ponents of the system.

2. The ratio of the experimental slope of the curve of log N against $1/T$ to the ideal slope, calculated from the latent heat of fusion, for any solute, is a measure of the relative internal pressures of the solute and solvent.

3. Not only may the latent heat of fusion of solids be determined but relative values for the internal pressures of many solids and liquids may be calculated from solubility data by the application of the principles developed.

4. The results of the calculations of relative internal pressures have been given and compared with those obtained by direct measurement or from other methods of calculation.

5. The principles entering into the procedure for calculating solubilities of organic compounds in various solvents have been discussed both for polar and non-polar substances. The limitations of the method have been pointed out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

A STUDY OF THE COBALTINITRITES OF BISMUTH AND CADMIUM

BY S. C. OGBURN, JR.

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Inorganic cobaltinitrites of the following elements have been previously prepared and described: potassium, sodium, lead, silver, lithium, thallium, barium, mercury (ous), strontium, zinc, magnesium, cobalt, ammonium, cesium and rubidium. This work has been done mainly by Aide and Wood,[1] Rosenheim and Koppel,[2] Cunningham and Perkin,[3] Burgess and Kamm,[4] and Drushel.[5] A survey of the literature, however, failed to disclose to the author any attempt at the preparation of the cadmium and bismuth compounds. This is, perhaps, due to their instability at formation, thus making their isolation by ordinary precipitation methods rather difficult.

Preparation of the Cobaltinitrite of Bismuth. Bismuthyl Cobaltinitrites

To a saturated solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, an equal quantity of a saturated solution of bismuth nitrate was added drop by drop, without shaking. A yellow-to-orange precipitate slowly appeared. At the end of 1 minute, it was filtered off by suction with as little agitation as possible. The precipitate was not washed,

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[1] Aide and Wood, *J. Chem. Soc.*, **77**, 1076 (1900).

[2] Rosenheim and Koppel, *Z. anorg. Chem.*, **17**, 42 (1898).

[3] Cunningham and Perkin, *J. Chem. Soc.*, **95**, 1562 (1909).

[4] Burgess and Kamm, *Am. J. Sci.*, **24**, 433 (1907); **26**, 329, 555 (1908).

[5] Drushel, THIS JOURNAL, **34**, 652 (1912).

but was dried well between filter paper and then in a desiccator over calcium chloride for several days. The filtrate was reserved and the dried compound was shown by analysis to contain bismuth 61.83 and 61.88% and cobalt 5.88 and 5.86%. The theoretical values for bismuth and cobalt in the normal salt, $BiCo(NO_2)_6$, which would be analogous to the sodium cobaltinitrite, are 38.304% and 10.86%, respectively. This difference of 23.55% (high) for bismuth, and of 5% (low) for cadmium was misunderstood at first, but when the filtrate was treated with more saturated bismuth nitrate solution, a distinctively yellow precipitate was formed, differing from the first. This indicated some abnormality and led to the preparation of the additional compounds and, eventually, to the assignment of formulas to the 3 compounds formed, which were substantiated and proved to represent a series of bismuthyl salts, and not a single simple bismuth cobaltinitrite. The normal bismuthyl salt, $(BiO)_3Co(NO_2)_6$, contains theoretically 61.9% of bismuth and 5.85% of cobalt; these values check very closely with those found in the above analysis.

The color and composition of this first precipitate were found to change readily with any change in conditions under which it was precipitated. If there was an excess of the sodium cobaltinitrite solution present, the precipitate dissolved, but it could be reprecipitated by the addition of more of the bismuth nitrate solution. When both solutions were not saturated upon such addition, the oxynitrate of bismuth was formed and thus contaminated the product. When the solution was allowed to stand longer than 1 minute, or was shaken excessively, another bismuthyl compound was formed which was found to contain a smaller percentage of the nitrite group.

This latter compound was directly prepared, as has been seen, by treating the filtrate from the orange precipitate with more of the saturated bismuth nitrate solution. Again, care was necessary not to shake the solution. A yellow precipitate of lighter shade than that of the $(BiO)_3Co(NO_2)_6$ compound was formed. This was carefully and rapidly filtered, dried, and analyzed, giving Bi, 64.90, 64.88%; Co, 6.12, 6.17%. These results conform to the formula, $(BiO)_3Co(NO_2)_5$, equivalent to 64.94% of bismuth and 6.13% of cobalt.

To the latter filtrate more saturated bismuth nitrate solution was added, the whole shaken vigorously and allowed to stand 5 minutes. A white crystalline precipitate (presumably bismuth oxynitrate from the excess of the bismuth nitrate used) settled and was filtered off. The filtrate was then diluted with distilled water to 10 times its former volume, and the mixture allowed to stand for 20 minutes. A white to light yellow precipitate was formed which was filtered off and by analysis showed an abnormal amount of bismuth, indicating that this salt was probably a mixed product of $(BiO_3)Co(NO_2)_5$, and $(BiO)_3Co(NO_2)_4$. The latter filtrate was then diluted with a large volume of distilled water, and the mixture allowed to stand for 20 minutes longer. A brick-red compound was precipitated which was shown to be $(BiO)_3Co(NO_2)_4$.

Analyses. Calc., Bi, 68.30; Co, 6.45. Found: Bi, 68.25, 68.21; Co, 6.49, 6.47.

When the concentration of the bismuth nitrate solution is changed, or when the precipitate is allowed to stand before filtration, mixtures of bismuthyl cobaltinitrites are formed, as two typical analyses show; in the first case, a mixture of the $-(NO_2)_5$ and the $-(NO_2)_6$ compounds (Bi, 63.31, 63.36%; Co, 5.98, 6.00%); and in the second case a mixture of the $-(NO_2)_4$ and the $-(NO_2)_5$ compounds (Bi, 65.52, 65.55%; Co, 6.21, 6.23%).

The $(BiO)_3Co(NO_2)_6$ compound was orange in color and the least stable of the three. The $(BiO)_3Co(NO_2)_5$ compound was yellow to orange. The $(BiO)_3Co(NO_2)_4$ compound was brick-red, and the most stable. Upon standing in the open, these compounds decomposed. Even standing in a drying desiccator longer than a week caused partial decomposition.

These bismuthyl compounds would seem to have the following coördination formulas: $[Co(NO_2)_6].3BiO$, $[Co(NO_2)_5(BiO)].2BiO$, and $[Co(NO_2)_4(BiO)_2].BiO$; thus in structure they bear a certain resemblance to the $[RuCl_4O_2].2Cs$ of Howe,[6] and $[OsCl_4O_2].2Cs$ and $[OsCl_3O_3].2Cs$ of Wintrebert,[7] as far as the valence problem is concerned.

In analyzing the bismuthyl compounds, the following scheme was carried out. The weighed sample was dissolved in 20 cc. of conc. nitric acid, and boiled until a colorless (or light pink) solution was obtained. It was then diluted with 200 cc. of water, and conc. ammonium hydroxide added until the mixture was strongly alkaline, when it was heated for 15 minutes and filtered. The white precipitated bismuth hydroxide was washed with distilled water and dried well, first between filter papers, and then in an electric oven at 110°, for 1 hour. At the end of this time, it was ignited and cooled to constant weight. The percentage of bismuth was then calculated from the bismuth oxide found.

The cobalt content was determined by boiling the filtrate from the above in a porcelain casserole with sufficient quantity of sodium hydroxide solution to insure complete precipitation of the cobalt hydroxide, indicated by the disappearance of the blue color. This usually proceeded so slowly that a small quantity of bromine water was added, and the solution again heated to boiling. The mixture was allowed to stand overnight, after which it was filtered and washed until the washings were neutral, and dried at 110° in an electric oven. It was then completely ignited, cooled and heated to constant weight. The percentage of cobalt was calculated from the cobalticobaltous oxide obtained. The nitrite content was obtained by difference.

Properties of the Bismuthyl Cobaltinitrites

Acids readily decompose these salts with the evolution of nitrogen peroxide. They are insoluble in ether, only slightly soluble in alcohol, and decomposed by water on standing. Sodium hydroxide solution and conc. ammonium hydroxide cause the precipitation of their respective hydroxides. They are all very hygroscopic, and range in color from yellow to brick-red.

Preparation of Cadmium Cobaltinitrite

Following previous methods of preparing cobaltinitrites it was found difficult to prepare the cadmium compound, due to its solubility in the reagents used. In order to increase the yield, a mixture of saturated solutions of sodium cobaltinitrite and cadmium sulfate was subjected to fractional crystallization. In an electric oven at 60°, evaporation slowly took place, and caused precipitation of the cadmium cobaltinitrite, as represented by the equation: $2Na_3Co(NO_2)_6 + 3CdSO_4 = \downarrow Cd_3[Co(NO_2)_6]_2 + 3Na_2SO_4$.

This separation of the desired product, however, was hindered by contamination of the precipitate with sodium sulfate, which crystallized from the mother liquor at high concentrations. This was overcome by evaporating the mixture nearly to dryness, and washing it thoroughly with cold water, in which the cadmium cobaltinitrite was found to be almost insoluble. The resulting solution was further evaporated and at

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[6] Howe, This Journal, **26,** 545 (1904).

[7] Wintrebert, *Thesis*, Bordeaux, **1902,** p. 82.

low concentration more of the bright yellow cadmium compound precipitated, thus increasing the total yield.

After the precipitate had been filtered and washed well with cold water, it gave by analysis, cadmium, 33.32%, and cobalt, 11.64%, which compared well with the theoretical values in the normal cadmium salt of formula, $Cd_3[Co(NO_2)_6]_2$, namely cadmium, 33.48%, and cobalt, 11.72%. The cadmium content was obtained by dissolving a weighed sample of the compound in the least possible amount of conc. hydrochloric acid, diluting with water and adding conc. ammonium hydroxide in excess, to bring about the reaction $CdCl_2 + 4\,NH_4OH = Cd(NH_3)_4Cl_2 + 4\,H_2O$. A small amount of potassium cyanide solution was then thoroughly stirred into the mixture, and a rapid stream of hydrogen sulfide run in: $Cd(NH_3)_4Cl_2 + 4\,KCN = 2\,KCl + K_2Cd(CN)_4 + 4\,NH_3$ and $K_2Cd(CN)_4 + H_2S = \downarrow CdS + 2KCN + 2\,HCN$......

The precipitated cadmium sulfide was filtered, washed well with cold water, dried and weighed. The percentage of cadmium was calculated on the basis of the cadmium sulfide found. The accuracy of this method of analysis was first checked by a "blank" determination.

The cobalt content was determined by treating the above filtrate in a manner similar to that described for the analysis of cobalt in the bismuthyl compounds. Tests were made in an attempt to detect water of crystallization, but the composition remained constant, even at 135°.

This compound ionizes as a complex salt into Cd^{++}, and $[Co(NO_2)_6]_2^{===}$, as was proved by the formation of sodium cobaltinitrite by double decomposition: $6NaNO_2 + Cd_3[Co(NO_2)_6]_2 = 3Cd(NO_2)_2 + \downarrow 2Na_3Co(NO_2)_6$.

Properties of Cadmium Cobaltinitrite.—Cadmium cobaltinitrite was found to be a hygroscopic, flaky compound, of bright canary-yellow color. It was only slightly soluble in cold water but was soluble in boiling water. Acids, alkalies, and common organic solvents, such as ether, carbon tetrachloride and chloroform, decomposed it to a greater or less degree. In the case of the alkalies, the respective hydroxides of cobalt and cadmium were formed. Its melting point could not be determined, as it decomposed at 175–180°. In solution it was very stable, differing in this respect from the majority of the other cobaltinitrites.

Summary

By simple double decomposition, 3 bismuthyl, and 1 cadmium cobaltinitrites were obtained from the action of sodium cobaltinitrite on a saturated solution of bismuth nitrate and cadmium sulfate, respectively.

The bismuth compounds $(BiO)_3Co(NO_2)_6$, $(BiO)_3Co(NO_2)_5$ and $(BiO)_3Co(NO_2)_4$ were obtained from the mother liquor by rapid filtration at the various stages of precipitation. Their structures accorded with Werner's theory of coördinated grouping, and bore a resemblance to the compounds, $[RuCl_4O_2].2Cs$ of Howe, and $[OsCl_4O_2].2Cs$ and $[OsCl_3O_3].2Cs$ of Wintrebert. The compound $(BiO)_3Co(NO_2)_4$ was the most stable. They ranged from yellow to orange in color, were insoluble in ether, and only slightly soluble in alcohol. Upon standing, either in solution or in the solid form, they readily decomposed. They were very hygroscopic, and unless care

was observed in the separation of one from the other at the proper time, intermixtures were formed.

Cadmium cobaltinitrite, $Cd_3[Co(NO_2)_6]_2$, was isolated from the mother liquor by fractional crystallization, and was obtained as a bright canary-yellow compound. It was found to be stable both in solution, and in the solid form. It was slightly hygroscopic, insoluble in cold water, and only slightly soluble in alcohol and ether, but dissolved readily in boiling water.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ELECTROMETRIC DETERMINATION OF SULFUR IN SOLUBLE SULFIDES

BY H. H. WILLARD AND FLORENCE FENWICK

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Introduction

When the bimetallic electrode system previously described[1] is used, the end-point in the electrometric titration of sodium sulfide[2] with an ammoniacal silver solution is unusually sharp. The e.m.f. rises slowly and sometimes irregularly at first, then there is a rise of 200 to 400 millivolts just before the end-point is reached, after which the completion of the reaction is marked by a very abrupt fall in potential. There is often a reversal of polarity during the titration which makes the first part of the rise apparently a fall. The proposed method is based upon the reaction used by Lestelle,[3] the precipitation of silver sulfide in alkaline solution by titration with standard ammoniacal silver solution. It is, however, much more simple and accurate than his visual determination of complete precipitation. The change in e.m.f. at the end-point is so great that it is never necessary to plot the curve.

Experimental Part

The sodium sulfide solution used in this work was prepared by absorbing 9 to 10 g. of hydrogen sulfide in a solution of 96 g. of sodium hydroxide and diluting to 6 liters.

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[1] Willard and Fenwick, THIS JOURNAL, **44,** 2516 (1922).

[2] This is by no means the first attempt to utilize an electrometric indicator for detecting the completion of the precipitation of an insoluble sulfide. A number of workers have studied this end-point in various solutions and with different electrode systems but have met with rather doubtful success. Dutoit and v. Weisse, *J. chim. phys.*, **9,** 578 (1911). Treadwell and Weiss, *Helvetica Chim. Acta*, **2,** 680 (1919). Pinkhof, "Over de toepassing der elektrometrische titraties," *Dissertation*, Amsterdam, **1919.**

[3] Lestelle, *Compt. rend.*, **55,** 739 (1862).