9-cm. fluted ashless filter paper. Use the filtrate to wash out the flask and pour this and any remaining precipitate through a 3-cm. fluted ashless filter. Do not wash unless non-volatile materials are present. In this case wash with a buffer solution made up as above saturated with hydrogen sulfide and cobalt sulfide. Dry the filters in the larger funnel at 100°, fold and transfer over white glazed paper to a small porcelain crucible. Burn off filter paper by heating strongly on a quartz plate. Transfer to a weighed porcelain boat, wiping out crucible and funnel with a shred of filter paper and place in furnace. Draw air slowly through the combustion tube and start the furnace. Roast for one-half hour after the tube glows dull red. Remove tube from furnace, without cooling the latter and allow to cool for three minutes. Pass hydrogen through slowly for several minutes and replace in furnace. Heat to 1000° for fifteen minutes and remove from furnace, the hydrogen being allowed to flow until the tube is quite cold. Weigh boat and metallic cobalt.

Summary

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

2. The precipitation of cobalt sulfide as a function of the acidity has been studied.

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THE QUANTITATIVE PRECIPITATION OF SULFIDES IN BUFFERED SOLUTIONS. II. NICKEL SULFIDE[1]

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The quantitative precipitation of metallic sulfides as a function of the acidity of the solution has been studied systematically only in the case of zinc sulfide[2] and of cobalt sulfide.[3]

Introduction.—The latter research revealed that nickel sulfide precipitates almost completely at about the optimum *P*H for cobalt sulfide. It was found also that metallic nickel, produced by the reduction of the oxide with hydrogen, was so pyrophoric as to make it difficult or impossible to weigh it in that form. The purpose of this research was to investigate more fully these two points.

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[1] Part of a thesis submitted by B. B. Westfall in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of the University of Maryland.

[2] Fales and Ware, This Journal, **41**, 487 (1919).

[3] Haring and Leatherman, *ibid.*, **52**, 5135 (1930).

Review of the Literature.—Fresenius[4] discusses the precipitation of nickel sulfide by ammonium sulfide in solutions buffered with ammonia plus ammonium chloride or with ammonium acetate plus acetic acid. Gooch[5] gives directions for precipitation with hydrogen sulfide in the presence of an ammonium acetate–acetic acid buffer. Baubigny[6] describes the estimation of nickel in nickel sulfate by the sulfide method; Cormimboef[7] describes the precipitation of nickel sulfide in solutions "acidified sufficiently." He stresses the method of washing the precipitate. The nickel sulfide is finally roasted to the oxide.

Apparatus, Materials and Method.—The theoretical aspects of this study are the same as those discussed in the first paper of this series on CoS.[3] Likewise the apparatus, materials and general procedure remain for the most part unchanged. Platinum Gooch crucibles were used as containers for the nickel sulfide and nickel oxide instead of the porcelain boats. Silica Gooches were also found satisfactory although more fragile. These crucibles were small enough to fit snugly into the end of the silica tube so that when air was drawn through it was obliged to go through the asbestos mat. A LaMotte color comparator block with brom cresol green color standards was used in the determination of the final *P*H after precipitation.

The asbestos used in the Gooch crucibles was a good grade of acid-washed material prepared for this purpose. It was chipped fine, reboiled with hydrochloric acid and washed until chlorine free.

The source of the nickel was the complex ammine salt, $Ni(NH_3)_4SO_4·6H_2O$, chosen chiefly because a large quantity of pure material was available. This had been prepared as follows. A saturated solution of recrystallized nickel sulfate hexahydrate was made in the cold. It was acidified with sulfuric acid and iron nails added to replace any copper present. Ammonium hydroxide was then added until a small amount of nickel hydroxide precipitated, and it was then aerated for about one week to remove any iron present by double displacement. The solution stood for about two weeks, being agitated occasionally, after which it was filtered. Concentrated ammonium hydroxide was then added until all the nickel hydroxide dissolved, and this mixture was allowed to stand for three days. The solution was filtered and the nickel ammine precipitated with 95% alcohol, washed with ammonium hydroxide, a mixture of equal portions of ammonium hydroxide and alcohol, alcohol, and last with ether.

A 5-g. sample, when neutralized with sulfuric acid, boiled with an excess of nitric acid and then boiled with an excess of ammonium hydroxide, gave no residue of ferric hydroxide on being filtered. A sample tested with Vogel's reagent (amyl alcohol and ether plus ammonium thiocyanate) gave no test for iron or cobalt. This is capable of detecting 0.01 mg. of cobalt per 10 cc. and the thiocyanate test for ferric iron is even more sensitive.

This salt was analyzed electrolytically (Treadwell–Hall)[8] and found to contain 22.67% of nickel. The theoretical composition gives 22.6651%.

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[4] Fresenius, "Quantitative Analysis," (Am. ed.), Vol. I, Sec. IIIC, p. 307.

[5] Gooch, "Quantitative Analysis," p. 108.

[6] Baubigny, *Compt. rend.*, **94**, 1183 (1882).

[7] Cormimboef, *Ann. chim. appl.*, **11**, 6 (1906).

[8] Treadwell–Hall, "Quantitative Analysis," **1919**, p. 147.

Description of Experiments

The efficiency of the buffer was first investigated by adding different amounts of acetic acid to a given amount of the solution containing approximately 0.2 g. of nickel as $Ni(NH_3)_4SO_4 \cdot 6H_2O$. Usually there was no ammonium acetate added as there would be approximately the equivalent of 34 cc. of 0.4 N ammonium acetate formed by the reaction of the acid with the salt. Acetic acid was added in excess to give the desired P_H, and the P_H taken, after dilution to constant volume (90 cc.), with the hydrogen electrode. The precipitation was carried out as described later, and the P_H taken on the filtrate with the indicator brom cresol green. The decrease in P_H during precipitation at P_H 4.4 (the optimum value) was found to be 0.16 unit.

About 0.89 g. of the nickel ammine was taken for the analysis. This contained 0.2 g. of nickel, which previous experience had shown to be a sample of the most desirable size. The samples were weighed out on a watch glass and then rinsed into a 300-cc. Erlenmeyer flask. Sufficient acid was added to neutralize the ammonia and to give the desired P_H. The contents of the flask were diluted to 65 cc. and the P_H determined electrometrically. The volume of the solution after rinsing the electrodes was 90 cc.

Precipitation was carried out as described by Haring and Leatherman[8] except that the solution before precipitation was heated to 90°, *not to boiling*, and the walls of the flask were not washed down. Also, just before the end of precipitation, the temperature was raised to 60°. This modification proved helpful in reducing the annoying adsorption of the nickel sulfide on the glass.

A portion of the filtrate was taken and the P_H determined colorimetrically, using the comparison method. The hydrogen sulfide was boiled off the remainder and the solution tested for nickel with dimethylglyoxime.[9] When 80 cc. of the hydrogen sulfide containing filtrate was taken, as was usually the case, and evaporated to 40 cc., there was nearly always a faint pink color developed momentarily, indicating that even at the most favorable P_H there was not quite complete precipitation. The test with dimethylglyoxime would indicate the presence of one part in four hundred thousand, or 0.0001 g. of nickel in the filtrate, which checks with the determination as the sulfide.

The amount of adsorption seems much more a function of the glass surface used, rather than anything else. If the glass is strained, local adsorption takes place on the strained area, whereas it may not on the rest of the surface. Of eight flasks used, two were found which gave almost no adsorption under any P_H values used, while others gave, particularly at the upper limit, adsorption so marked that nothing short of aqua regia would remove the sulfide from the walls of the container.

An entirely new technique was developed for the operations of filtration and roasting. These were both carried out in a platinum Gooch crucible. The mat was prepared in the usual manner, but the drying was carried out at 1000°. At this temperature it was found necessary to repeat the operation of washing and drying three times in order to reach constant weight. During filtration it was found essential to keep the Gooch full of liquid at all times. Washing was unnecessary since no non-volatile materials were present. It was found impossible to destroy completely the pyrophoric character of reduced nickel, even at 1000°. For this reason the nickel was

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[9] Brunck, *Z. angew. Chem.*, **20**, 834, 3844 (1907).

TABLE I

RESULTS OF EXPERIMENTS

Taken, g.	Found, g.	Initial P_H	Acid added (6.8 N), cc.	Final P_H	Error in parts/1000
0.2011	0.2013	6.81	0.06	4.90	+1
.2011	.2013	6.80	.06	4.90	+1
.2013	.2012	6.59	.20	4.80	−0.5
.2012	.2011	6.59	.20	4.80	− .5
.2011	.2009	6.19	.30	4.75	−1
.2013	.2014	6.18	.30	4.75	+0.5
.2011	.2010	5.79	.34	4.70	− .5
.2011	.2010	5.79	.34	4.70	− .5
.2012	.2011	5.41	.42	4.70	− .5
.2009	.2008	5.41	.42	4.70	− .5
.2013	.2012	4.78	1.40	4.45	− .5
.2011	.2012	4.78	1.40	4.45	+ .5
.2012	.2010	4.51	2.20	4.35	−1
.2011	.2008	4.47	2.20	4.30	−1.5
.2007	.2005	4.34	3.00	4.20	−1
.2007	.2004	4.41	3.00	4.20	−1.5
.2013	.2009	4.08	4.45	4.05	−2
.2013	.2005	3.95	5.20	3.90	−4
.2013	.2007	3.86	6.5	3.75	−3
.2018	.2002	3.44	30.2	3.40	−8
.2014	.1915	3.30	36.5	3.30	−49.5

weighed as nickel oxide, roasting being carried out at 1000° so as to insure decomposition of any nickel sulfate. The results of this study are displayed in Table I and Fig. 1.

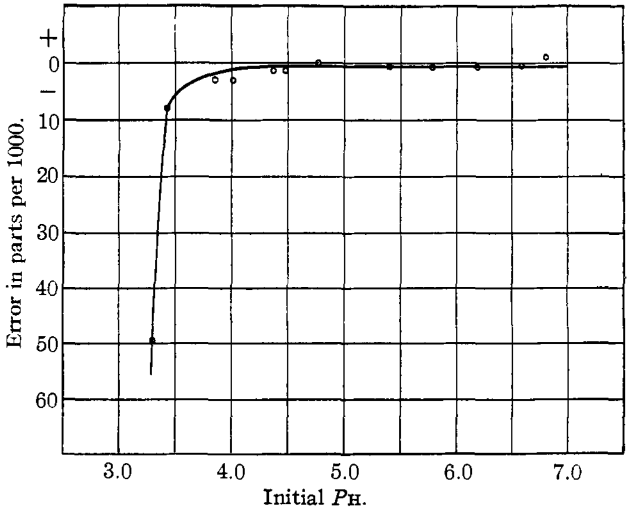

Fig. 1.—Relation between completeness of precipitation and initial acidity.

As will be evident, even at *P*H 7 there is no diminution in precision. The curve reveals that the optimum *P*H for nickel sulfide precipitation, *i. e.*, the lowest *P*H consistent with complete precipitation and reasonable time for the same, is 4.4.

Summary of the Method

A definite quantity of the material is weighed so as to give approximately 0.2000 g. of nickel. This is dissolved in 10–15 cc. of water, the *P*H is adjusted to 4.4 (the desired value) by adding 34 cc. of 0.4 *N* ammonium acetate and 2.8 cc. of 6.8 *N* acetic acid. The solution is then made up to a volume of approximately 90 cc. This is heated in the Erlenmeyer flask to about 90° (not to boiling). It is then connected with a source of hydrogen sulfide and the air expelled by the gas. After about five minutes the flask is rotated vigorously to aid precipitation by stirring. After precipitation the temperature is raised to 60° by heating on a water-bath. During this time it is connected to the generator. Precipitation is complete in slightly less than an hour. The solution is filtered from the precipitate by suction, using a Gooch crucible. It is *very* necessary that the crucible be kept full of liquid until this is complete, *i. e.*, until all the liquid and precipitate have been added. The crucible is then placed in the cold furnace and heated to 1000°, while a good current of air is drawn through, after which the crucible is cooled and weighed.

To test the method a sample of recrystallized nickel sulfate hexahydrate was analyzed for nickel content and the following results obtained.

TABLE II

RESULTS OF ANALYSES

Taken, g.	Found, g.	Initial *P*H	Final *P*H	Acid added, cc.	Error in parts/1000
0.1977	0.1976	4.61	4.3	2.8	−0.6
.1975	.1975	4.53	4.3	2.8	± .0

Summary

1. A precise method has been developed for the precipitation of nickel as sulfide and its subsequent determination as the oxide.

2. The precipitation of nickel sulfide has been studied as a function of *P*H.

3. Adsorption of metallic sulfides on glass surfaces appears to vary markedly with the state of strain of the glass.

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