chloride.

The separation of the magnesium from the boracic acid is effected by fusing the mineral with four times its weight of potassium carbonate and treating the residue with water.

The magnesia remaining undissolved can then be either weighed as such after washing with hot water, or, what is preferable, it may be converted into magnesium-ammonium phosphate (p. 16).

The boracic acid is determined as before, and the chlorine precipitated from the nitric acid solution of a separate portion as silver chloride (p. 17).

If the boracite (stassfurthite) contains water, determine this as directed in the analysis of boronatrocalcite.

Analysis of Silicates.

The compounds of silicic acid, by their different deportment with acids, may be divided into two groups, and may be distinguished as silicates decomposed, and silicates not decomposed, by acids.

To the first group belong, for example, allophane, analcite, botryolite, brewsterite, chabazite, cronstedite, datholite, dioptase, elaeolite, gadolinite, gehlinite, helvin, eulytite, lievrite, meerschaum, mellinite, mesotype, nepheline, okenite, orthite, pectolite, wernerite.

To the class insoluble in acids belong—

Albite, andalusite, augite, axinite, beryl, pumice-stone, chlorite, cyanite, diallage, dichroite, euclase, felspar, potassium and magnesium mica, garnet, carpholite, labradorite, rhodonite, oligoclase, pitchstone, pearlstone, petalite, pinite, serpentine, sillimanite, steatite, talc, turmalin, vesuvianite.

Determination of the Silicic Acid in Silicates Decomposed by Acids.—Ordinary hydrochloric acid is most commonly employed to effect the decomposition—very rarely concentrated nitric acid (for example, in silicates containing lead or silver oxides), or concentrated sulphuric acid (excellent for decomposing silicates containing aluminum).

Before, however, advancing to the actual analysis, it is necessary that the silicate should be extremely finely pulverized and then dried. The latter can generally be accomplished by heating the substance designed for analysis in an air-bath at 100° C. In case the silicate loses water of combination already at this temperature, the drying is performed at a lower degree, or over concentrated sulphuric acid.

Bring now a weighed portion of the powder into a platinum or porcelain dish, moisten it throughout with water, thus forming a pasty mass, then add hydrochloric acid, and apply heat upon a water-bath, constantly stirring the mass with a glass rod. The silicic acid almost invariably separates out as a gelatinous mass, and aided by a glass rod one may readily ascertain if any hard mineral material is present or not. However, it is well to mention that if gangue (quartz), or undecomposable silicates are mixed with the silicate, the gritty noise produced by rubbing with a glass rod may be due to their presence.

In decomposing the mineral with hydrochloric acid, the greater portion of the silicic acid will separate out (some silicates are perfectly soluble in dilute hydrochloric acid), although a portion will probably remain in the hydrochloric acid solution. For the complete separation of the same, in all instances evaporate the mass to dryness upon a water-bath, and heat the residue until hydrochloric acid no longer escapes, and a sandy, dry appearance is presented by it. When the silicate under examination contains neither ferric oxide nor alumina, the mass dried upon the water-bath can be advantageously heated for some time longer in an air-bath at 120° C.

In both cases the cooled mass is moistened equally with hydrochloric acid, and then heated for half an hour in a closed vessel, after which hot water is added with continued stirring, and the silicic acid then filtered. As the pores of the filter are greatly obstructed by the acid, it is better to wash the latter by decantation with hot water, and finally rinse it on to a filter.

The filtrate will always contain together with the oxides small quantities of silicic acid, even if the latter had been dried at 120° C. In all accurate analyses, therefore, the filtrate must be again evaporated, and the residue treated as heretofore.

After drying the precipitate ignite it and weigh. For this purpose inclose the precipitate in the filter, and ignite the same in a platinum crucible, at first over an ordinary burner until the paper has charred, then more strongly over a blast-lamp. When the contents of the crucible present a dark appearance—due to the unburned carbon of the paper—continue the ignition, with the crucible only partially covered, over an ordinary lamp, until the mass appears perfectly white. The ignition of the silicic acid over a blast-lamp should only be executed in a well-closed crucible, otherwise very considerable quantities of it may be very easily carried away by the strong current of air.

In all cases ascertain whether the silicic acid thus obtained is pure, or if it still contains undecomposed mineral. This is most simply discovered by heating a portion of the precipitate with hydrofluoric acid or ammonium fluoride, when no residue should remain.

Certain silicates contain titanic acid, which will separate out with the silicic acid, provided that the residue obtained in the first evaporation has not been mixed with a large quantity of hydrochloric acid, in which instance most of the titanic acid will be dissolved. For the estimation of the titanic acid the residue, left after treating the silicic acid with hydrofluoric acid or ammonium fluoride, is fused with potassium hydrosulphate, the fused mass dissolved in water, filtered if necessary, and the titanic acid precipitated by continued ebullition of the filtrate, through which a constant current of carbon dioxide is conducted and the evaporating water replaced. The titanic acid is washed with water and ignited with the addition of some solid ammonium carbonate. If some of the titanic acid has entered into the hydrochloric acid solution of the residue, it will be found with the aluminum or iron precipitate produced by ammonium hydrate. This precipitate is therefore fused with potassium hydrosulphate, the fused mass dissolved in cold water and hydrogen sulphide conducted into the filtrate to reduce any ferric oxide present to the ferrous state. After complete reduction the titanic acid in the liquid is precipitated as above directed.

Should this be the case, treat the entire precipitate in a similar manner, heating the residue with sulphuric acid, and adding this solution to that dissolved in hydrochloric acid.

The estimation of silicic acid in the presence of quartz has been already described (p. 84).

COURSE OF ANALYSIS FOR SILICATES DECOMPOSED BY ACIDS.

Natrolite.

MESOTYPE.

Composition.—Silicic acid, aluminum, sodium, water, with sometimes small quantities of ferric and calcium oxides.

The finely pulverized mineral, after being dried at 100° C., is treated with hydrochloric acid, and the above directions strictly followed.

The filtrate from the silicic acid is brought to boiling, and ammonium hydrate, free from carbonic acid, then added, causing the precipitation of the ferric and aluminic oxides. The boiling of the liquid should be continued until the odor of ammonia is no longer perceptible; the precipitate of the oxides is then immediately filtered, washed with boiling water, dried and ignited.

When ferric oxide is present, too intense ignition is to be avoided, because this will render the iron more insoluble and consequently more difficult to separate from the alumina.

When the quantity of calcium oxide is to any extent considerable, the precipitate of the aluminum is not perfectly pure. The liquid precipitated by the ammonium hydrate should then be acidified with acetic acid, neutralizing the excess of the latter, however, with ammonium. The solution should continue to give a slight alkaline reaction. Or, the supernatant liquid is poured from off the precipitate through a filter, the precipitate dissolved in hydrochloric acid, the solution strongly diluted with water, and the precipitation repeated.

The weighed aluminum oxide contains all the ferric oxide and generally also the small quantity of silicic acid that may have passed into solution. Digest the precipitate with fuming hydrochloric acid, removing the excess of acid by evaporation, and after filtering off the silicic acid, determine the iron volumetrically (according to pp. 75 and 80) in the filtrate.

The calcium oxide in the filtrate from the aluminum precipitate is thrown down as calcium oxalate upon the addition of ammonium oxalate, and by ignition converted into calcium oxide (p. 14). According to the quantity of calcium present there can very readily some alkali pass over into the precipitate. That the calcium oxalate may be entirely pure, it is necessary to re-dissolve the precipitate, after filtering, in hydrochloric acid and repeat the precipitation.

The filtrate contains, besides the ammonia salts, also the sodium in form of chloride. Evaporate the same to dryness in a platinum or porcelain dish, expel the ammonia salts by gentle ignition, and estimate the sodium chloride, after transferring the residue to a platinum crucible and igniting gently, covering the crucible during the ignition with a lid (p. 26).

The quantity of water in mesotype is obtained by igniting the mineral, previously dried at 100° C., in a platinum crucible, until constant weight is obtained. It is always well to use coarse powder or small pieces of the mineral for this purpose, because the fine powder can be readily carried away by the air-current from the lamp.

Prehnite.

Composition.—Hydrous silicate of calcium and aluminum oxides, generally combined with varying quantities of ferric and manganous oxides and the alkalies.

The analysis can be performed precisely as that of natrolite, only here a second precipitation of the aluminum and calcium oxides is absolutely required.

As prehnite generally contains but mere traces of manganese (0.3 per cent.), this may be precipitated as sulphide by the addition of a few drops of ammonium sulphide to the filtrate from the calcium oxalate.

The filtrate from the manganese sulphide is acidified with hydrochloric acid, heated until the liquid no longer yields the odor of hydrogen sulphide, and then filtered from any sulphur that may have separated. In the filtrate the alkalies are determined in the usual manner.

In estimating the water present it is well to observe that many varieties of prehnite contain organic substances, which of course blacken upon the application of heat, but gradually burn white. This being the case, the water should be determined directly by weighing (p. 36).

If it is desired to directly determine the organic matter present, this may be done according to a method to be subsequently described, *i. e.*, by heating a weighed portion of the mineral together with cupric oxide in a stream of oxygen gas, and weighing the carbon dioxide that is formed.

Datolite.

Composition.—Hydrous silicate of calcium, with calcium borate; sometimes aluminum and magnesium.

The finely powdered and dried mineral is subjected to the same mode of treatment as given in the analysis of natrolite. In the filtrate from the silicic acid precipitate the aluminum with ammonium hydrate free from carbon dioxide. The precipitate of aluminum oxide always contains boracic acid, which may be removed by pouring hydrofluoric acid over the dried precipitate placed in a platinum crucible, or mixing it with ammonium fluoride, adding a few drops of concentrated sulphuric acid, and applying heat whereby the boracic acid will be completely volatilized as boron fluoride. The sulphuric acid may be expelled by continuing the heating for some time, adding ammonium carbonate now and then.

In the filtrate from the aluminum oxide precipitate the calcium as oxalate, and in the filtrate from the latter throw down the magnesium as ammonium-magnesium phosphate (p. 16).

The boracic acid is generally estimated by loss. To determine it directly, mix a weighed portion of the silicate with four times its quantity of potassium carbonate, fuse, and boil the fused mass with water, washing the filtered residue with the same, and precipitate the silicic acid, aluminum and calcium with ammonium carbonate, removing, however, the final traces of silicic acid by ammonium-zinc oxide. (See p. 116.)

The liquid thus finally obtained perfectly free from silicic acid, alumina, and calcium oxide, is supersaturated with hydrofluoric acid, and evaporated to dryness. By treating the residue with a 20 per cent. solution of potassium acetate, the boron will remain behind as potassium borofluoride, which may be estimated as such. (See p. 121.)

Determine the water as directed in the analysis of Natrolite.

Olivine.

Composition.—Silicate of ferric and magnesium oxides.

Digest the dried mineral with hydrochloric acid, and separate the silicic acid as heretofore. The residue should, however, only be heated upon the water-bath to dusty dryness, because if heated strongly some of the ferric oxide will remain undissolved upon subsequent treatment with hydrochloric acid. The filtrate is heated with nitric acid or pulverized potassium chlorate added to convert ferrous oxide into ferric oxide, and the latter then precipitated from a boiling solution by the addition of ammonium hydrate (p. 24).

The magnesium is precipitated in the filtrate from the ferric oxide by sodium-ammonium phosphate (p. 16). When the olivine contains aluminum, the weighed precipitate of ferric oxide represents the combined weight of it and aluminum; therefore determine the iron volumetrically in a separate portion (p. 75 or p. 80).

Many olivines contain minute traces of copper, tin, manganese, and nickel. When this is the case, the first two metals may be removed by precipitating them with hydrogen sulphide in the filtrate from the silicic acid. When the quantity of the sulphides thus obtained is in any measure considerable, it would be advisable to digest them with a solution of sodium sulphide. The tin in the filtered liquid is then determined according to page 55, and the undissolved copper sulphide weighed as such.

When manganese and nickel are present precipitate them in the filtrate from the ferric oxide by adding a few drops of ammonium sulphide, and determine the magnesium in the filtrate.

By pouring a mixture of hydrochloric acid and hydrogen sulphide (p. 104) over the precipitate upon the filter produced by ammonium sulphide, the manganese will enter into solution, and may be reprecipitated as such and determined. By igniting the residual nickel sulphide with air contact, the oxide is formed and as such weighed.

Lievrite.

ILVAITE.

Composition.—Silicate of ferrous and ferric oxides; with generally small quantities of aluminum and manganous oxides.

The decomposition of the mineral is effected by hydrochloric acid, and the silicic acid separated by evaporating the liquid to dryness. (See Olivine, p. 130.)

Boil the filtrate from the silicic acid with nitric acid or potassium chlorate to oxidize the ferrous oxide to the corresponding higher compound, and precipitate the latter from its solution after the addition of sodium carbonate by the addition of sodium acetate (p. 73).

The precipitate contains not only the ferric oxide, but all the aluminum, and usually small quantities of silicic acid, which may be extracted by digesting the precipitate, after gentle ignition and weighing, with fuming hydrochloric acid, the excess of which is evaporated and the silica filtered off after diluting the solution with water. The aluminum is found by difference, if the found silicic acid and the iron calculated as ferric oxide are deducted from the original weight of the precipitate.

When ferric oxide is rendered insoluble by ignition in hydrochloric acid, it may be brought into solution by fusion with potassium hydrosulphate. (See p. 82.)

The liquid from the ferric oxide is mixed with ammonium oxalate (p. 13) for the precipitation of the calcium and the manganese thrown down in the filtrate as sulphide (p. 21) after previous neutralization with ammonium.

When determining the ferric in the presence of ferrous oxide proceed as heretofore directed (Magnetic Iron, p. 86). Dissolve the mineral in hydrochloric acid, conducting a stream of carbon dioxide into the solution during the operation, and bring the solution without filtering to a definite volume. Determine in the one-half the ferrous oxide with potassium bichromate (p. 79), and in the other the ferric oxide with stannous chloride (p. 80).

When concentrated sulphuric acid (see Chromic Iron, p. 88) has been used instead of hydrochloric acid for the decomposition of the mineral after diluting with water, the ferrous oxide may be determined in the one-half by means of potassium permanganate (p. 75).

Ultramarine.

Composition.—Aluminum, sodium, silicic acid, and sulphur, and generally slight traces of ferric oxide, calcium oxide, potassium, sulphuric acid and chlorine.

The pulverized substance is first dried and then digested with hydrochloric acid, when hydrogen sulphide gas is disengaged, and silicic acid, together with sulphur, separates out. When the decomposition is complete, the silicic acid is separated as usual, and the precipitate, consisting of silicic acid and sulphur, is ignited, which will volatilize the latter.

In the filtrate from the silicic acid the sulphuric acid is thrown down by the addition of barium chloride (p. 15), and any excess of the latter in the filtrate of the barium sulphate removed with sulphuric acid.

The aluminum in the filtrate from the barium sulphate is determined by double precipitation with ammonium hydrate, and the silicic acid that may be present in the filtrate is separated according to page 127. Since in the presence of sulphuric acid the latter invariably passes over into the aluminum precipitate, the latter should be strongly ignited (p. 37), which will render insoluble in hydrochloric acid any ferric oxide present; therefore, in order to estimate the iron volumetrically, fuse the precipitate with potassium hydrosulphate, and filter off the silicic acid after dissolving the fused mass in water, or determine the iron in a second portion of the substance.

Mix the filtrate from the aluminum hydrate with ammonium oxalate, determining the calcium as oxalate, and converting the latter into carbonate or oxide (p. 14).

The filtrate from the calcium precipitate is evaporated to dryness to determine the alkalies, and the residue ignited to expel ammoniacal salts. The sulphates thus obtained are then weighed (p. 37).

When potassium and sodium are present, their weighed sulphates are previous to their separation converted into chlorides (p. 47).

Sulphur Determination.—The conversion of the sulphur into sulphuric acid may be accomplished by following the method given at page 111, or by adding potassium chlorate to the finely divided mineral and pouring over it nitric acid (about 50 C. C.) of specific gravity 1.36. The vessel, covered with a watch-glass or funnel, is warmed upon a water- or sand-bath, potassium chlorate being added from time to time. When the oxidation is complete, and the liquid has become cool, add to it hydrochloric acid and evaporate to dryness, dissolving the residue in water and precipitating the sulphuric acid with barium chloride (p. 15) in the filtrate from the silicic acid.

Should the liquid to be precipitated contain undecomposed potassium chlorate or nitrate, the obtained barium sulphate will be rendered impure by barium chlorate or nitrate. The former of these impurities may be easily removed by digesting the ignited barium sulphate with dilute hydrochloric acid. The barium nitrate, however, is only imperfectly removed by it.

When employing this method, care should be exercised that the nitrates be completely decomposed previous to the precipitation with barium chloride. This may very readily be obtained by repeatedly evaporating the nitrate solution to dryness upon a water-bath, with frequent addition of strong hydrochloric acid.

It is, of course, understood that, in the calculation of the analysis, the amount of sulphuric acid existing as such must be deducted from that formed by the oxidation of the sulphur compound.

To estimate the amount of sulphur escaping as hydrogen sulphide, when ultramarine is treated with an acid, the evolved gas is converted into sulphuric acid.

For the execution of this operation, the following apparatus* is employed. (See Fig. 12.)

The flask *K*, of about 500 C. C. capacity, is connected on the one side with a carbon dioxide generator, upon the other with the absorption tube *a*, filled with pieces of glass. The latter, which may be replaced by a burette, provided with a side supply-tube, is about 60 Cm. long and 2 Cm. wide. The separatory funnel *b* is filled with a solution of bromine in hydrochloric acid, and *d* with hydrochloric acid. The bromine vapors that are evolved in the decomposition are absorbed by hydrochloric acid placed in an adjoining jar, into which the glass tube in *a*, bent at right angles (only indicated), dips.

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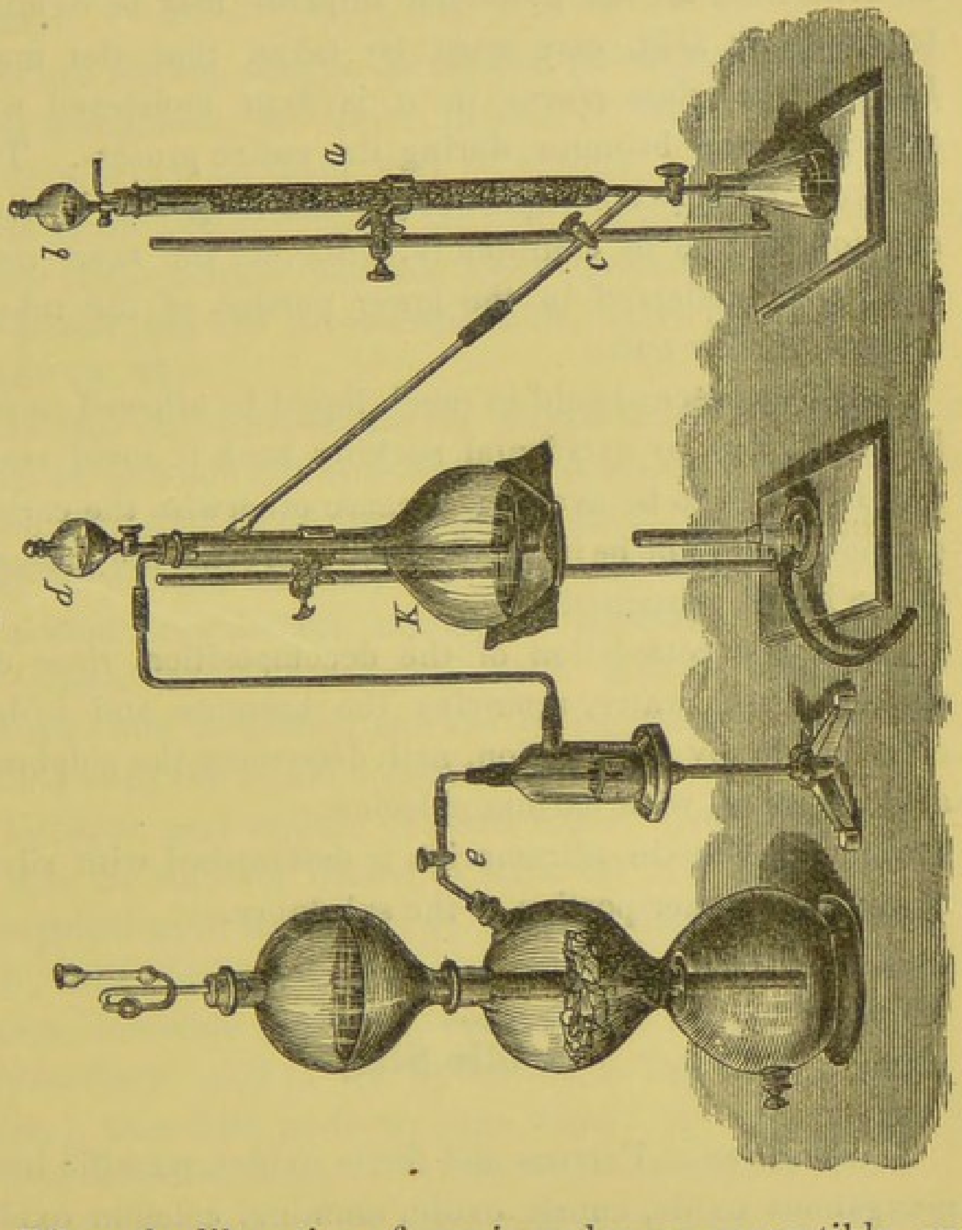
* Also been used in determining the sulphur in illuminating gas, cast iron, etc.

When the apparatus has been arranged, the weighed amount of ultramarine is brought into *K*, and then enough water added to just cover the end of the tube conducting in the carbon dioxide. Allow the bromine solution to pass from *b* into *a*, drop by drop, until the lower contracted part of the tube is filled, then gradually open the cork of the funnel *d*.

Fig. 12.



When the liberation of gas is no longer perceptible, on the addition of hydrochloric acid, the contents of the flask are heated slowly to boiling, while, at the same moment, the glass pinch-cock *e* is opened, and a continuous stream of carbon dioxide allowed to pass through the apparatus, until all the hydrogen sulphide has been expelled. The bromine oxidizes the latter perfectly to sulphuric acid. As this occurs, the bromine solution in the absorption tube *a* will be decolorized, and allowed to pass into a beaker placed beneath, and at the same time immediately replaced by opening the glass stopcock of the funnel *b*. In order that all the hydrogen sulphide may be oxidized to sulphuric acid, care must be taken that the upper half of the glass pieces in *a* is kept moistened with undecomposed bromine during the entire process. This we can readily accomplish, by permitting the bromine solution to drop in continually, while, at the same time, the liquid collected in the lower portion of the tube is allowed to flow out.

In no instance should so much liquid be allowed to collect in *a*, that by accidental sucking back it could reach *K*. It is also to be avoided, because otherwise the carbon dioxide would not be in condition to overcome the pressure of the liquid contained in *a*.

After the completion of the decomposition, rinse out the tube with water, removing the bromine and hydrochloric acid by evaporation, and determine the sulphuric acid, as usual, with barium chloride.

The chlorine in ultramarine is determined with silver nitrate in another portion of the substance.

Puddle Slag.

Composition.—Ferrous and ferric oxides, metallic iron manganous oxide, cupric oxide, alumina, calcium oxide, magnesia, silicic acid, sulphuric, phosphoric, and titanic acids.

Decompose the slag, finely powdered and dried at 100° C., with hydrochloric acid, separating the silicic acid as directed in the Natrolite analysis (p. 126). Titanic acid when present will be discovered with the silicic acid. (See p. 125.)

The method of analysis follows from the observations made in the analyses of iron ores; therefore, I refer to these.

When sodium acetate is used in the separation of iron from manganese, the latter, instead of being precipitated by ammonium sulphide, may be thrown down as the hydrate of the superoxide, by the addition of strong chlorine water to the filtrate, and this when ignited with access of air passes into the protosesquioxide, which is weighed as such* (p. 21).

To this end concentrate the filtrate from the iron precipitate, and add chlorine water to the boiling liquid until it smells decidedly of the reagent added. The oxidation may be considered complete when the liquid above the separated brown-black manganese appears red, owing to the production of permanganic acid. A few drops of alcohol may now be added, and the boiling renewed and continued until the liquid becomes colorless.

Bromine may replace chlorine water. Add a few drops of it to the solution heated to about 50° C. Heat should be applied until the excess of bromine has been expelled, *i. e.*, until the liquid becomes colorless, when the manganese binoxide is filtered, washed with water containing hydrochloric acid (1 vol. hydrochloric acid and 99 vols. water), then with perfectly pure water.

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* The oxidation of the manganese by bromine or chlorine will not be perfect in the presence of ammoniacal salts, and for this reason the iron is not separated according to the method described on page 72.

In the filtrate from the manganese determine the calcium oxide and magnesia as ordinarily done.

A separate portion of the substance is taken for the estimation of the ferrous when ferric oxide is present. The decomposition is best effected by heating with sulphuric acid in a sealed tube (p. 91). In using hydrochloric acid to dissolve the slag, if the ferrous oxide is to be determined with a permanganate solution, regard should be had to what was said on page 78. In this case it is decidedly more practical to determine the ferrous oxide with potassium chromate (p. 79).

In determining the metallic iron about 5 grms. of the slag are placed in a platinum dish, and to this is added a solution of copper sulphate, which causes a quantity of metallic copper ($CuSO_4 + Fe = FeSO_4 + Cu$) corresponding to the iron to be precipitated.

After protracted standing and frequent agitation, the copper, together with undecomposed slag, is filtered off, washed perfectly with water, and the residue digested with nitric acid, which dissolves the copper. The acid is evaporated, and the copper precipitated from the aqueous solution, acidified with hydrochloric acid, as copper sulphide.

When the slag contains copper *per se*, the corresponding amount ot copper sulphide is to be deducted.

It is of course understood that in the presence of metallic iron, which, upon treatment with hydrochloric acid, passes into solution as ferrous chloride, the amount of the latter will be considered when calculating the directly determined ferrous oxide.

The estimation of the phosphoric and sulphuric acids results most favorably when separate portions of the slag are fused with sodium carbonate, or sodium carbonate and silica. (See p. 83.)

Slags from the Smelting of Copper and Lead Ores.

Composition. — Ferrous oxide, alumina, manganous oxide, cupric oxide, lead, barium, calcium and magnesium oxides, alkalies, silicic acid, sulphuric acid and sulphur.*

Pulverize and dry the slag at 100° C., decomposing it with nitric acid, and separating the silicic acid as directed on page 123. When barium oxide is present barium sulphate will be mixed with it. To ascertain the amount of the latter, heat the weighed precipitate with hydrofluoric acid, or mix it with ammonium fluoride (p. 125), and determine the residual weight.† The silicic acid is represented by the difference.

When a considerable quantity of lead is present a portion of this may separate out with the silicic acid as crystalline lead chloride. This is very slowly dissolved when washed with water. This being the case, the residual silicic acid is washed with boiling water, and then transferred to the filter.

To determine the lead the filtrate is evaporated with sulphuric acid to expel the hydrochloric acid, and the lead weighed as sulphate (p. 49). When a considerable quantity of iron is present, some of the ferric oxide may very readily be involved with the lead precipitate, and it is therefore advantageous to continue the evaporation only until the greater portion of the hydrochloric acid has been driven away, then mix the liquid with ammonium hydrate

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* Besides these constituents these slags may contain arsenic, antimony, bismuth, zinc, cobalt, nickel, etc. For the determination of these substances refer to the analyses of *Refined Lead* and *Raw Copper*.

† Examine the residue qualitatively.

until the precipitate produced remains, then redissolve in sulphuric acid. To the liquid add one-third volume alcohol for the complete separation of the lead sulphate.

Expel the alcohol from the lead filtrate and precipitate and weigh the copper as sulphide (p. 48). When, however, arsenic and antimony are present, the precipitated sulphides should be digested with sodium sulphide, which will dissolve the arsenic and antimony sulphides (p. 87).

After separating the copper, expelling the hydrogen sulphide from the filtrate, and oxidizing the iron by the addition of nitric acid or potassium chlorate, the further analysis is executed according to the methods described on page 71, with the only difference that here the small quantity of manganese is best precipitated by chlorine. (See p. 137.)

The alkalies in the slag are determined in a separate portion. The filtrate from the silicic acid is treated first with hydrogen sulphide, then with ammonium sulphide and ammonium oxalate, and the filtrate heated with hydrochloric acid to destroy the ammonium sulphide, and after the expulsion of the hydrogen sulphide the liquid is evaporated to dryness with addition of oxalic acid or ammonium oxalate. The residue is gently ignited and extracted with water (p. 45). In the filtrate from the magnesia the alkalies are determined as sulphates. For the separation of potassium sulphate from sodium sulphate, see page 47.

If hydrogen sulphide is liberated when the slag is treated with a dilute acid, the sulphur is determined according to the method given on page 134.

The sulphuric acid is determined in a separate portion.

Clay.

As regards the mechanical analysis of clay, see Fresenius's article, "Investigation of the most important Nassau Clays," *Journ. f. prakt. Chemie*, lvii. 65. The elutriation apparatus of Fr. Schulze is also described in the *Journ. f. prakt. Chemie*, xlvii. 241.

Composition.—Hydrous silicate of aluminum, with variable amounts of ferric oxide (also ferrous oxide), calcium oxide, magnesia (often present as carbonate), alkalies, organic matter, and arenaceous quartz.

Clays are not perfectly decomposed by hydrochloric acid, but are in the rule when heated with sulphuric acid.* For this purpose the pulverized specimen dried at 100° C. is placed in a platinum dish, with an excess of sulphuric acid hydrate (equal volumes concentrated sulphuric acid and water), the whole heated to boiling, and the ebullition continued until all the sulphuric acid has been expelled. After cooling, this operation is repeated, and the residue, with addition of hydrochloric acid and the application of heat, finally dissolved in water.

The decomposition of clays with sulphuric acid succeeds very well when they, finely divided, are stirred up with sufficient concentrated sulphuric acid to form a paste, and then heated in a porcelain air-bath to 300° C. (Fig. 13.)

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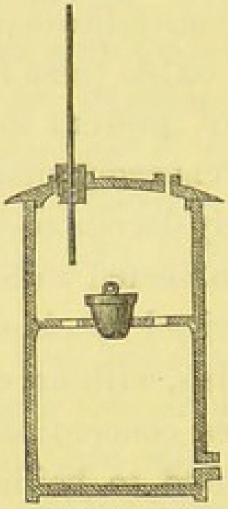
* If the heating with sulphuric acid is prosecuted in sealed glass tubes (see p. 91), the aluminum silicates are fully decomposed. If this process is not desirable, and if the clay is not perfectly decomposed by boiling with sulphuric acid hydrate, this may be effected by fusion with sodium carbonate. (See page 143.) The alkalies may be determined in a second portion by decomposing with hydrofluoric acid or ammonium fluoride (p. 144).

The decomposition is generally complete at the expiration of three or four hours. The residue should not yield a gritty sound when rubbed with a glass rod; this will, however, always occur to some extent when sand is present. When it is very gritty the residue is moistened again with sulphuric acid, and digested until it is fully expelled.

Fig. 13.



The silicic acid, insoluble in hydrochloric acid, after washing with water, is ignited and weighed. By subsequent boiling with a solution of sodium carbonate the quantity of arenaceous sand mixed with the silicic acid is obtained. The residual quartz should be examined for undecomposed silicates, viz., feldspar, etc.

The aluminum and calcium oxides are separated from each other as given in the analysis of Natrolite on page 126, and the magnesia and alkalies as directed on page 45.

When a ferruginous clay is being examined, the ferrous or ferric oxide had better be determined volumetrically in a second portion of the substance (p. 91), and the corresponding amount of ferric oxide subtracted from the weight of the alumina.

The carbon dioxide from the carbonates that may be present is estimated according to page 33.

Provided that the clay contains neither organic material nor ferrous oxide, the water may be determined by igniting a weighed portion of substance in a platinum crucible, or it may be directly estimated (p. 36) when the loss by ignition will approximately represent the quantity of water and organic substance.

The presence of carbonates renders this mode of estimation valueless, because of the simultaneous liberation of carbon dioxide.

Determination of the Silicic Acid in Silicates not decomposed by Acids.—When a silicate is mixed either with sodium or potassium carbonate and fused, there is produced, by the addition of an alkali, a silicate decomposable with acids. The object of the fusion of the silicate with an alkaline carbonate is, therefore, merely to withdraw from the former a portion of its silicic acid, converting it then into an analogous compound which acids will decompose.

In prosecuting the decomposition of a silicate in this manner, the substance, finely powdered and dried at 100° C., is thoroughly mixed, in a platinum crucible, with four to five times its weight of a mixture of sodium or potassium carbonate (5 : 7), then brought to fusion, until carbon dioxide no longer escapes, and the mass is perfectly liquefied. When a Bunsen burner has been employed in the fusion, the decomposition will require at least half an hour for its completion, whereas a blast-lamp will produce the same result in a much shorter (about ten minutes) period. If a platinum dish is at your immediate disposal, pour the liquid contents of the crucible into it, or place it upon a cold iron plate, when, after cooling, the contents may be easily loosened by pressing together the sides of the crucible. The fused mass and crucible are transferred to a beaker glass, and 20–30 times its quantity of water poured upon it, and heat applied. After disintegrating the mass thoroughly, add dilute hydrochloric acid, and assure yourself that complete solution is effected before evaporating the hydrochloric acid solution to dryness. The silicic acid is rendered insoluble* by evaporating the solution either in a porcelain or platinum dish, and heating the residue in an air- or water-bath to 120° C., until it becomes dusty-dry in its appearance. As regards the rest, proceed as directed on page 124. To assure yourself that all the oxides present have passed into solution, it is advisable to extract the residual silicic acid several times with warm hydrochloric acid before bringing it upon the filter.

The silicic acid, perfectly purified by washing with hot water, is dried, ignited, and weighed (p. 124).

Determination of the Alkalies in Silicates not decomposed by Hydrochloric Acid.—In the fusion of a silicate with an alkaline carbonate, the determination of the alkalies present in it is of course impossible, and some other means of decomposition must be used. A mixture of hydrofluoric acid and sulphuric acid, or pure hydrofluoric acid, or even ammonium fluoride, is resorted to in this case.†

When a silicate is heated with hydrofluoric acid or ammonium fluoride, a volatile fluoride of silicium is disengaged, while the fluorides of the oxides present compose the residue, and are dissolved as chlorides when heated

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* Under certain circumstances the silicic acid can remain entirely dissolved in the employed acid, particularly where too great an excess of alkaline carbonate has been used, or when a minute quantity of silicic acid is present.

† By previous ignition of the silicate, its subsequent decomposition by hydrofluoric acid or ammonium fluoride is rendered much easier.

with hydrochloric acid, with volatilization of the hydrofluoric acid.

Decomposition by means of Hydrofluoric Acid.—Bring the finely pulverized and dried silicate into a platinum dish, pouring over it concentrated hydrofluoric acid, or better, a mixture of sulphuric acid (equal parts of concentrated sulphuric acid and water), and concentrated hydrofluoric acid (1 part of sulphuric acid with two to three parts of hydrofluoric) and then apply heat to incipient ebullition. When the decomposition is complete,* evaporate the solution to dryness, expelling the sulphuric acid finally by heat; the latter, however, should not be too intense, because certain of the oxides (Al_2O_3 and Fe_2O_3) would otherwise be rendered very difficultly soluble. After cooling, heat the residue with concentrated hydrochloric acid, continuing the operation some time, with the frequent addition of water; and, should there still be some undissolved material, it may result from undecomposed substance; and when barium is present, it may be due to the barium sulphate. The residue should be examined qualitatively, and the above treatment finally repeated.

Decomposition by means of Ammonium Fluoride.—The employment of ammonium fluoride in the decomposition of silicates has some preference to hydrofluoric acid, because it is much more easily obtained; and certain silicates, also, that are only very slowly attacked by hydrofluoric acid, are very easily decomposed by ignition with ammonium fluoride.

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* Most silicates are very rapidly decomposed by this means, the decomposition being complete in about 5 to 10 minutes.

In analysis, the pulverized and dried silicate is mixed in a platinum crucible, with seven to eight times its quantity of ammonium fluoride, water added, and heat applied upon a water-bath until the mass becomes completely dry, when the ignition is continued over an ordinary Bunsen burner, until vapors no longer escape. The fluorides of the metals are decomposed by the addition of concentrated sulphuric acid, the excess of acid being evaporated, and the solution of the residue effected by means of hydrochloric acid.

All the oxides, which may be present, are in the hydrochloric acid solution. The manner of separating the alkalies is given elsewhere.

[*Decomposition by means of Calcium Carbonate and Ammonium Chloride.*—Mix 1 part of the pulverized substance with 8 parts of precipitated calcium carbonate and 1 part of pulverized ammonium chloride, place in a platinum crucible, and heat to full redness, but not too intensely, for 30 to 40 minutes. The crucible, with its contents (which should be in a coherent, sintered but not thoroughly fused condition), is placed in a beaker, covered with water, and heated to near the boiling point for half an hour. The whole is then brought upon a filter. The filtrate, containing the alkalies, calcium chloride and caustic lime, is treated with a little ammonium and with ammonium carbonate, in slight excess, and heated to boiling, filtered and the filtrate evaporated to dryness and gently ignited, to expel the ammoniacal salts. The residue is dissolved in a little water, and a drop of ammonium oxalate added, the mixture is heated, filtered, the filtrate evaporated to dryness, ignited, and the residual alkaline chlorides separated according to previous directions.—*Dr. J. L. Smith.*]

Felspar.

Composition.—Potassium-sodium-aluminum silicate, with ferric oxide, calcium oxide and magnesia.

For the determination of the silicic acid, alumina, ferric oxide, calcium oxide, and magnesia, fuse the pulverized mineral, dried at 100° C., with four to five times its weight of potassium-sodium carbonate, following the instructions given on page 143 for the separation of the silicic acid.

The aluminum oxide in the filtrate from the above is separated from the calcium oxide and magnesia by double precipitation with ammonium hydrate, free from carbon dioxide. (See Natrolite, p. 126.) When iron is present, this can be estimated volumetrically after the ignited precipitate has been dissolved in hydrochloric acid, or after the fusion with potassium hydrosulphate. When the iron is present in tolerably large quantity, it is best determined in a separate portion of the substance. The silicic acid that remains after dissolving the ignited alumina precipitate in hydrochloric acid must be deducted from the same and added to the already known amount of that acid.

In the filtrate from the aluminum the calcium oxide and magnesia are thrown down by ammonium oxalate and phosphorus salt (p. 32).

Alkali Determination.—In the decomposition of the mineral with hydrofluoric acid or ammonium fluoride, proceed as previously directed. After having obtained the hydrochloric acid solution, precipitate the aluminum with ammonium hydrate, and in the filtrate throw down the calcium with ammonium oxalate, removing the sulphuric acid with barium chloride, and separate the magnesia according to the method described on page 45.

The estimation of potassium in presence of sodium is accomplished with platinic chloride (p. 49).

[The method of Dr. J. Lawrence Smith is best adapted for the decomposition of the Felspar where the alkalies are to be estimated.]

Glass.

The analysis of porcelain or kaolin can be executed in a similar manner. (See also the analysis of Clay, p. 141.)

Composition.—Potassium, sodium, aluminum, calcium, magnesium, silicic acid, sulphuric acid, phosphoric acid.

In colored glasses regard must be had to the coloring metallic oxides that are present. If the glass contains merely potassium, sodium, aluminum, ferric oxide, calcium, magnesium, and silicic acid, the analysis is exactly analogous to that of Felspar.

When reducible oxides are present, viz., lead and tin oxides, sodium nitrate should be added to the mixture of carbonates used to effect the decomposition.

Should the glass under examination contain lead silicate, the silicic acid must be repeatedly boiled with water to dissolve the chloride of this metal, which may afterwards be precipitated as sulphide and determined (p. 29).

The filtrate from the lead sulphide, after the expulsion of the hydrogen sulphide and oxidation with nitric acid, is employed in the determination of the remaining oxides.

It is necessary when tin is present to digest the weighed silicic acid with ammonium sulphide and separate and determine the tin sulphide in the filtrate as directed on page 55. The filtrate from the silicic acid should also be examined for tin by precipitating it with hydrogen sulphide, and when lead is present the precipitate produced by hydrogen sulphide is digested with ammonium sulphide—determining the insoluble lead sulphide as such and supersaturating the filtrate with dilute sulphuric or hydrochloric acid (p. 55).

Instead of precipitating the aluminum with ammonium hydrate when manganese is present, neutralize the solution with sodium carbonate and precipitate it with sodium acetate, preparing thus for the subsequent precipitation of the manganese by bromine or chlorine (p. 137).

When cobalt is present with manganese, it will also be precipitated as sesquioxide by chlorine or bromine.

This being the condition of affairs, it would be better to throw down both metals, in the filtrate from the aluminum, as sulphides by means of ammonium sulphide, dissolving them in hydrochloric acid, with the addition of nitric acid, and precipitate the cobalt as nitrite of sesquioxide of cobalt and potassium (p. 22). Throw down the manganese in the filtrate as carbonate (p. 21).

The aluminum is also thrown down by sodium acetate when zinc oxide is present, and the latter removed from the filtrate by the addition of hydrogen sulphide (p. 109).

The sulphuric acid may be precipitated in the filtrate from the silicic acid by adding barium chloride, and the excess of the latter removed with sulphuric acid.

In the analysis of glass containing phosphoric acid, after the separation of the silicic acid the former acid is precipitated with metallic tin, and the oxides determined as heretofore in the filtrate.

Pistacite.

Composition.—Silicate of alumnia, ferric oxide and calcium oxide, together with ferrous oxide (manganous oxide), magnesia, potassium, sodium and water.

In determining the silicic acid and oxides, the alkalies excepted, the finely pulverized and dried mineral is fused with potassium and sodium carbonates, and the silicic acid determined as directed on page 143.

The filtrate from the silicic acid is heated with nitric acid and potassium chlorate to oxidize the ferrous oxide to the corresponding higher oxide, and this and the aluminum then separated from the manganese and alkaline earths, after neutralization with sodium carbonate, by boiling with sodium acetate (p. 73).

The manganese is then thrown down in the filtrate with bromine or chlorine (p. 137). The calcium oxide and magnesia are determined in the filtrate in the usual manner.

Ferric and ferrous oxides may be estimated very well volumetrically (p. 75 and p. 80) in the solution of a separate portion of the substance, decomposed by heating it with sulphuric acid in a sealed tube (p. 91).

The entire quantity of iron, calculated as ferric oxide, is deducted from the weighed alumina-iron precipitate.

Cook, to prevent the oxidation of the ferrous oxide, conducts the decomposition of the mineral in an atmosphere of carbon dioxide and steam. For this is used a water-bath with a constant niveau (Fig. 14 and 15), at the upper end of which is attached the tube *a*, which is connected with a Kipp carbon dioxide generator.

That the glass funnel *d* may be supported, the edge of the cover of the water-bath is provided with a deep channel. The cover ring bearing the platinum crucible contains a number of small perforations, through which, upon boiling, the water almost filling the water-bath rushes, causing the channel to be constantly filled with water, thus obstructing the entrance of air between the channel and the funnel edge.

First, ascertain by preliminary examination the least quantity of hydrofluoric acid, to which must be added sulphuric acid of 1.5 sp. gr., in order that the mineral may be decomposed; then place the pulverized substance (about 0.5 grm.) in a platinum crucible, pouring the mixture of sulphuric and hydrofluoric acid upon it, and stirring during the operation with a platinum spatula. Place the platinum vessel upon the perforated ring of the water-bath, put the funnel into position and fill the channel with water, at the same time dislodging the air in the funnel with a stream of carbon dioxide. When the decomposition is finished, the heating upon the water bath is interrupted, carbon dioxide conducted again into the funnel, and at the same time a continuous stream of cold water allowed to flow through the water-bath, which will hasten the cooling of the platinum crucible.

Fig. 14.

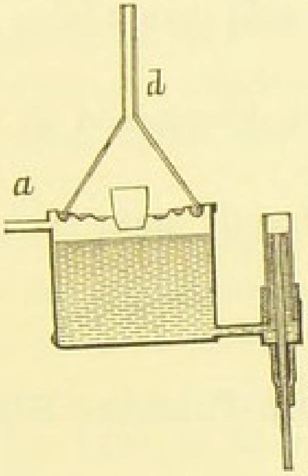
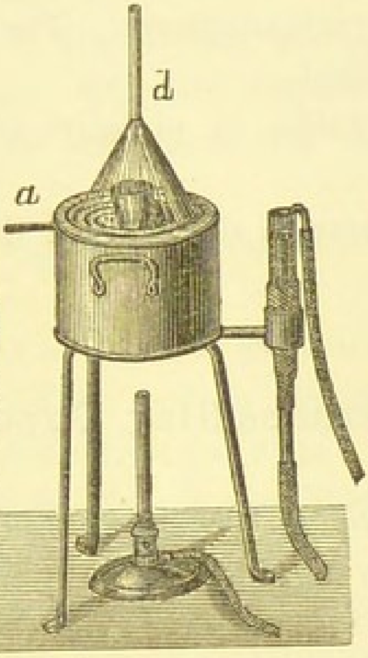


Fig. 15.



It may happen at times that the contents of the crucible will sinter tightly together, thus obstructing the further action of the acid. When this occurs, remove the lamp under the water-bath, fill the funnel with carbon dioxide, and stir the crucible contents with a strong platinum wire passed through the funnel tube. After washing the particles that may have adhered to the wire back into the crucible, discontinue the carbon dioxide stream, and renew the application of heat from the water-bath.

Before determining the ferrous oxide with permanganate solution, be certain the hydrofluoric acid used does not contain any substances which have a decomposing effect upon the permanganate. The acid should have previously been purified.

The alkalies in pistacite are determined as in Felspar (p. 147).

The water is determined directly most accurately (p. 36).

Blast-furnace Slag, Cupola-furnace Slags, etc.

Composition.—Ferrous and ferric oxides (sometimes metallic iron), manganous oxide, alumina, copper, lead, zinc, calcium oxide, magnesia (alkalies), silicic acid, titanic acid, sulphuric acid, phosphoric acid and sulphur (as calcium sulphide).

The slag finely divided and dried, when not soluble in hydrochloric acid, is decomposed by fusion with the carbonates of potassium and sodium, the silicic acid being removed as in Natrolite. When titanic acid is present an excess of hydrochloric acid is taken to dissolve the residue, and the silica is examined according to page 125.

In the filtrate from the silica, after the previous reduction of the ferric oxide by means of sulphurous acid (p. 87), precipitate the lead and copper as sulphides, if present, and dissolve the latter in nitric acid, and effect the separation of the metals by the addition of sulphuric acid. (See Brass, p. 49.) If, however, but one of these two metals exists in the solution, the precipitate produced by hydrogen sulphide may be determined by ignition in a stream of hydrogen.

The filtrate, free from hydrogen sulphide, is warmed with nitric acid or potassium chlorate to change the ferrous to ferric oxide, and the latter precipitated, together with the aluminum, by means of sodium acetate (p. 73). The precipitate should be examined for silicic as well as titanic acid (p. 82 and p. 125).

After adding acetic acid to the filtrate, precipitate the zinc with hydrogen sulphide. After the expulsion of the latter, the manganese may be separated with chlorine or bromine (p. 137).

The calcium oxide and magnesia are determined in the filtrate in the usual manner.

Ferrous oxide in presence of ferric is estimated according to one of the methods described in the analysis of Pistacite (p. 149), or Magnetic Iron (p. 86).

The metallic iron found in the slag is determined according to page 138.

When the alkalies are determined, take a second portion of the slag and decompose it with ammonium fluoride, precipitating the hydrochloric acid solution with hydrogen sulphide, and proceed in general as directed when analyzing Copper and Lead Slags (p. 139).

When calcium sulphide occurs in the slag, the sulphur is estimated by the oxidation of the hydrogen sulphide with a hydrochloric acid solution of bromine (p. 134).

The sulphuric and phosphoric acids are estimated as in Hematite (p. 79).

Turmalin.

Composition.—Ferrous and ferric oxides, manganese oxide, aluminium oxide, calcium oxide, magnesia, potassium, sodium, lithium, silicic acid, boracic acid, hydrofluoric acid (phosphoric acid) and water.

Determination of the Silicic Acid and Boracic Acid.—Fuse the finely pulverized mineral, previously dried at 100° C., with four times its weight of potassium carbonate. The fused residue is heated with water, and, after filtering off the insoluble portion, subject it to a thorough washing with hot water. Boracic acid, a portion of the silicic acid and aluminum will be found in the filtrate. The latter are precipitated with ammonium carbonate and ammonium zinc oxide. (See p. 116.) The boracic acid is removed as boro-potassium fluoride by supersaturating the liquid, entirely free of silicic acid and aluminum, with hydrofluoric acid. (See the Determination of Boracic Acid in Boronatrocalcite, p. 121.)

The insoluble residue remaining after fusion with potassium carbonate, and the precipitate produced by ammonium carbonate and ammon-zinc oxide, are both decomposed by hydrochloric acid, and the silicic acid taken out as in Natrolite (p. 126).

The estimation of the oxides is most satisfactorily prosecuted by decomposing a separate portion of the mineral with a mixture of hydrofluoric and sulphuric acids. The analysis is similar to that of Pistacite (p. 149). For the separation of potassium, sodium and lithium, the method described in the analysis of Psilomelane is the most satisfactory (p. 103).

When the turmalin contains phosphoric acid, this is generally found with the iron and aluminum precipitate. It is advisable to determine this in a separate portion (p. 83), or in the weighed precipitate (see analysis of Mineral Water), and deduct it from the aluminum and iron.

The fluorine is most commonly estimated by difference. A direct method for its estimation is given on page 115. The precipitate finally produced upon the addition of calcium chloride is, when boracic acid is present, calcium fluoride, calcium carbonate and borate. When treated with acetic acid the latter goes into solution with the calcium carbonate.

The water present may be ascertained according to page 36. A porcelain tube may advantageously replace one of glass.

Zircon.

Composition.—Zirconium oxide, ferric oxide, calcium oxide and silicic acid.

The decomposition of the mineral, either by means of acids or fusion with alkaline carbonates, is attended with difficulty, and is only successful when potassium fluoride in hydrofluoric acid is employed for the purpose. The process is analogous to that followed in the analysis of Chromite (p. 88). After the fusion, hydrochloric acid is added to the mass, and the solution, which is then evaporated, is treated with ammonium hydrate, causing the precipitation of the zirconium, which, after being washed, is ignited and weighed as ZrO_2. The same precautions should be observed here which have been previously enjoined in the determination of aluminum (p. 37). When the zircon contains iron, the latter will be precipitated together with the zirconium. This may be prevented if sufficient tartaric acid is previously added to the solution, so that neither iron nor zirconium will be thrown down upon the addition of the ammonium hydrate. The iron can then be precipitated with ammonium sulphide and the iron sulphide as given on page 90, filtered and finally converted into ferric oxide.

The filtrate is evaporated to dryness in a platinum dish, and the residue ignited to destroy the tartaric acid. The combustion of the carbon may be hastened by moistening the residue with a saturated solution of ammonium sulphate, and then applying a gentle heat. The final traces of carbon may be easily perfectly oxidized, if, finally, the operation be repeated with small quantities of ammonium nitrate. If, excepting the alkalies introduced by the decomposition of the mineral, no other oxides (calcium, etc.) are present, boil the residue repeatedly with water, and determine the residual zirconium oxide. When the contrary is the case, the residue must be heated with ammonium fluoride, and the hydrochloric acid solution precipitated with ammonium hydrate as above. The calcium is then removed from the filtrate as calcium oxalate.

To obtain the silicic acid, decompose a second portion with the alkaline carbonates, add hydrochloric acid to the fused mass, and do as directed on page 143.

Pyrites.

Composition.—Sulphur and iron; traces of arsenic, antimony, gold, copper, nickel (cobalt, manganese), calcium oxide, magnesium oxide and quartz.

In most instances in the analysis of pyrites the determination of the sulphur is all that is required. Its conversion into sulphuric acid is best effected by fuming nitric acid (p. 111), or potassium chlorate and nitric acid (p. 133).

A very suitable oxidizing agent for pyrites is a solution of bromine in concentrated hydrochloric acid, which with the application of heat will, in a short time, convert the sulphur into sulphuric acid. The bromine solution is at first allowed to act in the cold, and, subsequently, warmed gently, not allowing the temperature, however, to rise to the fusing point of the separated sulphur, which, if once fused to a globule, will demand a large expenditure of time to change it to sulphuric acid. When the oxidation is complete, the solution is evaporated to remove bromine, hydrochloric and silicic acid. The sulphuric acid is determined as barium sulphate in the filtrate (p. 15).

Very often it is preferred to oxidize the pyrites by fusion with some substance yielding oxygen, and for this purpose a mixture of sodium and potassium nitrates is most commonly taken. The results obtained, when this method is followed, are not very accurate, because the barium sulphate produced is impurified by the corresponding nitrate, which salt is very difficultly removed, either by washing with hot water or subsequent digestion with dilute hydrochloric acid. Very satisfactory results are obtained when potassium chlorate is substituted for the nitrate.*

The finely divided substance is mixed in a platinum crucible with a mixture of six parts sodium carbonate and one part potassium chlorate, then fused over an ordinary Bunsen burner until gas bubbles no longer escape. Treat the fused mass with water, filter off the residue, and wash it with water containing sodium carbonate, until the washings acidulated with hydrochloric acid yield no precipitate with barium chloride. Hydrochloric acid is gradually added to the filtrate to distinct acid reaction, the carbon dioxide expelled by boiling, and precipitation caused by barium chloride.

When any potassium chlorate remains undecomposed in the fused mass, the hydrochloric acid solution must be warmed until the liquid ceases to impart the odor of chlorine gas, which is most perfectly accomplished by a partial evaporation of the solution.

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* The fusion with sod. carb. and potassium chlorate is preferable also to the oxidation with nitric acid, because in the latter case the barium sulphate is likely to contain iron. (See p. 84.)

Arsenic and Antimony Determination.—The estimation of these substances may very easily be combined with that of the sulphur. The aqueous solution of the fused mass obtained by sodium carbonate and potassium chlorate is reduced to a definite volume, determining in the one measured portion the sulphuric acid, as before directed, whilst the remainder is employed for the estimation of the arsenic and antimony. For this purpose acidify the alkaline liquid with hydrochloric acid, and precipitate both metals as sulphides, which may be separated according to page 164.

Gold Determination. — The residue remaining after fusing the pyrites with sodium carbonate and potassium chlorate, and treating with water, is taken for the estimation of the gold. As the quantity of the latter is extremely small, a large amount of substance must be used, and the decomposition executed in a Hessian crucible. The residue, insoluble in water, consisting principally of ferric oxide, is ignited in a stream of hydrogen gas, and the reduced iron (nickel, cobalt, etc.) dissolved in nitric acid. The residue that remains is dissolved in aqua regia, the silica filtered off, and the liquid evaporated to dryness on a water-bath. A few drops of dilute sulphuric acid are added to the aqueous solution of the residue, and the liquid heated some time with a concentrated ferrous sulphate solution. The metallic gold that separates out is washed then ignited in a porcelain crucible and weighed.

Determination of Iron, Copper, Manganese, Cobalt, Nickel, and the Alkaline Earths.—These substances are determined either in the solutions of the mineral in aqua regia, or in nitric acid and potassium chlorate, or, better, in the insoluble residue remaining after treating the fused mass obtained by fusion with soda and potassium chlorate (estimation of sulphur, antimony and arsenic) with water.

When the pyrites has been decomposed with aqua regia or nitric acid, the latter is removed by repeated evaporation with hydrochloric acid, the residue is dissolved in the same acid, diluted, and the liquid freed from silicic acid by filtration is reduced with sulphurous acid (p. 87). After the complete reduction of ferric to ferrous oxide, hydrogen sulphide is conducted into the liquid, and the filtered sulphides digested with a solution of sodium sulphide. The insoluble copper sulphide is washed with water containing hydrogen sulphide, then ignited in a current of hydrogen and weighed (p. 48).

Finally, after the expulsion of the hydrogen sulphide from the filtrate and the oxidation of ferrous to ferric oxide with nitric acid aided by heat, separate the iron, manganese, cobalt and nickel according to page 104.

As the ferric oxide may contain some silicic acid and also the alumina that is present, the precipitate should be again dissolved in dilute sulphuric acid and the iron determined by titration, either with stannous chloride (p. 80) or permanganate solution (p. 75).

After the destruction of the ammonium sulphide by hydrochloric or sulphuric acid (p. 105), the calcium and magnesium are precipitated in the usual manner with ammonium oxalate and sodium-ammonium phosphate.

When that portion of the fused mass insoluble in water is used in the determination of the oxides, it is dissolved in hydrochloric acid, and, after separating the silica as usually done, separate in the filtrate the oxides as above described.

Mispickel.

Composition.—Iron, arsenic (antimony) and sulphur.

The mineral may be either decomposed with aqua regia or with potassium chlorate (p. 133). In both instances the nitric acid is expelled by repeated evaporation to dryness with addition of hydrochloric acid, and, after bringing the latter solution to a definite volume, the sulphuric acid is precipitated in a measured portion, or the entire solution is treated with barium chloride, the excess of the latter in the filtrate being removed by dilute sulphuric acid.

For the separation of the arsenic (antimony) from the iron, precipitate the first as sulphides. As, however, the arsenic acid is so extremely slowly precipitated by hydrogen sulphide gas, it is more practical, to previously convert it into arsenious acid, which is easily thrown down as sulphide. Either sulphurous acid or the solution of a sulphite (see potassium or sodium hydrosulphite, p. 87) will serve as a reducing agent. Hydrogen sulphide is now conducted into the liquid until its odor is strongly predominant, and the arsenic (antimony) tersulphide filtered off.

When the mineral does not contain antimony, the precipitate may be dissolved in hydrochloric acid with the aid of potassium chlorate, and the arsenic acid then precipitated from an ammoniacal solution as ammonium-magnesium arseniate (p. 69).

When antimony is present the hydrochloric acid solution is treated according to page 165.

The filtrate from the arsenic sulphide, after the expulsion of the hydrogen sulphide, is oxidized with nitric acid or potassium chlorate and the ferric oxide precipitated by ammonium hydrate (p. 24).

Chalcopyrite.

Composition.—Copper, iron, sulphur and quartz.

All the constituents may be determined in the same solution if the method described (p. 133) be carefully followed (oxidation of the sulphur compounds with potassium chlorate and nitric acid). The filtrate from the residual quartz is repeatedly evaporated with hydrochloric acid to expel the nitric acid, and the sulphuric acid then precipated by barium chloride. The excess of the latter is gotten out with dilute sulphuric acid.

The copper in the liquid filtered from the barium sulphate is determined as sulphide (p. 48), and the iron, after the removal of the hydrogen sulphide and oxidation of the liquid with nitric acid, is precipitated by ammonium hydrate as ferric hydrated oxide.

In most analyses of chalcopyrite, the estimation of the copper is the most important subject. It may be determined as cuprous sulphide or as metallic copper. To estimate it in the latter form, be sure to drive out the last traces of nitric acid if it has been employed in the decomposition of the mineral. This may be accomplished by heating the filtrate from the quartz to boiling, and gradually adding to it a concentrated solution of ferrous sulphate acidified with sulphuric acid, until the liquid becomes dark-brown in color and the liberation of gas is no longer visible. When all the nitric acid is reduced, undecomposed ferrous salt should still be present in the liquid. This is readily ascertained by adding potassium ferricyanide to a drop of the liquid.

Cadmium or zinc will cause the separation of copper in a metallic form.*

Of the volumetric methods for the determination of copper, only the two in most frequent use will be described.

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* For the electrolytic separation of copper as a method for determination in ores, see Fresenius, Journ. f. Analytische Chemie, Jahrg. 8, p. 23, and Jahrg. xi. p. 1.

Copper Determined with Sodium Hyposulphite.—When the solution of a cupric salt is mixed with a potassium iodide solution, cuprous iodide is precipitated, and a quantity of iodine, equaling that contained in cuprous iodide, separates:—

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

The separated iodine is determined with a sodium hyposulphite solution (p. 96), and one atom of iodine corresponds to one atom of copper.

In the estimation of copper according to this method, the copper sulphide, as above obtained, is dissolved in nitric acid, and this then fully expelled by evaporation with addition of dilute sulphuric acid.

The aqueous solution of the residue is mixed with an excess of potassium iodide and starch solution, and sodium hyposulphite added from a burette, until the blue color of the starch iodide first disappears.

When, in estimating copper in ores, absolute accuracy is not required, the nitric acid solution may be saturated with ammonium hydrate, the iron oxide filtered off, and the solution after acidulation with hydrochloric acid treated as first directed.

The precipitated ferric oxide, however, invariably contains some cupric oxide. To dissolve as much as possible of this, the filtered and imperfectly washed precipitate is again dissolved in hydrochloric acid and the precipitation with ammonium hydrate repeated.

Copper Determined with Potassium Cyanide.—By supersaturating the solution of a copper salt, *e. g.*, copper nitrate, with ammonium hydrate, a deep-blue colored liquid of cupric ammonium nitrate [$Cu(NO_3)_2 4NH_3$] is produced. Upon the addition of a potassium cyanide solution to this liquid, the blue coloration immediately disappears, as the cupric ammonium nitrate is altered to colorless potassium copper cyanide:—

$$Cu(NO_3)_2 4NH_3 + 4KCN = [Cu(CN)_2 2KCN] + 2KNO_3 + 4NH_3.$$

The end of the reaction, therefore, will be indicated by a perfect disappearance of the blue color of the solution.

The value of the potassium cyanide solution employed is fixed with an ammoniacal copper solution of known strength. This solution is prepared by dissolving 10 grms. of copper in nitric acid and diluting the liquid saturated with ammonium to 1 litre.

This method, however, affords unreliable results, even if in the standardization of the solution, and in the actual titration, similar conditions are always observed. It has recently been recommended for the determination of copper in ores poor in the metal (especially for the estimation of copper in Mansfield slate); and, in addition, Steinbeck suggests the following process: Pour over five grms. of the pulverized slate 40–50 C. C. commercial hydrochloric acid of 1.16 sp. gr., adding to this 6 C. C. dilute nitric acid (equal vols. water and nitric acid of 1.2 sp. gr.), and heat upon a water-bath for half an hour, finally bringing the liquid to boiling, which should be continued ten to fifteen minutes. By this means all the metals contained in the ore are dissolved (Cu, Pb, Zn, Fe, Mn, Co). The insoluble portion is filtered off, and the copper thrown down from the filtrate with zinc.

The final reduction of the copper solution may be recognized by mixing a drop of the liquid with ammonium hydrate (p. 58); the supernatant liquid is then poured off, the residual copper washed (p. 58), and dissolved in 8 C. C. nitric acid of the above-mentioned concentration. To the cooled liquid are added 10 C. C. of ammonium hydrate (prepared by mixing 2 vols. water and 1 vol.

ammonium of sp. gr. 0.93), and then titrated with potassium cyanide.

The value of the potassium cyanide solution is fixed with a copper solution of like concentration as the one about to be determined. Here, also, equal quantities of nitric acid and ammonium are to be used.

Mohr advises that the ore be dissolved in nitric acid and sulphuric acid, or hydrochloric, nitric, and excess of sulphuric acid, and that the solution then be evaporated to dryness. The filtered liquid is free from hydrochloric and nitric acid and lead, and upon the direct addition of zinc the copper may be obtained pure (free from lead). It is better then to immediately weigh the copper than to redissolve and determine it volumetrically.

Nickel Matte.

COPPER MATTE.

Composition.—Nickel, cobalt, zinc, iron, copper, lead, arsenic, antimony, sulphur, and gangue.

Digest the finely pulverized substance with aqua regia until pure gangue remains, and expel the nitric acid by repeated evaporation with hydrochloric acid. If the gangue does not become white upon evaporating the residue with dilute hydrochloric acid, it should be fused with potassium hydrosulphate and the hydrochloric acid solution of the residue added to the other.

After the reduction of the arsenic acid with sulphurous acid or potassium hyposulphite, saturate the liquid with hydrogen sulphide gas, and filter off the sulphides thus obtained. By digesting these with sodium sulphide,*

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* As copper sulphide is somewhat soluble in ammonium sulphide, the latter cannot, therefore, be used for the separation of antimony and arsenic.

arsenic and antimony are dissolved,* and are reprecipitated as sulphides upon the addition of dilute hydrochloric or sulphuric acid to the filtered liquid. (See p. 52.)

The sulphides are separated by dissolving them in aqua regia, and adding so much tartaric acid to the solution that the subsequent addition of ammonium hydrate will cause no precipitation. When the added tartaric acid was insufficient the ammonium hydrate will produce a precipitate, which, after the removal of the supernatant liquid, may be dissolved in an excess of the acid. From this solution magnesium chloride will only precipitate arsenic acid as ammonium-magnesium arseniate, which is determined as directed on page 69.

After acidulating the filtrate with hydrochloric acid the antimony is precipitated as antimony tersulphide, and determined either as such or converted into antimoniate of antimony (p. 53).

The insoluble copper and lead sulphides, after perfect washing with water containing hydrogen sulphide, are dissolved in nitric acid, with addition of hydrochloric acid, and the liquid evaporated with dilute sulphuric acid (p. 49). In the filtrate from the lead sulphate, after expelling the alcohol, determine the copper as oxide (p. 14), or as metallic copper (p. 58), or volumetrically (p. 162).

The filtrate from the hydrogen sulphide precipitate is boiled to expel the excess of the precipitant, and nitric acid then added to oxidize the iron, which is thrown down upon the addition of ammonium hydrate. As the ferric oxide contains weighable quantities of zinc, cobalt, and nickel, the imperfectly washed precipitate is dissolved in hydrochloric acid, the solution neutralized with ammo-

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* When antimony and arsenic are present in rather large quantities, the sulphides digested with sodium sulphide and insoluble, are fused with soda and sulphur (p. 54).

nium hydrate and carbonate (p. 72), and the iron precipitated by boiling. The ferric oxide thus obtained should be examined for cobalt and nickel, and the precipitation finally repeated.

In separating zinc from nickel, proceed as directed on page 62. When the zinc sulphide is not perfectly white, the separation should be repeated.

Cobalt and nickel are precipitated in the filtrate by the addition of ammonium hydrate and sulphide. This is best executed in a flask that may be readily closed. An excess of ammonium sulphide should be avoided, as nickel sulphide is somewhat soluble in it. In case the filtrate is colored brown, due to the nickel held in solution, add mercurous nitrate to it. The mercury sulphide that forms carries down with it the nickel sulphide, and upon igniting the precipitate the former will again be volatilized.

The dried sulphides are dissolved in hydrochloric acid* with addition of nitric acid, and the filter, freed as much as possible from the precipitate, incinerated, and the ash added to the solution. The diluted liquid is then treated with sodium hydrate in a porcelain or platinum dish (p. 22). The precipitate, consisting of the hydrated oxides of cobalt and nickel, after being washed perfectly by decantation with hot water, is reduced in a current of hydrogen, and the metals formed, as above directed (p. 22), treated with water, and again ignited. They are generally rendered impure by small quantities of silicic acid, iron or alumina; therefore, dissolve them in nitric acid, filtering the solution from the silicic acid, and precipitate the iron by neutralizing the solution with ammonium hydrate, and supersaturating with ammonium

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* When manganese is present, the sulphides are previously treated with hydrochloric acid and hydrogen sulphide. (See p. 104.)

carbonate. Filter off the precipitate, dissolve it, and repeat the precipitation. By ignition in a hydrogen current the ferric oxide will be reduced to the metallic state, and, together with the silicic acid, deducted from the cobalt and nickel.

For the estimation of the cobalt and nickel, evaporate the filtrate from the ferric oxide and ignite the residue to expel all ammoniacal salts. In the hydrochloric acid solution of the residue, precipitate the cobalt as potassium cobaltic nitrite. (See p. 104.) The addition of sodium hydrate to the filtrate will produce the precipitation of the nickel.

When there is relatively much cobalt present with the nickel, it is more practical to convert these into potassium nickel cyanide and potassium cobalt cyanide, and then precipitate the nickel as sesquioxide from an alkaline solution of these compounds. For this purpose, supersaturate the nitric acid solution of the sulphides with potassium hydrate, and add to this hydrocyanic acid, until the precipitate dissolves and the liquid very distinctly imparts the odor of the hydrocyanic acid. By boiling this solution for some time (about one hour), replacing the water that is evaporated, the double cyanide of cobalt and potassium in the solution is mostly converted, with the liberation of hydrogen, into potassium cobalticyanide, whilst the double cyanide of potassium and nickel remains unchanged. By conducting chlorine gas into this solution, or warming it with bromine water or sodium hypochlorite, in which case care must be preserved that the liquid continues to be alkaline, the nickel will be precipitated as sesquioxide, which upon ignition passes into protoxide. The latter compound can readily have alkali adhere to it, therefore it is advisable to ignite the precipitate in a stream of hydrogen and determine the nickel as metal (p. 23).

For the determination of the cobalt, the filtrate is mixed with nitric acid until the liquid reacts only slightly alkaline, and mercurous nitrate is then added to it. The cobalt falls as cobaltic mercuric cyanide, which, after washing and ignition in a stream of hydrogen, becomes metallic cobalt. The metal should be tested for alkali (p. 22).

In analyses of nickel-matte, the determination of the cobalt and nickel demands the most consideration, and the course of analysis, in consequence, may be considerably simplified.

Proceed at first as above directed, removing from the solution everything precipitated by hydrogen sulphide gas. Separate in the filtrate, as heretofore, the iron from the zinc, cobalt and nickel. The filtrate from the iron precipitate, which must necessarily be concentrated, is mixed with sodium carbonate to alkaline reaction, the precipitate that is produced being dissolved in acetic acid and sodium acetate (50 C. C. of a solution of the concentration 1 : 10) added. From this solution the metals are precipitated by hydrogen sulphide, the liquid being heated continuously to about 20° C. The filtrate from the sulphides of cobalt and nickel (zinc), which continues to impart the odor of the precipitant, is neutralized with ammonium hydrate and slightly acidulated with acetic acid, which will cause a meagre precipitation of nickel and cobalt sulphides. This precipitate may be transferred to a separate filter. To remove the zinc co-precipitated with cobalt and nickel, we are obliged to dissolve the sulphides in hydrochloric acid, aiding their solution by the addition of nitric acid and evaporating the liquid to dryness, and mixing the hydrochloric acid solution of the residue with ammonium chloride. A sufficiently large quantity of the latter is added, so that for about 5 grms. of it there are 0.2 grm. zinc oxide. Upon evaporating this solution to dryness and gently igniting the residue, all the zinc will be volatilized in the form of chloride, together with the ammonium chloride, and metallic cobalt and nickel will remain. These are dissolved in hydrochloric acid with some nitric acid, and precipitated from this solution with potassium hydrate. The oxides thus obtained are, as heretofore, reduced and ignited.—*Fresenius.*

For the mere determination of the copper in the matte, the already described process may be followed.

The sulphur is best determined in a separate portion of the material.

Copper or Lead-speiss.

REGULUS.

These are obtained in the smelting of copper ores containing antimony or arsenic, or lead ores containing arsenic and nickel, and are in composition antimony and arsenic compounds of iron, cobalt and nickel, together with sulphides of copper, lead, silver, bismuth, iron and zinc.

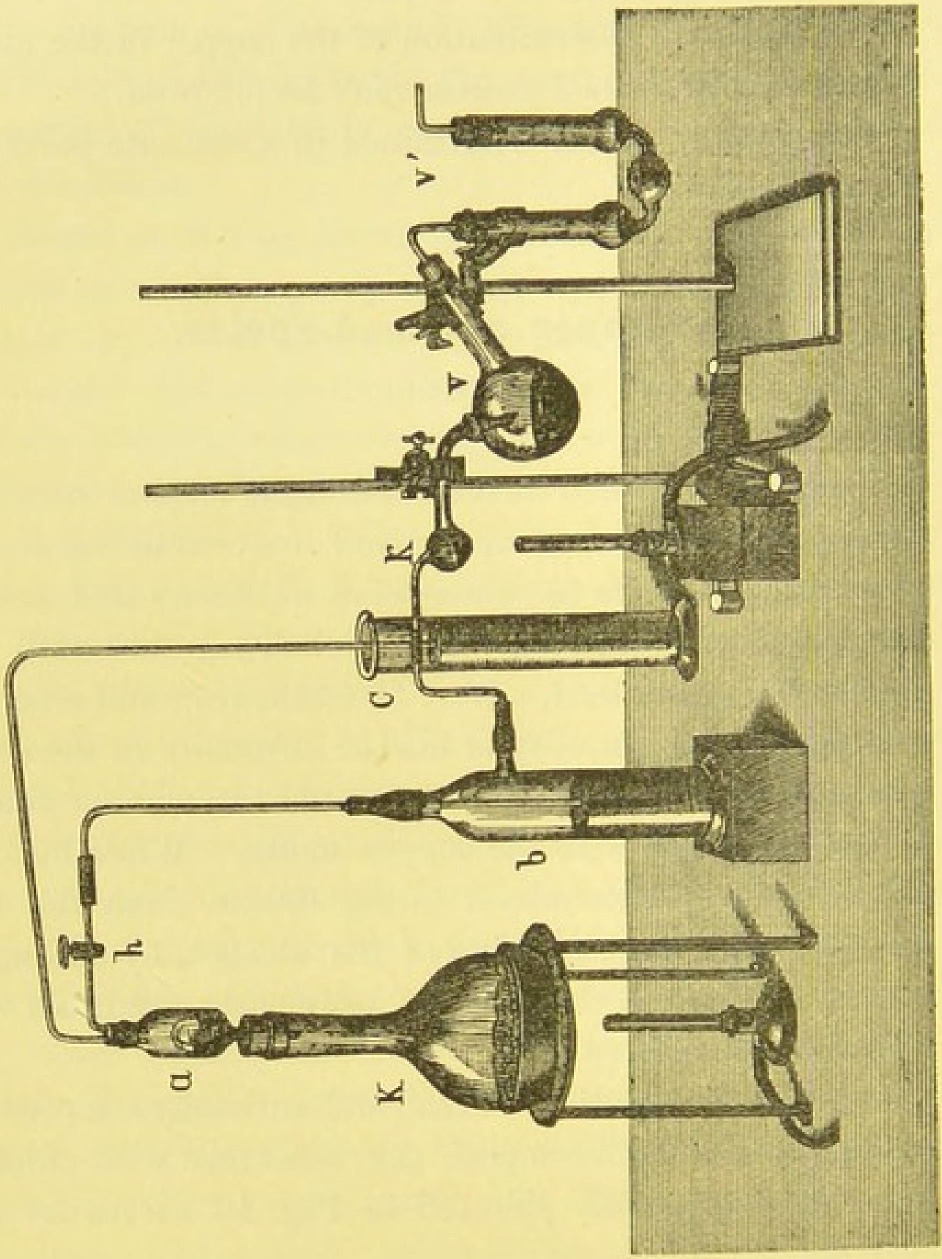
Provided the quantity of lead or antimony in the speiss is small, the analysis may be executed in a manner similar to that employed with the copper matte. When bismuth is present, it is determined in the filtrate from the lead sulphate, after the expulsion of the alcohol, by adding an excess of water to the solution previously saturated with hydrochloric acid (p. 56).

When large quantities of lead and antimony are present, it is advisable to decompose the substance with chlorine gas. The apparatus pictured in Fig. 16 serves for this purpose.

The bulb-tube *k*, of difficultly fusible glass, containing the finely pulverized substance, stands in connection with the chlorine generator and also the receivers *v* and *v'*.

The downward-inclined limb of the tube almost dips into the liquid of the receiver *v*. The generating flask *K* contains coarsely powdered manganese dioxide, which, when heated with hydrochloric acid, generates chlorine gas, which is dried by its passage through the flasks *a* and *b*, containing concentrated sulphuric acid.

Fig. 16.



To be able to properly regulate the gas flow, a glass tube, bent at right angles, is inserted in the flask *K* and immersed in the potassium hydrate contained in the cylinder *C*, so that upon the entire or partial closure of the stopcock *h* the chlorine will be conducted into the potassium hydrate and there absorbed. *v* and *v'* are partially filled with a mixture of equal volumes of hydrochloric and tartaric acid. The chlorine gas is conducted away by connecting the extreme limb of the receiver *v'* with an aspirator or a glass tube, bent at right angles, the end of which dips in a solution of dilute potassium hydrate.

As chlorine gas attacks caoutchouc corks very readily, ordinary corks are employed, and the tubings, connected by pieces of gum, are closely pushed together.

When the apparatus is arranged, conduct a gentle but continuous stream of chlorine gas over the contents of the glass-bulb, and continue this as long as any decomposition of the substance occurs, which is indicated by the warming of the bulb. The contents of the latter are now gently heated, the flow of the gas being at the same time increased, the temperature rising gradually; not, however, becoming so great as to cause the bulb to fall into a red glow. By this process the volatile chlorides (arsenic, antimony, a portion of the zinc and iron), and sulphur as chloride are driven from the bent tube into the receivers *v* and *v'*, the chlorides being dissolved, and the sulphur oxidized to sulphuric acid.*

When, upon the application of heat to the bulb, the sublimation of the chlorides no longer occurs, drive the

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* Under certain circumstances the sulphur choride is only partly oxidized to sulphuric acid; this can occur when the substance has been heated so intensely by the chlorine that the sulphur chloride was volatilized before the receiver had filled with chlorine gas. For this reason the chlorine stream must be carefully regulated by partial closure of the glass stopcock, which will prevent too intense warming of the bulb contents and the volatilization of the sulphur chloride.

sublimate in the bent tube, the stopcock *h* being closed, with the aid of a gas-flame, as much as possible into the receiver, and sever the tube immediately behind the bulb, and by proper inclination of the receiver dissolve the chlorides that may adhere to the glass tube.

The contents of the receiver are transferred to a beaker glass, and the sulphuric acid precipitated with barium chloride (p. 15). If sulphur has separated out in the receiver, it is brought upon a weighed filter, dried at 100° C., and its weight ascertained.

After removing the excess of barium with dilute sulphuric acid, precipitate the arsenic and antimony with hydrogen sulphide. The obtained sulphides are separated according to page 165.

By saturating the filtrate from the sulphides with ammonium hydrate and sulphide, the iron and zinc will be precipitated as sulphides.*

The latter are filtered with exclusion of air, washed with water containing ammonium sulphide, then dissolved in hydrochloric acid with addition of potassium chlorate, and added to the principal solution.

The non-volatile chlorides of copper, lead, silver, bismuth, cobalt and nickel (iron and zinc) remaining in the bulb are dissolved in dilute hydrochloric acid, and separated according to methods already described.

Miargyrite.

Composition.—Silver, antimony (arsenic), sulphur and gangue.

The mineral is very easily decomposed by chlorine gas;

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* It will not do to add the filtrate directly to the solution of the metals remaining in the bulb-tube *k*, because the tartaric acid will prevent the precipitation of the oxides by certain reagents.

after the decomposition the bulb-tube contains silver chloride* and gangue, which are separated as directed under Galenite.

In regard to the compounds that have passed over into the receiver, refer to the preceding analysis.

Tetrahedrite.

Composition.—Copper, antimony, arsenic, silver, lead, iron, zinc, sulphur and gangue.

The decomposition here is also effected by chlorine. The receiver will contain antimony, arsenic and sulphur, as well as iron and zinc. After the separation of the antimony, arsenic and sulphuric (p. 172) acid, precipitate the iron and zinc with ammonium sulphide, dissolve the precipitate in hydrochloric acid with addition of nitric acid, and proceed according to page 108.

The bulb-tube contains the chlorides of copper, silver and lead, with gangue, and sometimes also iron and zinc. These should be dissolved in hydrochloric acid (silver chloride and any gangue present remain behind), and are separated in the manner described on page 152.

Furnace-Bears.

Sows.

These form alloys of iron (principal constituent), copper, silver (gold), molybdenum, vanadium, cobalt, lead, nickel, zinc, with sulphides and phosphorus compounds of these substances, containing besides larger or smaller quantities of carbon and silicic acid.

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* The silver is best determined by cupellation in a separate portion. (See Galenite.)

These substances are completely dissolved by heating them with nitric acid or aqua regia, leaving behind carbon and silicic acid. The separation of the metals succeeds more readily when the decomposition has been effected by chlorine gas. In case a large quantity of iron is present, it is, however, necessary, in order that the obstruction of the bent tube be prevented, to employ a tube of difficultly fusible glass provided with two bulbs, so that the second bulb is in a proper condition to take up the larger quantity of the ferric chloride. The ignition in a stream of chlorine is continued until ferric chloride is no longer sublimed, and then you may be assured all the molybdenum chloride has also been volatilized. In decomposing with chlorine gas, the latter should be introduced slowly when beginning, and this is to be particularly observed when the substance exists in a finely pulverized state. Heat is only applied to the tube when there is no longer any perceptible action noticed in the cold. When the operation is complete, the receiver will contain, besides the sulphur and phosphorus chlorides, the iron, vanadium, and molybdenum in form of chlorides. In the bulb-tube may be found the remaining chlorides, as well as the iron residue, carbon and silicic acid.

The contents of the receiver are used for the determination of the oxides, whilst the sulphuric and phosphoric acids are estimated in a separate portion of the substance. (See below.) Continue conducting hydrogen sulphide gas* into the liquid until the solution above the precipitate has become perfectly colorless. As molybdic acid is altered very slowly to sulphide, the solution, containing the formed

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* When vanadium is not present, supersaturate the liquid with ammonium hydrate and sulphide, which will dissolve the molybdenum sulphide and leave the iron. (For the further process, see Pyromorphite.) The residual iron sulphide is converted into oxide.

molybdenum oxide, will possess a blue color, even after protracted treatment with this reagent.

The absorbed chlorine, upon the other hand, decomposes a rather large quantity of hydrogen sulphide, and it is, therefore, owing to the easy volatilization of the dissolved chlorides, not advisable to previously expel the chlorine by the application of heat.

The precipitate of molybdenum sulphide is transferred to a filter dried at 120° C., washed with hot water, and dried at the same temperature until constant weight is obtained. An aliquot portion of the precipitate is then heated in a stream of hydrogen and the residual MoS_2 determined.

The filtrate from the molybdenum sulphide contains the vanadium and the iron. Ammonium hydrate is mixed with this until it yields an alkaline reaction, and yellow ammonium sulphide then added in excess. By continued digestion with ammonium sulphide upon a water-bath the entire quantity of vanadium is dissolved; the residue is iron sulphide, which may be dissolved in hydrochloric acid, and after oxidation with nitric acid, precipitated as hydrated ferric oxide.

For the estimation of the vanadium the solution in ammonium sulphide is mixed with nitric acid and evaporated to dryness. The residue is mixed with several times its weight of saltpetre, and gradually heated to fusion in a porcelain crucible. Extract the residue with water, neutralize with nitric acid; the liquid must, however, continue to react alkaline, and precipitate the vanadic acid as ammonium vanadate. To this end, after concentrating the solution as much as possible, and while warm, add to it a saturated solution of ammonium chloride and one-third volume alcohol. After several days the ammonium vanadate will have separated perfectly, and may then be washed at first with a saturated ammonium chloride solution, and the latter finally replaced by alcohol.

By gradual ignition of ammonium vanadate with access of air it is converted into (V_2O_5) vanadic acid. To prevent the reduction of the latter the precipitate must be carefully separated from the filter, and this incinerated upon a platinum wire, after having moistened it with ammonium nitrate, and then dried. The chlorides remaining in the bulb-tube are dissolved in hydrochloric acid, and the carbon transferred to an asbestos filter. Its quantity is determined by mixing it with cupric oxide, and oxidizing it in a stream of oxygen to carbon dioxide, which is absorbed by soda-lime, then weighed. For the remaining points of this operation, see the analysis of Cast Iron.

When silver is present it will remain with the carbon, after treating the chlorides with hydrochloric acid. If it is desirable to determine the silver simultaneously with the carbon, ignite the residue in a stream of hydrogen, which will cause the reduction of the silver chloride to metal, which is then dissolved in dilute nitric acid, and the silver determined as chloride in the liquid filtered through an asbestos filter (p. 47).

The separation of the chlorides dissolved in hydrochloric acid (residue of the bulb-tube after decomposition with chlorine gas) may be effected by reference to the preceding examples.

To estimate the sulphuric acid dissolve a separate portion of substance in nitric acid or aqua regia, and expel the excess of nitric acid by repeated evaporation with hydrochloric acid, and precipitate the sulphuric acid in the aqueous acidified solution of the residue with barium chloride.

Phosphoric Acid Determination.—Supersaturate the nitric acid solution of the substance with sodium carbonate, evaporate and fuse the residue in a silver or platinum crucible with an equal weight of a mixture consisting of equal parts of potassium nitrate and sodium carbonate. The fused mass is extracted with water, the solution supersaturated with ammonium sulphide and digested some time upon a water-bath, whereby the molybdenum is dissolved as sulphide and precipitated as such upon the addition of hydrochloric acid. The acidified solution is heated until it no longer imparts the odor of hydrogen sulphide, and the phosphoric acid is then thrown down in the filtrate, after previous neutralization with ammonium hydrate by the addition of magnesium chloride to the liquid (p. 25).

All the vanadic acid will be found in the filtrate from the magnesium ammon-phosphate, provided that a sufficient quantity of hydrochloric acid had been employed for the decomposition of the ammonium sulphide.

Stibnite.

Composition.—Antimony, sulphur (iron, lead, copper, arsenic).

When the mineral contains nothing but antimony, iron and sulphur, a finely pulverized portion of it may be oxidized either with aqua regia, or potassium chlorate and nitric acid. If antimonic oxide separates out in this operation, decant the liquid from it, and bring it into solution by treating it with a mixture of hydrochloric and tartaric acid, or tartaric acid is directly added to the aqua regia solution.

The liquid freed from excess of acid is precipitated with barium chloride, after the previous addition of tartaric acid, which is done to prevent the precipitation of any antimonic oxide.

The excess of barium chloride in the filtrate is precipitated by sulphuric acid, and the antimony in the filtrate thrown down as sulphide, and determined according to page 53.

Determine the iron by adding ammonium hydrate and sulphide to the filtrate from the antimony sulphide. After the complete separation of the iron sulphide, which is hastened by warming the liquid, it is filtered away from air-contact, washed with hydrogen sulphide water, and dissolved in hydrochloric acid with addition of potassium chlorate or bromine water. Ammonium precipitates from this solution hydrated ferric oxide, which is determined according to page 24.

If the above-mentioned metals, especially lead, are present in the stibnite, it must be decomposed with chlorine. The chlorides of arsenic, antimony, sulphur and iron are sublimed and then separated as on page 172.

As stibnite is decomposed very easily already at ordinary temperatures by chlorine gas, to prevent a too rapid volatilization of sulphur chloride (see remark, p. 171), the stream of chlorine must be regulated and allowed to pass through the bulb in a weak current.

In the bulb-tube are the chlorides of lead and copper and the iron residue. These are dissolved in water with addition of hydrochloric acid, and the copper and lead separated according to page 49.

The iron is precipitated as hydrated oxide in the filtrate from the copper sulphide.

In many instances in the analysis of stibnite the estimation of the antimony is all that is desired; this is accomplished either gravimetrically or volumetrically. For the gravimetric determination of antimony, supersaturate the solution which has been obtained with ammonium hydrate and sulphide, and digest for some time upon a water-bath, following carefully the directions inserted on page 52. In the presence of copper, sodium sulphide should replace ammonium sulphide. When considerable quantities of other metals are mixed with antimony in stibnite, one will not succeed in dissolving all the antimony sulphide in alkaline sulphides; therefore the residual sulphides should be fused with sodium carbonate and sulphur (p. 54).

Hydrochloric or sulphuric acid precipitates the sulphide of antimony from its solution in the alkaline sulphides, and it is then further treated according to the method given on page 52. The antimony sulphide may be decomposed by hydrochloric acid, and the evolved hydrogen sulphide gas conducted into a bromine solution (p. 135). The antimony is calculated from the amount of sulphuric acid that has been obtained.

$$Sb_2S_3 \ : \ 3BaSO_4, \text{ etc., or } BaSO_4 \ : \ \tfrac{2}{3}Sb.$$

The volumetric determination of antimony depends on the principle that the antimonic oxide in an alkaline solution is converted by iodine into antimonic acid and hydriodic acid:—

$$HSbO_2 + 2I + H_2O = HSbO_3 + 2HI.$$

If for the decomposition an iodine solution of known strength (about $\frac{1}{10}$ normal solution, which is made by dissolving 12.7 grms. iodine in potassium iodide solution and diluting to 1 litre) has been taken, two atoms of the employed iodine will correspond to one molecule of antimonic oxide. To ascertain when the reaction is complete, add starch paste to the solution, and, as soon as the liquid becomes blue from the starch iodide, the oxidation of the antimony oxide is finished.

The antimony tersulphide is dissolved in hydrochloric acid, heat applied until the odor of hydrogen sulphide has disappeared, and the solution then mixed with tartaric acid or Seignette salt and supersaturated with sodium hydrocarbonate. After the addition of some starch paste, the iodine solution is allowed to flow from the burette until the blue color of starch iodide appears.

If t C. C. iodine solution have been used, and a represents the quantity of iodine in 1 C. C. of the solution, we have:—

$$2I : HSbO_2 = at : x \quad \text{or} \quad 2I : Sb :: at : x.$$

The standardization of the iodine solution is best fixed with antimony tartrate, and it is advisable that the same conditions be preserved in the titration (similar concentration, equal volumes tartaric acid and sodium hydrocarbonate).

Burnonite.

Composition.—Lead, copper (iron) and sulphur.

The pulverized mineral is decomposed with chlorine gas, and the analysis executed as heretofore.

Zinkenite.

Composition.—Antimony, lead (silver, copper, iron), sulphur.

The same mode of decomposition may be used here as in the preceding examples. As zinkenite is soluble in hydrochloric acid (excepting the silver that may be present, which will remain as silver chloride), the metals may be determined in this solution. The liquid is supersaturated with ammonium hydrate and sulphide (when copper is present use sodium sulphide), and the directions given on page 52 strictly followed.

When the sulphides of lead, silver, copper and iron have been perfectly washed, they are dissolved in nitric acid, and the lead precipitated as lead sulphate (p. 49).

The alcohol is expelled from the filtrate, and the silver then thrown down as chloride. In the filtrate from this, precipitate the copper as sulphide (p. 48).

Expel the hydrogen sulphide, oxidize the solution with nitric acid or potassium chlorate, and precipitate the iron by ammonium hydrate.

When hydrochloric acid has been employed in bringing the mineral into solution, the sulphur must be determined; this is best accomplished by following the method described in the analysis of Ultramarine (p. 134).

According to Wöhler, zinkenite ignited in a current of hydrogen loses its entire quantity of sulphur as hydrogen sulphide, and there remains pure antimony-lead (silver, copper, iron). The analysis is carried out by heating a weighed portion of the sample, placed in a porcelain boat, which is inserted in a porcelain combustion tube, in a stream of hydrogen gas. The mixture of hydrogen sulphide and hydrogen is conducted into a bromine solution (p. 134), and the sulphur calculated from the sulphuric acid that has been formed.

When the decomposition is finished, the residue in the boat is dissolved in nitric and tartaric acids and examined as already directed.

Ullmannite.

Composition.—Antimony, nickel and sulphur.

The mineral can also be decomposed by chlorine gas. The nickelous chloride remaining in the bulb is dissolved in dilute hydrochloric acid and precipitated with sodium hydrate. By ignition of the nickelous oxide in a current of hydrogen it is converted into metallic nickel (p. 23).

Niccolite.

KUPFERNICKEL.

Composition.—Nickel, arsenic (iron, lead, sulphur).

The finely powdered mineral is dissolved in *aqua regia*, and the nitric acid removed by repeated evaporation with hydrochloric acid. After the reduction of arsenic to arsenious acid by means of sulphurous acid, the arsenic (and lead) is precipitated with hydrogen sulphide. Upon digesting the sulphides with ammonium sulphide, the arsenic sulphide will be dissolved. The undissolved lead sulphide is ignited in a stream of hydrogen and weighed (p. 30).

The arsenic sulphide is reprecipitated when hydrochloric or sulphuric acid is added to the ammonium sulphide solution. It is then converted into magnesium arseniate. (See p. 68.)

As there is but a trifling amount of iron in niccolite, it is separated from nickel by double precipitation with ammonium hydrate and carbonate. The instructions on page 166 should be followed out here.

Determine the sulphur in a separate portion by oxidizing the mineral with nitric acid or aqua regia.

Linnaeite.

COBALT-KIES.

Composition.—Cobalt and sulphur.

The finely pulverized mineral is decomposed either by aqua regia or potassium chlorate, and the solution freed from nitric acid by repeated evaporation with hydrochloric acid, and then mixed with barium chloride. The excess of the latter is precipitated by dilute sulphuric acid, and the cobalt determined in the filtrate as hydrated oxide, which is converted into metallic cobalt (p. 22).

If accurately agreeing measuring vessels are at command, the solution of the substance may be reduced to a definite volume, and the measured volumes used in determining the sulphuric acid and cobalt.

Cobaltite.

Composition.—Cobalt, iron (copper, antimony), arsenic and sulphur.

The course of analysis to be pursued may be readily determined from what has been learned from preceding examples. Cobaltite is decomposed by nitric acid alone, and the acid expelled by evaporating the solution with hydrochloric acid. In the aqueous solution of the residue, acidified with hydrochloric acid, precipitate the sulphuric acid with barium chloride and the excess of the latter with sulphuric acid. Or, we can use an aliquot portion of the solution for the estimation of the sulphuric acid. Before precipitating the arsenic, antimony and copper with hydrogen sulphide, first reduce the arsenic to arsenious acid with sulphurous acid or potassium hyposulphite, and separate the metals by digesting them with sodium sulphide. The copper sulphide that remains, after being washed with water containing hydrogen sulphide, may be weighed as such (p. 48). The sulphides of arsenic and antimony that have been dissolved are precipitated according to page 165 and estimated.

The filtrate from the above precipitate contains yet the cobalt and iron. Bring the solution to boiling to expel the hydrogen sulphide, then add enough nitric acid to convert the ferrous into ferric salts and separate the latter from cobalt by double precipitation with ammonium hydrate and carbonate. (See Nickel Matte, p. 166.)

To precipitate the cobalt as hydrated oxide, the ammoniacal salts must be first expelled by ignition, or the cobalt may be separated as sulphide. In doing this follow strictly the description mentioned under Nickel Matte.

Arsenical Cobalt.

Composition.—Cobalt, iron, arsenic and sulphur.

Proceed precisely as in the analysis of Cobaltite. As the mineral contains a very considerable amount of iron, its perfect separation from the cobalt can only then be insured, when the first obtained precipitate of ferric oxide is redissolved in hydrochloric acid and the precipitation with ammonium hydrate and carbonate repeated.

Cerrusite.

Composition.—Lead oxide (ferric and calcium oxides) and carbon dioxide.

The pulverized mineral is dried at 100° C. and dissolved in dilute nitric acid, and the lead precipitated either (p. 49) as sulphate, or as sulphide (p. 57).

Oxidize the filtrate, after expelling the hydrogen sulphide gas, with nitric acid, and precipitate the small quantity of ferric oxide with ammonium hydrate and subsequently the calcium with ammonium oxalate (p. 13).

The carbon dioxide is determined in another portion of the substance (p. 33).

Galenite.

Composition.—Lead (antimony, arsenic, copper, silver, gold, zinc, iron), sulphur and gangue.

Galenite that is rich in antimony is most advantageously decomposed by chlorine gas. If nitric acid or some other oxidizing agent is used to cause solution, the separated lead sulphate is invariably impurified by antimony.

In the decomposition with chlorine gas the receiver will contain the sulphuric acid, antimony, arsenic and also a portion of the iron and zinc. For the analysis of these substances refer to page 172.

The bulb-tube will contain the chlorides of lead, silver, copper and the non-volatilized portions of iron and zinc. The separation of these substances will easily follow from the numerous examples and their treatment, which have already been given. The course of analysis is briefly indicated as follows: Dissolve the contents of the bulb in dilute hydrochloric acid; the greater portion of the lead will separate as chloride and dissolve again by repeatedly boiling with water. The insoluble portion is silver chloride and gangue.* After concentrating the solution precipitate the lead with dilute sulphuric acid, and the copper in the filtrate with hydrogen sulphide gas (p. 50).

The filtrate, as heretofore, must be boiled and nitric acid added to oxidize the iron, which is then separated from the zinc by sodium acetate. The zinc in the filtrate is determined as sulphide.

If the decomposition of galenite is effected by strong nitric acid, a large portion of the lead will separate as sulphate. This may be dissolved and separated from the

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* Generally the silver is determined by refining (see below). To estimate the gangue in presence of silver chloride, ignite the residue in a stream of hydrogen, whereby metallic silver and a compound of silver and silica are produced. The silver will be perfectly dissolved when the residue is warmed with dilute nitric acid. The silica and gangue separate fully when the liquid is evaporated upon a water-bath. The aqueous solution of the residue may be employed for the estimation of the silver.

gangue by repeated boiling with hydrochloric acid. Or, the nitric acid solution may be evaporated to dryness with sulphuric acid, thus causing complete separation of the lead (p. 49). In this case, the joint weight of lead sulphate and silica is determined, and the mass then digested with a solution of ammonium acetate or tartrate. The lead sulphate dissolves completely. The gangue residue is weighed and the difference in the two weights will indicate the amount of lead sulphate.

The other metals will be found in the filtrate from the lead sulphate, and may be separated according to methods already described.

Ordinarily, in the analysis of galenite, the determination of the lead and silver is all that is wished, therefore the following methods are almost exclusively used:—

25 grms. of the pulverized ore are mixed in a wrought-iron crucible with from 2 to 3 times the quantity of soda, the mass covered with a layer of borax and the crucible placed either in the hot muffle of an assay furnace or directly in the coke fire of a wind oven. When the contents of the crucible have become liquid, the air entrances are closed, causing a depression in the temperature, and the crucible is allowed to remain for ten minutes in the fire, which, however, is dependent upon the fusibility of the lead mixtures contained in the ore. When the liquid mass is no longer disturbed by gas bubbles, lift the crucible out of the oven, unite the lead globules by tapping upon the crucible, pour out first the slag and then the liquid lead that has collected on the crucible bottom in a metallic globule. With a certain amount of practice one can soon acquire the art of pouring out the lead perfectly free from slag, and obtain a regulus which can be immediately weighed. When slag is mixed with the lead, remove it by breaking up the regulus and weigh the lead after having washed it.

The reduced lead contains the entire quantity of silver* present in the ore. To determine this, the lead must be expelled, that is, converted by oxidizing ignition into lead oxide. To accomplish this the lead is placed in a previously ignited cupel, and this then set in a glowing muffle. As soon as the lead is melted, by a partial opening of the draught the heat must be so regulated that the assay does not become too hot, which would cause a partial oxidation of the silver, which would then be absorbed by the cupel, together with the lead oxide. Again, when the temperature sinks too low, the assay will become rigid (freeze). When the latter occurs, it is exceedingly difficult to bring the assay into propulsion.

The point when all the lead has been expelled is easily recognized; the smooth color of silver appears upon the metallic globules where thin coverings of lead oxide had been. The hot cupel is then taken from the muffle, and the globule of silver, while still hot, is smoothed over with a small steel anvil to free it from adhering lead oxide.

When gold is present in galenite, it will be discovered in the silver globule. The silver is dissolved in dilute nitric acid, in a weighed porcelain crucible, the residual gold thoroughly washed by decantation with hot water (this can be executed without the slightest loss whatever), and its weight determined after slight ignition.

Wulfenite.

Composition.—Lead molybdate.

The mineral is readily decomposed by fusion with a mixture of equal parts of sodium carbonate and sulphur.

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* To estimate the silver in ores poor in lead, mix them with lead oxide not containing any silver, and reduce them as above directed.

The procedure is the same as given at page 55, the fused mass being extracted with water. The molybdenum exists as sodium-molybdenum sulphide in the solution, and may be separated from the latter as sulphide by the addition of hydrochloric acid to it. The decomposition is best effected at a boiling heat, this being maintained until all the hydrogen sulphide is removed. The molybdenum sulphide is transferred to a filter weighed at 120° C., washed with hot water, and an aliquot part of the precipitate dried at the same temperature and ignited in a stream of hydrogen. The residue is MoS_2.

The residual lead sulphide is weighed as such, after having been perfectly washed with water containing hydrogen sulphide (p. 20).

Pyromorphite.

GREEN AND BROWN LEAD ORE.

Composition.—Lead phosphate and chloride, sometimes with the sulphate and arsenate and calcium fluoride.

To determine the lead oxide, calcium oxide, phosphoric acid, and arsenic acid, the finely pulverized mineral is digested with nitric acid until it all has passed into solution, when the liquid is evaporated to dryness on a water-bath, with addition of hydrochloric acid. As the nitric acid will counteract the precipitation of the arsenic acid by hydrogen sulphide, the residue is again moistened with strong hydrochloric acid, the evaporation repeated, and solution finally effected by hydrochloric acid. After pouring off the supernatant liquid, the separated lead chloride is dissolved by successive washings with water, and a stream of hydrogen sulphide conducted through the liquid which had previously been reduced by sulphurous acid. The precipitate, sulphides of arsenic and lead, is digested with ammonium sulphide, the insoluble lead sulphide ignited in a stream of hydrogen, and the arsenic tersulphide reprecipitated from its solution upon the addition of dilute hydrochloric acid. The sulphide is converted into ammon-magnesium arseniate and determined (p. 69).

Sulphuric acid is added to the filtrate from the above sulphides, the solution evaporated, and the calcium determined as sulphate (p. 29).

Neutralize the filtrate with ammonium hydrate and precipitate the phosphoric acid by adding magnesium chloride (p. 25). In the presence of sulphuric acid, some of it is likely to contaminate the magnesium precipitate; it is, therefore, necessary to redissolve the imperfectly washed precipitate in hydrochloric acid and reprecipitate by addition of ammonium hydrate and some more magnesium chloride solution.

Proceed in determining the chlorine as directed (p. 117).

The sulphuric acid is precipitated by barium chloride (p. 15) in the nitric acid solution, after the excess of the latter acid has been evaporated.

The determination of the fluorine in the presence of phosphoric acid, lead, etc., is accompanied by many difficulties and cannot be accurately estimated, and must therefore be calculated by difference.

Lead Matte.

Composition.—Lead, copper, iron (silver, antimony, nickel, zinc), sulphur.

The finely pulverized substance can be decomposed by chlorine gas, and the analysis indeed conducted throughout similarly to that described on page 170.

Red Lead.

Composition.—Besides the lead tetroxide, the commercial red lead contains generally small quantities of arsenic, antimony, copper, silver, iron, zinc, calcium, silicic acid and carbon dioxide.

If, in the production of red lead, the lead oxide has not been perfectly oxidized, there is formed a mixture of lead tetroxide and oxide. The quantity of the latter may be determined by digesting the finely pulverized substance dried at 100° C., with a solution of neutral lead acetate, in which the oxide is easily soluble. The insoluble tetroxide is transferred to a weighed filter and dried at 100° C., until the weight becomes constant.

The impurities occurring in red lead are determined by dissolving the substance, dried at 100° C., in dilute hydrochloric acid. Should lead chloride perchance separate out, it may again be dissolved by treating it repeatedly with hot water. Any silver chloride or silicic acid* present remains undissolved. Filter, and evaporate the filtrate with addition of sulphuric acid to determine the lead (p. 49).

The arsenic, antimony, and copper are precipitated by hydrogen sulphide in the filtrate from the lead sulphate. The first two are separated with sodium sulphide and determined as directed on page 165. After washing the insoluble copper sulphide with water containing hydrogen sulphide, ignite and weigh it.

For the estimation of silver in red lead take at least 25 grms. and form a lead regulus by fusing the substance with soda and borax. The silver will remain in the cupel after the expulsion of the lead (p. 186).

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* Silver chloride and silicic acid are separated according to page 185.

Iron, zinc and calcium are determined as usual in the filtrate from the precipitate produced by hydrogen sulphide.

Ascertain the quantity of carbon dioxide according to page 33. Sulphuric acid must be used to decompose the lead tetroxide, because hydrochloric acid would form with it free chlorine and lead chloride.

Cinnabar.

Composition.—Mercury sulphide, ferric and manganic oxides (copper), calcium oxide and alumina.

Sulphur Determination.—It may be oxidized to sulphuric acid by treating the finely pulverized substance with aqua regia, or nitric acid and potassium chlorate (p. 133), or even with bromine in a hydrochloric acid solution (p. 156).

Another method is based upon the oxidation of the sulphur by chlorine in presence of a caustic alkali (sodium or potassium). Suspend the pulverized substance in dilute potassium or sodium hydrate, and while applying heat continue the introduction of chlorine into the liquid until the red color of cinnabar has been changed to the red-brown of mercuric oxide; or until the oxide has been fully converted into the white chloride. After acidifying the solution with hydrochloric acid, precipitate the sulphuric acid as usual (p. 15).

Determination of the Mercury and remaining Oxides.—A solution of the substance in aqua regia is evaporated with addition of hydrochloric acid to dryness upon a water-bath. The hydrochloric acid solution of the residue is boiled with sulphurous acid to reduce ferric to ferrous oxide, and the mercury then precipitated by hydrogen sulphide.

The mercuric sulphide (HgS) is brought upon a filter dried at 100° C., washed with water, and dried at the same temperature until the weight becomes constant.

The mercuric sulphide is invariably mixed with sulphur when the reduction with sulphurous acid has been omitted or imperfectly executed. To remove this impurity pour carbon disulphide from time to time over the dried precipitate until a drop of the filtrate evaporated upon a watch-glass does not leave a residue of sulphur. When the quantity of sulphur is large, it is better to dissolve it in warm sodium sulphite. Spread out the filter upon a glass plate, wash the precipitate into a porcelain dish, and then digest it with sodium sulphite. After drying the filter, again fold it and filter off the mercuric sulphide, which is washed with cold water and then dried.

This method is not applicable in the presence of copper, because the sulphide of the latter is with difficulty separated from that of mercury. In this case mix the hydrochloric acid solution with an excess of phosphorous acid, which will reduce mercuric chloride to insoluble mercurous chloride (Hg_2Cl_2). After standing twelve hours in a moderately warm place, bring the precipitate upon a filter dried at 100° C.; wash with hot water, and dry at the above temperature until constant weight is obtained.

The copper is determined as sulphide in the filtrate (p. 50).

The filtrate from the latter contains yet the remaining oxides, the separation of which has already been given on page 71.

If the estimation of mercury in any of its ores is all that is desirable, this may be easily accomplished by precipitating it in metallic form by means of stannous chloride. With the hydrochloric acid solution absolutely free from nitric acid, mix a clear solution of stannous chloride (obtained by dissolving tin in hydrochloric acid) in excess, and heat to boiling. By this process we have the mercuric chloride perfectly reduced to the metallic state, and stannic chloride produced at the same time. When the precipitate has perfectly subsided, decant the clear supernatant liquid, and unite the globules to one mass, which is very easily done by again heating the residue with some stannous chloride and a few drops of hydrochloric acid. Wash the mercury by decantation at first with water containing hydrochloric acid, and finally with pure water, then transfer it to a tared porcelain crucible. The greater portion of the water adhering to the metal may be removed with filter paper. The crucible is, however, placed in a desiccator containing sulphuric acid, and the weight of the perfectly dried metal determined.

When cinnabar contains considerable quantities of other metallic compounds, it is by far advisable to effect its decomposition in a stream of chlorine gas, thus causing the volatilization of the mercury as chloride, and determining it in the receiver.

Molybdenite.

Composition.—Molybdenum sulphide.

The mineral is decomposed precisely as lead molybdate, viz., by fusion with sodium carbonate and sulphur. Hydrochloric acid will precipitate the molybdenum sulphide from the aqueous extract of the fused mass. Determine it according to page 188.

When other metals are mixed with the molybdenite, they remain as sulphides upon dissolving the fused mass in water.

Always estimate the sulphur in a second portion of the substance, fusing it with a mixture of sodium carbonate and potassium chlorate (p. 157).

Bismuthinite.

Composition.—Bismuth (copper, lead, gold, tellurium, arsenic, iron, cobalt, nickel), sulphur.

Digesting with concentrated nitric acid will perfectly decompose the mineral, and when an insoluble residue remains, fuse it with potassium hydrosulphate. After driving off the excess of nitric acid upon a water-bath, mix hydrochloric acid with the solution, and upon diluting this with a large quantity of water, bismuth oxychloride will separate out, and this may be converted into metallic bismuth by pursuing the course given on page 56.

The filtrate contains the other oxides. To estimate the tellurium, evaporate the nitric acid, dissolve the residue in dilute hydrochloric acid, and separate the tellurium as metal by heating its solution with sulphurous acid or potassium hydrosulphite. If the solution was dilute, or very small quantities of tellurium were present, to render the precipitation complete, the liquid should be allowed to stand for several days in a warm place. The separated tellurium is washed by decantation with sulphurous acid, and dried upon a filter dried at 100° C., until the weight is perfectly constant.

When gold is present in the bismuth ore, it is simultaneously separated with the tellurium. The weighed precipitate is treated with nitric acid, which will cause the solution of the tellurium, leaving the gold. Or both metals are dissolved in aqua regia, the nitric acid removed by evaporation, and the hydrochloric acid solution of the residue reduced by a concentrated solution of ferrous sulphate, which will throw down metallic gold.

The separation of the remaining oxides from tellurium in the gold filtrate may be found in what precedes.

Uraninite.

PITCH-BLENDE.

Composition.—Uranium protosesquioxide, with variable quantities of lead, copper, bismuth, arsenic, antimony, sulphur, selenium, vanadium, iron, manganese, cobalt, nickel, zinc, calcium, magnesia, sodium, carbon dioxide, silicic acid and water.

It has been recommended, when selenium occurs in this mineral, to determine it by heating the finely powdered substance in a current of chlorine (p. 170), causing the volatilization of the chlorides of bismuth, arsenic, antimony, sulphur and iron, and all the selenium. When the decomposition is complete, the liquid contained in the receiver is warmed gently on the water-bath to expel the chlorine, and the selenium precipitated in metallic form by reducing the solution with sulphurous acid or potassium hydrosulphite. The course of procedure is analogous to that followed in the determination of tellurium in the preceding example (p. 194).

The vanadium, too, may be best determined in a separate portion of substance. Fuse the powdered substance in a silver crucible about an hour with an equal weight of potassium nitrate, and lixiviate with water, which will dissolve all the vanadium as potassium vanadate. After neutralizing this liquid with nitric acid the vanadium is precipitated by the addition of ammonium chloride (p. 175).

The remaining oxides are determined by digesting the powdered substance with nitric acid. If a residue remains, this is decomposed by heating it with a mixture of nitric and sulphuric acids and filtering off the silicic acid. When the excess of acid has been driven away, reduce the arsenic to arsenious acid, and precipitate with hydrogen sulphide the metals thrown down by this reagent. Arsenic and antimony (selenium) are separated by treating their sulphides with ammonium sulphide, or, when copper is present, with sodium sulphide. The sulphides not soluble in ammonium sulphide are dissolved in nitric acid, and lead and bismuth separated according to the method given on page 55. The filtrate from the bismuth contains the copper which is determined as sulphide (p. 50).

The filtrate from the hydrogen sulphide precipitate neutralize with ammonium hydrate, carbonate and sulphide, adding the first in excess to prevent the precipitation of uranium by the last. Since, however, when considerable quantities of iron, cobalt, etc., are present, a portion of the uranium is likely to remain with their sulphides, dissolve the latter in hydrochloric acid, with addition of nitric acid, and precipitate ferric and uranic oxides (with small quantities of cobalt and nickel) by ammonium hydrate. It is necessary to redissolve the precipitate in hydrochloric acid and repeat the precipitation to get rid of the co-precipitated oxides. To separate the iron from the uranium, ignite the dried residue in a stream of hydrogen, thus reducing the iron to metal and uranium sesquioxide to protoxide. Dilute hydrochloric acid now added to the residue will perfectly dissolve the iron. The uranium oxide (UO) is re-ignited in a current of hydrogen and weighed.

The principal quantity of uranium will be discovered in the ammonium sulphide solution filtered from the sulphides. If any nickel has been dissolved, the liquid will possess a brown color. The addition of a few drops of mercurous nitrate to it will clear the solution (p. 166). Acidulate the liquid with hydrochloric acid, expel the hydrogen sulphide, and precipitate the uranium in the filtrate with nitric acid. The hydrated uranic oxide thus obtained is changed by ignition in a current of hydrogen to uranous oxide.

The cobalt, nickel, zinc, manganese and calcium are separated, according to page 104, in the filtrate from the iron-uranium precipitate.

The alkaline earths and alkalies are in part contained in the filtrate from the uranium precipitate, but the greater portion of the calcium will be found in that from the iron-uranium precipitate.

The carbon dioxide and sulphur are determined in separate portions, the first according to page 33, and the sulphur after page 133.

If upon the addition of hydrochloric acid to the mineral hydrogen sulphide be disengaged, the method of estimating the carbon dioxide must be somewhat modified. (See the analysis of Soda.)

Wolframite.

Composition.—Tungstic acid, ferrous oxide, manganous oxide (calcium oxide and magnesia).

The mineral is only with difficulty decomposed by acids, but this is readily remedied by fusing it with four times its weight of potassium or sodium carbonate. The aqueous extract of the fused mass will contain all the wolfram as potassium (sodium) tungstate. The oxides of iron and manganese remain undissolved. After washing they are dissolved in hydrochloric acid, and separated as heretofore directed (p. 71).

The tungstic acid may be precipitated as such from an alkaline solution, or as tungstate of mercurous oxide.

To separate the acid as such from an alkaline solution, supersaturate the latter with hydrochloric acid, evaporate to dryness upon a water-bath, and heat the residue for some time at about 120° C. The alkaline chlorides are dissolved in water, hydrochloric acid being added, and the insoluble tungstic acid being filtered off, washed with water containing hydrochloric acid, and then ignited with air access. To avoid any reduction of the acid by the carbon of the filter, obtain the latter as free as possible from the precipitate, and after moistening it with a few drops of ammonium nitrate and drying, incinerate it upon a platinum wire. If the tungstic acid is not pure yellow in color, it is moistened with a few drops of nitric acid, and the ignition in an open tube repeated.

To determine the tungstic acid as tungstate of mercurous oxide, neutralize the liquid with dilute nitric acid to slight acid reaction, drive out the absorbed carbon dioxide by heat, and add then a sufficient quantity of mercurous nitrate. Ammonium hydrate is now added, drop by drop, until the precipitate assumes a brown color, and it has subsided; filter and wash it perfectly with water containing mercurous nitrate. After ignition with access of air, the residue is tungstic acid (WO_3).

Scheelite.

Composition.—Calcium tungstate, frequently also small quantities of magnesia and cupric oxide.

Scheelite is completely decomposed either by hydrochloric or nitric acid. The solution is evaporated to dryness, the residue heated to 120° C., and hydrochloric acid poured over it. The insoluble tungstic acid is determined as in the preceding example.

In the filtrate from the above the calcium and magnesium are estimated in the usual manner.

The cupric oxide may be precipitated by hydrogen sulphide.

Refined (Soft) Lead.

Composition.—Lead, with small quantities of silver, copper, bismuth, antimony (arsenic), cadmium, iron, zinc, nickel (cobalt, manganese).

Take for the analysis 200–500 grms. of lead, according to its purity, 200 grms. usually being sufficient. After cleaning the lead, hammer it out, upon a steel anvil, into a thin plate of 0.05 Cm. thickness, and divide it into pieces of about 2 or 3 Cm. length. These are introduced into a flask, and 250 C. C. of concentrated nitric acid of sp. gr. 1.4 poured over them, and the whole diluted with 500 or 600 C. C. distilled water. The solution will be considerably hastened by warming the flask and its contents upon a water- or sand-bath. When the evolution of the gas is too violent, remove the flask for a short time; not long enough, however, to cool the liquid sufficiently to cause the separation of lead nitrate.

The solution is generally complete and perfectly clear after three hours, providing the quantity of antimony in the lead does not exceed .02 or .03 per cent. When lead antimoniate separates from the solution, filter the liquid and wash the residue completely with water. Mention will hereafter be made for the further treatment of the residue. The nitric acid solution is brought into a 2 litre flask, provided with a mark, and 170 C. C. dilute sulphuric acid (1 part concentrated H_2SO_4 and 2 parts water) added, which will produce a precipitation of the lead sulphate. Add water to the mark. Shake the flask well and allow the precipitate to subside, then remove the principal portion of the supernatant liquid with a siphon filled with the same liquid, without carrying away any lead sulphate. 1750 C. C. of the clear liquid are evaporated to dryness, and the residue ignited, until white vapors of sulphuric acid hydrate appear. When cool, add 50 or 60 C. C. of water and filter off the slight quantity of lead sulphate that may have separated. As it may very probably contain a small quantity of antimony, dissolve it in hydrochloric acid and precipitate it with hydrogen sulphide. The antimony sulphide is separated from the lead by treating the precipitate with ammonium sulphide, and adding hydrochloric acid to this filtered solution (p. 52). The acidified liquid is in the mean time preserved. Conduct a stream of hydrogen sulphide into the filtrate from the lead sulphate, maintaining, during the operation, a temperature of about 70° C. to facilitate the reduction of arsenic to arsenious acid. When the precipitate has fully subsided, filter it off and digest it with a solution of potassium or sodium sulphide, and precipitate again the sulphides of arsenic and antimony in the solution by the addition of hydrochloric acid. This precipitate is combined with the antimony sulphide obtained above, washed with water, and the adherent sulphur removed by carbon disulphide, after drying the filter or substituting alcohol for water in washing.

If lead antimoniate remained when the lead was dissolved in nitric acid, dissolve it in hydrochloric acid with addition of tartaric acid, and add hydrogen sulphide. The antimony (arsenic) sulphide thus obtained can be brought upon the same filter with the sulphides obtained by precipitation with potassium or sodium sulphide.

The dry filter is placed in a rather large porcelain crucible, and fuming nitric acid poured upon it. When the fibres of the paper have been perfectly destroyed, and the greater portion of the nitric acid removed by evaporation, dilute with water, and add in excess sodium carbonate and some nitrate. After evaporation the residue is fused and heat applied, until the fused mass becomes perfectly white. Lixiviate the cooled residue and wash the insoluble sodium antimoniate first with water and then with alcohol. Dissolve the residue in hydrochloric and tartaric acids, and precipitate the antimony with hydrogen sulphide.

The filtrate from the sodium antimoniate contains sodium arseniate and some antimony. Expel the alcohol and acidify the solution with dilute sulphuric acid, evaporating the nitric acid and precipitating the arsenic and antimony with hydrogen sulphide. (See above.) Pour over the washed sulphides on the filter a cold, concentrated ammonium carbonate solution, dissolving by this means the arsenic tersulphide, and leaving the antimony. For the complete removal of the arsenic, repeat the operation several times, employing small quantities of an ammonium carbonate solution. The addition of hydrochloric acid to the filtrate will reprecipitate the arsenic. After driving away the carbon dioxide by the application of heat, add more hydrogen sulphide, bring the precipitate upon a weighed filter, and dry it at 100° C.

The two precipitates of antimony tersulphide are filtered and washed. Fresenius suggests that in this case the filtering be done through a small glass tube, drawn out at the lower end, and above the contraction fitted loosely with asbestos. The tube is dried and then weighed. When the antimony sulphide has been washed, and the tube dried, a stream of carbon dioxide is conducted through it, the antimony being heated until it becomes black, when the carbon dioxide is replaced by air and the tube again weighed.

Or, the antimony sulphide is transferred to a small filter, washed with water containing hydrogen sulphide and ammonium nitrate, and then a small quantity of a warm, ammonium sulphide solution poured over it. This liquid is allowed to flow into a weighed porcelain crucible, the filter washed with water and the solution then evaporated upon a water-bath. By digesting the residual antimony sulphide with nitric acid, it is readily converted into antimoniate of antimonic oxide. (See p. 53.)

The results prove fully as accurate if the tersulphide of antimony is determined volumetrically (p. 179).

Instead of separating arsenic and antimony according to the above-mentioned method, their sulphides may be dissolved in hydrochloric acid with addition of potassium chlorate, and the arsenic acid, then precipitated after the addition of tartaric acid, as ammonium magnesia arseniate (p. 69). The antimony in the filtrate is thrown down with hydrogen sulphide, and determined as above.

The copper, cadmium, etc., sulphides, insoluble in potassium sulphide, are dissolved in dilute nitric acid (1 part HNO_3, sp. gr. 1.2, and 2 parts H_2O), and the solution then evaporated with dilute sulphuric acid, until the white vapors of the latter appear. If any lead sulphate remains upon treating the residue with water, filter it off and wash it with water containing sulphuric acid.

For the separation of the bismuth from the other metals, neutralize the liquid with sodium carbonate—the solution must, however, react acid—add some potassium cyanide, and heat gently upon a water-bath. Wash the potassium bismuth cyanide, and dissolve it in nitric acid, precipitating the bismuth as carbonate. For this purpose mix the solution with a slight excess of ammonium carbonate, and heat it for some time to boiling. The bismuth carbonate is filtered, washed and ignited. The residue is bismuth oxide (Bi_2O_3).

To the filtrate from the potassium bismuth cyanide add more potassium cyanide to prevent the precipitation of the copper, and mix in sodium or potassium sulphide. The precipitate of silver and cadmium sulphide is washed perfectly with water, and then dissolved in dilute nitric acid. On the addition of a few drops of hydrochloric acid to the liquid, the silver will be completely precipitated (p. 47).* Concentrate the filtrate and precipitate the cadmium as carbonate (p. 64).

The copper is present in the filtrate from the silver and cadmium sulphides. This is slightly acidified with hydrochloric acid, heated until the odor of hydrocyanic acid has disappeared, and the copper then precipitated by hydrogen sulphide (p. 48).

The original filtrate from the hydrogen sulphide precipitate, containing zinc, iron, etc., is mixed with ammonium hydrate and sulphide, and the sulphides obtained filtered off. Should any nickel sulphide pass into solution, which is most generally the case, separate it again by the method described on page 166.

By treating the sulphides directly upon the filter with hydrochloric acid and hydrogen sulphide water (see p. 104), iron, zinc and manganese will be dissolved. The sulphides of nickel and cobalt constitute the residue. Oxidize the solution with nitric acid, and separate the iron and zinc by repeated precipitation with ammonium hydrate (p. 109). The ferric oxide is ignited and weighed.

Acidify the filtrate from the ferric oxide with acetic acid, and precipitate the zinc with hydrogen sulphide (p. 19). After the solution has stood twenty-four hours, filter off the precipitate and weigh it.

Concentrate the filtrate from the zinc precipitate by evaporation, and mix it with ammonium hydrate and sulphide. When the manganese sulphide has stood twenty-

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* The quantity of silver is most accurately ascertained by refining 50 grms. of lead. For a gravimetric determination, dissolve 200 grms. of the lead in nitric acid, and dilute this solution strongly with water. Add to this a few drops of dilute hydrochloric acid, and filter after the precipitate of silver chloride has fully subsided. By ignition in a current of hydrogen gas, this is converted into metallic silver.

four hours, filter it off and determine it as mentioned on page 21.

The sulphides of nickel and cobalt, insoluble in dilute hydrochloric acid, are dissolved by it upon addition of a few drops of nitric acid, and the solution evaporated almost to dryness, and mixed with ammonium hydrate to distinct alkaline reaction. If this produces a slight precipitation, filter this, and in the filtrate throw down the cobalt and nickel by boiling with sodium hydrate. (See p. 166.)

In the calculation of the analysis, the space occupied by the lead sulphate must be regarded. 100 grms. lead converted in sulphate occupy 23 C. C., 200 grms. 46 C. C. Therefore, when calculating, the 1750 C. C. are not to be referred to the 2000 C. C., but to 2000—46=1954 C. C. or to 179.12 grms. soft lead.

The analysis of "work lead" may be similarly executed. 10 or 15 grms. substance are sufficient for this purpose. When sulphur is a constituent of the lead, it is determined according to page 134.

Hard Lead.

In analyzing this substance the determination of the antimony is most frequently required. The following method may therefore be used: Reduce the lead to a fine state, and fuse 2 grms. of it, in a porcelain crucible, with four times its quantity of a mixture of sulphur and soda. The fused mass is boiled with water, and when the residue has subsided the supernatant liquid is poured into a flask of 250 C. C. capacity. After digesting the residue with sodium or potassium sulphide, bring this liquid into the same receptacle and dilute up to the mark. 100 C. C. of the sodium sulphide solution passed through a weighed filter are precipitated with dilute sulphuric acid, and after washing and drying the precipitate it is freed from the excess of sulphur by pouring carbon disulphide over it. The antimony sulphide is dissolved in strong hydrochloric acid with addition of tartaric acid, and sodium hydrocarbonate mixed with it. Add starch-paste to the solution, and titrate it with an iodine solution. For the rest, see page 179.

The metals occurring in Hard Lead, which are not dissolved when the fused mass is treated as directed, are determined according to already known methods. Or, another portion of the substance may be dissolved in nitric acid, and the analysis executed similarly to that of Soft Lead.

Antimony.*

The investigation of metallic antimony may be made according to the method employed in the above analysis of Hard Lead. After fusion with soda and sulphur, and treating the fused mass with water, the residue will consist of the sulphides of lead, cadmium, copper, bismuth, iron, nickel, manganese and zinc, whilst in the solution are antimony, tin and arsenic. These latter substances may be separated as directed in the method described on page 66.

Estimate the sulphur after page 134. Use a mixture of hydrochloric and tartaric acids to effect the decomposition.

Zinc (Spelter).

It contains between 0.5 and 2 per cent. lead; also iron, cadmium, arsenic, and sometimes antimony, manganese, copper, tin and sulphur.

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* The antimony in antimony slags is estimated as directed in the analysis of Hard Lead.

A piece of zinc, weighing from 50 to 100 grms., is suspended by a platinum wire, in a rather large beaker, filled to one fourth its volume with dilute sulphuric acid, so that the piece of zinc will be immersed about one-half in the liquid. After dissolving a sufficient quantity of the metal, filter the liquid rapidly through a folded filter, afterwards washing it. By this means a solution of pure zinc sulphate may be obtained; because, as long as zinc is present, none of the other metals will be dissolved in sulphuric acid. The impurities will be partly deposited upon the zinc, or remain upon the filter. The insoluble zinc is freed from the spongy deposit, rinsed with water, dried and weighed. The portion of zinc in solution is represented by the difference in the weight.

Digest the spongy deposit and the residue, upon the filter, with nitric acid, and evaporate to dryness. Treat the residue with dilute nitric acid, when any tin that may be present will remain undissolved as oxide, together with antimonic oxide, silica and carbon. The filtered precipitate is washed well, and after the incineration of the filter, fused in a silver crucible, with sodium hydrate. Antimony and tin are separated as directed on page 65. It is always best, when silica and carbon are present, to determine them in a separate portion of the substance, dissolved in nitric acid. The liquid is evaporated to dryness, and the residue warmed with dilute hydrochloric acid, leaving undissolved the carbon and silicic acid. Determine the carbon by burning it in a current of oxygen gas, and weigh the residual silicic acid in the porcelain boat. The purity of the silicic acid thus obtained must always be tested.

Treat the filtrate from the oxide of tin with hydrogen sulphide, heating it at the same time to about 70° C., and digest the sulphides with potassium sulphide.

The arsenic and antimony should always be determined in a separate portion of the substance (see below), because, in dissolving the metal, they partially escape as hydrogen compounds.

The sulphides not soluble in potassium sulphide are dissolved in nitric acid, and this solution evaporated to dryness, with addition of dilute sulphuric acid. The residue is taken up with water and alcohol, and the lead sulphate washed with dilute alcohol (p. 49).

Expel the alcohol first from the filtrate from the lead sulphate, then add ammonium and ammonium carbonate, and after protracted heating, filter off the cadmium carbonate. The latter is again dissolved in hydrochloric acid, and the precipitation repeated. The ignited precipitate is cadmium oxide (p. 64).

Precipitate the copper with hydrogen sulphide, after having acidulated the liquid with hydrochloric acid.

To the filtrate from the copper sulphide, add ammonium and ammonium sulphide, separating the sulphides produced as in the analysis of Soft Lead.

For the determination of the antimony and arsenic, dissolve 25 to 50 grms. of zinc in aqua regia, evaporating the excess of acid, and precipitating the metals as sulphides. The process described on page 165 may be used in their separation. When tin is present, it will occur with these, and the method of separation described on page 66 must then be employed.

If the zinc, when treated with sulphuric acid, liberates hydrogen sulphide, ascertained by conducting the gas stream into an alkaline solution of lead, the sulphur may be determined as in Ultramarine.

Black or Raw Copper.

Composition.—Copper, iron, lead, silver, arsenic, antimony, bismuth, zinc, nickel, cobalt, calcium, magnesium and sulphur.

Dissolve about 10 grms. of the substance in dilute nitric acid, and evaporate the solution to dryness, with addition of dilute sulphuric acid. Upon the residue pour sufficient water to dissolve the copper sulphate, then add alcohol. When too much of the latter is present, crystals of copper sulphate separate out and are with difficulty redissolved. It is, therefore, advisable to wash the insoluble lead sulphate at first with water containing sulphuric acid, and use alcohol after almost all the sulphate has passed into the filtrate. Supersaturate the latter with hydrogen sulphide, whilst the temperature of it is retained at about 70° C. The arsenic and antimony are dissolved when the sulphides are digested with potassium or sodium sulphide, and may be separated by already known methods (p. 165).

Dissolve the sulphides insoluble in potassium sulphide in nitric acid, and evaporate the solution to dryness. Treat the residue with water and a few drops of hydrochloric acid, which will dissolve the copper and bismuth and leave the silver chloride.

To determine the silver quantitatively, use the solution of a larger quantity of copper, and proceed as given on page 203.

In the filtrate from the silver chloride, precipitate the bismuth as oxychloride (p. 58).

The quantity of copper is found by difference. To determine it directly, reduce the filtrate to a definite volume, and precipitate an aliquot part with hydrogen sulphide.

Neutralize the filtrate with ammonium hydrate, and add ammonium sulphide to effect the precipitation of the zinc, nickel, etc. Separate them as heretofore.

The calcium and magnesium are in the ammonium sulphide filtrate, and for its further treatment to separate the metals see page 74.

The sulphur may be estimated by precipitating the nitric acid solution of the substance with barium chloride, or, what is decidedly preferable, according to the method given on page 134. In the latter instance, fuming hydrochloric acid is used to dissolve the copper.

Refined Copper.

Composition.—Contains, besides the constituents of the preceding example (however in smaller quantities), cuprous oxide and crystallized nickelous oxide.

For the determination of the coarse copper constituents, refer to the preceding example. Estimate the cuprous oxide by igniting a weighed portion of the copper in a stream of hydrogen gas, causing by this means a reduction to metallic copper. The cuprous oxide may be easily determined from the loss in weight. This method, however, is only applicable when the metal does not contain any sulphur, arsenic, or antimony. When free from the latter two, and containing sulphur, the method may still be employed, if the substance is weighed off in a porcelain boat and the latter placed in a tube of similar material. Connect the one end of the tube with an hydrogen generator, and the other with an absorption apparatus containing bromine dissolved in hydrochloric acid (p. 134). After the decomposition is complete, estimate the sulphuric acid, and the quantity of sulphur corresponding to this is deducted from the loss in weight.

Another method, that of Aubel, is based upon the fact that, upon the one hand, cuprous oxide and sulphuric acid yield copper and copper sulphate, while copper and silver sulphate replace each other to silver and copper sulphate:—

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$
$$Cu + Ag_2SO_4 = CuSO_4 + Ag_2.$$

216 parts of separated silver, therefore, correspond to 142 parts cuprous oxide.

According to Aubel, 0.5 grm. finely filed copper is mixed with 2.6 grms. silver sulphate and 15 C. C. sulphuric acid of 1.13 sp. gr. added. The whole is allowed to stand eight hours in a warm place, and frequently stirred. When the decomposition is complete, wash the metallic silver, ignite and weigh.

Tin.

The most common impurities are copper, lead, bismuth, iron, zinc, arsenic and antimony.

After oxidizing the metal with dilute nitric acid, and evaporating the excess of the latter, all the tin will remain as oxide. This, however, invariably contains weighable quantities of the other metals, particularly copper, lead and antimony. By fusing the washed residue with sulphur and soda (p. 54), and lixiviating with water, the first two metals remain as sulphides. The tin and antimony are in solution. These are reprecipitated as sulphides upon the addition of hydrochloric acid to the solution; they are separated according to page 54.

The sulphides not soluble in sodium sulphide are dissolved in nitric acid and added to the principal solution.

The course of analysis follows from the preceding examples.

Bismuth.

Composition.—Lead, silver, copper, arsenic, iron, cobalt, nickel and sulphur.

A rather large quantity of the metal is dissolved in dilute nitric acid, the excess of the latter evaporated, and the small quantity of silver present precipitated by hydrochloric acid. Add enough of the latter so that upon subsequent dilution with water, bismuth oxychloride will not be precipitated.

In the filtrate determine the bismuth as on page 58.

The filtrate contains the remaining bases, which are separated according to known methods.

Silver.

This generally contains traces of gold, lead, copper, antimony and arsenic.

To determine the quantity of gold present, dissolve 25 to 50 grms. of the substance in dilute nitric acid, free from chlorine, and proceed as given in the analysis of Galenite on page 187.

Cubical Nickel.

Composition.—Copper, arsenic, antimony, iron, cobalt, sulphur (carbon) and silicic acid.

For the method of analysis, refer to Nickel Matte, on page 164.

Cast Iron.

STEEL.

In making a complete analysis of the same, we have to consider: iron, manganese, copper, zinc, cobalt, nickel, chromium, aluminum, titanium, antimony, arsenic, calcium, magnesium, silica, phosphorus, sulphur, carbon, the latter partly chemically united and partly present as graphite.

Estimation of Iron, Manganese, Aluminum, Zinc, Cobalt, Nickel, Chromium, Titanium, Calcium, Magnesium and Silicon.—About 10 grms. of iron dust or borings are placed in a large platinum or a good porcelain dish, dissolved in hydrochloric acid, and the solution evaporated to dryness upon a water-bath. Moisten the residue with hydrochloric acid, add water and filter off the insoluble portion. The residue contains, besides the silica, the graphite present in the iron, iron phosphate, iron titanite, chromic and carburetted iron. Dry the precipitate, ignite it, together with the filter, in a porcelain crucible, and fuse it with an equal weight of a mixture of equal parts soda and saltpetre.*

Remove the residue from the crucible with water,† dissolve it in hydrochloric acid, and separate the silicic acid by evaporating the liquid to dryness. (See p. 143.) Dissolve the residue in dilute hydrochloric acid, filter off the silica, and add the filtrate to the principal solution, this

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* Iron samples, which do not contain any graphite (Spiegeleisen), and when dissolved leave a very slightly colored residue, may be fused with potassium hydrosulphate.

† If the fused mass is treated directly with hydrochloric acid in the platinum crucible, there can (as potassium nitrite is generally present in the residue) considerable quantities of platinum chloride be dissolved.

being then reduced to a definite volume (about 500 C. C.). Examine the silica for titanic acid (p. 125).

The hydrochloric acid solution not only contains the metals, but also the silicic and titanic acid that remain. The estimation of the latter may be united with that of aluminum and chromium. For this purpose an aliquot portion (about 200 C. C.) of the solution is oxidized with nitric acid or potassium chlorate and precipitated with ammonium hydrate (best in a platinum or porcelain dish). Heat the liquid until the odor of ammonia is only faintly perceptible. Filter off the precipitate (containing ferric oxide, alumina, chromium, silicic, phosphoric and titanic acids), and fuse it in a platinum crucible with potassium hydrosulphate. Lixiviate the fused mass with cold water, filtering off the silicic acid, and separating the titanic acid according to the method described on page 125.

To separate the ferric oxide from aluminum and chromium, mix the filtrate from the titanic acid with sufficient tartaric acid, so that, upon the addition of ammonium hydrate to alkaline reaction to the solution, no precipitate is produced; then throw down the iron in a closed flask with ammonium sulphide. The iron sulphide is not filtered until the supernatant liquid appears of a pure yellow color. The filtrate contains the aluminum, chromium and any phosphoric acid that may be present. Evaporate this to dryness, adding sodium carbonate and potassium chlorate, and ignite the residue to oxidize the carbon, with addition of ammonium sulphate or nitrate. (See p. 156.) Dissolve the residue in hydrochloric acid, and add sodium carbonate to precipitate the oxides of aluminum and chromium (together with phosphoric acid). By adding enough bromine water to the liquid, and warming, chromic acid will pass into solution, and may be determined as barium chromate according to the method given on page 89.

The aluminum precipitate contains the phosphoric acid. Wash well with hot water, ignite and weigh. Dissolve the residue in nitric acid, precipitating the phosphoric acid with ammonium molybdate (p. 25), and deducting its amount from the first precipitate.

To determine the manganese and zinc, oxidize an aliquot portion of the hydrochloric acid solution (about 250 C.C.) with nitric acid or potassium chlorate, and separate the ferric oxide and aluminum from manganese and zinc, after previous addition of an excess of aluminum chloride, by means of ammonium hydrate and carbonate (p. 72).*

As the solution contains a large quantity of iron compared with manganese, its precipitation must occur in an exceedingly dilute liquid, and the maximum quantity of ferric oxide in one litre of the liquid should not exceed 3.5 grms. The precipitate of ferric hydrate is washed by decantation with hot water, a small quantity of ammonium hydrate being finally added. The filtrate is concentrated by evaporation, and the slight quantity of aluminum (ferric oxide) that has been dissolved precipitated by ammonium hydrate. The filtered precipitate is again dissolved in hydrochloric acid, and the precipitation with ammonium hydrate repeated. Put the filtrate into a flask that can be closed, mix with it yellow ammonium sulphide (see p. 73—remark) in slight excess, and permit the whole to stand until the precipitate thus formed has fully subsided, when it is filtered. Wash the precipitate perfectly with water containing hydrogen sulphide, to which a little ammonium chloride has been added; rinse it then into a

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* If sodium carbonate and acetate and ammonium acetate (p. 73) are employed for the separation of iron and manganese, the ferric acetate will invariably contain weighable quantities of manganese, especially, as in the present case, when large quantities of iron are present with manganese.

porcelain dish, and pour acetic acid upon it. Nearly all the manganese sulphide will be dissolved; a portion of it, however, will remain with the zinc, cobalt, nickel and copper* sulphides. Filter the acetic acid solution, wash the residue and suspend it in hydrogen sulphide water containing hydrochloric acid, whereby the remainder of the manganese and the zinc will be dissolved. The nickel, cobalt and copper sulphides will be insoluble. Expel the hydrogen sulphide from the hydrochloric acid solution of the zinc and manganese, and separate these by boiling the solution with potassium hydrate. Add the slight precipitate of manganous hydrate thus produced to the acetic acid solution of the sulphide. Precipitate the manganese from its solution either in the form of sulphide or carbonate (p. 21).

After acidifying the alkaline filtrate with acetic acid, precipitate the zinc with hydrogen sulphide, and determine it as sulphide.

The sulphides of nickel, cobalt and copper, that were insoluble in hydrochloric acid, may be dissolved in a mixture of hydrochloric and nitric acid. Evaporate the nitric acid and precipitate the copper with hydrogen sulphide. After getting rid of the hydrogen sulphide in the filtrate, throw down the nickel and cobalt with potassium hydrate. These metals occur in such slight quantities that it appears perfectly useless to separate them. This may be done according to the method given on page 104.

The quantity of iron in cast iron is usually calculated by difference. For its direct determination a portion of the hydrochloric acid solution may be titrated either with potassium permanganate (p. 75), or stannous chloride (p. 80). In employing the first method, it is advisable

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* The copper is estimated in another sample of the iron. (See p. 217.)

to boil the dilute solution for some time, because it has absorbed hydrocarbons, which may readily decompose the permanganate, and then evaporate it to dryness with sulphuric acid. It is, of course, understood, that the solution, before titration with permanganate, is reduced by zinc.

The alkaline earths are present in the filtrate from the ammonium sulphide precipitate. Acidify the solution with hydrochloric acid, evaporate it to dryness, expel the ammoniacal salts by ignition, and separate the calcium and magnesium in the solution of the residue, according to the method given on page 32.

Separate Determination of the Manganese.

Very frequently in the analysis of cast iron the estimation of the manganese alone is required, and then an exceedingly short course may be pursued. The method of procedure is very plain, if we remember the previously described separation of iron and manganese. When the silicic acid has been removed, add hydrogen sulphide to the filtrate. Boil the filtrate from the copper sulphide to expel the excess of hydrogen sulphide, oxidize the iron with nitric acid or potassium chlorate, and precipitate it as previously directed. Concentrate the filtrate and get rid of the aluminum by a second precipitation with ammonium hydrate, and then add ammonium sulphide. Generally the quantities of cobalt, nickel, and zinc present are so small that the obtained manganese sulphide can be directly weighed. When the contrary is the case, suspend the precipitate in water strongly acidified with hydrochloric acid, and saturate with hydrogen sulphide water (p. 104). The manganese is reprecipitated as sulphide in the filtrate from the cobalt and nickel sulphides. The ignited precipitate must be examined for zinc.

For such an examination use 2–3 grms. of iron.

If we use sodium acetate instead of ammonium carbonate for the separation of iron from manganese, the latter may be precipitated as the hydrate of the binoxide, by means of bromine, and then determined as protosesquioxide (p. 137).

The separation of iron from manganese by precipitation with sodium acetate, as already intimated (p. 214), is not as accurate as with ammonium carbonate, because a portion of the manganese remains behind with the iron acetate. Therefore, when great accuracy is desired, the precipitate, after being imperfectly washed, is redissolved in hydrochloric acid, and the precipitation repeated.

Determination of Copper, Arsenic and Antimony. (Phosphorus.)

Dissolve about 10 grms. cast iron in aqua regia, in a large flask, and when there is no longer any visible action, evaporate the whole to dryness upon a water-bath, and heat the residue with dilute hydrochloric acid. The portion insoluble in aqua regia is fused with soda and saltpetre, and the aqueous solution of the fused mass added to the hydrochloric acid solution. After the reduction of ferric chloride and arsenic acid to ferrous chloride and arsenious acid, with sulphurous acid or potassium hyposulphite, the liquid is saturated with hydrogen sulphide gas, and the sulphides obtained filtered off. Digest the precipitate with potassium sulphide; the arsenic and antimony will be dissolved. They may be reprecipitated and determined according to page 165. The copper sulphide that remains insoluble is washed with water containing hydrogen sulphide, ignited in a stream of hydrogen, and weighed (p. 50).

When, in a complete analysis, copper, arsenic, etc., have been determined, the filtrate from the hydrogen sulphide precipitate may serve for the estimation of the phosphoric acid ; otherwise, a shorter course, described below, may be chosen. The expulsion of the hydrogen sulphide gas may be hastened by conducting carbon dioxide through the heated liquid, which is then mixed with ferric chloride sufficient to unite with all the phosphoric acid, the solution neutralized with sodium carbonate and solid barium carbonate then added. The precipitation should be performed in a flask that may be closed, and this allowed to stand until the supernatant liquid has become colorless. Filter off the precipitate, consisting of iron phosphate and hydrate, barium carbonate, etc., and dissolve it in the smallest quantity of hydrochloric acid possible, and after the removal of the barium with dilute sulphuric acid, precipitate the phosphoric acid in the filtrate with ammonium molybdate. (See p. 25.)

Sulphur Determination.

Performed exactly as described on page 134.

By the action of the bromine upon the hydrocarbons liberated when the iron is dissolved, reddish-yellow oil-drops of propylene bromide,* etc. are produced. These disappear upon the subsequent boiling of the liquid.

Fresenius, in his sulphur determinations, conducts the hydrogen sulphide and hydrocarbons, formed by the action of hydrochloric acid upon the substance, into an alkaline lead solution, and uses for this purpose the apparatus pictured in Fig. 17.

In K is introduced the weighed quantity of iron, and

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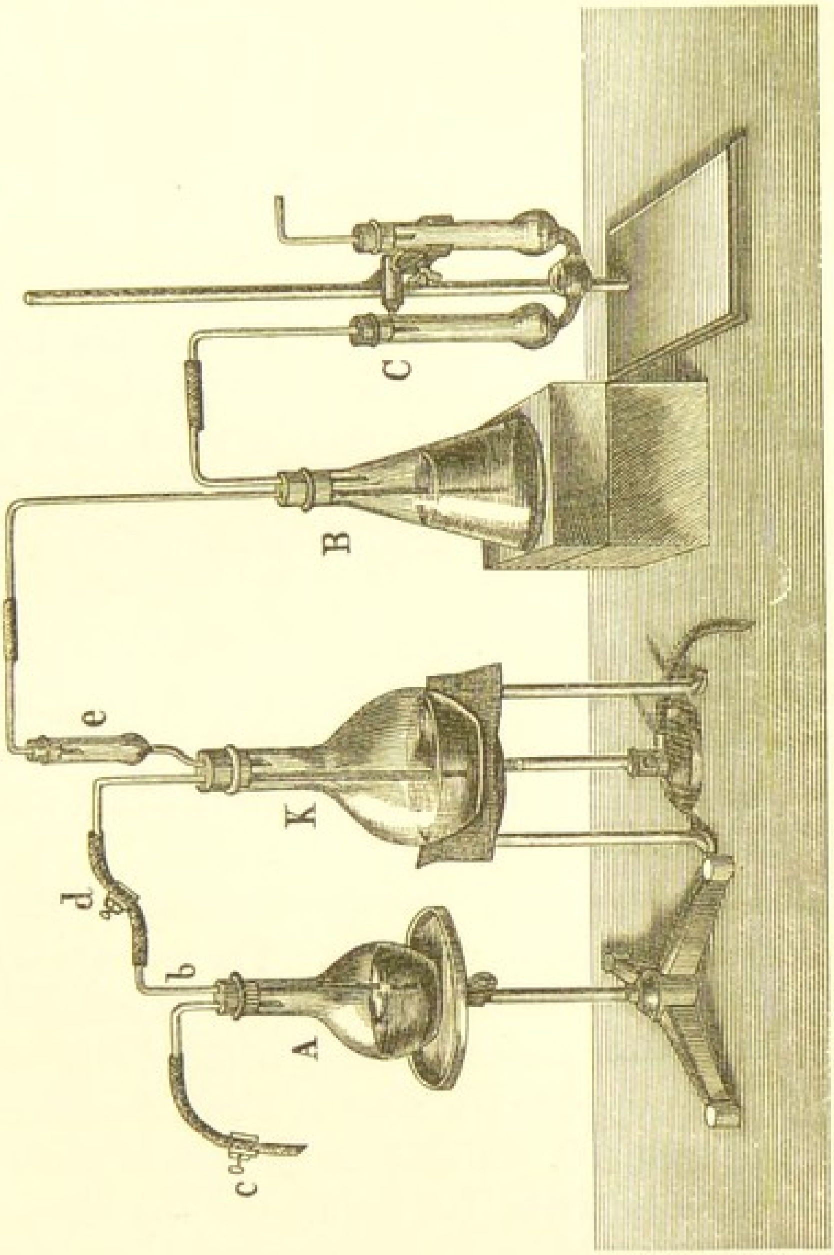
* Cloez, Berichte der deutschen chem. Gesellschaft, vii. 823.

water poured over it. A contains the hydrochloric acid serving for the solution of the iron. B and C contain a solution of lead oxide in potassium hydrate. Draw the tube *b* out of the liquid, open the pinch-cock at *c*, and fill

Fig. 17.



the entire apparatus with hydrogen gas purified by mercuric chloride and soda lime. This done, push the tube *b* into the liquid and open the pinch-cock again at *c*, which will cause a quantity of acid in A to flow over into

K; then close the pinch-cock at *d*, and hasten the solution of the iron by the application of heat. When there is not a sufficient quantity of acid present, open the pinch-cocks again at *c* and *d*, and proceed as heretofore. When the solution is complete, remove the tube *b* from the liquid, and allow a current of hydrogen gas to stream through the apparatus, the solution in K at the same time being brought to ebullition.

The lead sulphide in B and C is filtered, and the dried precipitate fused with soda and saltpetre. The aqueous solution of the residue contains the sulphuric acid. To remove the small quantities of lead that have been dissolved, pass a stream of carbon dioxide through it, acidify the filtrate with hydrochloric acid, and evaporate to dryness. In the aqueous solution of the residue, acidulated with hydrochloric acid, precipitate the sulphuric acid with barium chloride.

As it is very possible, in cases of difficultly soluble iron, that the liquid in B will be acid from the acid mechanically carried over, and that there will be a partial solution of the lead sulphide, Fresenius suggests that a horizontal cooler be connected with the flask K.

Gintl recommends the following method for the determination of sulphur in cast iron. The pulverized iron is mixed with twenty times its quantity of a rather concentrated and almost neutral solution of ferric chloride, then digested from eight to ten hours at a temperature ranging from 25° to 30° C. Almost all the iron is dissolved as ferrous chloride, whilst the residue consists of undecomposed iron, graphite, and iron phosphate, with all the sulphur. Filter the residue, wash, and fuse it in a silver crucible with a mixture of three parts saltpetre and one part alkaline hydrate. After acidifying the aqueous extract with hydrochloric acid, estimate the sulphuric acid as heretofore.

Phosphorus Determination.

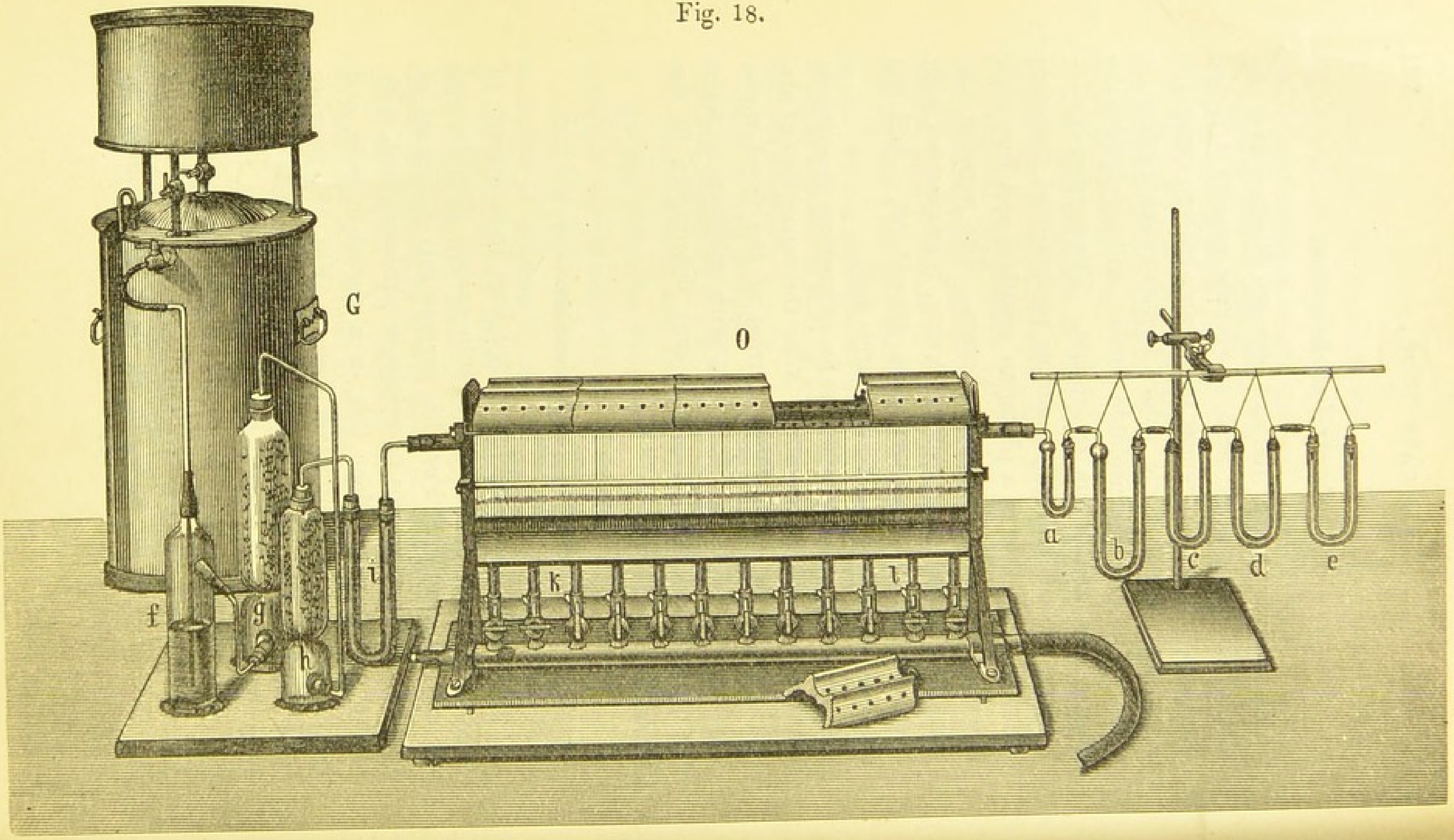
About five grms. of the cast iron are digested in a platinum dish with nitric acid of specific gravity 1.2, and then evaporated to dryness on a water-bath to cause the separation of the silicic acid. Dissolve the residue in nitric acid, filter the insoluble portion, and precipitate the filtrate with ammonium molybdate. The portion insoluble in nitric acid usually contains phosphorus; therefore incinerate the filter in a platinum crucible, and fuse with an equal weight of soda and saltpetre. The aqueous extract of the fused mass, after filtering, is evaporated with hydrochloric acid, and the silica filtered off. Add the aqueous solution to the first in nitric acid.

Gintl follows the same course in estimating phosphorus that he proposes for sulphur. After the separation of the silicic acid from the aqueous extract of the fused mass, the residue is dissolved in water, with addition of some nitric acid, and the phosphoric acid determined in the filtrate from the silicic acid.

Carbon Determination.

By burning the finely pulverized iron in a stream of oxygen the carbon is converted into carbon dioxide, and directly determined. For this purpose mix 4–5 grms. of iron in a rather spacious porcelain or platinum boat, with coarse cupric oxide; place this in a porcelain tube, and lay the latter in a combustion oven O (Fig. 18), serving for the analysis of organic compounds. The ends of the tube should extend beyond the oven. Connect the one end with the gasometer G, containing oxygen, the other with the tubes *a*, *b*, *c*, *d*, *e*. The oxygen, before entering the tube, passes through the vessels *f*, *g*, *h*, and *i*, of

Fig. 18.



which *f* contains concentrated potassium hydrate, *g* pumice stone moistened with concentrated sulphuric acid, *h* potassium hydrate in solid form, and *i* calcium chloride. The small U-shaped tube *a* is filled with small pieces of glass, moistened with about twenty drops of a saturated solution of chromic acid. The latter serves, upon the one hand, to decompose the sulphurous acid produced, and, upon the other, to enable the operator to observe the course of the analysis; *b* contains calcium chloride; *c* and *d* are five-sixths filled with soda-lime, and one-sixth with calcium chloride. (See p. 35.) These absorb the carbon dioxide, and are weighed before the analysis.*

To prevent carbon dioxide or water from entering the front portion of the tube, it is provided with the tube *e*, one limb of which, pointed towards the apparatus, is filled with potassium hydrate, the other with calcium chloride (p. 35).

When the various parts of the apparatus have been connected, the porcelain tube from *k* to *l* is warmed gently, and a stream of oxygen gas allowed to pass slowly through it. When the tube is once warm, the heat may be rapidly increased to an intense glow. When the iron glows, all the oxygen will be required for its oxidation, and during this time scarcely any gas-bubbles will be noticed in the tube *a*. When the oxidation is complete, the combustion of the carbon to dioxide will begin, and a regular stream of gas passes through the liquid in *a*. Ignition for a quarter of an hour will complete the combustion.

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* When the carbon dioxide, mixed with air or oxygen, is to be absorbed, soda-lime is preferable to potassium hydrate, because it may readily happen, when the oxygen is in preponderance, a portion of the carbon dioxide will not be absorbed.

The increase in weight of the tubes *c* and *d* will indicate the amount of carbon dioxide produced, and from this the quantity of carbon may be very readily calculated.

As already above mentioned, when employing this method the iron should be in a very fine condition. To obtain it in this form is a matter of no very little difficulty with certain varieties of iron. When the latter is the case the iron is dissolved in some suitable manner, and the carbon in the residue determined. Of the various methods recommended for this purpose, I will describe but three, which are convenient and reliable.

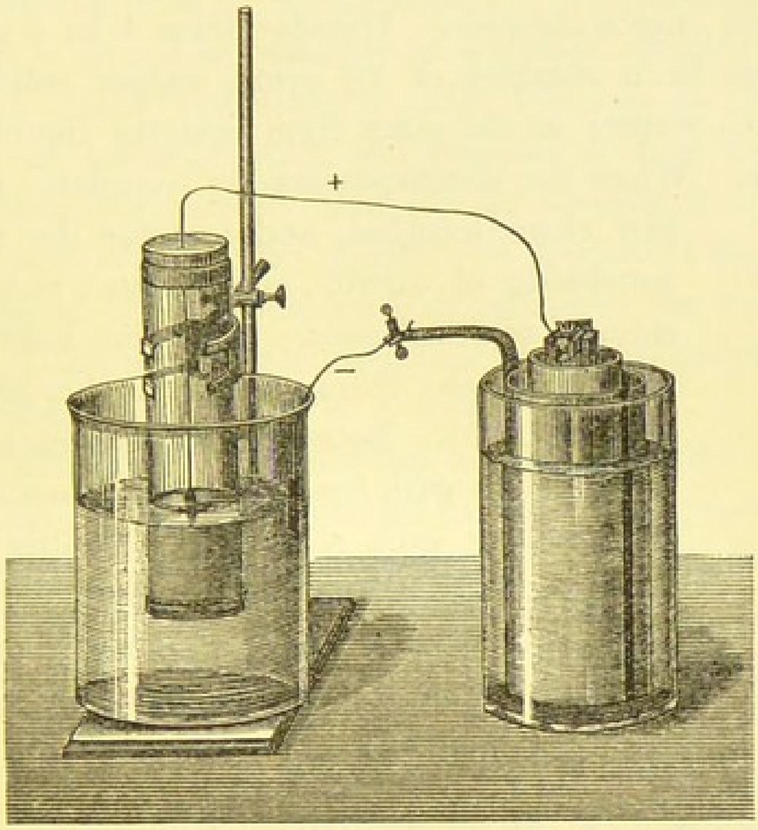
First Method.—Weyl found, that, if iron was dissolved in an electrolytic manner in hydrochloric acid, and when it served as the positive electrode, an amount of hydrogen equivalent to that of the iron would separate out at the negative pole. Suppose, that only a weak current was used in this decomposition, the iron would exist in solution in the ferrous state, whilst if the opposite were the case ferric chloride would be produced, and carbon would be separated at the negative pole.

Over the other two methods this one possesses one great advantage, viz., that entire pieces of iron may be used for solution.

A Bunsen "element" serves for the decomposition. A weighed piece of iron is attached with the aid of a platinum wire or a pincette to the wire of the positive pole and these immersed in a glass jar filled with dilute hydrochloric acid (Fig. 19). The jar, closed at the lower end with a bladder, is placed in a beaker-glass containing the same acid. Care must be taken to have the liquid in the glass jar and that surrounding it of the same level and not to allow the platinum point or wire to dip into the acid, because the current will be interrupted by the carbon separated out between the iron and platinum point.

A piece of platinum foil will answer splendidly as negative electrode, and may be attached just as the iron to the wire of the negative pole and dipped at the same moment with it into the hydrochloric acid. Solution commences immediately, and by bringing the electrodes near each other

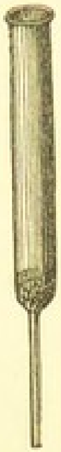
Fig. 19.



or removing them, the current may be so regulated that the iron will be dissolved only as ferrous chloride. The formation of ferric chloride is easily perceived by the yellow-colored threads dropping from the iron, and then the stream must be diminished, to obviate any loss of carbon. When, after the expiration of a few hours, a sufficient quantity of iron has been dissolved, remove the carbon adhering to the piece of iron, and after drying reweigh it. Collect the carbon upon a funnel loosely closed with ignited asbestos, and, after washing and drying, mix it with cupric oxide and burn in a stream of oxygen, just as above directed.

Second Method.—By suspending coarsely divided iron in a neutral solution of cupric chloride, the iron will be dissolved as ferrous chloride and the carbon remain behind. (Berzelius.) Ullgren has substituted copper sulphate for cupric chloride. Dissolve from 4 to 5 grms. of cast iron in a solution of 20 grms. copper sulphate in 100 C. C. water; at the same time heat the liquid gently and stir. When the decomposition is complete, pour off the clean solution, and transfer the residue, consisting of carbon, copper, etc., to a funnel stopped with asbestos. Berzelius used an apparatus of the form shown in the adjoining cut (Fig. 20). Below at the contracted part it is filled in with loosely placed asbestos. By constructing such a tube of difficultly fusible glass, the carbon may be immediately mixed with cupric oxide and the latter placed in a porcelain tube. The combustion is performed as heretofore.

Fig. 20.



Third Method.—To effect the solution of the iron Wöhler uses iodine; suspending the first in water and adding iodine gradually (for 5 grms. iron about the same amount of iodine). When the decomposition is complete, the residue is filtered through asbestos and burned in an oxygen stream.

Recently bromine has in many instances replaced iodine for this purpose. This is, however, less adapted to effect solution, the results obtained, generally being too low, and the reason for this may be readily explained by the formation of propylene bromide. (See p. 218.)

Graphite Determination.

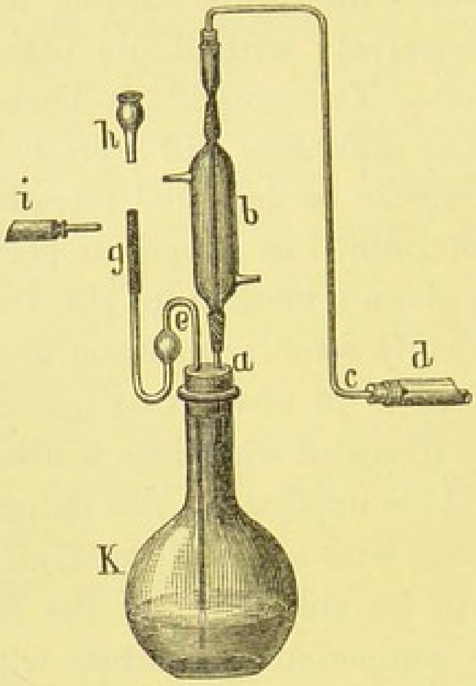
Carbon, as is known, exists in iron partly chemically united with it and partly as graphite. The latter remains insoluble, when the iron is dissolved in hydrochloric or sulphuric acid, whilst the chemically combined carbon escapes in the form of hydrocarbons. To determine the quantity of graphite, dissolve a weighed quantity (3–5 grms.) in dilute hydrochloric acid, filtering the residue through an asbestos filter, and washing it, first with hot water, then successively with dilute potassium hydrate, alcohol and ether. The graphite is burned in a current of hydrogen. The difference will represent the combined carbon, if the graphite be deducted from the entire quantity of carbon determined in a separate portion.

Fresenius has given a method for the direct determination of the chemically combined carbon in the presence of graphite. It consists in converting into carbon dioxide, the hydrocarbons liberated when iron is dissolved in dilute sulphuric acid. It is implied, in this determination, that, when iron is treated with sulphuric acid, all the chemically united carbon will be volatilized in the form of hydrocarbons, and no compounds of carbon will remain with the graphite. Before employing the method be satisfied that the residue remaining after treating the iron with dilute sulphuric acid and washing with hot water contains no hydrocarbons soluble in potassium hydrate, alcohol or ether. This is readily noticed because in using potassium hydrate it will be colored brown, and if alcohol or ether have been employed it would be noticed by the residue of organic matter remaining after these solutions have been evaporated to dryness.

The apparatus of Fresenius (somewhat modified) consists of the following parts (Fig. 21):—

K is a small flask of about 150 C. C. capacity, having a doubly perforated cork admitting the tubes *a c* and *e g*; *a c* is connected with the vertical cooler *b*. The funnel tube *e h* is severed at *g*, and may be either united with the funnel *h* or with the tube *i* containing soda-lime. The combustion tube *d* is attached at *c*. It is about 30 centimeters long and at the end directed towards *c*, half-filled with asbestos that has been well ignited. Behind the asbestos follows a layer of well-ignited, coarse-grained cupric oxide and finally an asbestos stopple. To catch the water and carbon dioxide, the end of the tube opposite *c* is joined with a calcium chloride tube, this with a weighed tube containing soda-lime and finally with one containing soda-lime and calcium chloride. This last tube serves solely to prevent the entrance, from without, of steam and carbon dioxide into the weighed soda-lime tube (p. 35).

Fig. 21.



The portion of the combustion tube *d* containing the cupric oxide is heated until it glows, and the weighed portion of iron, 1–1.5 grms., introduced in the flask K; *h* connected with *g*, and a sufficient quantity of dilute sulphuric acid (1 part sulphuric acid and 5 parts water) allowed to pass into K, and the funnel replaced by the tube *i*.

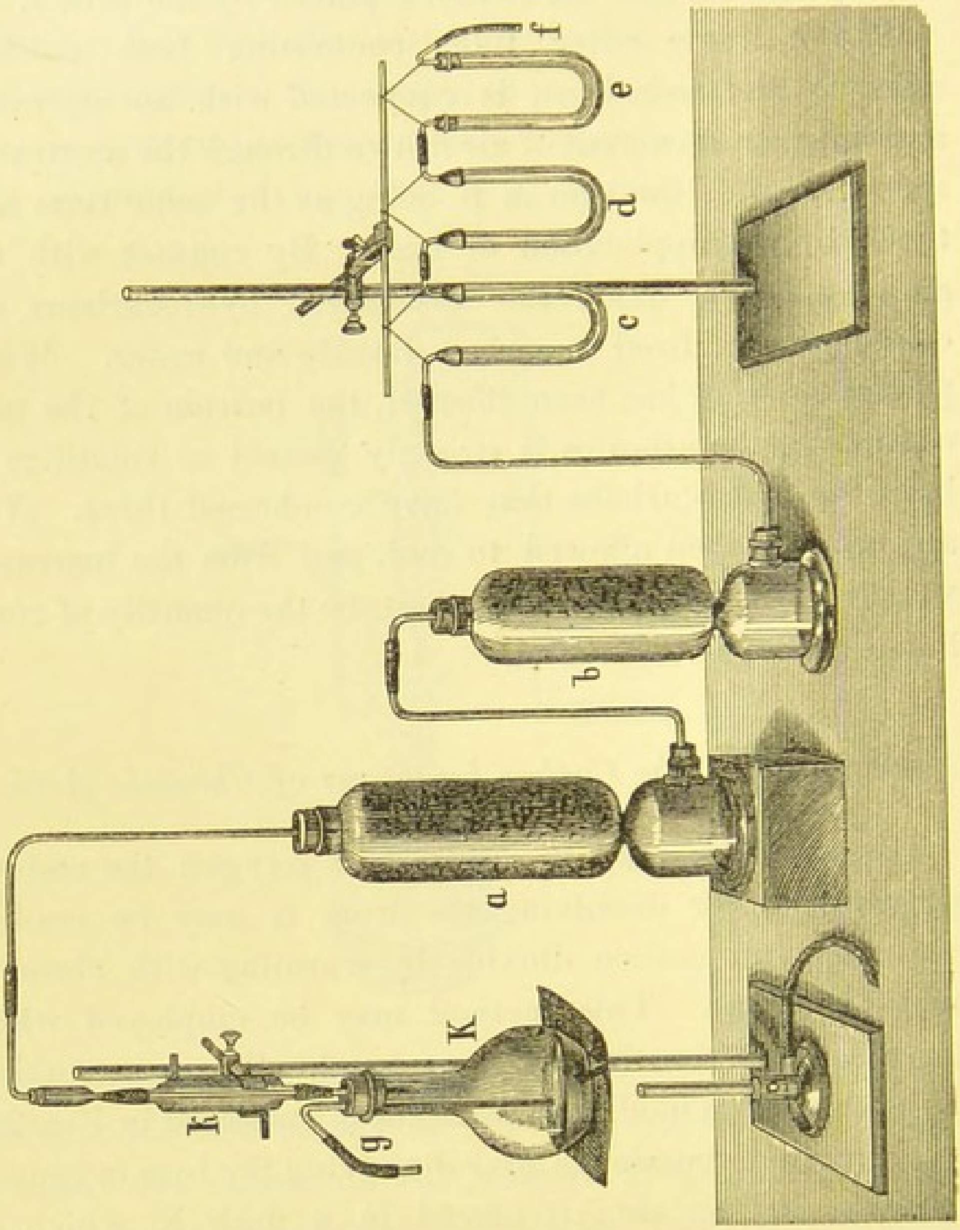
The extreme outer tube, containing both calcium chloride and soda-lime, is connected with an aspirator, and a constant current of air drawn through the apparatus, the solution of the iron in K being at the same time hastened by the application of heat. By contact with the glowing cupric oxide the disengaged hydrocarbons are completely oxidized to carbon dioxide and water. When perfect solution has been effected, the portion of the tube containing the asbestos is strongly ignited to volatilize or burn the hydrocarbons that have condensed there. The apparatus is then allowed to cool, and from the increased weight of the weighed soda-lime tube the quantity of combined carbon is calculated.

Oxidation of the Carbon by means of Chromic Acid.

Instead of burning in a stream of oxygen the residue remaining after dissolving the iron, it may be readily converted into carbon dioxide by warming with chromic acid (Ullgren). This method may be employed when there is no combustion oven at hand. The construction of the somewhat modified apparatus is indicated in Fig. 22.

The carbon remaining after dissolving the iron in copper sulphate, iodine, etc., is placed in a flask K, which is closed at *g* during the operation with a glass rod. Pour in about 40 C. C. of concentrated sulphuric acid, and after cooling add 8 grms. crystallized chromic acid. The carbon dioxide first passes the vertical condenser *k* (serving to condense the steam), then the jar *a*, containing pieces of pumice-stone saturated with sulphuric acid, and the calcium chloride flask *b*: *c* and *d* are the soda-lime tubes intended for the absorption of the carbon dioxide; *e* a protecting tube filled with soda-lime * (p. 35) and calcium chloride.

Fig. 22.



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* Ullgren employs pumice stone filled with potassium hydrate for the absorption of the carbon dioxide. The substance is prepared by dissolving 1 part potassium hydrate in 3–4 parts water, and adding, while constantly applying heat, small pieces

The contents of the flask are heated until there is a violent liberation of gas, and the temperature gradually increased until white vapors are visible in the cooler K. The heating is continued as long as gas liberation is perceptible, the lamp then removed, *f* connected with an aspirator and some air drawn out. The glass rod at *g* is replaced by a potassium hydrate tube, after pushing the glass tube, bent at right angles, into the liquid. Air is drawn through the apparatus for some time, and the tubes *c* and *d* finally reweighed.

Colorimetrical Determination of the Combined Carbon.

Eggertz has proposed a method for the determination of the combined carbon in cast iron and steel, which is based upon the fact that iron dissolved in nitric acid gives the solution a color more or less brown, in proportion to the amount of combined carbon present. For the purpose of comparison a solution of iron with a known amount of carbon will answer. The concentration is so arranged that every cubic centimetre contains as much carbon as will correspond to 0.1 per cent. carbon in iron. As these solutions lose their color very readily, Eggertz substitutes for them a solution of caramel in dilute alcohol, or an extract of burnt coffee in alcohol and water. These have the same color (see below). 0.1 grm. iron is now dissolved in a test-tube in 1.5–5 C. C. nitric acid of sp. gr. 1.2, and when solution is effected heated to about 80° C. on the water-bath. If the solution is complete, the cool, clear liquid is poured into a graduated tube, and the insoluble residue again treated with nitric acid until there is

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of pumice-stone, and finally evaporating the mixture almost to dryness. The pumice-stone, saturated with potash while yet hot, is introduced into the tubes.

no longer any liberation of gas. The solutions are united and diluted with water until the color is the same as that with which they are to be compared.

Britton has modified the Eggertz method in the following manner: A weighed portion of the finely divided iron (when there is present 0.3 per cent. carbon, take 1 grm. substance, and when the percentage is higher take less—not more than 0.5 grm. substance) is heated in a test-tube with 10 C. C. nitric acid, free from chlorine—sp. gr. 1.2—and after standing 10 to 15 minutes the clear solution is decanted and the residue again digested with 5 C. C. of nitric acid of the same strength until the iron is completely decomposed. The solutions are filtered through a dry filter and poured together in a reagent tube 12 Cm. long and 1.5 Cm. wide. For a comparison of the tints of color take 15 test-tubes of similar dimensions as the one above, and introduce into them different extracts of roasted coffee, water and alcohol, so that the tint in color of the first tube will correspond to that of 1 grm. of iron containing 0.02 per cent. of chemically combined carbon and dissolved in 15 C. C. of nitric acid, that of the second to a solution containing 0.04 per cent. carbon, that of the third to a solution containing 0.06 per cent. carbon, and the color tint of the 15th tube is equivalent to 0.3 per cent. of chemically combined carbon. These tubes are hermetically sealed and so arranged in a rack that between each two is sufficient room to stand the tube containing the solution to be tested.

According to Britton's experiments we can accurately estimate with this method the amount of carbon in iron to within 0.01 per cent.

Determination of the Nitrogen.

1. Determination of the nitrogen which is converted into ammonia when the iron is dissolved in hydrochloric acid.

In this determination the iron is placed in a tubulated retort and dissolved in hydrochloric acid, and the escaping gases conducted through a **U**-shaped tube partially filled with dilute hydrochloric acid. The latter operation has for its object the conversion of the ammonia escaping with the disengaged gases (hydrogen and hydrocarbons) into ammonium chloride. When the solution is finished pour the contents of the **U** tube back into the retort, and after adding sodium or potassium hydrate, subject the whole to distillation. (See p. 37.)

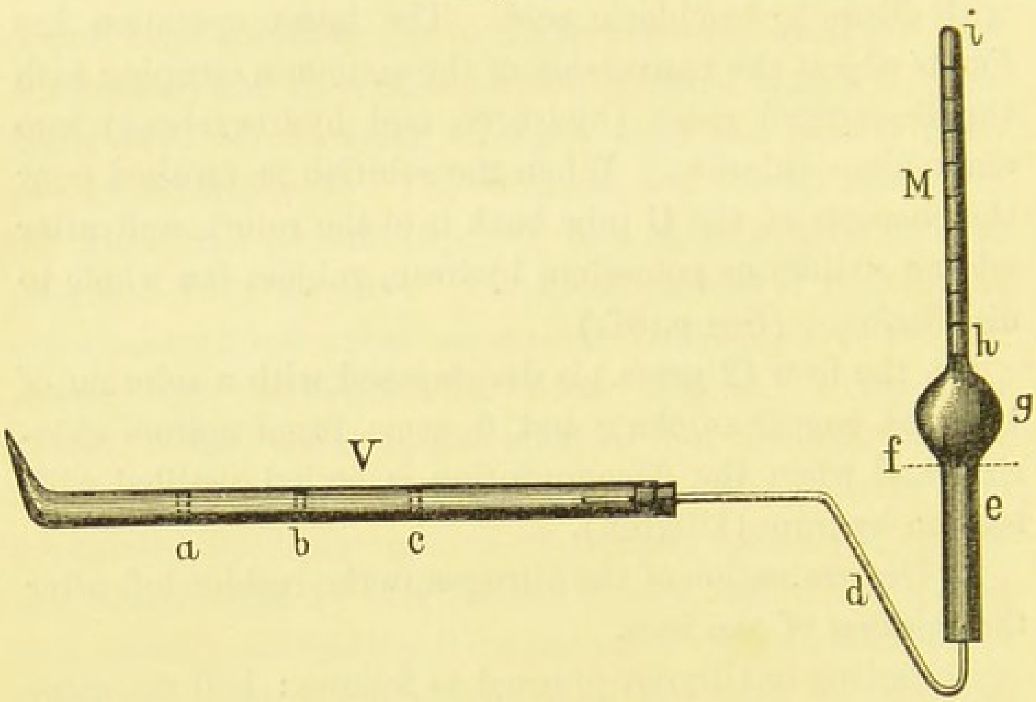
Or, the iron (2 grms.) is decomposed with a solution of 10 grms. copper sulphate and 6 grms. fused sodium chloride, and when the decomposition is ended distilled with sodium hydrate (Ullgren).

2. Determination of the nitrogen in the residue left after the solution of the iron.

According to Ullgren proceed as follows: Fill the combustion-tube (V) (see Fig. 23), 30 Cm. in length, to *a* with about 12 grms. of magnesite or sodium hydrocarbonate, place a loose stopple of asbestos next, and introduce from *a* to *b* the insoluble residue from the iron, dried at 130° C. and mixed with about 4 grms. of mercuric sulphate. Another stopple of asbestos is placed at *b*, and from *b* to *a* the tube is filled with coarse pumice-stone powder, which was previously mixed with mercuric sulphate and water, and afterwards dried. Finally, the anterior portion of the tube, after adding another asbestos layer, is filled with coarse pieces of pumice-stone saturated with a concentrated chromic acid or potassium chromate solution. This is intended to decompose the sulphurous acid that may be formed.

The combustion-tube is connected by *d* with a graduated tube M filled with mercury, and inverted in a mercury bath. The entire capacity of M is about 90 C. C.; the tube *i h*, divided into $\frac{1}{10}$ C. C., holds about 20 C. C., the bulb-portion about 40 C. C., and the lower extremity *e* about 30

Fig. 23.



C. C. 35–40 C. C. of a potassium hydrate solution (1 part potassium hydrate in 2 parts water) are now introduced into M by means of a bent pipette, and then 15 C. C. of concentrated tannic acid added, so that the mercury will stand about *f*. The air contained in the apparatus is expelled by heating the portion of the tube containing the magnesite, at the same time conducting the gas evolved into M. The portion *a b* is heated gently at first, while *b c* is in the mean time brought to a glow. When this point has been reached, the part *a b* is rapidly brought to a red heat, and held in this condition until the column of liquid in M no longer sinks. The final traces of nitrogen contained in the combustion tube are expelled by reigniting the magnesite. Remove the tube *d*, and with a small porcelain dish filled with mercury transfer the tube M to a tall and wide jar containing water, which will displace the mercury, potassium hydrate and tannic acid. Close the tube with the thumb or a gum cork, incline it, and rinse out the potassium hydrate that may yet remain in the upper portion of the tube. After allowing the tube to remain 15 or 20 minutes in the jar ascertain the temperature, note the barometer-stand, then elevate the tube with tongs until the liquid in M has the same niveau with that of the jar, and read off the volume of nitrogen.

Representing the volume of nitrogen read off by V, and the volume of the same at 0° C. and 760 Mm. barometric pressure by V′, and the barometer in millimetres by B, the temperature of the water according to Celsius by t, and the tension of the steam in millimetres by f, dependent upon the observed temperature, we have

$$V' = \frac{V(B - f)273}{760(273 + t)}.$$

Well, Spring and River Water.

According as these waters are used for domestic or practical purposes the analysis extends itself merely to the estimation of certain constituents. In the examination of a drinkable water the estimation of the iron, calcium, magnesium, alkalies, sulphuric, hydrochloric, nitric and nitrous acids (carbon dioxide), ammonia, organic substances, and the quantity of solid material usually come into consideration, whilst in the analysis of water for industrial purposes the determination of the alkaline earths (of the total and permanent hardness), ferrous oxide, sulphuric and hydrochloric acids, and the entire amount of substances is of interest.*

Determination of the Amount of the Solid Constituents, of the Ferrous Oxide, Calcium Oxide, Magnesia and Alkalies. —500 or 1000 C. C. water (still larger quantities when spring and river water are taken) are evaporated upon a water-bath in a weighed platinum dish. The residue is dried at 120° to 125° C., either in an oil or air-bath until constant weight is obtained. Pour water over the dried mass, adding hydrochloric acid to effect the complete solution. The dish is covered with a large watch-glass. Heat until bubbles of carbon dioxide no longer escape from the liquid, remove the cover, and again evaporate to dryness. By subsequent treatment of the residue with dilute hydrochloric acid, any silicic acid present will remain insoluble, and can be filtered, washed, dried and weighed.

For the precipitation of the ferric oxide the filtrate is mixed with ammonium hydrate to alkaline reaction, the precipitate filtered off and dissolved after being imperfectly washed, and the precipitation repeated. This second precipitation is absolutely necessary, because, especially in waters containing much calcium, the carbonate of the latter is invariably thrown down together with the ferric oxide.

The precipitate produced by ammonium hydrate contains not only silicic acid, but also aluminum and phosphoric acid. The quantitative determination of these latter constituents is in the present instance not necessary, while, upon the other hand, under many circumstances (especially when the water is employed for certain technical purposes)

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* For the determination of all the constituents, see Analysis of Mineral Water.

the determination of the iron in this precipitate is very important. Dissolve the precipitate, therefore, in sulphuric acid and determine the iron volumetrically after reducing it to the ferric state (p. 75). It is necessary that a very dilute solution of potassium permanganate be employed for estimating such small quantities of iron. A solution in which 1 C. C. corresponds to 0.001 grm. iron may be used. In well waters, containing large quantities of iron, the latter may be directly determined by adding potassium permanganate to the freshly-drawn water, acidified with sulphuric acid. In this instance it must also be ascertained how much permanganate would be required to color red a volume of distilled water equal to that employed, and this quantity subsequently deducted. The filtrate from the ferric oxide is mixed with an excess of ammonium oxalate or oxalic acid, the calcium oxalate filtered off and determined according to page 13.

To separate the magnesium from the alkalies, evaporate the filtrate to dryness in a platinum dish, and gently ignite the residue (p. 45). For the perfect separation of the magnesia, the filtrate is again evaporated, and the ignition repeated with addition of ammonium oxalate or oxalic acid.

The alkalies are determined by evaporating their solution to dryness with sulphuric acid upon a water-bath. By ignition the sulphuric acid and the ammonium salts are expelled. Finally (to convert the hydrosulphates into neutral sulphates) pieces of ammonium carbonate are added (p. 46). The sulphates are then weighed. To estimate the amount of potassium in the presence of sodium, proceed according to page 47 (Remark).

In the examination of water for technical purposes, certain inferences are drawn from the quantitative determinations of the calcium and magnesium oxides, and we then merely ascertain how much soap solution of known strength will be required for the decomposition of a measured quantity of water, or, as it is usually expressed, what *hardness* the water under consideration possesses.

If water, containing salts of the alkaline earths in solution, be mixed with a soap solution, these will separate as insoluble compounds of the fatty acids, and the acids previously combined with the alkaline earths, now united with alkali, will pass into solution. As soon as this replacement is complete, a lather is produced on shaking the solution, if the slightest excess of soap is present. This indicates the final reaction.

The units (amount) of calcium oxide (CaO) contained in 100,000 parts of water are termed the *degree of hardness.* Water, therefore, indicating 15 degrees of hardness, contains in 100,000 parts 15 parts of calcium oxide (or its substitute, magnesia), united with sulphuric, nitric, and hydrochloric acids or with carbon dioxide.

As is known, by boiling the water the greater portion of the carbonates (by the decomposition of the hydrocarbonate) will be precipitated, whilst the sulphates and chlorides will remain in solution. Therefore we speak of a *total hardness*, which is represented by the entire quantity of alkaline earths present, and of a *remaining* (*permanent*) hardness, which is indicated by the earths, which continue in solution after boiling. The difference between the two is the *temporary hardness*, which would approximately represent the amount of carbonates (hydrocarbonates) in the water.

Determination of the Total Hardness. Clark's Method.—As a normal liquid a soap solution will answer in which 45 C. C. will correspond to 12 Mgrms. calcium oxide dissolved in 100 C. C. H_2O. The soap suitable for this purpose is made by rubbing together 150 parts lead plaster with 40 parts of potassium carbonate. The mass is extracted with alcohol, filtered, the filtrate evaporated to dryness on the water-bath, and the residue dissolved in alcohol. For every 2 parts of the soap, take 100 parts of dilute alcohol (56° Tr.).

A solution of barium chloride will serve for the standardization of this soap solution. Dissolve 0.523 grm. of dry barium chloride in water, and dilute to 1 litre; then transfer 100 C. C. of this solution to a glass vessel provided with a cork, and having a capacity of 200 C. C., and allow the soap solution to pass in from the burette, until upon shaking the liquid there remains a permanent lather. The soap solution is then diluted with so much alcohol, that the production of a lather in 100 C. C. of the barium chloride will require 45 C. C. of the former. Then 45 C. C. will correspond to 12 milligrammes of calcium oxide in 100 C. C. of water.

For the estimation of the entire hardness of the water, proceed as in the standardization; pipette 100 C. C. of the above water into the glass provided with a cork, and add the soap solution gradually until the final reaction occurs. If the water under examination indicates more than 12 degrees of hardness, the end reaction is uncertain, and the titration must be performed in a more dilute solution. In this case take only 10 C. C. of the water, mixing with it distilled water to 100 C. C., and proceed as before.

Determination of the Permanent Hardness.—400 to 500 C. C. water are boiled for at least one half hour, and the evaporating steam continually replaced by distilled water. After cooling, the carbonates of the alkaline earths are filtered off, and the filtrate brought to the same volume as the originally employed liquid (400 to 500 C. C.). Take 100 C. C. to estimate the earths that may yet remain in solution, proceeding as previously directed. If we employ for the examination 100 C. C. of water, the tables of Faisst and Knauss given in the appendix afford a direct reading of the degree of hardness from the number of C. C. of the soap solution which has been used.

If, when determining the degree of hardness, we obtain a number not given in the table, take the number most nearly approaching it, and multiply the difference between the two by the fractions of a degree of hardness, which represent the difference of 1 C. C. of the soap solution. The product obtained is either subtracted from the degrees of hardness opposite the number taken in the table or added to it, according as the found C. C. of soap solution are deducted from those marked in the table, or the latter from the number of C. C. found by experiment. For example: 36 C. C. of soap solution have been used in one experiment; then the difference between 36 and $36.7 = 0.7$, which must be multiplied by 0.294; the product is 0.2058. In this instance we must deduct 0.2058 from 9.5, and obtain in consequence as the degree of hardness 9.2942. Or, 100 C. C. of water require 44 C. C. of soap solution, then $44 - 43.4 = 0.6$, to be multiplied by 0.31, and the obtained number then added to 11.5. The water corresponds, therefore, to $11.5 + 0.186 = 11.686$ degrees of hardness.

Determination of the Hydrochloric Acid.—It may be estimated either gravimetrically as silver chloride (p. 17) or volumetrically with silver nitrate, using potassium chromate as an indicator (p. 43). The amount of water used will depend upon the quantity of chlorides present. When very small quantities of the latter exist, it is necessary, particularly in the gravimetric determination, to previously concentrate the solution by evaporation.

Determination of the Sulphuric Acid.—Take 500 to 1000 C. C. water, depending upon the quantity of sulphates that may be present. Acidify the water with hydrochloric acid, and determine the sulphuric acid as barium sulphate. When upon testing qualitatively only a faint reaction for sulphuric acid has been obtained, the solution acidified with hydrochloric acid is concentrated before precipitation.

Where a comparison of different spring waters is desirable and great accuracy is not required, the sulphuric acid can be much more readily determined volumetrically. Take as a normal solution one containing 12.2 grms. barium chloride dissolved in 1 litre of water. A solution of potassium chromate of equal strength is also made. This is prepared by dissolving 7.365 grms. dry potassium bichromate in 100 C. C. of water. To this solution is added sufficient ammonium to convert the potassium bichromate into ammonium-potassium bichromate—the color of the liquid changing from red to yellow. Finally dilute to 1 litre. 1 C. C. of the barium chloride solution will correspond to 1 C. C. of potassium chromate. To carry out the method, first remove the carbonates of the alkaline earths by the continued boiling of the solution, replacing the escaping steam with distilled water, filter and precipitate the boiling solution with an excess of the normal barium chloride solution. 10 C. C. usually suffice for this purpose. The excess of barium chloride is titrated by potassium chromate. Pass the latter from a burette until the liquid over the precipitate appears slightly yellow. Tiemann[*] suggests that this slight necessary excess of potassium chromate be determined colorimetrically. The liquid is brought to a definite volume, about 150 C. C. (Tiemann effects the precipitation in a glass vessel provided with a mark), and 100 C. C. of the liquid, filtered through a dry filter, is transferred to a narrow jar of

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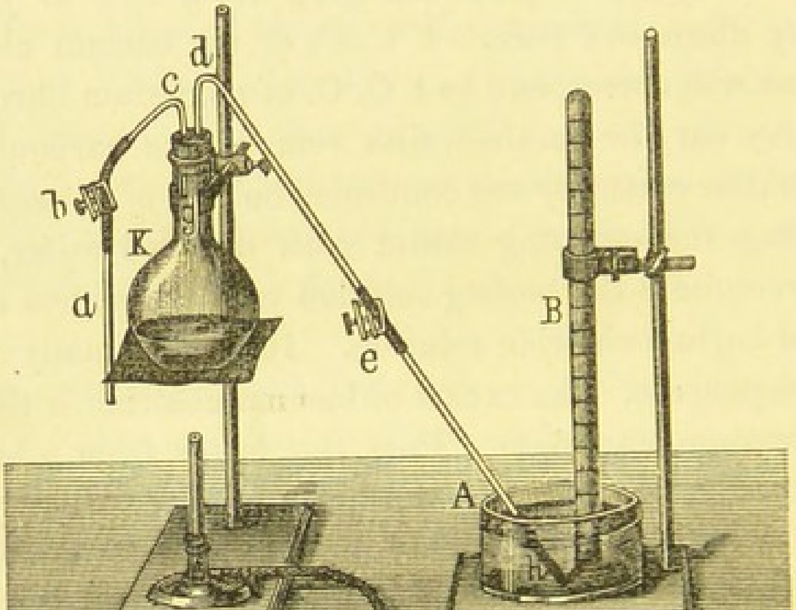
[*] Berichte der deutschen chem. Gesellschaft, 1873, p. 920.

colorless glass. Now, to 100 C. C. of water placed in another cylinder of similar dimensions as the first, add the normal chromate solution drop by drop, until the color tint agrees with that in the first tube. The amount of potassium chromate used which is equivalent to the excess of it taken in the first cylinder, is deducted from the entire number of C. C. taken for the titration of barium chloride.

Determination of the Nitric Acid. Tiemann's Modification of Schulze's Method.[*]—The method is based upon the decomposition of a nitrate by hydrochloric acid and ferrous chloride, and the measurement of the nitrogen oxide gas evolved :—

$$6FeCl_2 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 4H_2O + 2NO.$$

Fig. 24.



The apparatus shown in Fig. 24 is used for this purpose. K is a small flask containing about 150 C. C.,

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[*] See Berichte der deut. chem. Gesellschaft, 1873, p. 1041.

closed by a doubly perforated gum cork, one perforation of which contains *c g*, and the other the tube *d*. At *b* and *e*, both tubes are joined by means of closely fitting gum tubing to the tubes *a* and *e h*, and may be closed with pinchcocks. The bent end of the tube *e h*, to prevent its being broken, is covered with a piece of gum tubing. The tube *c g* about 2 Cm. below the cork (at *g*) is drawn out to a rather fine point, while the other tube is cut off immediately below the cork. A is a glass dish containing 10 per cent. sodium hydrate, B a narrow tube divided into $\frac{1}{10}$ C. C. and filled with sodium hydrate that was previously boiled.

100–300 C. C. of water are now concentrated in a porcelain dish to about 50 C. C., and the liquid together with the precipitate of the alkaline earths then rinsed into the flask K and boiled, and toward the close of the operation the tube *e h* is dipped into sodium hydrate, and the steam allowed to escape through it. If the air has been completely expelled from the apparatus, by pressing with the fingers upon the gum tube at *e*, the sodium hydrate will rapidly pass back in the tube *e h*, and this will be noticed by a gentle tap upon the finger pressed upon the gum connection. The pinchcock at *e* is closed and the boiling continued (the steam escapes through *g a*) until the residual liquid amounts to about 10 C. C. Remove the lamp, close the tube with a pinchcock at *b* and fill the limb *a b* with water. Notice whether air bubbles form at *b*, and remove them by pressing with the fingers upon the tube. The graduated tube B is now placed over the bent portion of the tube *e h*, so that the latter extends 2 to 3 Cm. into B. If a vacuum has formed in the flask K it will be noticed by the compression of the tubes at *e* and *b*, and then pour an almost saturated solution of 20 C. C. of ferrous chloride into a small beaker glass, dip the tube *a b* into it and let the liquid enter the flask through the opening at *b*. Through the same opening small quantities of concentrated hydrochloric acid are twice introduced and the pinchcock again closed. The flask is now gently heated until the tubes are somewhat distended at *e* and *b* by the pressure upon them, when the pinchcock is removed and the tube held shut with two fingers, until the pressure is sufficiently great to carry the nitric oxide into B. When the gas liberation diminishes, the flask is more strongly heated and this continued until the column of liquid in B no longer alters its niveau. At last nothing more than vapors of hydrochloric acid pass over and these are absorbed so violently by the sodium hydrate as to create a noise, similar to that noticed in the chlorine distillation according to Bunsen's method. The tube *e h* is now removed, and B is transferred by aid of a porcelain dish filled with concentrated sodium hydrate to a large glass cylinder containing water. (See p. 235.) By multiplying the C. C. of nitric oxide, calculated from the formula (p. 235), by 2.413, we obtain the corresponding number of milligrams of nitric acid (N_2O_5). By dividing this product by the number of C. C. of water used in the experiment, we obtain the quantity of nitric acid in 100,000 parts water.

This method is also applicable when the water has even large quantities of organic matter in solution. Care must be exercised that the water employed contains at least 3 milligrams of nitric acid. A rather large and measured quantity should be previously evaporated.

Determination of the Nitrous Acid. Trommsdorf's Method.—If the solution of a nitrite is mixed with potassium iodide, a starch solution and dilute sulphuric acid, there is produced the blue color of starch iodide,* which

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* $N_2O_3 + 2HI = 2I + H_2O + 2NO$.

is more or less intense according to the amount of nitrous acid present.

If different but measured quantities of a solution of potassium nitrite of known strength be added to equal volumes of distilled water, the conditions being the same, the iodine reaction can be induced by the addition of potassium iodide, starch and dilute sulphuric acid, and the quantity of nitrous acid in the water estimated by a comparison of the color tints.

As the starch solution of potassium iodide remains stable but for a short period, a starch solution of zinc iodide has frequently been made to replace it. The latter is put in closed vessels and kept in a dark apartment, where it will remain unaltered for quite a while.

Besides the starch solution of zinc iodide, there is required to carry out this method a solution of potassium nitrite of known strength.

To prepare the first, rub in a mortar 5 grms. of starch, together with a little water, and add the milky liquid to a boiling solution of 26 grms. of zinc chloride in 100 C. C. of water. Continue boiling the solution in a closed vessel until all the starch has been dissolved. 2 grms. of zinc iodide are now added, and the whole diluted to 1 litre, and filtered. Before making use of this solution, be satisfied that the addition of dilute sulphuric acid, after the previous dilution with water, causes no blue coloration.

The potassium nitrite solution is prepared by precipitating a concentrated solution of potassium nitrite with silver nitrate, and then filtering off the silver nitrite. The latter is washed, dissolved in the least possible amount of boiling water, and purified by recrystallization. 0.406 grm. of crystals dried between blotting paper are dissolved in hot water, and sodium or potassium chloride added until there is no longer a precipitate of silver chloride produced. The cold liquid without filtering off the silver chloride is diluted to 1 litre. When the precipitate has fully subsided, pipette out 100 C. C. of the clear solution, and dilute it with water to 1 litre.

1 C. C. of this liquid contains 0.01 milligram of nitrous acid.

To ascertain the amount of nitrous acid in a water, pour 100 C. C. of the latter into a narrow glass cylinder, the dimensions of which have been so chosen that the above volume will occupy a column of 18 or 20 Cm,, and add 3 C. C. of a zinc iodide starch solution and 1 C. C. of dilute sulphuric acid (1 : 3). If the iodine reaction occurs immediately or after a short time, the experiment must be repeated with a smaller quantity of water (10 to 50 C. C.), diluting the latter to 100 C. C. with distilled water, so that the blue coloration only becomes visible after some time. 2 to 4 cylinders of the same dimensions as those above are now filled with 100 C. C. water and 3 C. C. of a starch solution of zinc iodide, and 1 C. C. of dilute sulphuric acid added. The color tints of the four cylinders are contrasted with that of the water under examination. This is most satisfactorily done by placing successively the four cylinders side by side with the one under consideration, using a piece of paper as a background, and looking down from above through the liquid column. By this means we may succeed in ascertaining the exact or approximate quantity of nitrous acid in the water examined, if its color tint agrees with that of either one of the four cylinders. When only approximate results have been reached, the experiment must be repeated with other and varying quantities of potassium nitrite, until the color tint obtained corresponds perfectly with that of the water being examined. It is only when the quantity of nitrous acid in 100 C. C. of water is confined to a limit of 0.01 or 0.04 milligram, that this method affords reliable results.

Method of Feldhausen-Kubel.—The method is based upon the oxidation of nitrous to nitric acid by means of potassium permanganate. An excess of the latter is added and then titrated with a solution of ferrous ammonium sulphate. This method of determination is to be particularly recommended when the quantity of nitrous acid in 100 C. C. exceeds one milligram. The results, however, are not accurate when 100 C. C. of the water contain less than 0.1 to 0.2 milligram of nitrous acid (Tiemann).

For the decomposition of the nitrous acid, $\frac{1}{100}$ normal permanganate solution is taken. This is prepared by dissolving 0.34 to 0.36 grm. potassium permanganate in 1 litre of water. For a ferrous solution employ a liquid containing 3.92 grms. dry ferrous ammonium sulphate dissolved in 1 litre of water. The permanganate solution is so standardized that 1 C. C. of the same corresponds to 1 C. C. of the iron solution, and therefore to 0.19 milligram of nitrous acid. The procedure is precisely analogous to that described in the standardization of the permanganate solution (p. 75). 100 C. C. of the water are mixed with an excess of the above permanganate solution; 5 to 20 C. C. are usually required, according to the amount of nitrous acid present. 5 C. C. of dilute (1 : 3) sulphuric acid are then added, and the solution treated with ferrous ammonium sulphate until it becomes perfectly colorless. When an excess of the iron solution has been added, pass in permanganate from a burette until a slight coloration is perceptible.

To avoid the decomposition of any organic matter contained in the water by the permanganate, the maximum temperature of the solution should not exceed 25° C. A temperature of at least 15° C. is necessary for the conversion of nitrous into nitric acid.

Determination of the Ammonia. Method of Frankland and Armstrong.—The method is founded upon the deportment of ammonia and its compounds with potassium mercuric iodide. The quantity of the ammonia is determined colorimetrically, *i. e.*, by the greater or less coloration occasioned by the addition of potassium mercuric iodide to water. It is, of course, presumed that all bases precipitated by a normal alkaline solution (iron, calcium and magnesium) have been removed from the water, which is very easily done by the previous addition of some sodium carbonate and hydrate (1 part sodium hydrate free from ammonia and 2 parts water).

For a comparison of the obtained color tints a solution of 3.147 grms. dried ammonium chloride in 1 litre of water will answer. Dilute 50 C. C. of this solution with 1 litre of water; 1 C. C. of the latter will then correspond to 0.05 milligram ammonia.

3.144

To prepare potassium mercuric iodide (Nessler's Solution) dissolve 50 grms. of potassium iodide in 50 C. C. of hot water, and add a hot concentrated solution of mercuric chloride (20 to 25 grms.) until a permanent red precipitate of mercuric iodide is produced. Mix the filtrate with 300 C. C. of potassium hydrate (1 part of potassium hydrate in 2 parts water), and dilute with water to 1 litre.

The ammonia is estimated by pouring 300 C. C. of the water being examined into a glass cylinder, adding 2 C. C. of sodium carbonate and 1 C. C. of sodium hydrate (of the above concentration), and shaking up well. When the precipitate of the carbonates of the alkaline earths has subsided, transfer 100 C. C. of the clear liquid to a tall and narrow glass cylinder (see Nitrous Acid Determination), and pour into it 1 C. C. of the potassium mercuric iodide solution. In case a dark reddish-yellow or red color is produced, the ammonia percentage is too large; therefore a smaller volume of the liquid (5 to 50 C. C.), precipitated by sodium carbonate, must be diluted with distilled water to 100 C. C., so that the addition of the reagent to the liquid causes nothing more than a bright-yellow coloration. As for the rest, proceed as directed in the Nitrous Acid Determination: 100 C. C. of distilled water are mixed with 0.2 to 2 C. C. of the ammonium chloride solution, and 1 C. C. of potassium mercuric iodide, then compare the obtained colors. (See p. 246.)

The method only affords an accurate estimation of the ammonia, when the quantity of the latter extends from 0.005 to 0.1 milligram in 100 C. C. of water (Tiemann). When there is a large percentage of ammonia a corresponding amount of distilled water must be previously added.

For another method of determining ammonia, see Analysis of Mineral Water.

*Determination of the Organic Substances.** *Method of Kubel.*—Is based upon the oxidation of the organic substances in acid solution by potassium permanganate. The excess of permanganate added is titrated with oxalic acid:—

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + MnSO_4 + 10CO_2 + 8H_2O.$$

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* A former method for the estimation of the organic substances, and one which may, even at the present time, be in use, consisted in evaporating the liquid to dryness, drying the residue at 120° to 140° C., and then igniting the same to volatilize the organic substances, which were estimated by the difference in weight. As the carbonates of the alkaline earths lose carbon dioxide upon being strongly ignited, the residue was moistened with ammonium carbonate, and dried at 120° to 140° C., until constant weight was obtained. It is very evident that by the ignition of the residue not only the organic substances were expelled, but also the ammonia compounds, nitrates, etc. A portion of the calcium carbonate would be decomposed by the silicic acid, and the magnesium chloride would break up into magnesia and hydrochloric acid, etc.

Take a solution containing 0.32 to 0.34 grm. crystallized permanganate dissolved in 1 litre of water. This is standardized with a $\frac{1}{100}$ normal oxalic acid solution, having 0.63 grm. pure crystallized oxalic acid dissolved in 1 litre of water. In the standardization of the solution the conditions observed in the actual analysis must be followed. Proceed as follows:—

100 C. C. of distilled water together with 5 C. C. of dilute sulphuric acid are brought and boiled in a large flask of about 300 C. C. capacity. Run in 3 to 4 C. C. of the permanganate solution from a burette, and continue the boiling for five minutes, then reduce the permanganate, after removing the lamp under the flask, with 10 C. C. of a $\frac{1}{100}$ normal oxalic acid solution. Titrate the excess of oxalic acid with permanganate, *i. e.*, to the colorless, warm liquid add enough permanganate to cause a permanent red color.

In calculating the analysis it must be remembered that the 10 C. C. of oxalic acid, which were added, contain 6.3 milli grms. crystallized oxalic acid ($C_2H_2O_4 + 2H_2O$), and these correspond to 3.16 milligrams of potassium permanganate, or 8 milligrams (necessary for the oxidation of oxalic acid to carbon dioxide) oxygen.

When determining the organic substances in water proceed just as in the standardization of a solution. Take 100 C. C. of the water. It is of course understood that after the addition of 3 to 4 C. C. of permanganate the boiling will cause the disappearance of the red coloration, and therefore permanganate must be added until this no longer occurs.

The excess of permanganate, which was more than necessary for the oxidation of 10 C. C. of oxalic acid, will represent the quantity of permanganate decomposed by the organic matter in the water.

If x represents the number of C. C. which correspond to 10 C. C. of the oxalic acid, y the C. C. of permanganate decomposed by the organic matter, then $\frac{3.16.y}{x}$ will express the parts of permanganate, and $\frac{0.8.y}{x}$ the parts of oxygen necessary for the oxidation of the organic substances contained in 100,000 parts of water.

If, for example, 100 C. C. of water require 7.22 C. C. permanganate for the production of a permanent red, and if this liquid was then decolorized by 10 C. C. of the normal oxalic acid and 3.55 C. C. permanganate then added; and further, if 10 C. C. of the normal oxalic acid solution equal 8.5 C. C. permanganate solution, we have

$7.2+3.5=10.7$; $10.7-8.5=2.2$. C. C. permanganate.

100,000 parts of water require, therefore, for oxidation:

$\frac{2.2.\,3.16}{8.5}=0.8179$ parts potassium permanganate, corresponding to:

$\frac{2.2.\,0.8}{8.5}=0.2070$ parts oxygen.*

If the water under examination contains nitrous acid, this will have a decomposing effect upon the permanganate (p. 247), and therefore we must deduct for each part of nitrous acid in 100,000 parts water, 1.66 parts potassium permanganate. When ammonia or sulphuric acid is present, evaporate the water to about $\frac{2}{3}$ of its original

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* According to Kubel and Wood, 5 parts of organic matter are oxidized by 1 part of potassium permanganate; therefore, if the excess of permanganate given in milligrams were multiplied by five, it would give the amount of organic substances in 100,000 parts of water. Tiemann recently discovered this supposition to be false. He found that the absolute weight of the non-volatile organic matter in different waters stood in a different ratio to the quantity of permanganate necessary for the oxidation of the organic matter.

volume, and replace the evaporated portion with distilled water and then titrate the solution.

Schulze's Method.—This differs from the method of Kubel, in that the oxidation of the organic material is effected in an alkaline solution. After acidifying the red colored liquid with sulphuric acid, decolorize it again with oxalic acid, determining the excess of the latter with permanganate.

Proceed as heretofore, mixing the 100 C. C. of the water under examination with $\frac{1}{2}$ C. C. sodium hydrate (obtained from sodium and the solution of 1 part of sodium hydrate in 2 parts of water), and then add, according to the amount of organic matter present, 10 to 15 C. C. of a permanganate solution. The liquid is boiled about ten minutes (must remain red in color), and after cooling to 50° to 60° C., 5 C. C. of dilute sulphuric acid (1 : 3) and 10 C. C. of the normal oxalic acid are added. The colorless liquid is again mixed with permanganate until the red color is permanent. Calculate as before.

As regards the management of the final results, it is certainly the best to calculate the constituents in the uncombined state, that is, to simply give the amounts of chlorine, sulphuric acid, nitric and nitrous acids, silicic acid, also the quantities of calcium, magnesium, potassium, sodium, &c. in 100,000 parts of water.

Every combination of the acids present with the oxides is more or less arbitrary. In this connection I will merely mention that generally chlorine unites first with sodium (to form sodium chloride) and then with potassium. If any chlorine remains it may be regarded as combined with calcium. When there is sufficient chlorine to combine with the sodium and potassium, the remaining alkalies can be regarded as sulphates. The remainder of the sulphuric acid is joined with calcium ($CaSO_4$), and the rest of the calcium and magnesium calculated as carbonates. Nitric acid when present is generally joined with ammonia, and then with calcium. Nitrous acid is also combined with the ammonia. When large quantities of iron are present it may be regarded as combined with the carbon dioxide ($FeCO_3$). The silica is recorded as uncombined.

Mineral Water.

1. Work at the Spring.

The physical properties are first learned, the appearance, smell and taste of the water noted, also the quantity of the latter determined which flows within a minute from the efflux tube, and the temperature of the water as well as that of the air recorded. It is also necessary to ascertain what action it gives with red and blue litmus paper, and whether the change of color in the paper remains upon drying. If spongy deposits or solid sinter are found in the spring or efflux pipe, samples of these are collected and placed in closed bottles for future investigation.

Determination of the Hydrogen Sulphide.—When a portion of the water has been acidified with dilute sulphuric acid and shaken up in a flask not entirely full, the presence of this gas is detected very readily by its odor, or by the decolorization of paper slightly blued with starch iodide.

The quantity of the hydrogen sulphide is estimated with an iodine solution of known strength.*

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* $H_2S + 2I = 2HI + S$. This decomposition only occurs when the quantity of hydrogen sulphide does not exceed 0.04 per cent. When this is the case a measured quantity of the water is mixed with a sufficient amount of boiled distilled water.

Use an iodine solution containing 1 grm. iodine (dissolved in potassium iodide, p. 96) to the litre. Measure off a quantity of water, mix it with acetic acid and a dilute solution of freshly prepared starch, and while stirring the liquid pass from a burette drop by drop the iodine solution until the blue color of starch iodide remains permanent. Having in this manner ascertained how much iodine solution is necessary for the decomposition of the hydrogen sulphide, it would be well to repeat the experiment in such a manner that almost the entire quantity of the required starch solution is poured in a beaker glass and mixed with an equal quantity of mineral water. Add to the colorless liquid a few drops of acetic acid and some starch, and allow sufficient iodine solution to enter from the burette to produce a blue coloration in the liquid.

There only remains yet to learn how much iodine solution is necessary to color in a like manner an equal volume of distilled water, and deduct this quantity. The sulphur in warm mineral springs can only be determined with an iodine solution after the water has become perfectly cool. Although the cooling can be hastened very much by sinking the flask in cold water, yet the quantity of air which the mineral water absorbs upon filling is sufficient to decompose a certain amount of the sulphur compounds. It is therefore advisable to previously fill the flask to be used with carbon dioxide, and first remove the stopper when the vessel is immersed beneath the surface of the water.

To estimate the hydrogen sulphide volumetrically, two portions of the water are mixed with a solution of silver chloride in sodium hyposulphite and ammonium hydrate added to this and the flasks then carefully closed with glass stoppers. The precipitate produced is subsequently filtered off in the laboratory and oxidized with bromine water. In the filtrate from the silver bromide, after expelling the bromine, determine the sulphuric acid as barium sulphate

(p. 15).* Aqua regia may replace bromine in the oxidation of the silver sulphide.

When large quantities of hydrogen sulphide are present in mineral waters, in order to render an accurate determination of the sulphuric acid possible, we must either boil two portions of the water immediately at the spring, adding some hydrochloric acid, or if this cannot be done, precipitate the sulphur compounds in the water in closed flasks, with cadmium chloride. The sulphuric acid is then afterwards determined in the filtrate from the cadmium sulphide. The precipitate formed by the cadmium chloride may also be used to determine the total amount of sulphur combined with hydrogen or metal. Oxidize it with fuming nitric acid, and determine the sulphuric acid in the usual manner after evaporating the excess of nitric acid.

In case hyposulphurous acid is present, it may be estimated in the filtrate from the cadmium sulphide. Two fresh portions of the water are mixed with a cadmium solution and the warmed filtrate mixed with an excess of a silver nitrate solution. The precipitate—silver sulphide† and chloride—is filtered off, and the latter dissolved in ammonium hydrate and the sulphide in nitric acid. After evaporating the excess of the latter acid, the silver in the solution is estimated as chloride. 1 mol. silver chloride corresponds to 1 mol. of hyposulphurous acid.

Determination of the Ferrous Oxide.—A permanganate solution is here required which contains about 0.6 grm. crystallized permanganate, the strength of which has been previously determined, then acidify about 500 C. C. of the

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* Some springs yield a higher percentage of hydrogen sulphide by this method than by titration with an iodine solution.

† $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$.

water with dilute sulphuric acid, and add the permanganate until the known reaction occurs. For this purpose the beaker glass is placed upon a piece of white paper, and the color observed by looking through the liquid from above. It is also necessary to know how many C. C. of permanganate are consumed to produce the same color tint in an equal quantity of distilled water, and subtract this amount from the number of C. C. taken for the oxidation of the ferrous oxide.

This method is not applicable when the mineral water under examination contains hydrogen sulphide; then the iron must be determined gravimetrically. (See below.)

*Determination of the Total Carbon Dioxide.**—For this estimation take a solution of 1 part crystallized calcium chloride in 5 parts of water containing 10 parts of ammonium hydrate. This mixture should be prepared several weeks before being used, and preserved in a well-sealed flask. According to the quantity of carbon dioxide present, the measuring flask of 200–1000 C. C., filled with mineral water, is sunk as far as possible beneath the surface of the liquid, and the water sucked from the flask by means of a rubber tubing; this will enable one to fill the vessel with water from the lowest depths. For transportation this is then poured into a second flask intended for this purpose, and which contains sufficient of the clear calcium chloride solution to combine with the carbon dioxide. Rinse out the measuring flask with small quantities of boiled distilled water. Several such flasks are filled in a like manner and carefully corked. This is best effected by using corks covered with caoutchouc, which is previously moistened with water (Bunsen).

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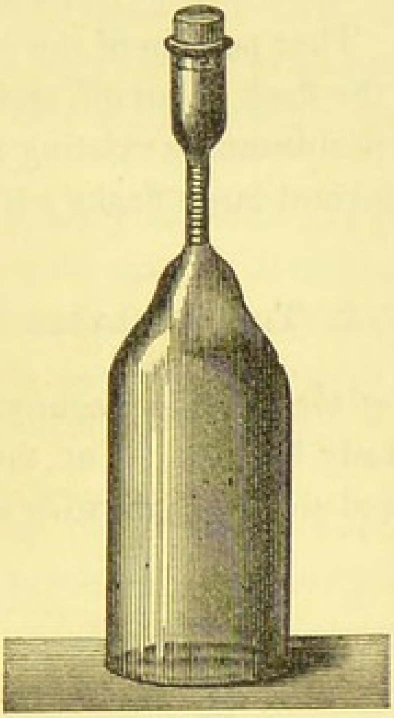
* For the determination of absorbed gases, etc., found in water, see Bunsen's "Gasometrische Methoden."

Determination of the Specific Gravity.—In mineral waters rich in gases it is best to prepare for the specific gravity determination at the spring. For this purpose flasks of 200–400 C.C. capacity are used (Fig. 25). This method of procedure was proposed by Fresenius. The neck of the flask is drawn out into a tube 50 Mm. long and 5–6 Mm. wide, upon which a millimeter scale is etched. The mouth is round and can be closed air-tight with a caoutchouc cork. To fill the flask close it with the thumb, immerse it as far as possible beneath the water surface, and allow enough water to enter to fill it to about the middle of the neck. The mouth is again covered with the thumb, the flask removed from the spring, and immediately closed with the caoutchouc cork, which for safety is wound around with a piece of cord.

Fig. 25.



Filling the Flasks.

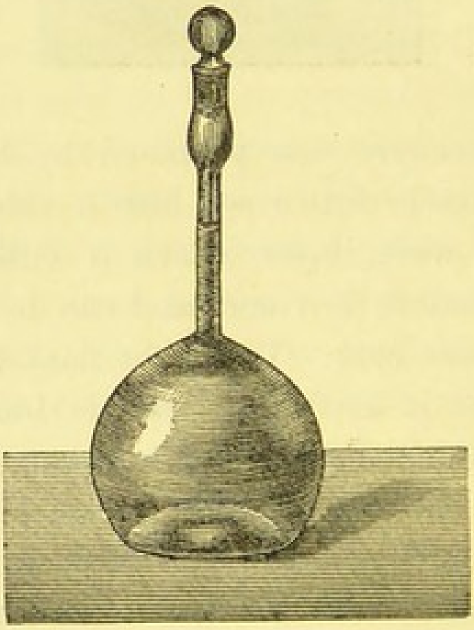
Wine or mineral water flasks are usually employed for the transportation of the water under examination to the laboratory. These are dipped as far below the surface of the liquid as possible, the water poured out, and the flasks refilled. The latter are corked with stoppers covered with caoutchouc. That portion of the cork extending beyond the neck of the flask is cut off, and when dry, sealed.

To estimate those substances existing in small quantities in the water, fill several large flasks with the same.

2. The Analysis.

Determination of the Specific Gravity.—If preparations for this have already been made at the spring, the flask used there is placed side by side with another filled with distilled water, and both allowed to stand for at least twelve hours in a suitable room, so that the temperature of both liquids becomes the same. The height of the

Fig. 26.



liquid in the first glass is noted and its weight then ascertained. Empty it and rinse it with distilled water from the second flask, and then refill with the same liquid to the height noted before. There now remains merely the determination of the weight of the empty flask, for which purpose it is rinsed out with alcohol and ether, then dried.

It is of course understood that the flask containing either mineral or distilled water is not to be put upon the balance until the exterior has been carefully dried with bibulous paper and cleaned.

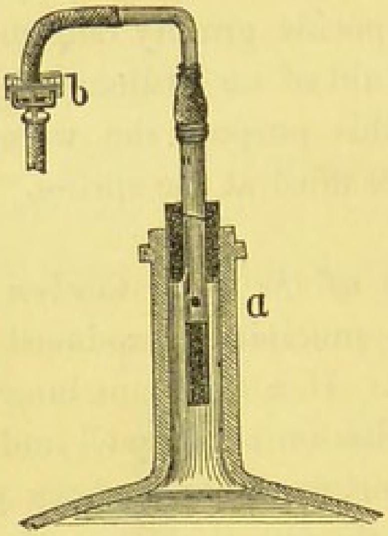
If it was not necessary to make any preparations at the spring for the specific gravity determination, it must be performed with aid of an ordinary piknometer (see Fig. 26), using for this purpose the water from one of the flasks which were filled at the spring.

Determination of the Total Carbon Dioxide.—Use for this purpose the precipitate produced at the well by the calcium chloride. If a sufficient interval has elapsed between the precipitation at the well and the time of analysis, so that the originally amorphous precipitate has become crystalline, the filtration (through a plaited or ribbed filter) can occur immediately, while otherwise the flasks must be warmed for some time upon the water-bath. The corks are then loosely fitted to prevent bursting of the flasks through the pressure induced by heating. The precipitate is rinsed into a small flask, and the carbon dioxide determined according to page 33.

As a measured quantity of water was taken at the spring for the precipitation of the carbon dioxide in the calculation of the amount of the same in the water, the sp. gr. of the latter must be regarded. To find the absolute weight of the water, it is only necessary to multiply the employed volume expressed in C. C. by the specific gravity.

Determination of the Total Carbon Dioxide in Mineral Waters Supersaturated with it.—Sometimes the case occurs that the carbon dioxide in flasks and other vessels containing the mineral water must be estimated; then not only the portion of carbon dioxide retained in the water by pressure, but also that remaining after the removal of this force is determined. Employ a sharp cork borer closed above with a perforated caoutchouc cork for this purpose. (See Fig. 27.)

Fig. 27.



A small round aperture is made at *a*. To better regulate the flow of the liberated gas stream, the glass tube bent at right angles is provided at *b* with a thumb-screw. The cork bore is pressed through the cork until the opening at *a* is below the latter. The gum tubing at *b* is connected with an aspirator (p. 34), and a slow stream of carbon dioxide is allowed to escape in the apparatus by a gradual opening of the thumb-screw. As soon as the bubbles of carbon dioxide cease to ascend in the liquid, pour out the contents of the previously tared flask into a solution of calcium chloride in order to determine the carbon dioxide remaining in the water. Proceed then as before.

Determination of the Total Amount of Solid Constituents.—A flask is filled at the spring and tared, its contents then poured into a platinum dish, and evaporated on a water-bath. Water rich in gas must be heated carefully, and it is advisable after each "filling-in" to cover the dish with a watch glass, until bubbles of carbon dioxide no longer escape.

The empty flask is rinsed out several times with distilled water and then reweighed. The residue in the platinum dish after the evaporation of the liquid is dried in an oil bath until the weight is constant.

By converting the weighed salts into sulphates (by treatment with dilute sulphuric acid and igniting with ammonium carbonate, p. 37), and taking the weight, this will serve as a control for the analysis. This must, of course, agree with the weight which is obtained when the found constituents (potassium, sodium, calcium, etc., iron excepted) are calculated as sulphates, deducting, however, the ferric oxide, silicic and phosphoric acids.

Determination of the Sulphuric Acid.—According to the quantity of sulphates present (ascertained previously by qualitative testing), the contents of one or several flasks are employed. In the latter instance the water is concentrated, with addition of hydrochloric acid, previous to the precipitation with barium chloride. For the estimation of the sulphuric acid in mineral waters containing hydrogen sulphide, see page 255.

Determination of the Chlorine.—Proceed as directed on page 240. Bunsen suggests, instead of converting the silver produced by the incineration of the filter into chloride, that the filter be reduced upon a weighed platinum wire, and the increase in weight of the latter ascertained.

When bromine and iodine are present in mineral water, they will be precipitated together with the chlorine, and must subsequently be deducted from it.

Determination of Bromine, Iodine, Fluorine and Boron (Boracic Acid).—As these elements occur usually in very minute quantities, and as a larger amount of water must be evaporated for their determination, the estimation ot each can be satisfactorily made in the same portion of water. The contents of a large flask filled at the spring are evaporated, care being taken that the water, by successive additions of sodium carbonate, continually shows a slightly alkaline reaction. This, however, is not necessary when the water belongs to the class of alkaline mineral waters. The residue is repeatedly digested with larger quantities of distilled water, and the insoluble portion transferred to a filter. The latter contains, besides the alkaline earths and magnesia, ferric oxide, manganese oxide, silicic acid, etc., and all the fluorine as calcium fluoride. Treat this residue with dilute hydrochloric acid to dissolve the carbonates of the alkaline earths, and also the oxides, iron, manganese, etc. Fuse the insoluble portion (sulphates of the alkaline earths, calcium fluoride and silicic acid) in a platinum crucible with sodium carbonate. The aqueous extract contains, together with sodium silicate, all the fluorine as sodium fluoride, whilst the alkaline earths remain as insoluble carbonates. For the separation of the silicic acid, and the determination of the fluorine as calcium fluoride, proceed as given upon page 116.

The aqueous solution obtained by digesting the residue left after evaporation (the filtrate from the carbonates and sulphates of the alkaline earths) is employed in the determination of the boracic acid, iodine and bromine, and divided into three weighed portions. To estimate the boracic acid, one portion is acidified with hydrochloric acid, then about 1 grm. magnesium chloride and some ammonium chloride added, and the whole supersaturated with ammonium carbonate. The liquid is evaporated to dryness in a platinum dish, and ammonium hydrate added from time to time during the evaporation, so that the solution continually yields an alkaline reaction; finally ignite the residue, consisting of boracic acid, magnesium chloride and magnesia. This is now repeatedly lixiviated with hot water, and the filtrate (to obtain the last traces of boracic acid) again brought to dryness, after adding magnesium chloride, and ammonium chloride and hydrate. The residue as thus obtained, after repeated extraction with water, is transferred, together with the first—also well washed—residue, to a platinum crucible, evaporated several times with small quantities of water, and finally ignited and weighed. A small portion of the substance is now tested qualitatively for boracic acid. When the latter is present, divide the residue into two parts, dissolving the one—larger portion—in cold nitric acid, and precipitating the chlorine as silver chloride, while the second portion is dissolved in hydrochloric acid, and the magnesium estimated as magnesium pyrophosphate (p. 16). (Bunsen.)

If A represents the weight of the mixture, consisting of boracic acid, magnesium chloride, and magnesia, B the weight of the obtained silver chloride, C the weight of the obtained $Mg_2P_2O_7$, and x the required amount of boracic acid, then:

$$x = A - \frac{Cl - O}{AgCl} \cdot B - \frac{2MgO}{M_2P_2O_7} \cdot C.$$

$$\text{or } x = A - 0.19142\ B - 0.36037\ C.$$

To determine the iodine in the second portion of the aqueous solution, different methods may be pursued. When the quantity of iodine is to any degree large, it is precipitated as palladious iodide (PdI_2). Acidify the liquid slightly with hydrochloric acid, and add palladious chloride or nitrate until the precipitation is complete. The palladious iodide, after standing 48 hours, is transferred to a weighed filter dried at 80° C., washed with warm water and dried again at 80° C. until the weight becomes constant. The precipitate is ignited in a porcelain crucible, and the quantity of iodine calculated from the residual palladium. When only small quantities of iodine are present, the following methods are preferable. Acidify the liquid slightly with hydrochloric acid, and separate out the iodine by means of a few drops of a solution of hyponitric acid in sulphuric acid, or with fuming sulphuric acid, and shake the liquid with carbon disulphide for some time in a closed vessel. When the iodine has been fully dissolved, pour off the supernatant liquid, wash out the carbon disulphide solution and rinse it into a small glass provided with a cork. A very dilute solution of sodium hyposulphite is allowed to pass in drop by drop, and stirred well after each addition, until the violet coloration of the liquid first disappears. The strength of the sodium hyposulphite is similarly determined, by shaking a few C. C. of an iodine solution of known strength (about $\frac{1}{100}$ normal solution) with carbon disulphide, and this then decolorized with sodium hyposulphite. Bunsen uses chlorine water of known strength for the separation and simultaneous determination of the iodine. For the estimation of minute quantities of iodine, the chlorine water saturated at the ordinary temperature is diluted to 20 times its bulk with water, and for larger quantities with double its volume of water. The strength of this solution is so determined that a measured portion of it (of the dilute chlorine water 100 to 150 C. C., and of the concentrated about 40 C. C.) is passed into potassium iodide, and the iodine that separates estimated with sodium hyposulphite (p. 96).

Acidify the liquid with hydrochloric acid and mix in enough chloroform so that upon shaking (in a closed tube) some C. C. of it remain undissolved, and then add chlorine drop by drop, shaking the liquid violently after each addition. This is continued until the violet color in the chloroform just disappears, or the yellow coloration produced by the separation of bromine just appears.

By employing palladium nitrate for the precipitation of the iodine as palladious iodide, the filtrate may be used for determining the bromine; it is, however, necessary to remove previously almost all the chlorine. Mix the liquid with sodium carbonate to alkaline reaction, evaporate to almost perfect dryness upon a water-bath, and repeatedly extract the residue with warm absolute alcohol. The alcoholic solution contains the entire quantity of bromine (combined with the potassium or sodium), together with small quantities of alkaline chlorides. Expel the alcohol by heating, and add a few drops of sodium hydrate. Now acidify with nitric acid and precipitate the bromine and chlorine by the addition of silver nitrate. The amount of bromine can be readily ascertained by the loss in weight which occurs when the weighed precipitate is heated in a bulb-tube, and a stream of chlorine gas is passed over it, until there is no longer a diminution in weight, and all the bromine replaced by chlorine.

We can estimate the bromine in the same liquid if the iodine has been before separated by pure hyponitric acid and sulphuric acid, without the addition of nitric acid. The bromine will then be contained in the liquid poured from off the carbon disulphide. Its determination in the presence of chlorine has already been mentioned.

Bunsen also makes use of titrated chlorine water for its determination. A third portion of the solution (see above) almost neutralized with sodium carbonate, and boiling in a porcelain dish, is evaporated to incipient crystallization, then slightly acidified with hydrochloric acid, and chlorine water allowed to enter the boiling solution, drop by drop, from a burette immediately above the surface of the liquid. Both bromine and iodine are liberated, coloring the liquid yellow, and are volatilized by continued boiling. As soon, however, as the liquid resumes its colorless condition, add a fresh quantity of chlorine water, and continue doing so until this no longer causes a coloration in the liquid.

We can find the amount of bromine if we deduct the C. C. corresponding to the iodine from the C. C. of chlorine water employed, and calculate the difference for bromine.

If the original liquid is colored by organic matter held in solution, it is evaporated in a platinum dish, with addition of sodium hydrate, and the residue then ignited in a silver crucible.

Determination of the Nitric Acid.—The estimation is made as directed on page 242. The determination of the nitric acid and ammonia may be combined. The residue (see further on) left after the expulsion of the ammonia by sodium or potassium hydrate may be used, and the nitric acid converted by warming with zinc into ammonia :—

$$KNO_3 + 7NaOH + 4Zn = (3ZnNa_2O_2 + ZnNaKO_2) + 2H_2O + NH_3.$$

Concentrate the retort contents still further. The decomposition with zinc dust is begun and the mixture of ammonia and water caught in a receiver containing dilute hydrochloric acid. (See p. 38.) (Bunsen uses 4 to 6 zinc iron spirals instead of the zinc dust. These can easily be made by winding strips of zinc and iron around a glass rod. They are cleaned with hydrochloric acid and water before being used.) After a lapse of twelve hours heat the retort on a water-bath, until the liberation of gas ceases, dilute with water and continue heating over a free flame until about half the contents have been distilled off.

As already mentioned on page 39, the ammonia may be conducted into a measured volume of normal oxalic acid (in this instance $\frac{1}{100}$ normal oxalic acid is sufficient), and that portion of the acid not neutralized with ammonia may be titrated with ammonium or sodium hydrate. (See Analysis of Soda.)

If, in this instance,

t represents the number of C. C. of oxalic acid used in the experiment,

a the weight of acid $(C_2H_2O_4+2H_2O)$ contained in one C. C.,

t_1 the number of C. C. of neutralized acid in the receiver after the dilution, then the water will contain $\frac{N_2O_5}{C_2H_2O_4+2H_2O}a\ (t-t_1)$ grms. nitric acid.

Determination of the Ammonia.—1000 to 2000 grms. of water are taken for this estimation. These are beforehand concentrated with addition of hydrochloric acid to a small bulk, either in platinum or porcelain vessels. Follow the method on page 37.

Determination of Calcium, Strontium, Barium, Magnesium, Iron, Manganese, Aluminum, and Phosphoric and Silicic Acids. (Organic Matter.)—About 5000 grms. of water* are acidified with hydrochloric acid and then evaporated to dryness in a platinum dish. The precautions already given above should be strictly followed. (See Determination of Solid Constituents.) The emptied

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* The amount of water to be evaporated depends upon the quantity of solid constituents; so that for this purpose greater or less quantities are employed.

flasks should always be rinsed out with dilute hydrochloric acid and water, because if they have stood any time calcium carbonate would very probably have separated out, and also ferric oxide in case this was present.

The perfectly dry residue must be heated to about 120° C. to effect the complete separation of the silicic acid, then moistened with hydrochloric acid, warmed on a water bath and dissolved in water. The silicic acid remains insoluble, and after filtering, washing and drying it is ignited and weighed (p. 124). If it is discolored by any organic material, treat after ignition with pure alcohol and ether. After the evaporation of these solvents the residue is weighed and regarded as " organic substance."*

The purity of the silicic acid is tested by treating it with hydrofluoric acid or ammonium fluoride, and the residual traces of barium or strontium sulphate (titanic acid) brought into solution and added to the rest of the liquid.

The filtrate from the silicic acid is warmed with addition of nitric acid, and the aluminum, ferric oxide and phosphoric acid precipitated by ammonium hydrate (best in a platinum dish). The precipitate (I.) is imperfectly washed with hot water, redissolved in hydrochloric acid, when there generally remains a residue of insoluble silicic acid (p. 131), and the precipitation of the aluminum, etc. with ammonium hydrate is repeated, in the filtrate from the same. Berzelius' method may be employed in the separation of the ferric oxide, alumina and phosphoric acid. The precipitate is fused in a platinum crucible, with six times its quantity of a mixture of 6 parts sodium carbonate and 1½ parts of silica, and the fused mass treated with water. The aqueous solution will contain besides the silicic acid, the excess of sodium carbonate,

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* For the determination of the organic matter by the ignition of the residue left upon evaporation, see page 249, remark.

and all the phosphoric acid combined with sodium. The silicic acid is separated by warming the liquid with ammonium carbonate and evaporating the filtrate with hydrochloric acid to dryness in a platinum dish. Add to the filtrate an excess of pure (free from aluminum) potassium hydrate and filter off the ferric oxide after digesting the solution for some time on a water bath. After washing with hot water dissolve the precipitate in hydrochloric acid, precipitate again with ammonium hydrate, wash, dry and ignite.

To remove the aluminum from the potassium hydrate solution acidify the latter with hydrochloric acid and add ammonium hydrate (p. 37).

The liquid from (I.) precipitate is transferred to a flask of suitable size, and the manganese thrown down with ammonium sulphide added in slight excess (Precipitate II.). To prevent the separation of calcium carbonate from the liquid upon standing, fill the flask with boiled water and cork it. The manganese sulphide may, however, contain slight traces of calcium carbonate; dissolve it, therefore, in acetic acid (any zinc, cobalt or nickel that may be present will be insoluble) and repeat the precipitation as before. This second filtrate is added to the first.

To separate the remaining substances the filtrate from the manganese sulphide (II.) is acidified with hydrochloric acid and warmed until the hydrogen sulphide odor is no longer perceptible. Filter off the sulphur, and after neutralizing with ammonium hydrate add an excess of ammonium oxalate. When the calcium oxalate has subsided, it is filtered off, washed and after dissolving in hydrochloric acid, is reprecipitated by ammonium hydrate and oxalate (Precipitate III.). By ignition the calcium oxalate is either converted into carbonate or oxide and weighed (p. 14).

When barium and strontium are present, they are found in the calcium precipitate. The latter may also contain traces of magnesium. To estimate these substances heat the weighed precipitate in a platinum crucible with nitric acid, until a clear solution is obtained, then evaporate on a water-bath. The residue contains the alkaline earths as nitrates. These are now digested with a small quantity of absolute alcohol, and after standing twenty-four hours the nitrates of barium and strontium are filtered off (p. 28). The filtrate contains the nitrates of calcium and magnesium. Evaporate this solution to dryness, dissolve the residue in hydrochloric acid, and, after again evaporating and redissolving in water, the calcium is precipitated as oxalate. The magnesium is separated by evaporating the filtrate to dryness and igniting the residue to expel all ammoniacal salts. This done, the residue is taken up in water acidulated with hydrochloric acid, and the magnesium thrown down by ammonium hydrate and phosphate (p. 16).

The nitrates of barium and strontium are dissolved upon the filter in hot water—the solution being then evaporated to dryness in a weighed platinum crucible and the residue dried at 140° C. until the weight becomes constant. The nitrates are converted into oxides by heat, and these then treated with hydrochloric acid. The solution of the chlorides is evaporated to dryness, the residue treated with absolute alcohol, when barium chloride will remain insoluble. Filter and wash with absolute alcohol. The washed barium chloride is dissolved in hot water, the solution evaporated in a platinum crucible, with addition of a few drops of sulphuric acid, to dryness, and the barium sulphate weighed.

After expelling the alcohol from the filtrate, the strontium is treated similarly.

The precipitate from the calcium oxalate (Precipitate III.) contains besides the magnesium small quantities of calcium. It is put in a platinum dish and evaporated to dryness, the ammoniacal salts expelled by heat and the residue dissolved in dilute hydrochloric acid. The magnesium is thrown down in this solution as ammonium magnesium phosphate (p. 16). To obtain the calcium contained in the magnesium pyrophosphate dissolve the latter in strong hydrochloric acid, precipitate with ammonium hydrate and again dissolve in acetic acid. From this solution the calcium is precipitated by ammonium oxalate.

Determination of Potassium and Sodium.—With waters containing large quantities of sodium chloride, the contents of one or two flasks will be sufficient for the prosecution of this determination, while otherwise a much larger quantity of water must be worked up. The water is concentrated in platinum vessels and whilst boiling precipitated with excess of barium hydrate. Evaporate the filtrate in a platinum dish, dissolve the residue in a very small quantity of water, and precipitate the filtrate with ammonium carbonate and hydrate. The filtrate from the barium carbonate is evaporated in a platinum dish, the ammonium salts expelled, and the aqueous solution of the residue again mixed with ammonium carbonate and hydrate.

If a precipitate of barium carbonate is produced, treat the filtrate as before, and continue evaporating and precipitating as long as ammonium hydrate and carbonate produce a precipitate. The final residue, free from ammoniacal salts, is dissolved in water, and the solution digested in a platinum dish for 24 hours with freshly precipitated oxide of mercury to precipitate the last traces of magnesia. The filtrate is evaporated in a platinum dish and ignited to expel the small quantity of mercuric chloride present, the residue is dissolved in as little water as possible, the filtrate evaporated to dryness in a platinum crucible with addition of hydrochloric acid, and the perfectly dry residue heated to a low redness, the crucible being well covered. The potassium and sodium are separated according to page 41.

The alkaline chlorides thus obtained are rendered impure by small quantities of magnesium chloride, and contain moreover all the lithium as chloride.

To determine the magnesium chloride the filtrate from the potassium-platinum chloride is evaporated upon a water-bath to expel the alcohol, and the residue rinsed into a long-necked flask. By boiling the liquid the air is expelled, and the flask is connected with a hydrogen generator and heat applied. By this operation not only the excess of platinic chloride, but also the double salt of platinum and sodium in the solution, is decomposed, with the separation of metallic platinum. As soon as the liquid has become colorless, the precipitate is filtered off and the magnesium in the filtrate thrown down in the usual manner. The magnesium pyrophosphate is calculated for chloride, and this deducted from the weighed alkaline chlorides (Laspeyres).

For the determination of the lithium see later.

Direct Determination of Sodium Carbonate.—It is frequently preferred, in the analysis of alkaline mineral water, to determine directly the amount of sodium carbonate held in solution. To do this boil 100–300 grms. of water for some time in a platinum dish, and filter off the separated carbonates of the alkaline earths, etc. etc. The precipitate is perfectly washed with water, and the filtrate halved. The one portion is evaporated to dryness with hydrochloric acid, and after the complete expulsion of the latter the chlorine in the residue is estimated in the usual manner. To calculate the sodium carbonate from the silver chloride obtained, there must be deducted from the latter the amount of silver chloride which corresponds to the sodium chloride existing in the solution. (See Hydrochloric Acid Determination.) It must also be borne in mind that, when compounds of bromine, iodine and sulphur are present, these are also converted into sodium chloride, and a quantity of silver chloride corresponding to the sodium sulphide, bromide and iodide must likewise be deducted. Finally there is always some magnesium passing into the filtrate as magnesium-sodium carbonate, which is changed to magnesium chloride. To determine the latter precipitate the magnesium in the second portion of the above filtrate in the usual manner, calculating from the magnesium pyrophosphate the quantity of silver chloride corresponding to it. The silver chloride that remains is calculated for sodium carbonate.

Determination of the Lithium and Detection of Cæsium and Rubidium.—Generally only slight traces of lithium compounds are found in mineral waters, and for their determination large quantities of the water are evaporated. If for the determination of the potassium and sodium a rather large quantity of water was taken, the lithium may be estimated at the same time with these. The filtrate from the metallic platinum is evaporated to dryness, and the residual chlorides of sodium and lithium extracted with ethereal alcohol. Proceed as directed later.

When a separate portion of water is used for the lithium estimation, the detection of the rubidium and cæsium may be carried on at the same time. For the removal of the alkaline carbonates, ferric oxide, manganese oxide, etc., proceed as in the estimation of boracic acid, bromine, fluorine and iodine (p. 262); evaporating the contents to dryness after adding sodium carbonate. The residue is repeatedly lixiviated with water, and the filtrate, after concentration and slight acidulation with hydrochloric acid, is precipitated in the cold with platinic chloride. The precipitate produced contains not only the double chlorides of potassium and platinum, but analogous salts of rubidium and cæsium, whilst the double chloride of platinum and lithium (together with sodium platinic chloride) remains in solution. The detection of rubidium and cæsium in the presence of potassium depends upon the greater solubility of the double chloride of potassium and platinum in water than the corresponding double salts of the other two. The platinum precipitate is filtered after standing 24 hours, and boiled up 25–30 times in a platinum dish with small quantities of water. Only enough water is added to cover the precipitate. If anything is deposited from the aqueous decantations on cooling, this is again subjected to the same treatment, added to the first residue, and examined in the spectroscope for calcium and rubidium.

To estimate the lithium decompose the double salts with hydrogen (p. 272), and boil the filtrate with barium hydrate to remove the alkaline earths. The excess of this reagent, as well as traces of calcium, are removed from the liquid by warming the latter with ammonium hydrate and carbonate. The filtrate is now evaporated in a platinum dish, and the residue gently ignited to expel the ammonium salts. Dissolve the residue in water, and acidify the liquid which must necessarily be filtered with hydrochloric acid. When large quantities of sodium chloride are present in the water, it is advisable to remove this as far as possible before extracting with alcohol. Concentrate the acidulated liquid, transferring the sodium chloride that has crystallized out to a funnel, washing it several times with cold water, and treating the mother liquor again in the same manner. (Bunsun.) At last the solution is evaporated to dryness on a water-bath, heated some time over a free flame to expel the water, then repeatedly exhausted with a mixture of absolute alcohol and ether. This process is continued until a small portion of the filtrate no longer yields the flame reaction of lithium, when the alcoholic solution is evaporated on a water-bath, the residue dissolved in water and tested with ammonium hydrate and carbonate, and notice taken of the precipitation of calcium. If this occurs, evaporate the filtrate, and precipitate the solution of the residue again with ammonium hydrate and carbonate. The residue finally obtained dissolve in dilute hydrochloric acid, and the sharply dried residue of the solution treat with ethereal alcohol. Any traces of sodium chloride that may remain are filtered off, and the lithium determined in the filtrate according to page 106.

Qualitative Detection of Copper, Bismuth, Lead, Arsenic, Antimony, Tin, Cobalt, Nickel, Zinc, Barium, Strontium and Titanium.—These elements exist in such minute quantities in mineral waters, that in most cases even very large amounts of water are not sufficient for their detection. The collected deposit or sinter at the mouth of the spring is particularly adapted for this purpose. It is perfectly purified and freed from adherent mineral water by washing with distilled water. For the detection of arsenic, antimony and tin, fuse a portion of the substance with an equal amount of a mixture of equal parts of soda and saltpetre, evaporating to dryness upon a water-bath the aqueous solution of the fused mass, with addition of dilute sulphuric acid. The aqueous solution of the residue is boiled with sulphurous acid to cause a reduction of the arsenic acid, and after expelling this the arsenic is precipitated by hydrogen sulphide. The sulphides of arsenic, antimony and tin are dissolved when the precipitate is treated with sodium or potassium sulphide; and by boiling this solution with an excess of sulphurous acid, and evaporating the liquid to one-third its volume, the antimony and tin are precipitated, whilst the arsenic is dissolved (p. 70). The further recognition is most safely insured by the flame reactions.

To detect the remaining metals digest a second portion of the spring deposit with hydrochloric acid, and evaporate to dryness on the water-bath. The residue is dissolved in dilute hydrochloric acid, and hydrogen sulphide conducted into the liquid. The precipitate produced is oxidized with fuming nitric acid to effect the destruction of any organic matter mixed with it. For the separation from arsenic, antimony and tin neutralize the solution with potassium hydrate, and digest with sodium sulphide. The insoluble sulphides are dissolved in nitric acid, and the lead removed with sulphuric acid. In the filtrate are copper and bismuth, which are separated by ammonium carbonate. The precipitates obtained should be more closely examined according to Bunsen's suggestion—reduction by particles of carbon.*

To get out the cobalt and nickel in cases where the sinter contains considerable iron, Bunsen recommends that the filtrate from the hydrogen sulphide precipitate, after the expulsion of the gas, be neutralized with sodium carbonate, and boiled with freshly precipitated manganese sulphide. Cobalt and nickel pass into the precipitate, and are afterwards separated from the manganese with acetic acid.

Barium, strontium, and titanium must be sought for in the usual manner in that portion of the sinter insoluble in hydrochloric acid. The residual silica should be examined for titanium (p. 125).

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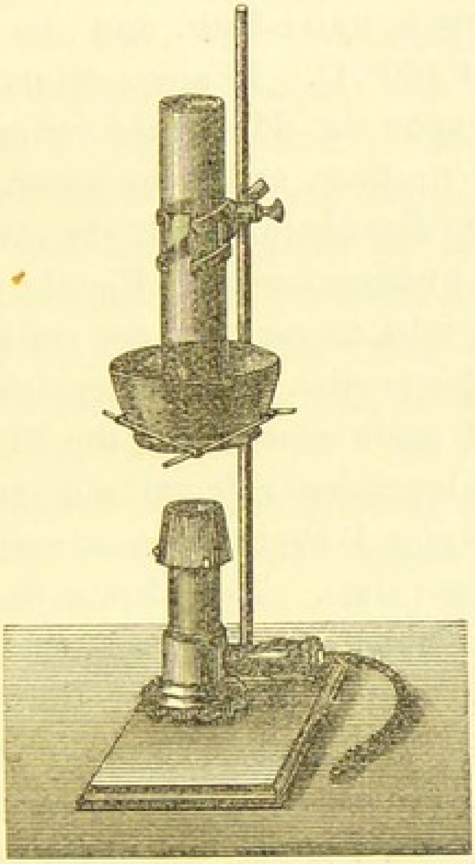
* See Bunsen's "Flammenreactionen," p. 53.

Ashes of Plants.

Composition.—Ferric oxide, alumina, manganic oxide, calcium oxide, magnesia, potassium, sodium, silicic acid, carbon dioxide, phosphoric, sulphuric, and hydrochloric acids.

Fig. 28.



To obtain the ash the parts of plants dried at 100° C., the seed, fruit, etc., are incinerated either in a muffle or in a large platinum dish at as low a temperature as possible. In all instances the latter method is applicable, if, according to F. Schulze, the air-draft be increased by a lamp chimney, extending some distance in the dish. (Fig. 28.) The incineration begins at a low red heat, and volatilization of the alkalies need not be feared.

When the weight of the dish becomes constant, the ash is finely pulverized, and preserved in a corked bottle. Transfer to a glass cylinder of about 300 C. C. capacity, and that can be well closed, about 10 grms. of ash, and 20 C. C. of water are then poured in, and the cylinder and the latter filled with carbon dioxide. Close the same and shake. Add more carbon dioxide, and shake, and repeat this operation until the liquid becomes colorless. The contents of the cylinder are rinsed into a dish, evaporated upon a water-bath, and the residue heated for some time at 160° C. If any calcium carbonate has crystallized out upon the sides of the cylinder, and cannot be removed by washing, add some water, and pass in a current of carbon dioxide to convert the calcium carbonate into the soluble hydrocarbonate. For the perfect removal of the alkaline salts extract the dry residue with water, bring the insoluble portion upon a filter dried and weighed at 100° C., and again concentrate the filtrate by evaporation. In this operation calcium sulphate usually separates out, and is also brought upon a weighed filter and preserved for some time. The filtrate from the gypsum is caught in a weighed dropping flask, care being exerted that no drops sprinkle the sides of the vessel, and that the point of the funnel does not come in contact with the filtered solution. (Bunsen.)

The aqueous extract of the ash contains, besides little quantities of the phosphates, the alkalies as carbonates, sulphates and chlorides. The residue consists principally, besides the silicic acid, of the carbonates and phosphates of the alkaline earths and also ferric oxide, alumina and manganese oxide (and manganese protosesquioxide).

Immediately after the filtration (having mixed the solution well) the aqueous extract of the ash is divided into five portions, determining in the first the chlorine by adding silver nitrate, nitric acid, and then applying heat. (See p. 17.)

The second portion serves for the sulphuric acid estimation, by precipitating it from a hydrochloric acid solution as barium sulphate.

For the estimation of the alkalies the third portion is boiled with barium hydrate, and the method of procedure followed which is fully explained at page 271.

The third portion is acidified with hydrochloric acid, and boiled to decompose the carbonates, then rendered alkaline with ammonium hydrate, and the precipitate produced dissolved in a small quantity of acetic acid. From this solution precipitate the traces of calcium by ammonium oxalate, and after creating an alkaline reaction in the filtrate by addition of ammonium, precipitate the phosphoric acid remaining in the filtrate from the ammonium-magnesium phosphate by addition of a magnesium chloride solution (p. 25).

When phosphoric acid is not present, the usual method for the separation of calcium and magnesium is followed. The carbon dioxide is determined in the fifth portion either by direct weighing (p. 33) or from loss in weight. (See Soda Analysis.)

For the analysis of the weighed residue of the ash insoluble in water, after having mixed it well in an agate mortar, pour over it nitric acid (about 2 grms.) containing some nitrous acid,* and digest upon a water-bath to complete solution. Evaporate the liquid to dryness with addition of nitric acid, and filter off the silicic acid. The filtrate is reduced to a definite volume, and the phosphoric acid estimated with ammonium molybdate in a measured portion (or when weighed, in a weighed portion, p. 25).

After removing the excess of nitric acid by evaporation,

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* This is added to dissolve the manganese protosesquioxide.

mix a portion or the entire quantity of liquid with a sufficient amount of lead acetate to precipitate the phosphoric acid, and remove the excess of the former in the filtrate by hydrogen sulphide (p. 114). Expel the excess of the latter reagent by boiling, convert the ferrous into ferric oxide, and precipitate the aluminum and iron in the boiling liquid with ammonium hydrate. It is advisable to redissolve in hydrochloric acid the filtered and imperfectly washed precipitate and repeat the precipitation. Iron and aluminum may be separated according to the methods given on pages 90 and 269. The precipitate may yet contain phosphoric acid, if the precipitation of the latter with lead acetate was effected in a very acid solution. The manganese is thrown down in the filtrate of the ammonium precipitate by a few drops of ammonium sulphide (see p. 21), and the excess of the latter destroyed with hydrochloric acid. The calcium and magnesium are separated as usual.

Instead of treating portions of the filtrate from the silicic acid for the estimation of the phosphoric acid and the bases, it is possible, if the method of Reissig be pursued, to effect the separation of the oxides simultaneously with the determination of the phosphoric acid. The liquid is mixed with a weighed quantity of pure tin (about 2–3 grms.) and fuming nitric acid (p. 115), then digested until oxidation ceases. When the precipitate of tin phosphate and oxide has fully subsided, filter off the clear supernatant liquid, wash the precipitate perfectly on the filter and digest in a platinum dish with a small amount of concentrated potassium hydrate.*

Dilute the alkaline liquid, containing potassium phosphate and stannate, in a litre flask with about 900 C. C.

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* Avoid an excess, as a precipitate insoluble in this reagent may separate out if care is not observed.

of hot water, and saturate the solution with hydrogen sulphide gas. If a precipitate of iron sulphide forms, filter it off, returning the filtrate to the flask again, and render the same slightly acid by the addition of dilute sulphuric acid. Fill the flask to the "mark" and determine its weight. After the tin sulphide has subsided—after twelve hours—filter about two-thirds of the clear liquid through a dry filter into a weighed flask and reweigh this. The weighed filtrate may be used to estimate the phosphoric acid. To this end, the liquid, strongly concentrated by evaporation and after neutralization with ammonium hydrate, is precipitated by addition of magnesium chloride (p. 25).

To ascertain the relative weight of the liquid used for the phosphoric acid determination to that of the entire quantity, it is only necessary to deduct the quantity of stannic sulphide corresponding to the metallic tin taken from the entire weight of the flask contents (about 1000 grms.).

Ferric oxide, alumina, etc., are in the filtrate from the tin phosphate and oxide. To remove any impurities (generally copper) introduced by the tin, conduct a stream of hydrogen sulphide into the liquid, treating the filtrate as above (oxidation with nitric acid, precipitation with ammonium hydrate, etc.).

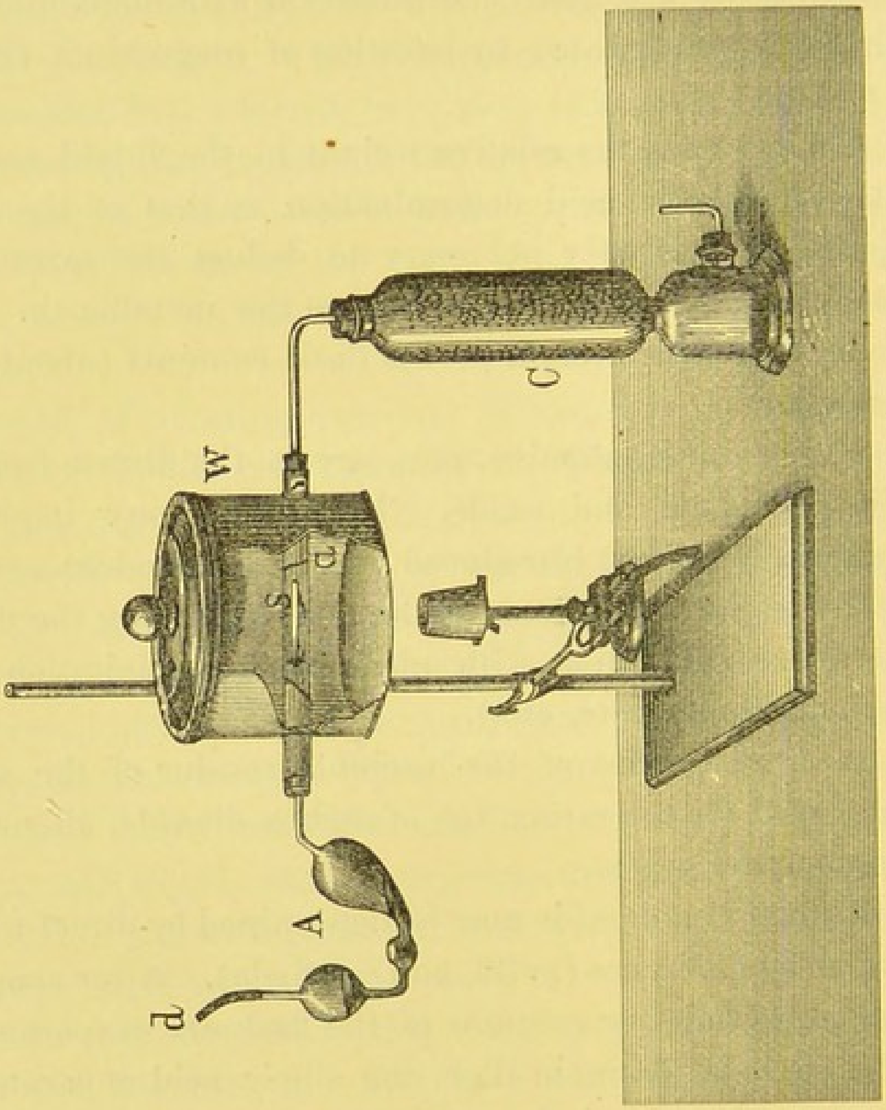
A fresh portion of the insoluble residue of the ash is employed for the estimation of carbon dioxide, silicic acid and sulphuric acid.

The carbon dioxide may be determined by direct weighing or by difference (p. 33, and see Soda). After complete decomposition the contents of the flask are evaporated to dryness in a platinum dish, the silicic acid separated as usual (p. 124), and the sulphuric acid precipitated with barium chloride in the filtrate from the silicic acid.

Guano.

Water Determination.—As guano dried at 100° C. or 120° C. loses a portion of its ammonia with the water, the latter cannot be determined by the loss in weight of a dried portion, but the volatilized ammonia must be also estimated. For this purpose Stohmann has constructed a special apparatus, the arrangement of which is shown in Fig. 29. W is a water-bath, in which the brass tube *a* is soldered, containing also the small boat serving to hold the guano. On one side there is connected with *a* the

Fig. 29.



calcium chloride flask C, and upon the other the pear-shaped tube A, which acts as a receiver for the ammonia. It contains a measured volume of oxalic or sulphuric acid of known strength (about 10 C. C. oxalic acid containing 0.63 grm. $C_2H_2O_4 + 2H_2O$, or 0.49 grm. sulphuric acid corresponding to 0.17 grm. ammonia).

Weigh off a portion (5 to 10 grms.) of the guano. Push the boat S into the tube *a*, and connect the latter with C and A; bring the water in W to boiling, and at the same time draw a current of air through the apparatus. As soon as the weight of the boat is constant, titrate the unneutralized oxalic acid or sulphuric acid with sodium or ammonium hydrate, and subtract the calculated quantity of ammonia from the loss in weight the boat has sustained.

Determination of the Non-volatile (fixed) Constituents in the Guano.—Proceed exactly as described in the analysis of the ash (p. 277), heating the residue from the water determination in a platinum dish at a very low temperature until the weight becomes constant. If alkaline carbonates are present, these may lose, according to the temperature, a portion of their carbonic acid; it is therefore necessary to moisten the ignited residue again with ammonium carbonate, and after gentle ignition reweigh. The resulting ash should be kept in a well-closed glass for the future determination of single constituents.

Determination of the Non-volatile Constituents—separately.—Usually the determination of phosphoric acid, sulphuric acid, calcium and the alkalies, is all that is necessary. As regards the phosphoric acid—heretofore it has been estimated in such a manner that a weighed portion of the ash was digested some time with nitric acid, and the phosphoric acid in this solution determined gravimetrically or volumetrically. Gilbert first called attention to the fact that, upon digesting the ash with nitric acid, the pyrophosphate that had been formed by ignition was not fully converted into the ordinary phosphoric acid, and consequently this acid existing in the residue as calcium pyrophosphate was thus withdrawn from the estimation. The conversion succeeds, however, readily and perfectly, if, pursuant with the suggestion of Gilbert, the incinerated guano be fused in a platinum crucible with four times its weight of a finely pulverized mixture of two parts soda and one part potassium chlorate.*

The fusion occurs at a low red heat and is continued until the ignited mass becomes white, when the heat is increased to a strong glow for a quarter of an hour. Pour out the liquid contents into a platinum dish (p. 40), digest some time upon the water-bath with addition of water, and add nitric acid finally to acid reaction. In the presence of silicic acid the solution is evaporated to dryness, and the residue dissolved in water and nitric acid. Determine the phosphoric acid in the filtrate from the silicic acid, volumetrically or gravimetrically. The precipitation with ammonium molybdate precedes the gravimetric determination (see p. 25). To convert the nitric acid into an acetate solution for the purpose of determining the phosphoric acid volumetrically, dissolve the precipitate produced by the addition of sodium hydrate in the least possible quantity of acetic acid. When iron and aluminum are present, their phosphates [$Fe_2(PO_4)_2$ or $Al_2(PO_4)_2$] will remain insoluble in acetic acid. If the precipitate is pure iron or aluminum phosphate, it is filtered off, washed with hot water, ignited, weighed, and the phosphoric acid contained in it calculated. If, however, the precipitate is

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* Saltpetre may replace potassium chlorate, and is preferable in case the substance analyzed leaves a difficultly combustible residue, rich in nitrogenous material.

a mixture of the two compounds in considerable quantity, and the determination of the phosphoric acid is to be accurate, the latter is separated from the bases by the method proposed on page 268. For the rest, see page 117.

The sulphuric acid is determined by digesting a second portion of the ash repeatedly with nitric acid, evaporating the solution to dryness on the water-bath, dissolving the residue in dilute hydrochloric acid, and precipitating the sulphuric acid in the filtrate with barium chloride.

The chlorine is most advantageously determined in the nitric acid solution of a third portion of the ash by evaporating it to dryness with sulphuric acid, forming calcium sulphate (p. 114).

The solution of a fourth part containing the alkalies is freed as much as possible from nitric acid, and these determined after boiling with barium water, and treating the filtrate with ammonium carbonate (p. 271).

In a complete analysis of the fixed constituents, all the substances present, excepting the alkalies, may be determined in the same solution. Fuse as above with soda and potassium chlorate, reducing the liquid filtered from the silicic acid to a definite volume. If the quantity of calcium sulphate in guano is to any degree considerable, the residual silicic acid will stubbornly retain a portion of it. Digesting the latter repeatedly with small quantities of nitric acid is then absolutely necessary.

The phosphoric and sulphuric acids are separated and determined as usual in a measured portion of the liquid. Before bringing the barium sulphate on a filter, boil it up repeatedly with water, and, after ignition, treat with dilute hydrochloric acid (p. 15).

To estimate the remaining constituents, the phosphoric acid is separated with tin from a second portion of the solution, and the method (p. 115) then followed in its particulars.

Determination of Constituents—soluble and insoluble in water.—For this purpose take about 10 grms. of undried guano, place it in a flask, and pour over it 200 C. C. of water; shake up several times, and immediately filter off the residue upon a filter dried and weighed at 100° C. The insoluble portion is perfectly washed (best with an exhaust pump) with small quantities of water, and dried at 100° C. until the weight is constant. By incinerating the residue (p. 277) the quantity of the fixed constituents is ascertained. The quantity soluble in water follows from the difference. If the entire quantity or a portion of the non-volatile constituents is to be determined in the aqueous solution, evaporate the filtrate to dryness in a platinum dish and ignite. The estimation of individual constituents —soluble or insoluble in water—is executed as above.

Determination of the Carbon Dioxide.—Many guanos contain carbonates in greater or less quantities; in this case the carbon dioxide is estimated according to page 33. (See Soda Analysis.)

Determination of the Total Carbon.—A portion of the substance previously dried at 100° C. is taken, and the carbon determined either according to page 221, by ignition in a stream of oxygen, or by oxidation with chromic and sulphuric acids (p. 229). As in the combustion of nitrogenous organic compounds with cupric oxide, nitrogen oxide gas is evolved, which is partially converted into nitrous acid, and as such absorbed by the soda-lime; therefore the anterior portion of the combustion-tube is filled with a layer of metallic copper, 12 Cm. long (copper wire rolls are best adapted), and this then ignited. In employing the first method it is further necessary, as the ash constituents readily retain carbon dioxide, to mix the guano before combustion with boracic acid, oxide of anti mony, or copper phosphate, which will perfectly expel the carbon dioxide. These latter agents may be disregarded if in the oxidation of the carbon we employ a mixture of nine parts lead chromate and one part potassium chromate. The formation of nitrous acid in this case is, however, more readily facilitated.

If the guano contains carbon dioxide for itself, this must, of course, be deducted from that obtained by combustion.

Determination of the Nitric Acid.—A weighed portion of the manure is extracted with cold water, the filtrate made alkaline with sodium carbonate, the precipitate filtered after standing some time, and a portion of the filtrate employed for estimating the nitric acid according to page 242 or page 266. When using the method subsequently described for the estimation of ammonia (by boiling with magnesia) the nitric acid determination can be made at the same time. Follow instructions given on page 266.

Determination of the Hydrochloric Acid.—A second portion of the undried guano is digested at a very low temperature with nitric acid, and the hydrochloric acid estimated by precipitation with silver nitrate.

Determination of the Oxalic Acid.—The method pursued is based upon the same principle as the valuation of manganese dioxide (p. 93) ; 2 mols. carbon dioxide correspond to 1 mol. oxalic acid ($C_2H_2O_4$). Mix the guano with an excess of pure manganese binoxide, and saturate with dilute sulphuric acid. The results are far more accurate if the carbon dioxide is not determined by loss in weight, but by direct weighing, as given on page 33. If the guano contains carbonates, the addition of dilute sulphuric acid precedes that of the manganese dioxide. The carbon dioxide is expelled by heat, the acid neutralized with sodium hydrate, manganese binoxide mixed in, and the method followed which has already been described.

Determination of the Uric Acid.—The uric acid is readily dissolved by gently warming the guano with sodium hydrate. Concentrate the filtrate by evaporation, and acidulate it with dilute hydrochloric acid. After standing twenty-four hours the separated uric acid is brought upon a filter, dried and weighed at 100° C., washed with small quantities of water (best with an exhaust pump), and dried at 100° C. until constant weight is obtained.

Determination of the Entire Nitrogen.—The method is founded on the principle, that nitrogenous organic substances, when fused with an alkaline hydrate, form alkaline carbonates, whilst the hydrogen of the alkaline hydrate combines with the nitrogen to form ammonia.

As an alkaline hydrate, there is generally employed a mixture of one part sodium hydrate with two parts oxide of calcium—the so-called soda-lime. The ammonia liberated by this process is either taken up in dilute hydrochloric acid, and the quantity of platinum-ammonium chloride and platinum determined (p. 39), or oxalic or sulphuric acid of known strength are used for this purpose. If 10 C. C. of an oxalic acid solution are taken with 0.63 grm. $C_2H_2O_4+2H_2O$, or 0.49 grm. sulphuric acid (see above, p. 283, Determination of the Water in Guano), these will correspond to 1.14 grms. nitrogen.

In the quantitative estimation of ammonium chloride, for the absorption of the ammonium produced, the apparatus of Varrentrapp and Will or that of Arendt and Knop is employed as receiver. (Figs. 30 and 31.)

The latter has an advantage over the other in that it possesses a second bulb, which will certainly prevent the acid from passing back into the combustion-tube. These forms of apparatus may be replaced by the absorption apparatus figured on page 170, which is particularly adapted to the employment of volumetric methods. To glow the soda-lime take a combustion-tube of difficultly fusible glass, and about 40 Cm. long, which is drawn to a point at one end, and bent upwards (Fig. 32). The back portion of the tube is filled with a layer of ignited soda-lime about 10 Cm. long,* the weighed quantity of guano then introduced, then another 10 Cm. layer of soda-lime

Figs. 30 and 31.

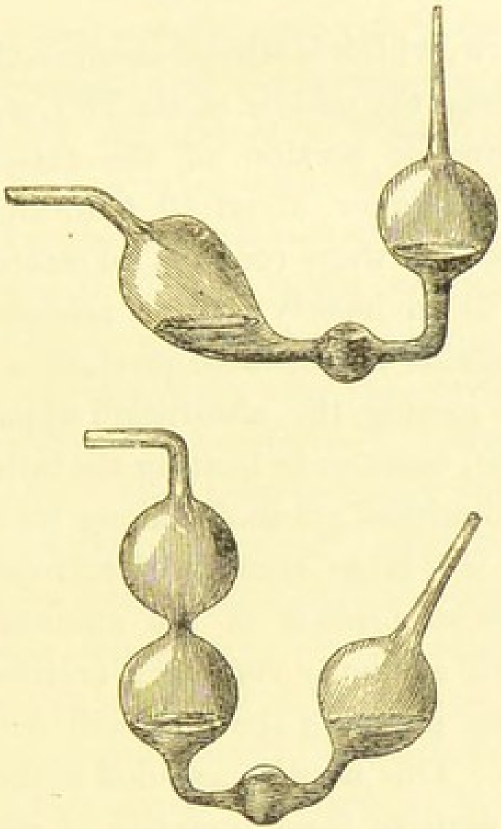

Fig. 32.

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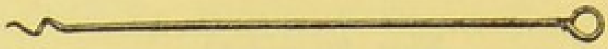
* Always test the soda-lime for nitrous acid.

filled in, which is well mixed with the guano. The mixing is effected by means of an iron wire (Fig. 33) shaped

Fig. 33.



like a cork-screw, which is stirred about in the tube, bringing the guano near the middle of the 20 Cm. layer of soda-lime. The anterior portion of the tube is filled with another soda-lime layer, about 10 Cm. long, so that between it and the cork there remains an unoccupied space of 4 to 5 Cm. Fill in loosely ignited asbestos, and by tapping on the outside of the tube produce a small channel within. After joining the absorption apparatus with the combustion-tube, commence heating the latter at the front, continuing the ignition gradually along its entire length.

When there is a large amount of nitrogen it can occur that during the absorption of the ammonia the hydrochloric acid will suddenly run back (retreat), and a portion of the same entering the tube will occasion the loss of the analysis. This may be avoided if the guano is previously mixed with an equal quantity of pulverized sugar, because the gaseous decomposition products of the sugar will dilute the ammonia gas, and the absorption will be less violent.

Determination of the Entire Quantity of Ammonia.—The ammonia in guano cannot be determined by the distillation of a weighed portion with sodium or potassium hydrate, because the protein substances contained in it (the guano) will also be decomposed with the liberation of ammonia. This latter decomposition, however, does not occur if calcium hydrate (milk of lime) or burned magnesia is substituted for the alkaline hydrate. As regards the employment of milk of lime, Schlössing, who proposed this method, found that the expulsion of the ammonia was only complete when the lime-water was allowed to act in the cold upon the substance to be decomposed. The decomposition should occur either under the well-ground bell-jar of a desiccator or a beaker glass, closed about with mercury. Hydrochloric (dilute), oxalic or sulphuric acid of known strength is taken as absorbent for the ammonia, and the vessel containing the acid is supported with the aid of a glass tripod or triangle directly over the dish filled with the guano and excess of lime-water. To prevent the loss of ammonia, it is advisable to add the milk of lime to the weighed guano, when every preparation is made for the absorption of the ammonia. Then rapidly place over the vessel the bell-jar or beaker. After standing twenty-four hours the decomposition is complete. One may be easily assured of this by introducing a moistened piece of red litmus paper under the jar, when its color should remain unaltered.

It is necessary, when using burned magnesia (Boussignault's method) to effect the decomposition of guano containing ammonia compounds, to boil the mixture, and follow exactly the course directed in the estimation by boiling with sodium hydrate (p. 38).

Superphosphates.

Composition.—The superphosphates contain not only calcium phosphate, but also varying quantities of calcium sulphate, calcium chloride, iron phosphate, free phosphoric acid, water, and generally sand, carbon and organic matter.

In most cases the valuation of these products consists in the estimation of the soluble, the so-called reverted, and the insoluble (crude) phosphoric acid.

For the complete analysis of superphosphates proceed precisely as in preceding examples. First of all, the water is ascertained in a portion by drying it at 160°–180° C. until constant weight is obtained.

The constituents soluble and insoluble in water are estimated by grinding about 10 grms. of the undried preparation in a porcelain mortar, with addition of cold distilled water, until the mass is perfectly divided; then filter and continue extracting the residue on the filter with small quantities of water (using the exhaust pump) until the filtrate no longer shows an acid reaction. The residue is reserved for further investigation, the filtrate reduced to a definite volume (500 C. C.), and four measured or weighed portions used in determining the organic substances and alkalies, the sulphuric, phosphoric and hydrochloric acids, and the alkaline earths.

The organic material and alkalies are ascertained by evaporating the first portion in a platinum dish to dryness, barium hydrate is added to alkaline reaction and again evaporated, and the weight of the residue, dried at 100° C., ascertained, then ignited as on page 277. The difference in weight will represent the organic material. Boil the ignited residue a second time with barium hydrate to separate calcium, magnesium, etc., and determine the alkalies in the filtrate according to page 271.

In the second portion of the solution the sulphuric and hydrochloric acids are estimated as usual. If the aqueous extract is strongly colored by dissolved organic substances, these must be destroyed to estimate the hydrochloric acid. Evaporate to dryness in a platinum dish, with addition of sodium and potassium nitrate, and determine the acid in the aqueous extract of the mass.

Phosphoric acid and the alkaline earths may be determined in the same (fourth) portion. The solution is evaporated to dryness with addition of sodium carbonate, the residue ignited and fused with a mixture of sodium carbonate and potassium chlorate (p. 284). The nitric acid solution of the cooled mass is rendered alkaline by sodium hydrate, mixed with acetic acid,* and the liquid reduced to a definite volume. In an aliquot portion determine the phosphoric acid either volumetrically or gravimetrically, the rest of the acetic acid solution being mixed with ammonium oxalate, and in the filtrate from calcium oxalate throw down the magnesium with ammonium hydrate and sodium phosphate (p. 16).

The further treatment of the portion insoluble in water follows from what has already been written (p. 283). Its weight is first determined by drying the residue, together with the filter ash, at 180° C., until the weight becomes constant, and ascertaining the percentage of organic material by the loss upon ignition. The residual fixed constituents are fused with sodium carbonate and potassium chlorate, proceeding in general as directed at page 284.

Nitrogen and ammonia are determined as indicated in the Guano analysis.

Determination of the Phosphoric Acid Soluble in Water.—The method follows from what has already been remarked in preceding examples. Two different methods serve for the extraction of the soluble acid—the digestion and washing processes. The first method consists in pouring gradually about 500 C. C. of cold distilled water upon a quantity of superphosphate, shaking repeatedly, and filtering the liquid after standing from 2 to 3 hours. The method results differently according to the time the substance is digested with water. It is not applicable when considerable quantities of ferric oxide and aluminum

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* When iron and aluminum phosphates remain undissolved, their quantity is determined in a separate portion (p. 284).

are contained in the superphosphate, because the soluble iron or aluminum phosphate gradually decomposes with water and separates as an insoluble tribasic phosphate of iron or aluminum (Rümpler). The results are consequently too low.

The *washing method* has already been described above. (Determination of the constituents of superphosphates —soluble or insoluble.) This yields the most accurate results.

As to the estimation of the phosphoric acid itself, pursue the course given on page 284; evaporate with sodium carbonate, and fuse the ignited residue with the same and potassium chlorate, precipitating the acid from the nitric acid solution with ammonium molybdate or titrating with a uranium solution.

Determination of the reverted Phosphoric Acid.—The residue after extracting the soluble acid with water is used. Fresenius discovered, that if this residue be treated with ammonium citrate (acid ammonium citrate) of sp. gr. 1.09, only the acid calcium phosphate $2CaO.H_2O.P_2O_5$ is dissolved whilst the undecomposed calcium phosphate existing in the superphosphate remains perfectly insoluble. After treating about 2 grms. of the superphosphate with water, the residue is washed perfectly with aid of a wash bottle filled with a solution containing 100 C. C. ammonium citrate of 1.09 sp. gr. into a beaker glass, this then digested for half an hour at a temperature of from 30° to 40° C. and filtered. The insoluble residue is washed out with a mixture of equal parts of the above ammonium citrate solution and two to three times as much water. The filtrate is evaporated to dryness in a platinum dish and the residue ignited alone and then with sodium carbonate and nitrate and the temperature greatly increased. After cooling the residue is treated with water, the liquid acidulated with nitric acid and heat applied until the solution is complete. Precipitate the phosphoric acid in the solution with ammonium molybdate, or titrate it with a uranium acetate solution (p 118).

The quantity of the reverted phosphoric acid may be indirectly calculated from the difference. In this case determine the entire quantity of phosphoric acid remaining after treating with water and ammonium citrate, both that soluble and insoluble in water.

If b represents the sought quantity of reverted phosphoric acid,
S the entire quantity of acid,
$a =$ portion soluble in water,
$c =$ the insoluble, then

$$S = a + b + c \text{ and } b = S - (a + c).$$

Bone Dust.

In a complete analysis not only the fixed constituents contained in the bones but also the fat and gelatigenous substances must be regarded.

The water is determined by drying a sample at 125° C.

For the estimation of the total amount of the fixed constituents proceed as directed in the analysis of Guano, and ignite 5 to 10 grms. of the undried powder, until the ash appears white. The residue is used in distinct portions for the estimation of the fixed constituents, proceeding as on page 283. In many instances in the analysis of bone dust merely the phosphoric acid is to be determined. The ignited residue (not necessary to be burned white) is fused with four times its weight of a mixture of two parts soda and one part nitre, proceeding as on page 283.

The fat is estimated by exhausting a weighed portion of the undried powder with anhydrous ether, the latter driven off, and the weight of the residue dried at 100° C. determined.

Gelatigenous substance cannot be directly determined: the amount of it is expressed by difference, if from the total weight of the fixed constituents, fat, carbon dioxide and water are deducted.

Nitrogen and carbon dioxide are determined as in Guano.

Bone Black.

Bone black presents a mixture of calcium phosphate, carbonate, and carbon, and contains generally small quantities of ferric oxide, magnesia, soda, sulphuric acid (fluorine), etc.

Determine the moisture by drying a sample at 120° C.

A second portion of the powder (about 5 grms.) is taken for the estimation of the carbon dioxide (after page 33), and the remaining constituents. The hydrochloric acid solution remaining in the apparatus is filtered through a weighed filter, and the residue dried at the same temperature until the weight is constant. This consists of carbon, the insoluble organic material, as well as sand and clay. By igniting to complete combustion of the carbon, sand and clay will remain; the quantity of carbon and other organic matter is expressed by the difference.

The hydrochloric acid solution filtered from the carbon, and containing calcium, magnesium, ferric oxide (alkalies), phosphoric and sulphuric acids is examined according to the method described in the analysis of Plant Ashes on page 277.

When hydrochloric acid is contained in bone black it is determined in a separate portion (p. 287).

Fuel.

According as the fuel under examination is to be applied, a perfect analysis (estimation of carbon, hydrogen, nitrogen, sulphur and ash), as well as an estimation of its technical value in producing heat effect and coke, etc., may be of interest and desirable.

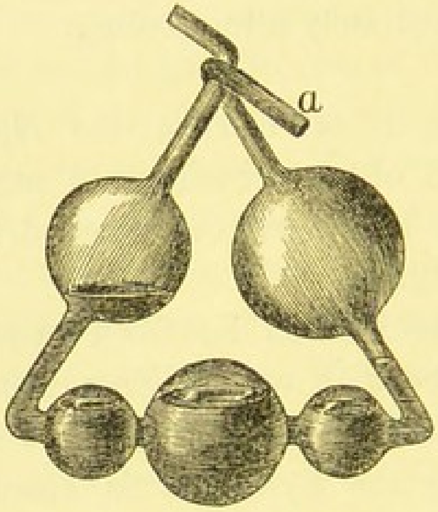
Determination of the Water.—The amount of water is expressed by the difference in weight of a finely pulverized and weighed sample dried at 125° C. Owing to the porous property of individual fuels, as well as their ability to absorb gases, it is necessary to weigh the substance in a tightly covered glass, and ascertain the weight of the dry sample immediately after cooling.

Determination of the Carbon and Hydrogen.—Determine the carbon either according to page 221, or if the estimation of the hydrogen is not needed, after the method of Ullgren (p. 229).

In applying the method described on page 221, replace the porcelain tube with one of glass about 60 Cm. long, and drawn out to a point at one end. Use lead chromate in burning. As the hydrogen is calculated from the water produced, care must be taken that the combustion tube and lead chromate are perfectly dry. The tube is most easily freed of moisture by moving it back and forth in a smoky flame, and sucking out the heated air with the aid of a long glass tube. While yet hot it is closed with a cork containing a calcium chloride tube, and allowed to cool. In the mean time the lead chromate may be heated in a copper or porcelain crucible, and, while warm, introduced into a tube or flask that can be well closed.

The filling with lead chromate and the substance is the same as described on page 288. After mixing well, the front portion of the tube is filled with a layer of lead chromate 15 Cm. long, and then, after creating a channel by tapping on the tube, a copper wire roll is introduced. To catch the water produced, the anterior part of the tube is connected with a calcium-chloride tube previously weighed, and this joined with the soda-lime tubes (p. 34) and the unweighed protection tube. As in using lead chromate no sulphurous acid is formed, the addition of a tube with chromic acid is not necessary (p. 223), and it is advisable, to enable one to control the course of the combustion, to substitute Liebig's bulbs (Fig. 34) for the soda-lime tube, and to insert this between the calcium chloride tube and that filled with soda-lime. So much potassium hydrate of 1.27 sp. gr. is filled in the apparatus that, upon sucking at the tube *a*, the large bulb will be about half-filled with liquid.

Fig. 34.



Owing to the nitrogen in the fuel the combustion cannot be made directly in a stream of oxygen, because this would favor the production of nitrogen trioxide, and the increase in weight of the apparatus would be far beyond the proper limit. The front portion of the tube is first heated to a faint redness, and the ignition gradually continued along its entire length. If almost all the carbon and hydrogen are in this manner oxidized to carbon dioxide and water, indicated by the retreating (sucking back) of the potassium into the large bulb, connect the drawn-out point of the tube with an oxygen gasometer, and continue heating for a quarter of an hour, with a slow current of oxygen passing through the tube. Now interrupt the combustion, and ascertain the increase in weight of the calcium chloride tube and both vessels intended for the absorption of the carbon dioxide.

When there is a high percentage of ash, and in the presence of carbonates, regard must be paid to the instructions on page 286.

Determination of Nitrogen.—(See p. 288.)

Determination of the Sulphur.—The process described on page 134 is very applicable in estimating the sulphur compounds (iron sulphide) contained in the material under investigation. A sample of the fuel is weighed* off in a porcelain or platinum boat, the latter shoved into a combustion tube, which is connected upon the one side with a gasometer filled with oxygen, upon the other with the absorption apparatus (p. 135) serving for the oxidation of the sulphur. On heating the sample in the boat in the oxygen stream, all the sulphur will be oxidized to sulphurous acid, which is conducted into a bromine solution and changed to sulphuric acid, and determined as barium sulphate (p. 136).

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* To analyze the ash, take for the determination about 10 grms. of substance.

Analysis of the Ash.

The residue from the above combustion will suffice for this analysis, which is executed as given on page 278.

Determination of the Heating Power. Method of Berthier.—Based upon Welter's law, according to which the quantity of warmth which combustibles afford upon ignition is proportional to the oxygen which was required for the combustion of the carbon and hydrogen contained in them. Although Favre and Silbermann have shown that the law of Welter is not exactly correct, it gives sufficiently accurate results for the technical valuation of material intended for heating purposes.

A gramme of the pulverized and dried material is placed in a crucible together with 40 grms. of litharge, and the mixture covered with 30 grms. more of the same substance, and gradually heated to a red glow, the entrance of reducing gases being avoided. The temperature must be so regulated that the litharge does not become liquid until the carbon has been burned. After ignition for three-quarters of an hour, the reduction will be complete. The liquid litharge is then either poured off from the lead (see p. 186), or the crucible, that has cooled slowly, is broken open, and the reduced lead freed from adhering litharge.

Thirty-four parts of reduced lead correspond to one part of pure carbon. If a represents the found quantity of lead, $\frac{a}{34}100$ expresses the relation of the burning value of the fuel to that of the pure carbon. ~~Was~~ Were there, for example, after the reduction of 1 grm. of the fuel, 10 grms. of metallic lead, its heating value would be $\frac{10}{34}100 = 29.41$ per cent. against that of the pure carbon.

Forchhammer used a mixture of three parts of litharge and one part of lead chloride, instead of the pure litharge, for the reduction. This in individual cases (*e. g.*, turf and wood) answered better than the pure litharge.

The presence of a large quantity of iron sulphide in the fuel renders the estimation inaccurate, because it has a reducing effect upon the litharge.

Determining the Coke.—This estimation is usually so executed that 20–40 grms. of the coarsely powdered and dried material (125° C.) are heated in a well-closed crucible over the gas lamp as long as combustible gases escape between the crucible edge and cover. When the gas liberation has ceased, the yet hot crucible is placed in a desiccator, and its weight determined immediately after cooling. If it is expected to obtain accordant results by this process, care must be taken that all the samples are examined, if possible, under like conditions, as gas pressure, similar lamps, and in one and the same crucible.

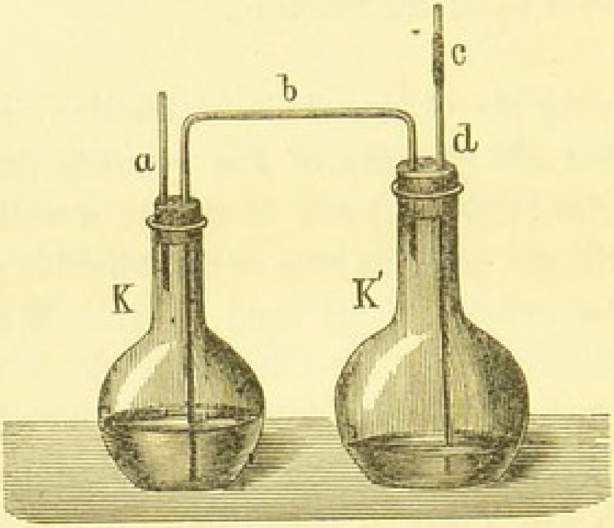
Soda Ash.

For the valuation of the commercial soda, generally the amount of sodium carbonate is all that is estimated, for which purpose two different ways may be pursued. Either the carbon dioxide is determined, or the aqueous solution of the substance is neutralized with an acid of known strength, and the sodium carbonate calculated from the found dioxide or from the volume of the standardized acid used.

In regard to the first process, the carbon dioxide is generally estimated by the loss of weight which the sample suffers when decomposed with acids, less frequently by the direct weighing of expelled carbon dioxide as described on page 33.

Of the many proposed forms of apparatus for determining the carbon dioxide by loss of weight, I will here mention more minutely only two—that of Fresenius and Will, and that of Mohr.

Fig. 35.



The first (Fig. 35) consists of two flasks, K and K′, which are connected by the glass tube *b*. K contains the sulphuric acid, serving for the decomposition of the sample; K′ for the solution of the carbonate. The glass tube *d* is closed at its exterior end *c* with a wax-ball, or better with a little plug of wood or small glass rod; the tube *a* is open at both extremities. Fill K about half its volume with concentrated sulphuric acid, and K′ to one-third its capacity with water, introducing then into the latter flask the sample of the soda ash,[*] dried at 100° C., and determine the weight.

The air in both vessels is diluted by sucking on a rubber tube attached at *a*, whereby a portion of the sulphuric acid passes over through *b*, toward K′, and the carbonate is decomposed. The liberated carbon dioxide must pass through the remaining sulphuric acid in K, as *d* is closed

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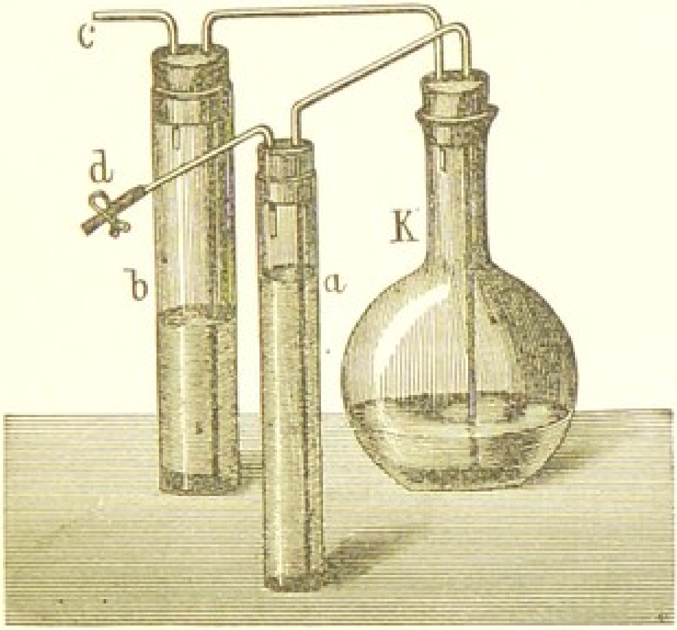
[*] The water in the soda is ascertained by igniting a separate portion.

at *c*. When the disengagement of gas in K′ ceases, suck again at *a*, and repeat this operation until all the sodium carbonate is fully decomposed. Finally all the sulphuric acid is allowed to pass over into K; this is attended with such an increase in heat in the contents of the flask that the carbon dioxide absorbed by the liquid will be rapidly expelled. The obstruction at *c* is removed, and by sucking at *a* the carbon dioxide contained in the apparatus is replaced by atmospheric air. After cooling, weigh the apparatus. The difference between the two weights will represent the amount of carbon dioxide.

Fig. 36.



If the soda contains sulphides, sulphites or hyposulphites (commercial soda-ash), there escape, besides the carbon dioxide, hydrogen sulphide and sulphurous acid. An excess of potassium chlorate is added to the solution of the sample, which oxidizes the above-mentioned gases to sulphuric acid. In the presence of chlorides the resulting perçentage is too high, due to the liberated hydrochloric acid gas, which may be avoided by the addition of silver nitrate.

In Fig. 36 is exhibited the construction of Mohr's apparatus, which may be particularly used to advantage if oxides are present, which form insoluble sulphates with the acid (*e. g.*, estimation of carbon dioxide in calcite). K is a flask of 100 C. C. capacity, intended for the decomposition of the substance; *a* contains hydrochloric acid; *b* contains concentrated sulphuric acid. Proceed as before. Suck on the tube *c*, and at the same time open the pinchcock at *d*. The latter is closed immediately when sufficient hydrochloric acid has passed from *a* to K, whereby the carbon dioxide must stream through *b*, and will be dried by the sulphuric acid. When the evolution of gas ceases, repeat the above, and finally permit the entire quantity of hydrochloric acid in *a* to enter the flask K. The pinchcock at *d* is opened; the carbon dioxide remaining in the apparatus is removed by drawing upon *c* with the mouth.

Another method of ascertaining the amount of carbonate in soda ash consists in using a standardized acid. The point of saturation is indicated by the litmus tincture, which has been added to the solution of the alkaline carbonate, changing in color from blue to red. As we know accurately the quantities of the different oxides which are necessary to form neutral salts with a certain acid, the quantity of carbonate may be calculated from the volume of acid employed.

For this purpose sulphuric, hydrochloric and oxalic acids are excellent. In manufactories, where similar determinations are daily executed, to escape any further calculation of the results, so-called *normal acids* are employed, *i. e.*, such as contain in 1 litre the molecule of the respective acid expressed in grammes. In using sulphuric or hydrochloric acids the preparation of a normal liquid is intolerably difficult and laborious. One is invariably obliged to fix the standard of such a solution by means of a separate experiment. As oxalic acid is gotten pure without much trouble, the use of it is preferable if it is desired to obtain an accurately standardized solution in a short time. A solution is usually employed which contains 6.3 grms. crystallized oxalic acid ($C_2H_2O_4 + 2H_2O$), and in certain cases one which has 0.63 grm. oxalic acid in a litre of water. Sulphuric acid and hydrochloric acid are generally made $\frac{1}{10}$ normal. This strength is approximately reached when sulphuric acid of sp. gr. 1.032 or hydrochloric acid of sp. gr. 1.018 are used.

Standardization of the Acid.—Chemically pure dry sodium carbonate will serve to begin with. As it is difficult to obtain it perfectly pure, the hydrocarbonate (sodium bicarbonate) is converted by gentle ignition into the neutral salt, and a weighed quantity (about 1 to 1.5 grms.) of the latter dissolved in water. This solution is mixed with some litmus tincture* (it is always advisable to add the same volume both in the standardization and in the subsequent analysis), and the acid to be titrated passed in gradually from a burette, until a slight reddening of the liquid occurs, then boil. By boiling, the carbon dioxide absorbed by the liquid, and which influenced the coloration of the litmus, will be expelled, and the liquid again become blue. Another portion of the acid is added, and the boiling repeated. Finally a point is reached when the next drop of acid will permanently redden the liquid, and the color not disappear, even upon protracted boiling. This point indicates the close of the reaction.

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* Treat the litmus cubes of commerce with alcohol, decant this and extract the residue with water. Acidify the aqueous solution with a few drops of sulphuric acid, and add an excess of barium hydrate. This latter substance is removed by conducting carbon dioxide into the solution, which is boiled and filtered. The litmus is kept in open vessels.

This method of standardization is rather tedious and time-consuming, and is especially not to be recommended if we have no idea of the amount of the acid present (in the application of the method, the amount of carbonate), and cannot calculate approximately the volume required for the decomposition. It is generally preferred (and this process is also more accurate) to add an excess of acid, and titrate this with an alkali solution of known strength. Mohr uses sodium hydrate for this purpose, 1 C. C. of which neutralizes an equal volume of acid. Such a solution possesses a specific gravity of 1.25, if acids of the above strength are taken. The sodium hydrate possesses the misfortune of invariably containing more or less carbon dioxide, which is liberated upon the addition of an acid and acts upon the color of the litmus tincture. If sodium hydrate is replaced by ammonium, the change from blue to red and the reverse will be quickly indicated, as no free carbon dioxide is present to cause any hindrance. The only inconvenience opposing the application of ammonium is its volatility. This, however, is easily avoided if a more dilute solution, one of about 0.993 specific gravity, is used.

The relation of the acid to the ammoniacal liquid (or sodium hydrate) is first fixed, by neutralizing a measured volume of the acid, mixed with litmus tincture, with ammonium hydrate until the red color changes to blue; then calculate from this how many C. C. of ammonium hydrate 1 C. C. of the acid equals. For the standardization of the acid, add an excess of the latter to the solution of sodium carbonate, and titrate the excess (when ammonium hydrate is used, not until the liquid is cool) with sodium or ammonium hydrate. It is superfluous to mention, that sodium or ammonium hydrate is added until the color of the liquid changes from red to blue.

If n C. C. of ammonium hydrate were used for the saturation of m C. C. of the acid, 1 C. C. of the acid will correspond to $\frac{n}{m}$ C. C. ammonium hydrate. Were r C. C. used for the supersaturation of the sodium carbonate solution, and for the titration of the excess t C. C. of ammonium hydrate, which would equal $\frac{m}{n}t$ C. C., there must have been necessary for the neutralization of the sodium carbonate $r - \frac{m}{n}t$ C. C. acid. If the latter is expressed by v, and if a grms. sodium carbonate have been used in the experiment, 1 C. C. of the acid will correspond to $\frac{a}{v}$ grms. sodium carbonate. From this the amount of anhydrous acid in 1 C. C. may be readily calculated. If, for example, in using sulphuric acid 1 C. C. of it equals a grms. sodium carbonate, the quantity of anhydrous sulphuric acid in 1 C. C. is calculated from the proportion—

$$Na_2CO_3 : SO_3 : : a : x.$$

The estimation of the quantity of sodium in any sample of soda is made exactly as in the standardization of the acid.

If the soda contains sodium hydrate, sulphide or hyposulphite, these are decomposed by the acid in titration, and incorrectly brought into the equation as sodium carbonate.*

To estimate sodium hydrate in the presence of sodium carbonate, precipitate the aqueous solution of the soda ash with an excess of barium hydrate, and determine the sodium hydrate in the filtrate, or an aliquot portion of it, with an acid of known strength. Follow the above instructions.

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* If a hyposulphite is not present, the other sulphur compounds can be oxidized with potassium chlorate and the aqueous solution of the residue titrated.

Both sodium sulphide and hyposulphite may be determined with an iodine solution of known strength (p. 253 and p. 95). The solution of a second portion is, for this purpose, acidified with acetic acid, starch paste added and then titrated with an iodine solution, thus ascertaining the quantity of hydrogen sulphide and hyposulphurous acid. A second portion is precipitated with an ammoniacal zinc solution or manganous sulphate; the sulphide of zinc or manganese is filtered off and the hyposulphurous acid determined with an iodine solution in the filtrate.

The quantity of the iodine solution required in the decomposition of the sodium sulphide is expressed by the difference.

Instead of deducting the C. C. of the normal solution corresponding to the amounts of sodium sulphide, etc., and calculating the sodium carbonate from the remainder of the used acid, it is sometimes preferred to estimate the sodium carbonate by a direct determination. For this estimation the precipitate of barium carbonate as above obtained is particularly adapted, the carbon dioxide in it being either determined with standardized hydrochloric acid or gravimetrically after the method given on page 33.

Fresenius* combines the carbon dioxide determination with that of the sodium sulphide, and uses an apparatus similar to that described on page 34. For the experiment a weighed sample of the soda is decomposed with hydrochloric acid in the flask. To condense the acid volatilized in the subsequent boiling, the bulb-shaped tube *b* is replaced by a vertical cooler (see Fig. 21, p. 228). The tubes *f* and *g* are arranged as before. To absorb the hydrogen sulphide, *g* is connected with two V-shaped tubes containing calcium chloride and pumice-stone filled with copper sulphate. These are joined to the soda-lime tubes

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* Zeitschrift für analytische Chemie, Jahrgang 10, p. 75.

k and *l*. The remaining parts of the apparatus described (p. 34) are not altered. The pumice-stone is filled with copper sulphate by saturating small pieces of the former with the latter (60 grms. pumice-stone and about 30 grms. copper sulphate), this then evaporated to dryness. The dry pieces are heated about four hours at 150°–160° C., then placed in closed vessels for preservation. The two tubes are filled the same as the soda-lime tubes ($\frac{5}{6}$ copper sulphate pumice-stone and $\frac{1}{6}$ calcium chloride). Proceed just as on page 35, with the difference that for the expulsion of the hydrogen sulphide the liquid contained in K must be boiled continuously for some time with a stream of air constantly passing through it. From the increase in weight of the tubes filled with copper sulphate pumice-stone and the two soda-lime tubes, we obtain the quantity of hydrogen sulphide and carbon dioxide.

If the soda contains a hyposulphite, care must be taken that this is decomposed by hydrochloric acid, with the formation of sulphurous acid. This would also be absorbed by the soda-lime and calculated as carbon dioxide. To render the method applicable under such circumstances, place between the second tube containing $CuSO_4$ pumice-stone, and the soda-lime tube *n*, a tube filled with chromic acid (see p. 223), and add another calcium chloride tube.

The soda of commerce always contains sodium chloride and sulphate, which are estimated in the usual manner. In the volumetric determination of hydrochloric acid with silver nitrate (p. 44), the solution of the substance is first neutralized with nitric acid, so that the liquid is only very slightly alkaline.

Pearl Ash.

Here the same determinations as in the preceding example are necessary. If soda is mixed with the pearl ash the titration with an acid is useless; the quantity of potassium carbonate in the presence of sodium carbonate must now be determined. To this end acidify the aqueous solution of the pearl ash with acetic acid, heat until the carbon dioxide is expelled, and precipitate the hot solution with lead acetate. After cooling reduce the liquid to a definite volume, and as soon as the precipitate has subsided pipette off a certain amount, which is treated with hydrogen sulphide to precipitate the excess of lead. The filtrate is evaporated to dryness in a platinum dish with addition of hydrochloric acid, and the sum of the alkaline chlorides ascertained (p. 26). The potassium chloride may be determined with platinic chloride (p. 42), or the chlorine (gravimetrically or volumetrically) estimated (p. 17 and p. 44), and from the found chlorides the corresponding carbonates calculated.

Crude Tartar and other Salts imparting an Acid Reaction.

To estimate the potassium hydrotartrate in crude tartar, titrate the aqueous solution of the same with sodium or ammonium hydrate. The amount of sodium and ammonium in their solutions is ascertained by an acid of known strength (p. 305).

The tartar is dissolved by boiling with a sufficiently large quantity of water and filtering off the residue of silicic acid. The filtrate is mixed with litmus tincture, and the alkaline solution (when cold, if ammonium hydrate is employed) added until the red color changes to blue.

In certain varieties of crude tartar no blue coloration occurs, but green instead, which indicates the final reaction fully as well.

The sodium or ammonium liquid of known strength can likewise be used in estimating other salt solutions having an acid reaction, *e. g.*, the estimation of potassium or sodium hydrosulphates, potassium hydro-oxalate, etc., and of course also for the estimation of free acids—sulphuric, hydrochloric, nitric, oxalic, citric, etc.

Soap.

In the valuation of soap the quantity of alkali, fat and moisture is to be determined.

The first of these may be accomplished by titration with sulphuric or hydrochloric acid. A weighed sample of the soap is dissolved in water, and so much acid added from a burette, until a drop of the liquid placed on litmus paper produces a red spot. If this operation occurs in a weighed porcelain dish, the same sample will suffice for the estimation of the amount of fat. The liquid neutralized with acid is allowed to cool, then decanted from off the solidified fat and the latter warmed with distilled water to remove the final traces of alkali inclosed in it. After cooling decant the water and dry the fat in a porcelain dish at 110° C., until constant weight is secured.

If the soap contains soda, the latter is determined by the estimation of the carbon dioxide (p. 33 or p. 302). Or, a weighed sample of the soap may be exhausted with absolute alcohol, and the insoluble sodium carbonate dissolved in water after filtering, and determined volumetrically.

The amount of water in soap is ascertained by drying a portion of the latter at 110°–120° C.

Nitre (Saltpetre).

Composition.—Potassium nitrate, together with nitrates of sodium, calcium and magnesium, and alkaline chlorides and sulphates.

If the saltpetre contains no other nitrates, the quantity of potassium nitrate is calculated from the nitric acid present.

[Another method of determining nitric acid may be inserted here.

It has been found that a thin plate of zinc, coated with copper (formed by placing the former metal in a solution of copper for a few minutes) decomposes water, particularly on warming, with the formation of zinc hydrate and the evolution of hydrogen.

The hydrogen so eliminated is capable of reducing nitric acid in combination to the state of ammonia—

$$NO_3K + 4H_2 = NH_3 + HKO + 2H_2O.$$

This reaction constitutes the basis of a method of determining nitric acid in nitrates.

About 25 to 30 grms. of thin sheet zinc are placed in a flask of about 200 C. C. capacity, and covered with a moderately concentrated and slightly warmed solution of copper sulphate. In about ten minutes a thick spongy coating of copper will be deposited on the zinc; the liquid is poured off the metals, which are now well washed with cold water, and covered with about 40 to 50 C. C. of pure water. Weigh out about 0.5 grm. of pure nitre into the flask, which is then placed in a sand-bath and connected with a condensing arrangement. The liquid is gradually heated to boiling and distilled for about an hour. The distillate is poured from a receiver, and evaporated to dryness in a porcelain basin over the water-bath with an excess of platinum tetrachloride, and the double salt treated as usual.]

Or, as already mentioned on page 242, the nitrates are decomposed by ferrous salts in the presence of hydrochloric acid, with the formation of ferric oxide, water and nitrogen oxide. To estimate the nitric acid, heat a sample of the salt with exclusion of air (see Fig. 5) together with a weighed quantity in excess of iron or ferrous ammonium sulphate (p. 77), and add hydrochloric acid. When the decomposition is complete, determine the remainder of the unoxidized ferrous salt with permanganate or potassium bichromate (p. 75 and p. 79), or determine directly with stannous chloride the ferric oxide that has been formed (p. 80). The calculation is readily made from the formula (p. 242).

When the valuation of saltpetre is to be determined, which contains not only potassium nitrate but also other nitrates, the preceding method is not applicable. Nothing other than a potassium determination is to be relied upon. The nitrates are for this purpose converted into chlorides, which is accomplished by repeatedly evaporating them to dryness with fuming hydrochloric acid or by several ignitions with ammonium chloride. The potassium is determined as double chloride of platinum and potassium. (See p. 42.)

If compounds of calcium and magnesium are present, they must be first removed (p. 45).

The sulphuric and hydrochloric acids are determined according to page 15 and page 17.

The moisture is ascertained by drying the samples at 120° C.

Gunpowder.

Composition.—Nitre, carbon, sulphur (and water).

The usual method for the analysis of gunpowder consists in drying a sample over concentrated sulphuric acid in a desiccator or at 70° C., and washing it upon a weighed filter with hot water to perfectly remove the nitre. The filtrate is evaporated to dryness in a weighed platinum dish, the residue dried at 120° C. and weighed. The difference in weight represents the total amount of carbon and sulphur. To estimate the latter exhaust the dried residue with carbon disulphide or with ammonium sulphide. The sulphur may also be calculated by difference if the carbon dried at 100° C. is ascertained, or in using carbon disulphide the filtrate is evaporated to dryness and the residual sulphur dried carefully at 70° C. and weighed.

[*Use of Platinum Vessels.*

As platinum vessels are so commonly used, the subscribed notes should be observed.

The following bodies should not be treated in platinum vessels :—

1. The caustic alkalies as well as baryta and strontia and their nitrates at a red and melting heat.

2. Fusible metallic sulphides or mixtures of sulphides with carbon ; thus, in particular, the alkaline sulphides.

3. Phosphates and carbon, which at a high heat give rise to platinum phosphide.

4. Metals that are easily fused, or mixtures of the oxides with substances which reduce them (carbon). These form fusible alloys with platinum.

5. Chlorine, and all mixtures that liberate chlorine, either in the cold or by heat; for instance, fusible mixtures of a metallic chloride and a nitrate, of ammonium sulphate and chloride.

Platinum crucibles may be cleaned by fusing borax or potassium bisulphate in them. They are afterwards digested in dilute acid, or scoured with fine round sand and water.]

TABLES FOR THE CALCULATION OF ANALYSES.

	Atomic and molecular weight.	100 parts contain
Aluminum	Al 27.3	
Aluminum oxide	Al_2O_3 102.48	53.28 Al
Antimony	Sb 122	
Antimoniate of teroxide of antimony	SbO_2 154	79.22 Sb
Antimony sulphide	Sb_2S_3 340	71.76 Sb
Arsenic	As 74.9	
Magnesium pyro-arsenate	$Mg_2As_2O_7$ 309.4	48.42 As
Ammonium-magnesium arsenate	$2MgO(NH_4)_2O+As_2O_5+H_2O$ 379.34	39.49 As 60.53 As_2O_5 80.44 As_2O_3
Barium	Ba 136.8	
Barium sulphate	$BaSO_4$ 232.62	58.81 Ba 65.67 BaO
Barium silico-fluoride	$BaSiFl_6$ 279.4	48.96 Ba 54.67 BaO
Beryllium	Be 9.3	
Bismuth	Bi 210	
Bismuth oxychloride	BiOCl 261.5	80.30 Bi
Boron	B 11	
Boracic acid	B_2O_3 70	31.42 B
Boro-fluoride of potassium	$KBFl_4$ 126.1	8.73 B 27.75 B_2O_3
Bromine	80	
Silver bromide	AgBr 188	42.55 Br
Cadmium	Cd 112	
Cadmium oxide	CdO 128	87.50 Cd
Cadmium sulphide	CdS 144	77.77 Cd 88.88 CdO
Cæsium	Cs 133	
Calcium	Ca 40	
Calcium oxide	CaO 56	71.42 Ca
Calcium carbonate	$CaCO_3$ 100	40.00 Ca 56.00 CaO
Calcium sulphate	$CaSO_4$ 136	29.41 Ca 41.17 CaO
Cerium	Ce 92.16	
Chlorine	Cl 35.5	

Tables for the Calculation of Analyses—continued.

	Atomic and molecular weight.	100 parts contain
Silver chloride . .	AgCl 143.5	24.73 Cl
Carbon . . .	C 12	
Carbon dioxide . .	CO_2 44	27.27 C
Calcium carbonate .	$CaCO_3$ 100	44.00 CO_2
Chromium . . .	Cr 52.4	
Chromic oxide . .	Cr_2O_3	68.57 Cr
Barium chromate . .	$BaCrO_4$ 253.4	20.67 Cr 29.54 Cr_2O_3 39.62 CrO_3
Lead chromate . .	$PbCrO_4$ 323.4	16.20 Cr 23.62 Cr_2O_3 31.04 CrO_3
Cobalt	Co 59	
Cobaltous oxide . .	CoO 75	78.66 Co
Copper . . .	Cu 63.3	
Cupric oxide . .	CuO 79.3	79.82 Cu
Copper sulphide . .	Cu_2S 158.6	79.82 Cu
Didymium . . .	Di 94.96	
Erbium . . .	E 112.6	
Fluorine . . .	Fl 19	
Calcium fluoride . .	$CaFl_2$ 78	48.71 Fl
Gold	Au 196.7	
Hydrogen . . .	H 1	
Water	H_2O 18	11.11 H
Iodine	I 127	
Silver iodide . .	AgI 235	54.04 I
Palladious iodide . .	PdI_2 360.5	70.45 I
Indium . . .	In 113.4	
Iridium . . .	Ir 196.8	
Iron	Fe 56 Fe_2O_3 160	70 Fe 90 FeO
Lanthanum . . .	La 92.8	
Lead	Pb 207	
Lead oxide . . .	PbO 223	92.82 Pb
“ chloride . .	$PbCl_2$ 278	74.46 Pb and 80.21 PbO
“ sulphide . .	PbS 239	86.61 Pb and 93.29 PbO
“ sulphate . .	$PbSO_4$ 304	68.31 Pb and 73.59 PbO

Tables for the Calculation of Analyses—continued.

	Atomic and molecular weight.	100 parts contain
Lithium	Li 7	
Lithium chloride	LiCl 42.5	16.47 Li 35.29 Li_2O
Lithium sulphate	Li_2SO_4 110	12.72 Li 27.27 Li_2O 77.27 LiCl
Magnesium	Mg 24	
Magnesia	MgO 40	60.00 Mg
“ pyrophosphate	$Mg_2P_2O_7$ 222	21.62 Mg 36.03 MgO
Manganese	Mn 55	
Manganese sulphide	MnS 87	63.21 Mn 81.60 MnO 90.80 Mn_2O_3
Manganese protosesquioxide	Mn_3O_4 229	72.05 Mn 93.01 MnO 103.49 Mn_2O_3
Mercury	Hg 200	
“ sulphide	HgS 232	86.20 Hg
Mercurous chloride	HgCl 235.5	84.92 Hg 84.92
Molybdenum	Mo 95.6	
“ sulphide	MoS_3 191.6	49.90 Mo
Nickel	Ni 59	
Nickelous oxide	NiO 75	78.66 Ni
Niobium	Nb 94	
Nitrogen	N 14.01	
Ammonium chloride	NH_4Cl 53.38	26.24 N 31.87 NH_3
Am. plat. chloride	N_2H_8PtCl 444.94	6.297 N 7.65 NH_3 8.09 NH_4
Osmium	Os 198.6	
Oxygen	O 16	
Palladium	Pd 106.5	
Phosphorus	P 30.96	
Magnesium pyrophosphate	$Mg_2P_2O_7$ 221.52	27.95 P 63.98 P_4O_5 85.59 PO_4
Calcium phosphate	$Ca_3P_2O_8$ 309.30	45.82 P_2O_5 63.24 H_3PO_4

Tables for the Calculation of Analyses—continued.

	Atomic and molecular weight.	100 parts contain
Platinum . . .	Pt 197	
Potassium . . .	K 39.04	
Potassium chloride .	KCl 74.41	52.47 K
Potassium sulphate .	K_2SO_4 173.9	63.19 K_2O 44.89 K 54.08 K_2O
Potassium plat. chloride	K_2PtCl_6 487	16.03 K 19.31 K_2O 30.56 KCl 35.71 K_2SO_4
Rhodium . . .	Rh 104	
Rubidium . . .	Rb 85.4	
Ruthenium . . .	Ru 104	
Selenium . . .	Se 79.4	
Silver	Ag 107.6	
" chloride . .	AgCl 143.03	75.27 Ag
Silicon	Si 28	
Silicic acid . . .	SiO_2 59.92	46.73 Si
Sodium . . .	Na 22.99	
" chloride . .	NaCl 58.36	39.39 Na 53.07 Na_2O
" sulphate . .	Na_2SO_4 141.80	32.42 Na 43.68 Na_2O
Strontium . . .	Sr 87.2	
" sulphate . .	$SrSO_4$ 183.02	47.64 Sr 56.36 SrO
Sulphur . . .	S 31.98	
Barium sulphate . .	$BaSO_4$ 232.62	13.75 S 34.33 SO_2 41.19 SO_4
Tantalum . . .	Ta 182	
Tellurium . . .	Te 128	
Thallium . . .	Tl 204	
Thorium . . .	Th 115.6	
Tin	Sn 118	
Tin oxide . . .	SnO_2 150	78.68 Sn
Titanium . . .	Ti 50	
Titanic acid . . .	TiO_2 82	60.97 Ti
Tungsten . . .	W 184	
Tungstic acid . .	WO_3 231.88	79.35 W
Uranium . . .	Ur 120	

Tables for the Calculation of Analyses—continued.

	Atomic and molecular weight.	100 parts contain
Uranous oxide . .	UrO 135.96	88.26 Ur
Uranium protosesquioxide . . .	Ur_3O_4 423.84	84.94 Ur
Vanadium . . .	Vd 51.3	
Yttrium . . .	Y 61.7	
Zinc	Zn 64.9	
" oxide . . .	ZnO 80.86	80.26 Zn
" sulphide . .	ZnS 96.88	66.99 Zn
Zirconium . . .	Zr 90	
" oxide . .	ZrO_2 121.92	73.82 Zr

Table for the Tension of Aqueous Vapor for Temperatures from 10° C. to 25° C.

Temperature.	Tension.
10° C.	9.165 Mm.
11 "	9.792 "
12 "	10.457 "
13 "	11.162 "
14 "	11.908 "
15 "	12.699 "
16 "	13.536 "
17 "	14.421 "
18 "	15.357 "
19 "	16.346 "
20 "	17.391 "
21 "	18.495 "
22 "	19.659 "
23 "	20.888 "
24 "	22.184 "
25 "	23.550 "

Table for the Calculation of the "Degree of Hardness" from the number of C. C. of the Soap Solution employed.

Employed soap solution.	Degree of hardness.
3.4 C. C.	0.5
5.4 "	1.0
7.4 "	1.5
9.4 "	2.0
The difference of 1 C. C. of the soap solution =	0.25
11.3 C. C.	2.5
13.2 "	3.0
15.1 "	3.5
17.0 "	4.0
18.9 "	4.5
20.8 "	5.0
The difference of 1 C. C. of the soap solution =	0.26
22.6 C. C.	5.5
24.4 "	6.0
26.2 "	6.5
28.0 "	7.0
29.8 "	7.5
31.6 "	8.0
The difference of 1 C. C. of the soap solution =	0.277
33.4 C. C.	8.5
35.0 "	9.0
36.7 "	9.5
38.4 "	10.0
40.1 "	10.5
41.8 "	11.0
The difference of 1 C. C. of the soap solution =	0.294
43.4 C. C.	11.5
45.0 "	12.0
The difference of 1 C. C. of the soap solution =	0.31

INDEX.

Ammonium platinic chloride, p 39

ERRATA.

Page 109, line 18 from above, *read* "desirable" *for* "preferable."
" 300, " 5 from below, *read* "were" *for* "was."

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