(Eq. 3) $\Delta F_T = -354{,}800 - 12.38T \ln T + 2.24 \times 10^{-3}T^2 + 145.6T$ (1000 to 2000° K.)

Equation (3) is derived from above values for ΔF_{1000} and ΔS_{1000} and the following equations for the heat content of boron (Eq. 4) and oxygen (Eq. 5) in addition to equation (2a) for liquid B_2O_3

(Eq. 4) Boron: $H_T - H_{1000} = 3.01T + 0.96 \times 10^{-3}T^2 - 3970$ (1000 to 2000° K.)

(Eq. 5) Oxygen: $H_T - H_{1000} = 8.034T + 0.213 \times 10^{-3}T^2 - 8247$ (1000 to 3000° K.)

Equation (4) was derived from the values $C_{p_{1000}} = 4.93$ cal./g. f. w. and $C_{p_{2600}} = 8.00$ (estimated); equation (5) was calculated from the values given in the tables of Johnston and Walker[13] at 1000, 2000 and 3000° K.

Equations (4) and (5) are of an abbreviated form intended for use only above 1000° K. They have been used in this high temperature region instead of the longer type ordinarily used by Kelley[14] over the entire range above 273° K.

Summary

1. The heat content above 298° K. has been determined for crystalline B_2O_3 to near the melting point and for glassy B_2O_3 to 1777° K.
2. The heat of the reaction B_2O_3 (crystals) $\rightarrow$ B_2O_3 (glass) has been determined at 298.1° K. as 4360 ± 20 cal./g. f. w.
3. The free energy of the reaction B_2O_3 (crystals) $\rightarrow$ B_2O_3 (glass) is calculated to be 2600 cal./g. f. w. at 298.1° K.
4. Entropy of B_2O_3 glass is calculated to be 18.9 ± 0.3 at 298.1° K.
5. An equation has been derived for the free energy of formation of liquid B_2O_3 at temperatures above 1000° K.

[14] K. K. Kelley, *Bur. Mines Bull.*, 371 (1934).

BERKELEY, CALIFORNIA RECEIVED JULY 21, 1941

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Entrainment of Cobalt by Tin(IV) Sulfide

BY JOHN F. FLAGG

It has been recognized for some time that the precipitation of tin(IV) sulfide in the presence of cobaltous ion results in contamination of the precipitate with cobalt. Auger and Odinot,[1] who first noted this effect, found that cobalt appeared in the precipitated tin(IV) sulfide at acidities so high that the tin(IV) ion itself was incompletely precipitated. They noted also that the amount of cobalt entrained was almost inversely proportional to the acidity of the solution, and finally concluded that the separation of cobalt and tin by this method was not feasible.

A study in somewhat greater detail was made by Feigl,[2] who determined the amount of cobalt entrained at various concentrations of cobalt and tin. His study was not exhaustive, as the few determinations were part of other work designed to support the "Coördination Theory" of co-precipitation.

The research of Kolthoff[3] and co-workers has made it evident that entrainment is not a simple process, that it is often the result of several processes, and is a function of acid concentration, temperature, time of standing, and concentration of the ions involved to an extent not previously recognized.

From this viewpoint, an investigation of the cobalt—tin problem has seemed desirable. Furthermore, the availability of radioactive isotopes of cobalt provides a convenient tool for attacking such a problem. The use of radioactive cobalt facilitates the quantitative analysis of precipitates for the small amounts of cobalt entrained, and it becomes possible to work at lower concentrations of cobalt than hitherto has been feasible.

The work reported here is a study of the entrainment of cobalt by tin(IV) sulfide from solutions varying in concentrations of tin and cobalt, as well as acidity, time of standing, and temperature of precipitation. Data also are presented to show that this troublesome analytical phenomenon can be successfully eliminated by using acrolein as a flocculating agent. Radioactive cobalt has been used exclusively in these studies.

Experimental Part

Preparation of Reagents.—A solution of tin(IV) chloride was prepared by dissolving Baker Analyzed $SnCl_4$-

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[1] Auger and Odinot, *Compt. rend.*, **178**, 710 (1924).

[2] Feigl, *Z. anal. Chem.*, **65**, 25 (1924).

[3] For review, see Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).

$5H_2O$ in six molar hydrochloric acid and diluting until the acid strength was approximately one molar. Chlorine gas was passed through the solution for fifteen minutes, followed by nitrogen until chlorine was no longer detectable in the solution. Analysis of 50.00-ml. portions for tin by precipitation as stannic acid, conversion to the oxide and weighing, gave an average value of 0.3704 g. Sn/50.00 ml. Aliquot parts of this solution were taken for the experiments.

Radioactive cobalt was obtained by bombardment of iron with protons in the University of Rochester cyclotron. The surface of the metal which had been exposed to the proton beam was etched repeatedly with small portions of hydrochloric acid containing a few drops of nitric acid until the radioactivity had been completely removed. In this way only a small amount of iron came into solution to contaminate the cobalt, and it was removed by precipitation with excess ammonium hydroxide. As expected, some cobalt was carried down with the iron, but the amount remaining was more than adequate for the experiments. It is to be noted that no inactive cobalt was added during the separation; consequently, the radioactive cobalt had a specific activity of one, and a negligible mass (save, of course, for any undetectable amount of cobalt that may have been present in the iron). This "indicator" cobalt was made up to 50.00 ml. in a volumetric flask, but as the activity was higher than needed for some experiments, portions of this stock solution were diluted to give other indicators of desired activity. The activity of these solutions was checked regularly.

Solutions of inactive cobalt were prepared from Merck Reagent Grade cobalt sulfate, and were standardized electrolytically. Aliquots of the standardized solutions were diluted in Normax volumetric flasks when lower concentrations were desired.

The acrolein used in the second part of the study was obtained from the Eastman Kodak Company. It was stabilized with hydroquinone, and the preparation used without further purification.

Hydrogen sulfide was obtained in tank from the Ohio Chemical and Mfg. Co. It was washed with dilute hydrochloric acid before use.

All other chemicals were of the reagent grade, and were used without further purification.

Procedure.—The first experiments involved the determination of the cobalt entrained in the tin(IV) sulfide precipitate as a function of the concentration of the cobalt. To a certain amount of tin was added the desired amount of inactive cobalt, indicator cobalt, hydrochloric acid, and water to make 100 ml. The amounts of tin used varied from 7.4 mg. to 111 mg., and sufficient six molar hydrochloric acid was added to make the hydrogen ion concentration 0.3 molar, or 1 molar, depending on the experiment.

The mixture was treated in a 125-ml. Erlenmeyer flask with a rapid stream of hydrogen sulfide gas for five minutes, either at room temperature or at elevated temperature. The flask was stoppered and allowed to stand, with frequent shaking, for fifteen minutes at the temperature of precipitation. Experiments in which the flask was shaken mechanically gave, within experimental error, similar results.

After standing, the precipitate was filtered on a Hirsch funnel containing an asbestos mat. Of several methods of filtration tried, this proved most satisfactory. The colloidal tin(IV) sulfide did not run through the filter; the precipitate was easily and effectively washed, and the whole operation required much less time than filtration through paper, or centrifugation. The filtered precipitate was washed with five ten-ml. portions of acid of the same strength and temperature as the mother liquor, and saturated with hydrogen sulfide. That this quantity of wash liquid was adequate was proved by negative chemical tests for cobalt (thiocyanate–amyl alcohol; α-nitroso β-naphthol; ammonium sulfide), on the last portion of wash liquid and by tests for radioactivity with the Geiger-Müller counter.

Following the filtration, the precipitate and the asbestos mat were returned quantitatively to the precipitation flask and digested with aqua regia. The solution was filtered through a fresh mat on the Hirsch funnel, flask and filter were thoroughly washed, the solution transferred and

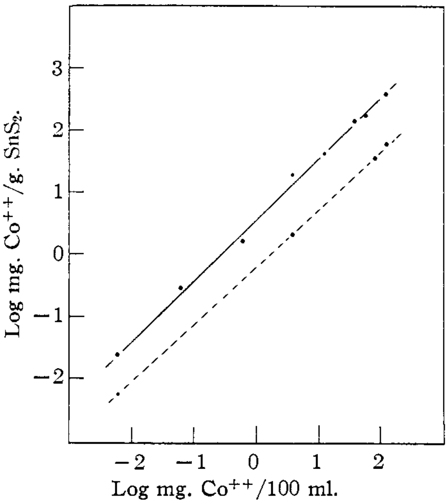

Fig. 1.—Entrainment at 0.3 molar $[H^+]$: solid, 23° broken, 95°.

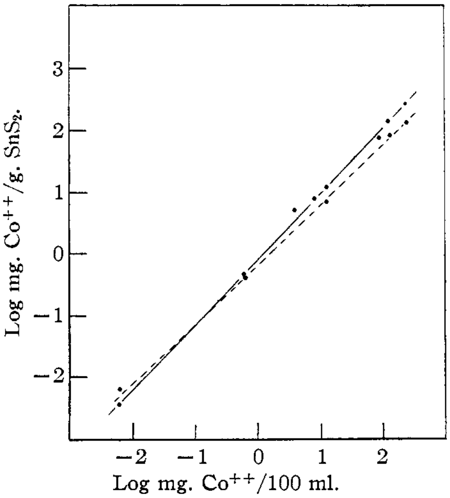

Fig. 2.—Entrainment at 1 molar $[H^+]$: solid, 23°; broken, 95°.

evaporated to dryness in a 100 ml. beaker. The residue was taken up in 2.00 ml. of six normal hydrochloric acid, and its activity measured in a counter of the type described by Bale.[4]

It was necessary to prove that all or any fraction of the radioactive indicator would be carried along through the above series of operations. To do this, a known amount of indicator cobalt was precipitated, together with some inactive cobalt, by ammonium sulfide. The precipitate was treated exactly as a tin(IV) sulfide precipitate; of the 268 ± 7.7 counts/min. originally added, 262 ± 7.7 counts/min. were recovered in the final operation.

The number of counts taken on any one sample was never less than 500, which was sufficient to give a probable error of not more than three per cent. All experiments were run in duplicate and the average value was used in making the plots. The results, plotted in the form of a log $\mathbf{x}/\mathbf{m}$ *vs.* log $\mathbf{c}$ relation, are shown in Figs. 1 and 2.

In a number of other cases, the filtrate and washings from the original precipitation were evaporated, and the activity determined. The activity found in this way, plus the activity in the tin(IV) sulfide precipitate, equalled the amount originally added, within experimental error. However, determination of the cobalt entrained was by the direct method in all cases.

In one experiment, cobalt was added after precipitation of the tin(IV) sulfide, rather than before. The difference in the amount of cobalt entrained was within the limit of experimental error.

Experiments were run to determine whether increased amounts of cobalt could be incorporated into the precipitate of tin(IV) sulfide upon longer times of standing. Solutions were prepared containing 0.0058 mg. of cobalt, radioactive cobalt, 37 mg. of Sn(IV) ion, and hydrochloric acid to make the hydrogen ion concentration 0.3 molar. A second series was prepared containing 580 mg. of cobalt, and with all other quantities the same. The tin(IV) ion was precipitated as usual, and the solutions allowed to stand for the periods indicated. The results are given below.

Time	% cobalt found in precipitate
Series I	
15 min.	26
35 min.	47
160 min.	61
13 days	100
Series II	
15 min.	3.1
120 min.	2.9
5 days	2.0

Experiments with Acrolein.—From the interesting work of Caldwell and Moyer,[5] it appeared that an organic flocculating agent might serve to coagulate the colloidal tin(IV) sulfide, and at least render it more easily filtered. Acrolein was chosen as a flocculating agent, and a number of experiments were carried out using 0.5 ml. of it in the solutions from which precipitation was to be made. Again, the acidity, temperature, composition, and times of standing before filtration were varied, and the technique followed in these experiments was exactly as described above.

The acrolein was markedly effective in flocculating the tin(IV) sulfide. Furthermore, the precipitate obtained was light yellow in color, as contrasted with a chocolate colored precipitate normally obtained in the presence of moderate amounts of cobalt. If the acrolein was added after precipitation in the presence of cobalt, the precipitate was flocculated, but retained its dark brown color.

The effect of acrolein in preventing entrainment by the tin(IV) sulfide was studied at concentrations of cobalt ranging from 0.0058 mg./100 ml. to 580 mg./100 ml.; at 0.3 and 1 molar hydrogen ion concentration; and at 23 and 70°. Thirty-seven mg. of Sn(IV) ion was used, and the precipitate filtered after fifteen minutes. At the lowest concentration of cobalt, the amount found in the precipitate was zero under all conditions, within the limits of experimental error. Shaking the solutions for three hours at room temperature in one molar hydrochloric acid failed to introduce cobalt into the precipitate, although in 0.3 molar acid about one per cent. of the cobalt was found in the precipitate. With 58 mg. of cobalt present, none was entrained, within the limits of experimental error, under any of the conditions tried. With 580 mg. of cobalt present, none was entrained at 0.3 molar and 1 molar acid concentration and 70°. However, at these same acidities and room temperature, 3.5 and 1.4 mg., respectively, were entrained. Obviously, a second precipitation of the tin in these cases would free it completely from cobalt.

In these experiments the specific activity of the cobalt was kept as uniform as possible by increasing the amount of indicator cobalt as the concentration of inactive cobalt increased. Thus the sensitivity of the method for large concentrations of inactive cobalt was maintained.

X-Ray Studies.—With the coöperation of Mr. John F. Bonner of the University of Rochester School of Medicine and Dentistry, powder diffraction patterns were taken of the tin(IV) sulfide, precipitated with and without the aid of acrolein, and after various periods of aging. The precipitates were allowed to age in contact with the solution, then were filtered and dried in a vacuum desiccator. The dried precipitates were ground with starch[6] and introduced into capillary tubes prior to making the diffraction patterns.

Tin(IV) sulfide which had been aged for one month gave the sharpest pattern, while tin(IV) sulfide which had been precipitated in the presence of acrolein and aged for fifteen minutes gave the least distinct pattern. Samples precipitated in the presence of acrolein showed barely more distinct interference maxima if aged for three hours before filtration.

Samples precipitated cold in the absence of acrolein and aged for fifteen minutes or three hours, showed definite patterns; these were somewhat stronger if the aging took place at about 95°. The actual differences among these intermediate cases were slight, but it might be concluded that a rise in temperature of 70° for fifteen minutes produced roughly the aging equivalent to three hours' standing at room temperature.

Discussion

The data show an influence of both acidity and

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[4] Bale. *Radiology*, **35**, 184 (1940).

[5] Caldwell and Moyer, THIS JOURNAL, **57**, 2372, 2375 (1935); **59**, 90 (1937).

[6] G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 270.

temperature on the entrainment when precipitation is made in the absence of acrolein. The decrease in entrainment with increasing acidity is doubtless the result of a decreased concentration of sulfide (or hydrosulfide) ions on the surface of the precipitate. Opportunity for the formation of hydrogen sulfide would be increased at the higher concentration of hydrogen ions. This would, in turn, reduce the chance for cobalt sulfide to form on the surface of the precipitate. (That cobalt actually is entrained as the sulfide seems probable, since the precipitate is brown in color.)

The effect of increased temperature in reducing the entrainment is more pronounced at the lower acidity, and roughly the same amount of cobalt is carried down in 0.3 molar acid at 95° as in 1 molar acid at 23° (or 95°).

The action of acrolein in flocculating the precipitate of tin(IV) sulfide doubtless can be explained as in certain other cases.[5] The removal of adsorbed sulfide (or hydrosulfide) ions from the surface of the precipitate by the acrolein is again the chief factor in preventing entrainment of the foreign ion.

The fact that the precipitate of tin(IV) sulfide obtained under these conditions is micro crystalline, as shown by the X-ray diffraction patterns, indicates that no aging takes place. This would result from a large decrease in surface, and consequent reduction of the solubility of the precipitate. As no evidence of postprecipitation of cobalt on tin(IV) sulfide thus prepared was found, it may be supposed that the surface remains covered by the acrolein and its addition products, or that it remains completely bare of any adsorbed layer of ions capable of reacting with the cobalt.

Certain practical aspects of this study might be mentioned in connection with the separation of cobalt and tin. If tin is to be separated as the sulfide in the absence of a flocculating agent, the least entrainment will occur at about 95° from 0.3 molar hydrochloric acid, or from 1 molar acid, regardless of the temperature. However, it is suggested that the precipitation be made in the presence of acrolein, preferably at about 60°. The advantages are: (1) speed in flocculation, filtration, and washing of the tin(IV) sulfide; (2) freedom of the precipitate from cobalt. The disadvantages are: (1) contamination of the filtrate with acrolein and its addition products; (2) the necessity for working in good ventilation. The method obviously operates most favorably for the isolation of tin, when cobalt is to be disregarded.

Summary

1. Freshly precipitated tin(IV) sulfide entrains cobaltous ion by a process which follows a log **x/m** *vs.* log **c** relation. The entrainment is decreased by increase of temperature and(or) acidity of the solution.

2. The entrainment of cobaltous ion by tin(IV) sulfide can be made negligible by precipitation in the presence of acrolein.

ROCHESTER, N. Y. RECEIVED JULY 3, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Syntheses in the Pyrazine Series. IV. 2-Sulfanilamidopyrazine

BY JOSEPH W. SAUSVILLE AND PAUL E. SPOERRI

In view of the valuable bacteriostatic properties exhibited by many heterocyclic sulfanilamide derivatives, it was considered worthy to prepare 2-sulfanilamidopyrazine. For this purpose, aminopyrazine prepared by a method of Gabriel and Sonn[1] which has been modified and improved by Hall[2] and Hall and Spoerri[3] was condensed with N-acetylsulfanilyl chloride. In the line of synthesis of aminopyrazine, however, considerable difficulty was met in isolating pure pyrazine-2,3-dicarboxylic acid after alkaline oxidation of quinoxaline with permanganate. For this reason and also because the method of the previous investigators was found to be very long, a shorter, more direct means of isolating the acid was devised.

While the latter work was in progress, the first ionization constant of pyrazine-2,3-dicarboxylic acid was determined from the half-neutral point in electrometric titrations at the hydrogen electrode. The value of the constant is $1.7 \times 10^{-3} \pm 0.4 \times 10^{-3}$. The second carboxylic group was

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(1) Gabriel and Sonn, *Ber.*, **40**, 4850 (1907).

(2) Stanley A. Hall, Thesis, Polytechnic Institute of Brooklyn, June, 1939.

(3) Hall and Spoerri, THIS JOURNAL, **62**, 664 (1940).