THE PRECISE DETERMINATION OF COBALT

AS THE SULFIDE

by

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Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial ful-
fillment of the requirements for the
degree of Doctor of Philosophy.

1927.

UMI Number: DP70454

UMI

Dissertation Publishing

UMI DP70454

ProQuest

ACKNOWLEDGMENT

Table of Topics

Introductory Statement

An examination of the standard analytical text-books discloses the fact that the methods by which cobalt can be determined quantitatively are not numerous and that those already developed are in many cases open to objections either because of the manipulative detail involved or because of susceptibility to error. Also from a qualitative standpoint it is evident that the separation of cobalt from the other members of the third group as the sulfide has not been fully studied.

The present work was, therefore, undertaken with a twofold objective in view. It was first desired to develop a satisfactory method for the quantitative determination of cobalt. The method once developed was to be used to study the completeness of precipitation of cobalt as the sulfide in solutions of varying pH values. The solutions were to be buffered in order to keep them at the desired pH value.

Review of Literature

A perusal of the literature on the subject reveals the fact that the precipitation of cobalt as the sulfide has been used very little as a direct method for the quantitative determination of the metal and furthermore so that no study has been made of the effect of p^H value upon either the completeness of precipitation or the character of the precipitate. Treadwell (1) discusses the precipitation of cobalt by ammonium sulfide. His directions for the precipitation are: "Put the solution into a flask, add ammonium chloride then ammonia just in excess, then ammonium sulfide as long as a precipitate is produced, fill up to the neck with water, cork and allow to stand for twelve to twenty-four hours in a warm place. In the moist state exposed to the air the sulfide oxidizes to the sulfate. In washing the precipitate after filtering, therefore, water containing ammonium sulfide is employed and the filter is kept full. It is advisable also to mix a little ammonium chloride with the wash water but its quantity should be gradually decreased, and the last water must contain none." The sulfide is then redissolved in aqua regia containing an excess of hydrochloric acid and the cobalt is weighed as the metal after precipitation and reduction of the hydroxide. Treadwell adds that there are no sources of error in the precipitation with ammonium sulfide. This statement will receive further comment in the course of this paper.

R. W. Landrum (2) goes a little further than Fresenius. In Landrum's method, "cobalt, manganese and nickel are precipitated together as sulfides and filtered off. The manganese is dissolved from the precipitate with cold hydrogen sulfide water acidified with one-fifth its volume of hydrochloric acid (sp. Gr. 1.11). The residue of cobalt is burned in a porcelain crucible, dissolved in aqua regia and evaporated with hydrochloric acid. The platinum and copper, if they are present, are thrown down by passing hydrogen sulfide through the solution. The filtrate is made ammoniacal and the cobalt is pre-cipitated with hydrogen sulfide. This is filtered off and washed with water containing a small quantity of ammonium sulfide. The precipitate is either ignited and weighed as oxide or reduced in hydrogen to metallic cobalt, taking care to cool it thoroughly in an atmosphere of hydrogen before allowing it to come in contact with the atmosphere of the room, as finely divided cobalt is decidedly pyrophoric and oxidizes readily, particularly if reduced at a low temperature." This latter statement will be commented on further.

One investigator, Low, (3) has precipitated cobalt as the sulfide in buffered acid solution. After the metals of group two have been removed by hydrogen sulfide he proceeds as follows: "boil the filtrate until the hydrogen sulfide is completely expelled and then add ammonia in slight excess. Now acidify slightly with acetic acid, add one to two grams of sodium acetate, heat to 70 or 90 degrees Centigrade and saturate with hydrogen sulfide. The nickel and cobalt

are precipitated as sulfides. Filter and wash with hot water. The
filtrate may still contain small amounts of nickel and cobalt. Con-
centrate it and add colorless ammonium sulfide. Make slightly acid
with acetic acid, warm and filter. If a precipitate is obtained,
collect it on a separate filter. Repeat this testing of the filtrate
until no further precipitation is produced.

Wash the precipitated sulfides from the filters, as completely
as possible, into a small porcelain dish or casserole. Try and wash
the filters and add the ash also. Dissolve the whole in hydrochloric
acid and a little nitric acid. The solution now contains nickel,
cobalt and possibly zinc. To remove the latter, evaporate to small
volume, add two or three grams of ammonium chloride. Pausanias (4).
evaporate to dryness on a water bath and then heat carefully until
all the ammonium chloride is expelled. The zinc is driven off at
the same time. Then cool dissolve the residue in nitrohydrochloric
acid and expel the excess of acid by evaporating nearly to dryness.
The cobalt is then precipitated as hydroxide with potassium hydroxide
and some bromine water. After ignition of the hydroxides the results
are reported as combined nickel and cobalt unless nickel is to be deter-
mined separately, in which case it is precipitated as the hydroxide by
red mercuric oxide while cobalt is retained in solution in the form of
potassium cobaltiocyanide.

There are numerous cases where cobalt has been determined
by weighing up as the metal in the final step. For example, Pausanias

5.

(5), Burgess (6), Low (7), and Scott (8).

An investigation which partially parallels the one under discussion was carried out with zinc by Maloo and Ware (9). Zinc was precipitated as the sulfide from carefully controlled buffer mixtures composed of ammonium formate and formic acid. The completeness of precipitation as a function of hydrogen-ion concentration was fully studied in the same manner as in the present investigation. The sample was finally weighed as the sulfate and not as the metal.

The literature reveals no further work differing greatly in principle from that already cited.

Discussion of Principles

Inasmuch as this investigation has to do with the development of a method for the quantitative precipitation of cobalt as the sulfide and with the completeness of precipitation in buffered solutions of varying hydrogen-ion concentration, it will be advisable to discuss some of the principles involved.

The method is based on the relative insolubility of cobalt sulfide in solutions of low acidity. The small amount remaining in solution may be considered to be fully dissociated into cobalt and sulfide ions. Likewise the dissolved sulfide is in equilibrium with the solid sulfide so we may write: $CoS_{Solid} \rightleftharpoons CoS_{Dissolved}$ and $CoS_{Dissolved} \rightleftharpoons Co^{++} + S^=$. The concentration of the dissolved sulfide is constant under these conditions and hence $\frac{CoS_{Diss.}}{CoS_{Solid}} = K_s$, where K_s is the solubility constant. Also $\frac{[Co^{++}][S^=]}{CoS_{Diss.}} = K_1$, where K_1 is the dissociation constant. Since $CoS_{Diss.}$ is a constant the last equation may be written $[Co^{++}][S^=] = K_{S.P.}$, where $K_{S.P.}$ is the familiar solubility product constant. The quantities $[Co^{++}]$ and $[S^=]$ are the effective ion concentrations or activities. A distinction must be drawn between concentration of dissolved sulfide and activity. The ratio of the activity to the total concentration of the electrolyte is the activity coefficient or the thermodynamic degree of dissociation. Creighton and Fink (10). Whenever concentrations are mentioned activities are to be understood unless otherwise stated. Hence the solubility product constant is the product of the activities of cobalt and sulfide ions which determines the amount of cobalt sulfide

which remains in solution. This activity product is fixed and definite. If one of the quantities involved in the product is increased the other must decrease as required by the solubility product constant.

The solubility product of cobalt sulfide quoted in Landolt-Bornstein (11) is the value calculated by Bruner and Zawadzki (12) by use of the modified equation of Bodlander, namely $\frac{Q}{2.23100} = E_A + E_K - .029 \log L$. In this equation Q is the heat of formation of the sulfide, E_A is the discharge potential of the anion, E_K that of the cation and L is the solubility product. The value given for cobalt sulfide is 3×10^{-26}. The value given for beta zinc sulfide is 1.2×10^{-23} and for nickel sulfide 1.4×10^{-24}. On the other hand, the value quoted by Seidell (13) from work done by Weigel (14) in 1906 by use of the electrolytic conductivity method, assuming complete dissociation and hydrolysis, for the solubility of cobalt sulfide in water at 18 degrees, gives a solubility product of 1.7×10^{-9}. This value is extremely different from the one in Landolt-Bornstein. The results obtained in the present investigation are more nearly in accordance with the value quoted by Seidell so that the discussion will be conducted in the light of the latter value.

In order that the solubility product be satisfied and a precipitate form, the product of the activities of sulfide ion and cobalt ion must equal 1.7×10^{-9}. If the salt is somewhat soluble the concentration of unionized salt must also be equalled. Chapin (14a).

9.

Consequently cobalt sulfide will either dissolve or fail to precipitate, as the case may be. The object of this investigation was to find the point at which incomplete precipitation begins. This was to be done by systematically lowering the pH value by small increments. It is, of course, obvious that the precipitation of cobalt sulfide itself will lower the pH value as a result of liberation of mineral acid until precipitation ceases unless steps are taken to suppress this lowering. A means of bringing about this suppression lies in the use of alkaline solutions or suitable buffer solutions.

The action of so-called buffer solutions may be most clearly explained by means of the theory of mixed electrolytes. Creighton and Fink (17). Whenever two binary electrolytes are present in solution, their four ions may react to form the four undissociated substances, the amount formed of each being governed by the equilibrium equations applicable to the respective substances. When all the four possible products are strong electrolytes, the ions react to but a negligible extent. The case is quite different, however, when one of the possible products is a weak electrolyte. For example, if ammonium and acetate ions (ammonium acetate) are introduced into a solution containing hydrogen and chlorine ions (hydrochloric acid), there is a great tendency for the acetate and hydrogen ions to combine to form undissociated acetic acid for $K_{HAc} \dfrac{[H^+][Ac^-]}{[HAc]} = 1.8 \times 10^{-5}$.

Since this ratio must always be satisfied, it is evident, therefore, that hydrogen and acetate ions must unite with one another to form undissociated molecules of acetic acid. Furthermore, this

union must proceed until the activities of these ions are reduced and
the activity of undissociated molecules is increased to such an extent
that the product of the activities of the ions divided by the activity
of the undissociated molecules is equal to 1.8×10^{-5} . This results
in the conversion of practically all of the ammonium acetate into
acetic acid. The reaction which takes place in this case may be
written: $\overset{+}{NH_4} + \overset{-}{Ac} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{NH_4} + \overset{-}{Cl} + HAc$.

or, omitting those substances which occur on both sides of the equation,
simply: $\overset{+}{H} + \overset{-}{A} = HA$. Similarly when a solution of a strong base is
added to a solution of a salt of a weak base, the weak base is
"liberated".

If to a liter of pure water one cubic centimeter of 0.01 normal
hydrochloric acid were added the pH value would drop from 7 to 5,
while the addition of the same quantity of 0.01 normal sodium hydroxide
would bring about a similar rise in the pH value. On the other hand,
if the solution of acid or alkali were added to a liter of a solution
of a weak acid, HA, and its salt, MA, the resulting change in pH would
be scarcely appreciable. In the latter case change in pH on the
addition of acid or alkali is opposed by the reaction: $\overset{-}{A} + \overset{+}{H}$ HA
or $HA + \overset{-}{OH} = H_2O + \overset{-}{A}$.

This power of certain solutions to resist change in PH on the
addition of acids or alkalis has come to be known as buffer action
and the solutions which exhibit this action are termed buffer solutions.

Buffer solutions evidently possess a reserve acidity or alkalinity

Since in accordance with the law of mass action $[H^+] = \dfrac{[HA]}{[A]} K_a$
it follows when $[H^+] = K_a$ or $[A] = [HA]$ that the reserve acidity and alkalinity of a buffer solution will be equal.

Thus if one wishes a solution of $[H^+] = 1 \times 10^{-5}$, which shall have equally effective buffer action towards added acid or added base, an acid with a dissociation constant close to this value is selected and mixed with the proper amount of its alkali salt.

Since in the present work it was necessary to obtain varying pH values, the solution of acetic acid used was made up sufficiently strong that it could be diluted to varying degrees to give any desired pH when mixed with a fixed quantity of its ammonium salt. The stock solution of acid prepared was 6.8 molar and a pure solution of this acidity would give a pH of approximately two as calculated by the equation $[H^+][Ac] = Ka [HAc]$ and as experimentally confirmed.

An experimental study was made of the effect on pH of adding varying amounts of the stock solution of acid to a constant volume, twenty-five cubic centimeters, of 0.4 molar ammonium acetate, subsequently diluting with water to a constant volume of 65 cubic centimeters. When the pH values had been obtained, 58.6 cubic centimeters of 0.1 molar hydrochloric acid were added in different cases in order that an indication might be obtained of the effectiveness of the buffer action. This quantity of hydrochloric acid is equivalent to that which would be set free during the precipitation by hydrogen sulfide of 0.25 grams of cobalt metal in the form of the chloride. The data obtained follow:

Table Showing pH of Various Buffer Mixtures and Effect of
Added Mineral Acid.

cc acetic acid (6.8N)	pH	pH after adding 38.6 cc 0.1N HCl	Resulting drop in pH
0	6.373	4.734	1.639
1	4.603		
3	4.218	3.922	0.296
5	3.996	3.693	0.303
10	3.682	3.449	0.208
15	3.465	3.265	0.220
20	3.247	3.102	0.245
25	3.221	3.043	0.278
35	3.096		
40	2.978	2.840	0.135

The results are shown graphically by the accompanying curves.
(Graphs I and II.) Graph I was used as a guide in obtaining mixtures
of desired pH value preparatory to the actual precipitation of
cobalt samples.

In the precipitation of cobalt as the sulfide, the concentration
of sulfide ions, which in turn depends upon the pH value, determines
to a large extent the optimum conditions. If ease and certainty of
complete precipitation alone are to be considered, then a pH value of
5 or even 6 would be most desirable. However, under such conditions
the sulfide ion concentration is relatively so great and consequently

Graph I.
pH of various mixtures before and, as indirectly determined, after precipitation.

Before precipitation (1)

After addition of HCl (2)

cc. Acetic Acid

pH

Graph II.
Curve showing increase in buffer action as concentration of acetic acid is increased.
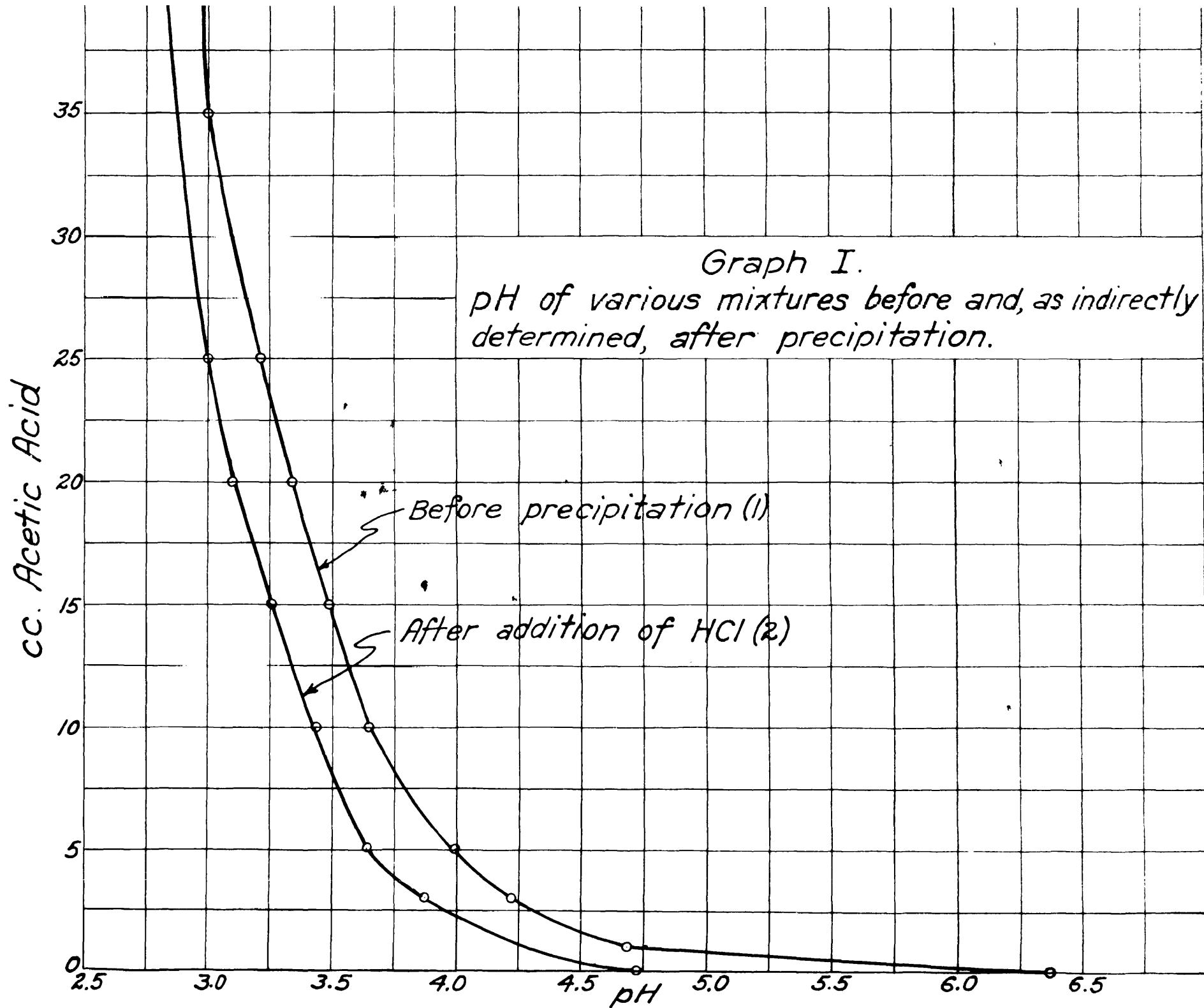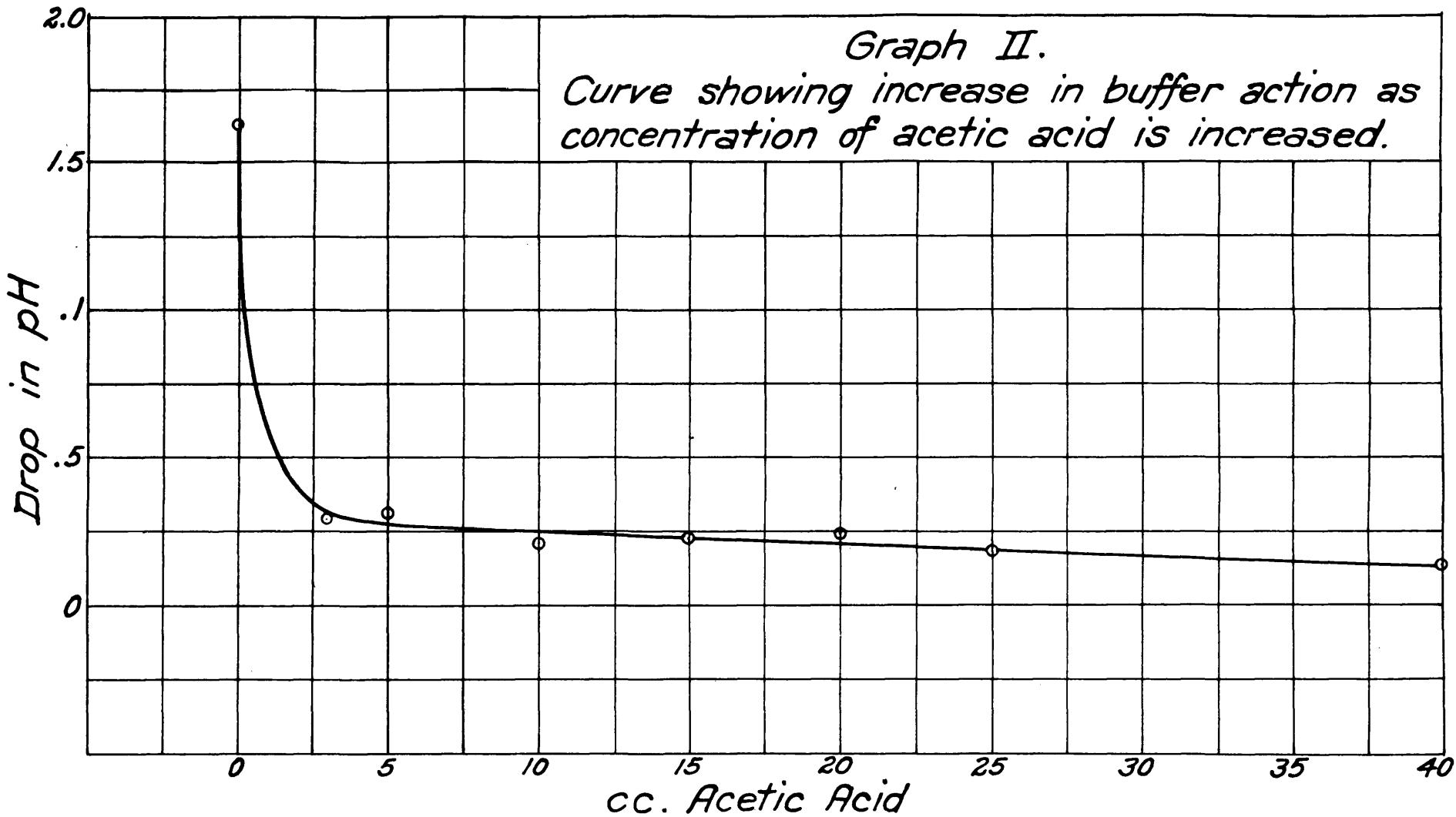
the number of crystal nucleii formed so large that the cobalt sulfide precipitated has a gel-like structure because of its enormous surface. The factor of washing makes this form of the precipitate most undesirable but there is still a more important objection. This is the propensity to oxidation of the sulfide to the sulfate. The more surface possessed by the precipitate the greater this propensity. This is indicated by a simple form of the equation for the velocity of heterogeneous reactions, that is $\frac{dx}{dt} = kS(a-x)$, Getman (17a), where S represents the area exposed and x denotes the amount of solid oxidized in the time t, k being a constant. This equation must, of course, be integrated before it can be used. The tendency to oxidation forbids the precipitation of the sulfide in so weakly acid solutions and points to the highest possible limit of acidity. Furthermore, Graph II shows that buffering action is relatively small at these high pH values. However, this upper limit is unsuitable for the reason that the element of saturation is involved. If saturation of the solution with hydrogen sulfide is not complete the active mass of sulfide ion will not be at a maximum and precipitation will be incomplete. The resultant of these factors and the curve shown elsewhere in this paper point to a pH value of 3.95 as being optimum. Under these conditions the precipitate is in the form of relatively large crystals, is quick settling and easily washed without danger of oxidation if reasonable care be exercised.

In roasting the precipitate several considerations enter. In the first place, the precipitate becomes partially converted only to the sulfate instead of entirely to the oxide. The temperature of de-

composition of cobalt sulfate is placed at 720 to 770 degrees

Centigrade. This factor, therefore, sets an absolute minimum temper-

ature. There are still other elements to be considered. Time is of

importance and a higher temperature shortens the time for roasting.

The same temperature is used for the reduction as for roasting and a higher

temperature is required for the reduction for the reason that cobalt

reduced at low temperature is quite pyrophoric and could not be weighed

with accuracy. If a temperature of 1000 degrees Centigrade is used for

reduction the pyrophoric nature of the reduced cobalt entirely disappears.

This might possibly be explained by sintering of the cobalt crystals at

the higher temperature.

Description of Apparatus

The method as finally adopted involves no accurate volumetric measurements, all precise measurements being gravimetric. The balance used was carefully calibrated for sensitivity. The weights were accurately calibrated by the Richard's substitution method, (17b).

The hydrogen ion measurements were made with a Leeds Northrup Students' potentiometer. The hydrogen electrode used was a platinized platinum, Hildebrand type bubbling electrode. The normal calomel electrode was used as reference. The hydrogen was purified by passing successively through alkaline pyrogallate, alkaline permanganate and water, after being generated in a Kipp generator by the action of thirty percent sulfuric acid on zinc.

The hydrogen sulfide was generated in a Kipp apparatus and passed in succession through absorbent cotton and two bottles of distilled water.

The furnace used for roasting and reducing the sulfide was an ordinary electric combustion furnace capable of reaching a temperature of 1000 degrees Centigrade.

The materials were all of "reagent" quality. Blanks were run on the acetic acid and ammonium acetate and a constant weight of 0.2 milligram subtracted from all determinations to take care of added non-volatile impurities. Stock solutions of acetic acid and ammonium acetate were made up in sufficient volume to permit the same solutions to be used throughout the work. The water used at all times was a

high grade of distilled water (specific conductivity 2×10^{-6} mhos) .

The prime requirement in the case of the substance to be studied, namely cobalt, was that it should be easily and quickly available in a form which possessed a definite composition, was stable under ordinary conditions, and could be weighed up with ease and dispatch.

First, of course, it was necessary to free the cobalt from the impurities present. The source of supply was "Baker's Analyzed" cobalt chloride hexahydrate which contained, according to the label, five hundredths percent of nickel and a smaller percent of iron. The method of purification was the usual one for cobalt and the one which was used by Baxter and Coffin (18) in their atomic weight determination of cobalt. It consists of the preparation of chloropentammine-cobaltichloride, Biltz (19), which precipitates in a pure condition in the presence of nickel. Iron is removed previously when the cobalt solution is made ammoniacal. The cobalt complex is redissolved, after filtering and washing thoroughly with one to one hydrochloric acid, in dilute ammonia. It is then reprecipitated by making the solution strongly acid with hydrochloric acid, and finally filtered and washed with dilute acid as before. Two precipitations were considered sufficient since the cobalt obtained thereby failed to show any trace of nickel by use of dimethylglyoxime or the presence of iron on the addition of ammonia.

Once the cobalt was purified it had to be converted into a form possessing the characteristics mentioned above. Baxter and Coffin, loc. cit., used anhydrous cobalt chloride as their source of supply but the difficulties involved in preparing this and keeping it in a pure anhydrous form were prohibitive in this investigation. It was

then thought that the stable hemihydrate might be obtained but the time required to secure the latter in a form entirely free from excess moisture and other hydrates was unreasonably long. Even the hemihydrate is not stable under all ordinary conditions.

An attempt was next made to prepare a standardized, concentrated aqueous solution of cobalt chloride which could be weighed out in a weight burette. On standing, however, the solution hydrolyzed to an appreciable extent. A small volume of semi-normal hydrochloric acid added to the solution would prevent this hydrolysis, but, even so, the solution was not immune to changes in composition due to evaporation.

It was finally decided to reduce the cobalt to the metallic state and use the pure metal as the starting point. The metal has all the desired characteristics and is easily converted into any desired salt by dissolving in the appropriate acid. The decision to use the metal as the stock material came as a result of a change in analytical procedure. It was originally proposed to follow in part the procedure or Fales and Ware, loc. cit., in their work with zinc. After precipitating zinc as the sulfide, these investigators converted the sulfide to the sulfate and weighed it as such. It was found in the case of cobalt sulfide impossible to bring about complete conversion to the sulfate without too great danger of loss or some of the material. This was because nothing short of aqua regia would dissolve cobalt sulfide. As a consequence of this, the plan of procedure was changed and the sulfide, after roasting, was reduced to cobalt metal.

It will readily be seen that if the end-product is cobalt metal, by using cobalt in the same condition as the starting material an excellent check is had on the accuracy of the analysis.

A word might be said at this point in regard to a difficulty encountered in the roasting and reduction of the sulfide. The original plan was to burn off the oven-dried precipitate in a crucible and then transfer it to a weighed short length of Pyrex glass tubing one centimeter in diameter for roasting and reduction. The sulfide was heated until the Pyrex tube softened, which requires a temperature of over eight hundred degrees Centigrade. During the heating, the sulfide was exposed alternately to the oxygen of the air and to a stream of hydrogen. Even though treatment might be continued for hours, never in any case did the weight of the reduced metal decrease to the theoretical value. This fact may have been due to two reasons. First, not all of the sulfur trioxide may have been driven off. Secondly, cobalt reduced at low temperatures is quite pyrophoric (R. W. Landrum loc. cit.) and the material as it was weighed up may have been contaminated with oxide. At any rate, it was found necessary to abandon this plan of procedure and substitute the one which was used henceforth. This will be described in another place.

Discussion of Method and Results

Preliminary investigation indicated that two-tenths gram of
metallic cobalt was the most suitable quantity for precipitation as
the sulfide under the conditions selected. The metal was poured out
upon a small watch glass, the total weight carefully determined by
the method of swings, and approximately two-tenths gram accurately
weighed out into each of two three hundred cubic centimeter Erlenmeyer
flasks. About five cubic centimeters of concentrated hydrochloric
acid were added to each and the tops of the flasks immediately cover-
ed with watch glasses, to protect against loss from effervescence.
The flasks were placed on water baths and warmed until all the metal
was in solution. The acid solutions were rinsed out into two hundred
fifty cubic centimeter beakers and evaporated to dryness. Each beaker
was then set on an asbestos-covered hot plate until the chloride had
assumed the bright blue color of the anhydrous salt. This latter
step was taken to insure complete removal of excess acid.

In the qualitative separation of the various groups of metals
cobalt is precipitated as the sulfide from an alkaline solution,
but it is well known that it will be completely precipitated from
solutions the pH values of which are much less, provided steps are
taken to neutralize the acid liberated during the precipitation.
It was, therefore, next a question of finding a suitable buffer
material. Preliminary investigation had disclosed the fact that

moist cobalt sulfide is spontaneously oxidized to the sulfate by the oxygen of the air. See also Treadwell (20). It is also a known fact that aqueous hydrogen sulfide solutions exert a peptizing action on sulfides. Hammarsh (21). It becomes, therefore, a matter of preventing loss into the filtrate by these two opposing influences. If a buffer solution containing a non-volatile solute were to be used the non-volatile matter would have to be washed out of the precipitate, and this washing would expose the precipitate to loss by peptization if hydrogen sulfide water alone were used or yet to loss by solution if the precipitate were washed sufficiently with a hydrogen sulfide solution containing a volatile electrolyte. In view of these conditions a volatile buffer material, namely ammonium acetate-acetic acid, was selected. By using this material all washing was eliminated. However, still another precaution was taken which was the use of two filter papers. A very rapid filtering, ashless, plaited filter paper of fine texture (Whatman No. 40) was used. The bulk of the precipitate was quickly poured into the first paper which was also contained in diameter, and then any precipitate adhering to the flask was washed by means of the filtrate from the first paper upon a smaller paper, also plaited, of three centimeters in diameter. In this way, no liquid was poured over the precipitate after it had dried to the least extent.

When the cobalt chloride had been freed of excess acid as described above, the buffer mixture was added in the proper concentration, and

the volume adjusted roughly to sixty-five cubic centimeters. The amount of buffer to be added was determined by calculating the amount of acid liberated during precipitation of the weight of metal taken, and then adding a considerable excess of buffer material as a safety margin.

It was found that twenty-five cubic centimeters of approximately 0.4 normal ammonium acetate would answer this requirement very well, and this constant volume of solution was added to the sample. The volume of acetic acid to be added in each case was determined by the pH value desired. By making the total volume up to sixty-five cubic centimeters with water and determining the pH value of the solution in the same beaker in which the evaporation was carried out, the final volume was between ninety and one hundred cubic centimeters. The difference between these two volumes represent of the amount of water required to rinse the electrodes and beaker. Only the initial pH value was determined because no equilibrium could be obtained in the hydrogen sulfide saturated filtrate. Hydrogen sulfide apparently acts as a poison to the platinized platinum electrode. The necessary information as to the effect of the acid liberated during the sulfide precipitation was obtained by adding hydrochloric acid in equivalent amount to the various buffer mixtures as explained earlier in this paper.

When the initial pH value had been determined, the solution was ready for precipitation. In preliminary work it was found that the sulfide had a striking tendency to be adsorbed on the walls of the flask. Apparently this tendency was less when the solution was

heated, and, furthermore, the precipitation was more rapid from hot
solutions. Also the precipitate was more compact at the higher temper-
atures. In the light of those facts all precipitations were carried out
in solutions which were heated just to the boiling point immediately
before hydrogen sulfide was passed in. A further precaution which was
found to be very helpful in preventing adsorption consisted of washing
down the sides of the flask thoroughly with distilled water before
heating. Hydrogen sulfide was not passed into the cobalt solution but
simply into the space above the latter. All air was driven from the
system by the incoming gas and during this time care was taken to have
the cobalt solution free from all agitation, as it was found that if the
solution was agitated and thereby splashed on the walls above the liquid
surface adsorption was greatly increased. Ordinarily the flask should
not be agitated before five minutes have elapsed and then a rotating move-
ment is given to the contents. The hydrogen sulfide is then confined
by pinching off the rubber exit tube and a slight positive pressure
of the gas is built up. Precipitation continues as the solution cools
and it more certain to be complete if a rapid rotating movement is given
to the flask at intervals. As a result of this agitation the precipitate
very soon settles out leaving a crystal-clear supernatant mother liquor.

The pH value of the solution exerts very interesting and important
effects upon the character of the precipitate as well as upon the rate
and completeness of precipitation. If the pH value at the start of the
precipitation is near the neutral point the entrance of the hydrogen

sulfide into the space above the liquid is accompanied by black
streamers of sulfide penetrating down through the liquid. Precipi-
tation goes on rapidly even when the solution is perfectly free from
agitation. Upon subsequent shaking the precipitate settles out in a
very bulky flaky form leaving only a shallow depth of clear super-
natant liquid. As the pH value decreases the rate of precipitation
slows down and the bulkiness of the precipitate decreases steadily.
Finally at the upper limit of hydrogen ion concentration the pre-
cipitate has become so compact that it forms only a thin layer on a
small area on the bottom of the flask. It may also be said at this
point that as the upper limit of acidity is approached it becomes
very difficult to obtain complete precipitation. The reason for this
is probably the same as that discussed by Weiss (22) with regard to
the acid separation of zinc. With a given set of conditions the
precipitation of zinc or of cobalt as the sulfide ceases when the
pH value decreases to a certain value. The reaction between hydrogen
sulfide and the cobalt or zinc salt is reversible and at a given
acidity more sulfide can be precipitated if the active mass of the
hydrogen sulfide in the solution be increased. Of course, in the
presence of hydrogen ions from another source the active mass of the
hydrogen sulfide, namely the concentration of sulfide ions, can be
increased only to a certain definite limit. As the pH value of the
solution decreases it becomes increasingly difficult to attain this
limit because the factor of saturation of the solution with hydrogen
sulfide becomes more important and a longer time must be allowed for
the precipitation to insure that the saturation value for hydrogen

sulfide at the given pressure and temperature has been reached. In no case is the passage of the gas discontinued before the solution has cooled to room temperature. At the upper limit of acidity it is necessary to allow the solution to set in contact with hydrogen sulfide over night.

The filtration of the sulfide has already been described. After filtration the smaller filter is placed inside the larger one and the whole dried in the oven at 100 degrees Centigrade. It is during this drying that the oxidation of the sulfide is especially noticeable. When the precipitate is removed from the oven the whole paper has assumed a purple color due to cobalt sulfate. After the drying has been completed the paper is removed from the funnel and held over a white glazed paper, on which side a crucible, while it is folded carefully and placed in the crucible. The latter is then set on a quartz plate strongly heated by a Bunsen burner and the paper slowly burned off. The crucible is next set over an open flame and heated to red heat until all carbon is burned off. The residue of mixed oxide, sulfate and sulfide is transferred to a weighed porcelain boat which sets on the white glazed paper thus affording protection against loss of material. The funnel and crucible are both wiped clean with a small piece of ashless filter paper which is carefully dried and placed in the boat with the sulfide. Any sulfide spilled on the paper is also wiped up with the filter paper.

The porcelain boat and its contents are then placed in a quartz combustion tube, which is inserted into the electric combustion furnace.

The heating of the furnace is not started until the boat is in it

becomes sudden heating of the small amount of filter paper in the

boat produces gases inside the tube which often leads to more or less

violent explosions inside the tube with resulting loss of material

from the boat. By means of an ordinary water suction pump a slow

current of air is drawn through the quartz tube to facilitate roast-

ing. The roasting is continued for one-half hour from the time the

interior of the tube has begun to glow at dull red heat. The furnace,

of course, does not come up to full heat for some little time but

this length of time appears to be sufficient. At the end of the time

the tube which is held at each end by clamps is displaced and

stands is lifted bodily from the furnace. After the boat inside the

tube has ceased to glow, that is, within two or three minutes, a slow

stream of hydrogen is led through the tube until most of the air is

displaced. The gas currents should never be so violent as to produce

loss of the feathery material from the boat. The tube is then placed

back in the furnace which has not been allowed to cool and heated at

the full heat of the furnace for twelve or fifteen minutes, after

which it is removed and allowed to cool with hydrogen still passing

through it. When the tube and boat have become cool the boat is re-

moved and weighed forthwith.

Bliss and Marg, loc. cit., found that the accuracy of the method

for zinc decreased with rising pH values. The same was not found true

for cobalt. The complete set of values for the range of acidity in-

vestigated in this research is given in the following table:

Table Showing Completeness of Precipitation of Cobalt as the Sulfide
from Solutions of Varying Acidity

Ct. Taken	Ct. Found	pH	Cubic Centimeters Acid Added	Error in Parts per 1000
			0.0	1.0
			0.0	1.2
			0.2	0.5
			0.2	1.5
			1.5	0.5
			1.5	1.5
			3.0	0.5
			3.0	1.5
			4.5	1.5
			4.5	0.5
			5.5	1.1
			5.5	0.5
			7.5	0.9
			7.5	1.5
			9.0	1.0
			9.0	1.5
			12.0	2.0
			12.0	2.0
			16.0	6.0
			16.0	6.4
			70.4	70.4

The first column gives the weight in grams of cobalt metal taken, the next column the weight found, the third the initial pH value, and the fourth the number of cubic centimeters of acetic acid required to give the pH value in the third column. The last column gives the error in parts per thousand. Only the initial pH values are given because it was found impossible by reason of electrode poisoning to determine the final pH values of the hydrogen sulfide saturated filtrate. The effect of added acid is shown in another table given previously. The volume of acetic acid to be added in each case to give a desired pH value was subject to some variation. This is explained by the nature of the technique.

When the last traces of mineral acid were expelled from the cobalt chloride preparing it for precipitation by setting it on a hot plate some hydrochloric acid was lost from the salt itself. This is explained by the partial hydrolysis of the cobalt chloride molecule to yield one molecule of the basic chloride and one molecule of hydrochloric acid. The degree of this hydrolysis varies with the intensity of heating and this explains the variation in the pH value obtained with different samples to which were added a constant amount of acetic acid. The volume of ammonium acetate added is not shown in the above table but it was twenty-five cubic centimeters in each case.

When the complete set of values had been obtained a curve was constructed to show the variation in accuracy of the determination with the initial pH value. The error in parts per thousand was plotted as

Graph III.
Relation between Completeness
of Precipitation and Initial pH.
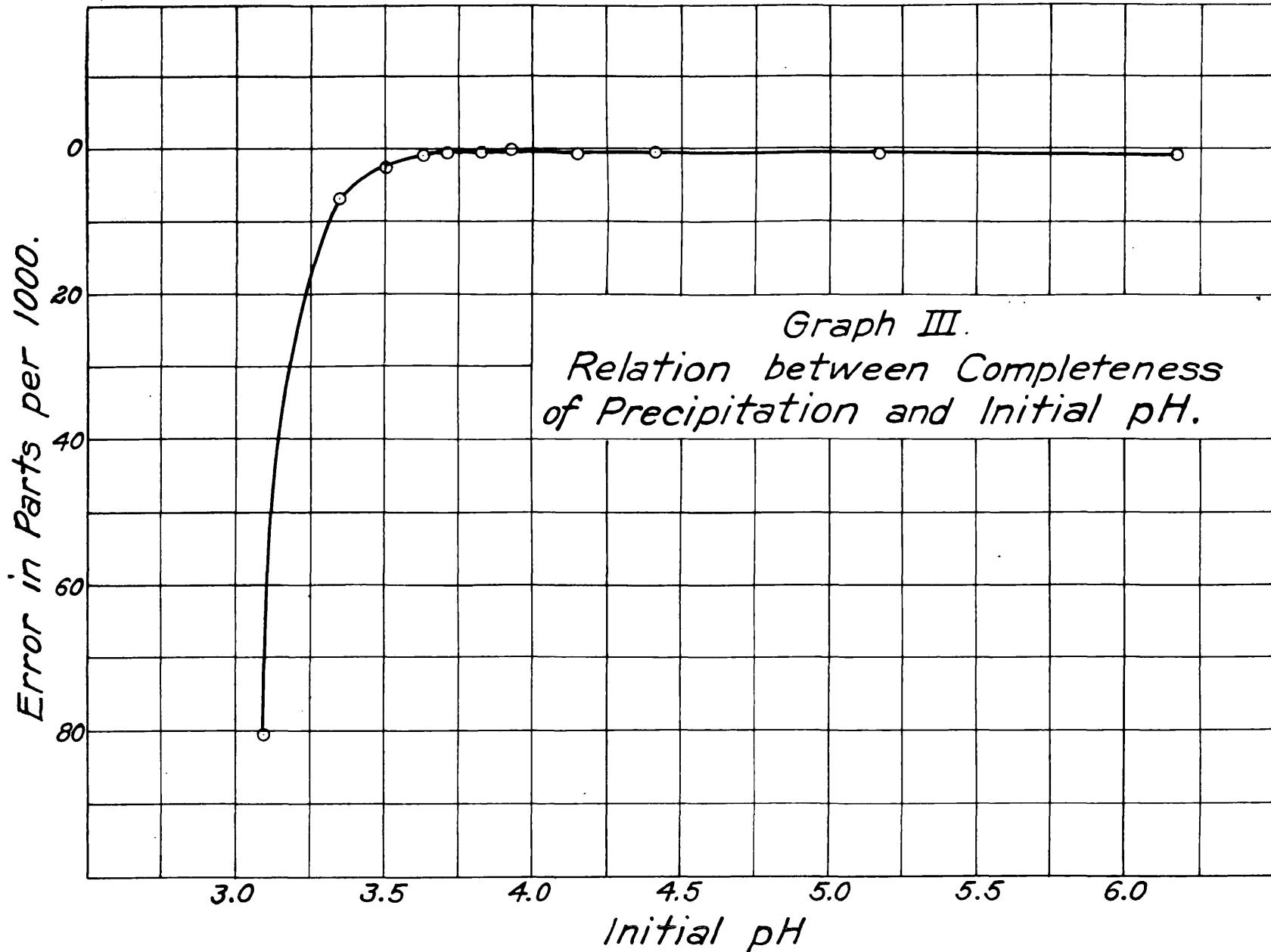
ordinates and the pH values as abscissae. The curve is here shown
(Graph III). The point of greatest accuracy was selected from the curve
while taking into account various other factors. The acidity selected
must provide for desirable filtering properties in the precipitate and
reasonable ease in obtaining complete precipitation. A pH value of
3.93 was found to fulfill all of these requirements. The precipitate
was so compact and granular as to permit washing with little or no
danger of loss by oxidation even when washed very thoroughly. A
series of three determinations involving six samples were made in
solutions of this acidity and the results are given below:

Table Showing Accuracy of Determination Under Optimum Conditions for Precipitation as the Sulfide

Wt. Taken	Wt. Found	pH	Cubic Centimeters Acid Added	Error in Parts per 1000
.2033	.2034	3.922	4.5	0.5
.2006	.2004	3.922	4.9	-1.0
.2066	.2065	3.939	4.5	-0.5
.2044	.2043	3.930	4.5	-0.5
.2027	.2027	3.948	4.5	0.0
.2035	.2036	3.914	4.5	0.5

An investigation was conducted to determine the effect of concentration on the accuracy of the method. The variation in concentration was obtained by changing the volume rather than the weight of sample. The volume was increased to two hundred cubic centimeters, that is, approximately doubled, and a set of samples determined. The results follow:

Wt. Taken	Wt. Found	pH	Cubic Centimeters Acid Added	Error in parts per 1000
.2014	.2012	5.914	5.8	1.0
.2040	.2037	5.897	6.8	1.5

It will be seen that the error, while not appreciably increased, is approximately twice that found when the volume is half as great. This is what would be expected, granted that the error found in the precipitation from a volume of one hundred cubic centimeters is due to solubility of cobalt sulfide. Doubling the volume obviously should double the quantity of cobalt sulfide lost in solution.

This fact may be conveniently illustrated by an actual calculation, using the value for the solubility product quoted in Seidell, namely 1.7×10^{-9}. $[Co^{++}][S^{--}] = 1.7 \times 10^{-9}$, therefore, $[Co^{++}] = 1.7 \times 10^{-8}$ or .000012 moles per litre. This is equivalent to .00069 grams per litre or .00024 grams in 100 cubic centimeters. In 200 cubic centimeters the weight dissolved would be .00048 grams, that is, twice as great. This is twice as much as was experimentally found, and would seem to indicate that the value quoted by Seidell is not

entirely correct. There are highly undesirable features involved
in using a greater volume for precipitation. In the first place a
longer filtering time is required. It becomes extremely difficult
to obtain complete precipitation. A much greater time must be allow-
ed for passing of hydrogen sulfide, and greater care exercised in
general. It will also be noted that the amount of acid required to
give the desired pH value is greater in the case of the larger volume.

It was also thought advisable to ascertain the effect of ammonium
salts on the accuracy of the method. While using the usual volume of
approximately ninety-five cubic centimeters, twenty-five grams of
ammonium chloride were added. The following table gives the results:

Wt. Taken	Wt. Found	pH	Cubic Centimeters Acid Added	Error in Parts per 1000
.2040	.2037	3.854	4.5	1.5
.2019	.2017	3.868	4.5	1.0

No decrease in accuracy was noted but it was not apparent that
the ammonium salt exerted a salting out effect as is supposed to be
the case with zinc, Treadwell and Hall (22a). It will be seen that the
pH values obtained are lower than usual with the amount of acid added.
This is possibly due to the neutral salt effect or hydrolysis of the
ammonium chloride.

It seemed likely that cobalt and nickel could be determined
together by precipitation as the sulfides and nickel subsequently
reprecipitated from the dissolved metals by dimethyl glyoxime after
the combined weights had been determined. This would give the weight
of cobalt by difference. Experimental work with nickel alone disclosed

apparently insuperable difficulties in the way of this plan. Nickel is

said to be more difficult to precipitate completely as the sulfide than

is cobalt, Fresenius (23). Nickel precipitated at the most favorable

pH for cobalt did show a trace of residual nickel in the filtrate when

the latter was tested with dimethyl glyoxime. This reagent produced a

slight coloration in the solution but it was not until the solution

had stood for some time that any definite precipitate of nickel dimethyl

glyoxime was formed. It may be said therefore that nickel is completely

precipitated under the same conditions as is cobalt. However, when

nickel sulfide is roasted and reduced under the same conditions as those used

the cobalt the reduced metal exhibit extremely pyrophoric properties.

This apparently absolutely prevents the determination of nickel in this

way. Work is about to be conducted in the catalyst laboratory of the

Fixed Nitrogen Research Laboratory to determine whether flushing out

the hydrogen from the hot tube after the reduction by some inert gas

such as nitrogen will destroy this pyrophoric nature of nickel, Tr.

P. H. Emmett (24).

Separation from Interfering Metals

A method is of greater value if provision is made for separation from interfering metals. The materials used for studying this problem were synthetic solutions containing cobalt, nickel, aluminum, iron, zinc and manganese. The barium carbonate method, Treadwell and Hall (25) was investigated first as a means of removing aluminum and iron. The method is apparently satisfactory but involves manipulative details and addition of certain materials which should be avoided. Consequently the ammonium hydroxide-ammonium chloride method was substituted and found to be more satisfactory.

Zinc can be removed after iron and aluminum by the ammonium thiocyanate method, Treadwell and Hall (26). However, the pH value of the solution must be more carefully controlled than is provided for by the usual directions for the method because cobalt and nickel will be precipitated in the presence of ammonium thiocyanate, at least at the pH furnished by sodium bicarbonate solutions. In order to avoid any doubt the solution must be adjusted to a pH of two to three before the addition of the thiocyanate because the latter exerts a poisoning effect upon the electrode. The zinc sulfide is precipitated from a hot solution and filtered when cold. The precipitate must be washed with hydrogen sulfide water containing ammonium thiocyanate and not with water containing some other ammonium salt as suggested by Treadwell. If washed with an ammonium chloride solution, traces of "ordinary" ammonium thiocyanate solution, or traces of cobalt or nickel contained on the paper will be precipitated. When the zinc

has been removed, the hydrogen sulfide remaining in the solution can be very readily removed by drawing air through the solution for several hours. This is a method which eliminates any danger of loss such as might arise from ebullition if the solution is boiled to expel hydrogen sulfide.

The method as followed after aluminum, iron and zinc are removed is to precipitate nickel with dimethyl glyoxime, Brunck (27) filter and evaporate the solution until the addition of the buffer solution will not increase the volume beyond one hundred cubic centimeters. The pH value cannot be determined in the solution because the materials present poison the electrode. Hence it is necessary to know the amount of acetic acid that must be added to give a pH of approximately four. The acidity must not be decreased beyond this because of danger of precipitating manganese. If conditions are very carefully controlled cobalt is precipitated quantitatively in the presence of the various materials in the solution. Occasionally, in spite of precautions, cobalt appears to form complexes with organic residues in the solution and does not precipitate completely. If the acidity is kept at the optimum for cobalt precipitation, namely pH 3.93, the likelihood of loss from this cause is negligible.

A change in procedure from that described above which appears promising but which was not investigated is precipitation of cobalt and nickel together as the sulfides. In such a case sulfides and filter paper would be dissolved in aqua regia containing an excess of hydrochloric acid. The chloride solution would be evaporated to

degrees to remove excess acid and nickel precipitated from solution with dimethyl glyoxime. The solution would then be again evaporated to dryness and all organic matter destroyed with aqua regia containing an excess of hydrochloric acid. From this point on the procedure would be the same as previously described.

The solubility product of manganese sulfide is large and no difficulty is experienced with manganese. As a preliminary an ammonium acetate-acetic acid solution of manganese chloride at a pH of 3.9% was saturated with hydrogen sulfide. No precipitate of manganese sulfide was obtained. When cobalt is precipitated in the presence of manganese or other metals whose sulfides are soluble acetate in the usual proportions to give a pH of four or thereabouts and was previously saturated with both hydrogen sulfide and cobalt sulfide.

washing of the precipitated cobalt sulfide is necessary. In this investigation the washing solution contained acetic acid and ammonium sulfide.

Usually the filtrate was tested by the Vogel test, Treadwell (28) to determine whether or not an appreciable quantity of cobalt had failed to precipitate. This was done to save time. If the filtrate showed too much cobalt the precipitate was dissolved and fresh samples carried through. This plan was necessary only where complete precipitation was uncertain, that is, at the upper limits of acidity. In order to see the Vogel test in this way it was necessary to know the sensitivity of the test. A solution of known cobalt content was made up and tests made with this solution. Tests are

made in the literature for a test when only two hundredths of a milligram of cobalt is present. The tests carried out indicated that the test could be obtained with one hundredth of a milligram of cobalt or even less. The test was unmistakable with one hundredth of a milligram.

Method Finally Chosen

The method as finally selected consisted, first, of the removal of iron and aluminum as follows. Treadwell and Hall (29): "To the acid solution containing five grams of ammonium chloride and not more than 0.2 gram of iron and aluminum in 200 cubic centimeters of solution, add a few drops of 0.2 percent solution of methyl red in alcohol and heat just to boiling. Carefully add normal ammonium hydroxide drop by drop until the color changes to a distinct yellow. Boil two minutes and filter promptly. Wash with hot two percent ammonium nitrate solution until free from chlorides. The precipitate contains ferric, aluminum, titanium and zirconium hydroxides. Greater accuracy is obtained if the precipitate is dissolved and reprecipitated."

Only one modification of this procedure was necessary. The color of the solution prevented the use of methyl red as an indicator and litmus paper was substituted.

The slightly ammoniacal filtrate is evaporated on the water bath to about one hundred cubic centimeters by which time all ammonia is expelled and the solution is practically neutral. The pH value of the solution is obtained and while hydrogen is still bubbling through the solution very dilute hydrochloric acid is added drop by drop until the pH value has dropped to approximately 2.5. The solution is then transferred to an Erlenmeyer flask and for every eighty cubic centimeters or solution ten cubic centimeters of one to five ammonium sulfocyanate solution is added. The solution is then heated just to

boiling and hydrogen sulfide passed into the solution while it is cooling to room temperature. The precipitated zinc sulfide is filtered and washed thoroughly with one to five ammonium sulfoganate solution saturated with hydrogen sulfide.

The filtrate is freed of hydrogen sulfide by bubbling air through it for some hours and if the volume is not greater than 500 cubic centimeters nickel is at once precipitated by adding an alcoholic solution of dimethyl glyoxime to the hot slightly acid solution and ammonia added to slight alkalinity. The precipitate is filtered off and washed with hot water.

The filtrate is evaporated almost to dryness on the water bath, the predetermined volume of buffer mixture added, the volume adjusted to 100 cubic centimeters and cobalt precipitated immediately according to the method as already described. The pH value of the solution is not determined in this case because of materials present which are poisonous to the electrode.

Analysis of Cobalt Oxide

An attempt was made to obtain a cobalt ore from the United States Bureau of Standards but none was available. A request of the Oxford-Cobalt Silver Mining Company of Cobalt, Ontario, yielded the reply that cobalt ores varied so much in composition that a sample of definite cobalt content would be very difficult to obtain. Finally a sample of cobalt oxide was obtained from the Deloro Smelting and Refining Company, Ltd. of Deloro, Ontario. This was concentrated black oxide and contained 70.88% of cobalt. The percentage of nickel was given as 0.76. This left roughly seven percent of the sample to be taken up with siliceous matter, zinc, copper, aluminium, iron, etc.

The sample taken for analysis was three-tenths gram as it was desired to have a cobalt residue of approximately two-thirds that amount. The oxide was dissolved in hydrochloric acid containing a little nitric acid. A small amount of siliceous matter remained undissolved. Enough additional hydrochloric acid was added so that when the solution was diluted to one hundred cubic centimeters, five to seven cubic centimeters of concentrated acid would be present, Scott (56).

Hydrogen sulfide was then bubbled through the hot solution until it had cooled to room temperature. A small amount of second group metals precipitated and were filtered off with the siliceous matter. The hydrogen sulfide was then removed by bubbling air through the solution and iron and aluminium removed as above described. Zinc and nickel were next removed in order named.

Cobalt was last removed. One of the samples failed to precipitate completely presumably because of the formation of an undissociated organic cobalt complex. The solution retained an extremely deep red color. The other solution became clear when the cobalt precipitated. When the precipitates were filtered, washed and finally reduced to the metal, the weight of the sample which failed to decolorize was found to be, according to the stated percentage, 1.35% low.

The following table gives the results for the other sample:

Wt. Taken	Wt. Found	Dyes in Parts per 1000
.2145	.2140	1:
70.86%	70.70%	

Lack of time prevented the running of further samples but it may be said that of all the several samples analyzed in developing the method for the separation, none failed to precipitate completely in the presence of whatever products were present as derivatives of dimethyl glyoxime, ammonium thiocyanate and traces of alcohol. However, because of this danger of incomplete precipitation it might be advisable to eliminate organic materials as described above.

Summary

A method has been developed for the quantitative precipitation of cobalt as the sulfide and subsequent determination of cobalt as the metal.

The completeness of precipitation of cobalt as the sulfide has been studied as a function of pH.

The effect of ammonium salts, temperature and concentration on completeness of precipitation has been investigated.

The completeness of precipitation of nickel as the sulfide under conditions optimum for cobalt precipitation has been investigated.

Methods have been developed for the separation of cobalt from interfering metals e. g. nickel, zinc, aluminium, iron and manganese.

A sample of crude cobalt oxide has been analyzed by the method developed.

The error of the method when cobalt alone is present has been found to be less than one-tenth of one percent and in the presence of interfering metals less than two-tenths of one percent.

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