The activities of ammonia in the mixtures were calculated by the approximate method of Lewis and Randall,[9] taking the activity equal to the concentration in pure liquid ammonia.

Summary

1. The surface tension of liquid ammonia at 0, 10 and 20°, and its temperature coefficient were determined.

2. By the differential method of Ramsay and Shields the molecular weight of liquid ammonia is found to be 24.5.

3. Surface tension and density of water–ammonia mixtures from 50–100% NH_3 at 20° are given for the first time.

4. A method is shown whereby the surface tension and density of a solution may be determined in the same sealed tube without removing the contents.

5. Surface tensions of water–ammonia mixtures follow closely values to be expected from the rule of admixtures except in the middle region, where a divergence of less than six dynes occurs.

6. Assuming divergence to be due to adsorption, it is shown that adsorption of ammonia in the surface is small, amounting from one to five per cent. of the normal surface concentration.

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THE QUANTITATIVE PRECIPITATION OF SULFIDES IN BUFFERED SOLUTIONS.[1] I. COBALT SULFIDE

BY MALCOLM M. HARING AND MARTIN LEATHERMAN

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Introduction

The separation of metals by means of sulfide precipitation in acid or basic solution has long been practiced. However, the regulation of the degree of acidity and the conditions under which a thoroughly satisfactory precipitate may be obtained have not been the subject of much careful study. Fales and Ware[2] carefully investigated the conditions under which zinc sulfide might be precipitated quantitatively, but practically nothing else is available. Such a study on cobalt sulfide seemed desirable because the methods for the determination of this element are neither so numerous nor

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[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

[1] Part of a thesis submitted by Martin Leatherman in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Maryland.

[2] Fales and Ware, THIS JOURNAL, **41**, 487 (1919).

satisfactory as might be wished, and because solid cobalt sulfide behaves so peculiarly when treated with acids.

Review of Literature.—Fresenius[3] and Landrum[4] both discuss the precipitation of cobalt sulfide by ammonium sulfide, but neither takes up acidity control. Both convert the sulfide to oxide and reduce the latter with hydrogen for the final weighing. Low[5] describes a method whereby cobalt sulfide is precipitated, together with nickel sulfide and traces of zinc sulfide, in a solution buffered with ammonium acetate. The cobalt and nickel mixed are weighed as oxides. No details are given as to the *P*H maintained, the character of the precipitate, etc.

Theoretical.—The physical character of a precipitate is conditioned, among other factors, upon the rate of formation. The latter is largely governed by the ionic concentrations concerned. Since the concentration of sulfide ion is dependent upon the hydrogen-ion concentration, the use of a buffer to control the acidity in sulfide precipitations is very desirable.

Apparatus.—The weights used were carefully calibrated. The measurements of *P*H were made using a Hildebrand type bubbling electrode. A small electric resistance furnace equipped with a silica tube was used for the roasting and reduction. Porcelain boats were used to hold the cobalt sulfide.

Materials.—The hydrogen, made by the action of zinc on 30% sulfuric acid, was purified by passage through alkaline pyrogallate, alkaline permanganate and distilled water.

The hydrogen sulfide was passed through absorbent cotton to filter out spray and then through two bottles of distilled water.

All materials were of "reagent" quality. Blanks were run on the acetic acid and ammonium acetate, and a constant weight of 0.2 mg. subtracted from all determinations to allow for the non-volatile impurities. Stock solutions of these reagents were made up in sufficient volume to permit the same solutions to be used throughout the work.

The water had a specific conductance of 2×10^{-6} mhos.

Metallic cobalt was used as the raw material in all experiments. It was purified from a good grade of $CoCl_2 \cdot 6H_2O$ by the chloropentamminecobaltic chloride method described in Biltz–Hall and Blanchard.[6] The chloride from the purification process was precipitated as sulfide, roasted and reduced with hydrogen to produce the metal in a very suitable form. No trace of nickel was detected by the dimethylgloxime method, or of iron by addition of ammonia. It had been hoped that the purified hexahydrate

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

[4] Landrum, *Trans. Am. Ceramic Soc.*, 12, 144 (1910).

[5] Low, "Technical Methods of Ore Analysis," p. 191.

[6] Biltz–Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," 1909, p. 173.

might be weighed out directly, but it is sufficiently efflorescent to make its use inadvisable. The anhydrous form is easily made but cannot be weighed out with certainty without the most extreme precautions.[7]

Discussion of Experiments

About 0.2 g. of metallic cobalt was found to be a suitable quantity for these experiments. This amount was weighed out into a 250 cc. beaker and dissolved in 5 cc. of concentrated hydrochloric acid. The solution was evaporated to dryness on an asbestos-covered hot-plate until all the chloride showed the bright blue color of the anhydrous salt and there was no odor of hydrochloric acid; 25 cc. of 0.4 *N* ammonium acetate, 40 cc. of water and sufficient 6.8 *N* acetic acid to produce the desired acidity were added and the *P*H measurement made.

Ammonium acetate was chosen as the salt of the buffer mixture used for the following reasons. Moist cobalt sulfide is readily oxidized by oxygen from the air. Hence washing with pure water will yield low results due to loss of soluble sulfate. Washing with hydrogen sulfide water is likewise inadvisable due to the tendency shown by many sulfides to peptize under such conditions. Therefore, for good results, non-volatile materials except cobalt salts should be absent at this point. Ammonium acetate is completely volatile and maintains the acidity desired and hence is eminently suitable for the purpose; 25 cc. of 0.4 *N* solution was found to provide an ample margin of safety in nullifying the effect of the acid liberated.

*P*H measurements could not be made with the hydrogen electrode on the mother liquor after precipitation since hydrogen sulfide poisons the electrode. The effect of the liberated acid was ascertained indirectly. Varying amounts of 6.8 *N* acetic acid were added to 25 cc. of 0.4 *N* ammonium acetate and the whole made up to 65 cc. The *P*H was determined, 38.6 cc. of 0.1 *N* hydrochloric acid was added and the *P*H redetermined. This quantity of hydrochloric acid is equivalent to that liberated when 0.25 g. of cobalt is precipitated as sulfide. At the *P*H finally selected (3.93) the decrease in acidity caused by precipitation was found to be 0.28 *P*H units. Since but 0.2 g. of cobalt was used in analysis, the decrease would be even smaller than this.

The initial *P*H having been determined, the solution was transferred back to the Erlenmeyer flask. The beaker and electrode washings had by this time increased the volume to about 95 cc. Hydrogen sulfide was then passed through the flask, *but not through the solution*, for about five minutes, after which the exit was closed and the pressure allowed to rise to the maximum produced by the Kipp generator. This was maintained throughout the period of precipitation. Preliminary experiments had revealed that cobalt sulfide is powerfully adsorbed by glass and that this

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[7] Baxter and Coffin, THIS JOURNAL, **28**, 1580 (1906).

adsorption is prevented by using a hot solution, by washing down the walls of the flask just before admitting hydrogen sulfide, and by having no agitation during the first few minutes of precipitation. Accordingly the solution was heated just to boiling prior to precipitation, the flask walls were immediately washed down and there was no agitation for at least the first five minutes of precipitation. Heating likewise increased the speed of precipitation and made the precipitate more compact. Giving the contents of the flask a gentle swirling motion after the earlier stages of precipitation also served to speed up this operation. The precipitation period was always continued until the contents of the flask were at room temperature (forty-five minutes to one hour). For the very low *P*H values, precipitation was continued overnight. The precipitate always settled quickly, leaving a crystal clear mother liquor. At the higher *P*H values precipitation was very rapid and the precipitate flocculent and very bulky. The speed of precipitation diminished with diminishing *P*H, and the precipitate was very compact, forming an exceedingly thin layer in the bottom of the flask.

Filtration was carried out as expeditiously as possible. A rapid filtering, "ashless," fluted filter paper of 9 cm. diameter was used. The bulk of the precipitate and mother liquor was poured through this filter. Then the filtrate was used to wash out of the flask and onto a 3 cm. filter the remaining precipitate. In this way no liquid was poured over the precipitate after it had dried to the least extent. As stated previously, non-volatile materials should be absent at this point so that washing will be unnecessary. If this is impracticable, washing may be carried out by using as wash water a buffer solution of the same *P*H as that used in precipitation, previously saturated with hydrogen sulfide and cobalt sulfide. The filtrate was always tested for cobalt by means of Vogel's test.[8] This test was found to be sensitive to 0.01 mg. of Co^{++} per 10 cc. of solution. By this means it was proved that each precipitation had been made as complete as possible under the conditions.

The procedure of Fales and Ware[2] could not be followed from this point because sulfuric acid, even when hot and concentrated, appeared to have little effect on the cobalt sulfide. Therefore instead of weighing as the sulfate it was decided to roast and reduce to the metallic state.

The filter papers and precipitate were dried at 100°, then burned in a porcelain crucible until carbon was removed. The residue was transferred to the porcelain boat, roasted at a dull red heat for half an hour, then reduced in hydrogen at 1000° for twelve to fifteen minutes, cooled in hydrogen and weighed as metal. It was found that a reduction temperature even as high as 800° was insufficient to destroy completely pyrophoric cobalt. The results of this study are displayed in Table I and Fig. 1.

[8] Treadwell, *Z. anorg. Chem.*, **26**, 105 (1901).

TABLE I

SHOWING COMPLETENESS OF PRECIPITATION OF COBALT AS THE SULFIDE FROM SOLUTIONS OF VARYING ACIDITY

Taken, g.	Found, g.	*P*H	Acid added, cc.	Error in parts per 1000
0.2015	0.2013	6.15	0.0	−1.0
.2360	.2357	6.15	.0	−1.2
.2035	.2034	5.17	.2	−0.5
.2015	.2012	5.18	.2	−1.5
.2005	.2004	4.40	1.5	−0.5
.1997	.1995	4.44	1.5	−1.0
.1890	.1891	4.16	3.0	+0.5
.1826	.1823	4.16	3.0	−1.6
.2022	.2021	3.93	4.5	−0.5
.2047	.2048	3.93	4.5	+0.5
.2226	.2223	3.82	5.5	−1.3
.2286	.2284	3.83	5.5	−0.9
.2109	.2107	3.72	7.5	−0.9
.2266	.2263	3.71	7.5	−1.3
.2081	.2079	3.63	9.0	−1.0
.2027	.2024	3.63	9.0	−1.5
.2007	.2003	3.52	12.0	−2.0
.2023	.2018	3.50	12.0	−2.0
.2124	.2110	3.36	16.0	−6.6
.2021	.2008	3.35	16.0	−6.4
.1795	.1634	3.09	32.5	−90.8
.1832	.1697	3.10	32.5	−70.4

As will be noted, precipitation was complete, within 0.5%, at a *P*H of about 3.6. No appreciable increase in error was noted at high *P*H values

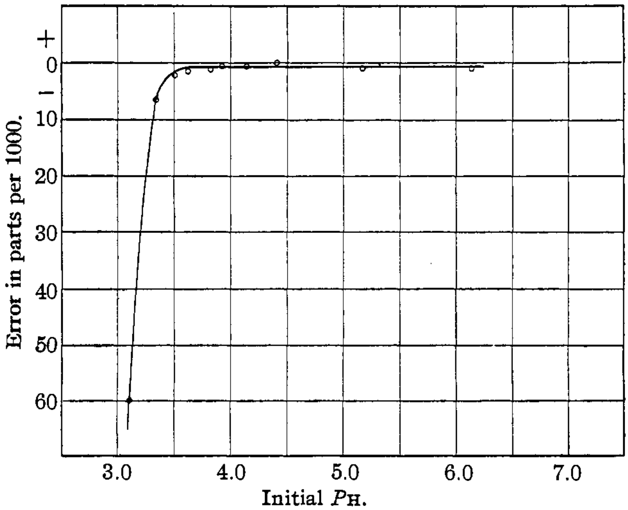

Fig. 1.—Relation between completeness of precipitation and initial acidity.

such as was found by Fales and Ware[2] with zinc sulfide. As already stated, the *P*H value selected for the quantitative precipitation of cobalt sulfide should be as low as is consistant with complete and fairly rapid precipitation. At *P*H 3.93 these conditions were met. The precipitation is complete in less than one hour and the precipitate compact and granular so that only a very small filter is needed. The *P*H values recorded in Table I are the initial values, *i. e.*, before precipitation. The slight variations in *P*H observed between duplicates is doubtless due to the fact that there was a small loss of hydrogen chloride when the chloride solution was evaporated to dryness. To test out the method, six more determinations were made at this *P*H with results as recorded in Table II.

TABLE II

SHOWING ACCURACY OF DETERMINATION UNDER OPTIMUM CONDITIONS FOR PRECIPITATION AS THE SULFIDE

Taken, g.	Found, g.	*P*H	Acid added, cc.	Error in parts per 1000
0.2033	0.2034	3.92	4.5	+0.5
.2008	.2006	3.92	4.9	−1.0
.2066	.2065	3.94	4.5	−0.5
.2044	.2043	3.93	4.5	− .5
.2027	.2027	3.95	4.5	± .0
.2035	.2036	3.91	4.5	+ .5

It was thought that nickel and cobalt might be determined simultaneously by this method. If so, nickel could be determined separately in the metallic product by the dimethylglyoxime method and cobalt by difference. Investigation showed that nickel sulfide is precipitated practically completely at the same *P*H as cobalt sulfide. However, the much more highly pyrophoric nature of nickel prevented the obtaining of accurate results. This investigation is to be pursued further.

A few determinations were made to investigate the effect of concentration and the influence of ammonium salts. Although the results cannot be considered conclusive, large quantities of ammonium salts and a low concentration of cobalt ion appear to diminish somewhat the precision of the method.

Summary of the Method

Prepare an aqueous solution containing about 0.2 g. of cobalt preferably as chloride. Free acid should be absent. Add 25 cc. of 0.4 *N* ammonium acetate, 4.5 cc. of 6.8 *N* acetic acid and 70 cc. of water. Heat to boiling in a 300-cc. Erlenmeyer flask, remove from flame, wash down and saturate with hydrogen sulfide under slight pressure until the solution has reached room temperature (forty-five minutes suffices). Do not agitate for at least five minutes at the start. Afterward swirl around occasionally. Pour most of the mother liquor and precipitate through a

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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[Contribution from the Dohme Laboratory of Physical Chemistry at the University of Maryland]

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).