

[CONTRIBUTION FROM THE INTERNATIONAL NICKEL COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

A New Method of Studying Basic Metal Salts Applied to Certain Basic Salts of Nickel

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A procedure is described for investigating basic metal salts by precipitation at constant pH. Standardized nickel salt and potassium hydroxide solutions were added from burets to an alkaline reaction medium so that the pH of the latter remained constant. The composition of the precipitate was immediately calculable from the buret readings. Application of this method to an investigation of freshly precipitated basic nickel sulfates, chlorides and nitrates showed their composition was determined by the pH of the reaction medium. These basic nickel salts are metastable; their composition approaches nickel hydroxide at rates which are influenced by the temperature, the pH, and the neutral salt content of the reaction medium. No wholly satisfactory explanation for these observations is available.

Introduction

Precipitated basic metal salts have been the subject of some investigation during the last 30 years in spite of the general difficulty of isolating and determining discrete, stoichiometric species. Several different experimental approaches have been made to elucidate the composition and structure of such materials. These may be illustrated by, (1) the extensive electrometric studies of Britton and co-workers in which the pH of the reacting medium was followed as alkali was added slowly to various metal salt solutions,^{1,2} (2) the extensive X-ray studies on basic salts by Feitknecht and co-workers,³⁻⁵ (3) thermometric and conductometric studies,^{6,7} and (4) analysis of variations in equilibrium pH upon dilution of the reaction medium.⁸ Most of the basic salts for the above investigations were prepared by adding alkali to a metal salt solution. During an investigation of methods of preparing high-purity nickel hydroxide, the results of which will be reported later, a study was made of the factors influencing the formation of the basic salts of nickel, primarily so that they could be avoided. The nickel salts were added to an alkaline reaction medium. This paper describes a volumetric experimental method which was developed for the determination of the average composition of a basic nickel salt precipitated under alkaline conditions and indicates some of the properties of the materials produced.

If a soluble metal salt is added to an alkaline reaction medium, the pH of that medium decreases as hydroxide ions are consumed by the formation of a basic metal salt or metal hydroxide precipitate. However, if during the course of the precipitation, a strong alkali solution is also added to the reaction medium at such a rate as to maintain the initial pH, one has an approximate measure of the hydroxide content of the precipitate. Thus, if x equivalents of a neutral metal salt solution are added to an alkaline reaction medium and if y equivalents of alkali must also be added to maintain the initial pH, then the average composition of the precipitate may be represented as $x - y$ equivalents of metal salt in some combination with y equivalents of metal hydroxide. The ratio y/x ,

which is readily calculated from buret readings, represents that fraction of the anionic equivalents of the precipitate which are hydroxide; the remaining anionic equivalents of the precipitate, $x - y$, are of the same type as in the metal salt added. In the general case, if x equivalents of a neutral metal salt, whose composition may be represented by the formula M_aA_m , are added to an alkaline reaction medium along with y equivalents a strong alkali metal hydroxide solution to maintain constant pH, then the composition of the precipitate may be represented as $\frac{x - y}{ma} M_aA_m \times \frac{y}{m} M(OH)_m$, where m is the valence of the metal, M , and a is the valence of the anion, A .

Experimental

Apparatus.—The precipitations were carried out in a covered 2-liter crystallizing dish shown schematically in Fig. 1. The pH of the reacting solution was measured with a glass electrode by a Leeds and Northrup Universal pH Potentiometer. An agitator, with four 15-mm. long blades turning at 1250 r.p.m., was located off-center and provided vigorous mixing of the reacting solutions. Possible complications due to pick-up of acidic gases from the air were avoided by covering the dish and by bubbling a stream of nitrogen through the reaction liquor.

Materials.—C.P. nickel salts (sulfate, chloride and nitrate), were used as 3 to 4 normal solutions. The potassium hydroxide solution was prepared by dissolving C.P. KOH pellets to make about a 4 normal solution; its carbonate ion content was removed as $BaCO_3$ by the addition of barium hydroxide. "Deionized" water was used exclusively and all solutions were standardized by well-established methods.

Procedure.—In the first series of experiments, the objective was to determine the influence of the pH of the reaction medium upon the composition of the precipitate. Standard KOH solution was added to 1.5 liters of water contained in the reaction vessel until the pH reached a desired, predetermined value. Then nickel salt solution was introduced slowly from a buret; and additional potassium hydroxide solution was simultaneously admitted from a buret at a rate sufficient to maintain the pH essentially constant. At five or six evenly-spaced intervals during the course of the addition of 50 ml. of the nickel salt solution, the precipitation was interrupted. The pH was adjusted as closely as possible to the initial value by adding small quantities of salt or alkali as required and the buret readings were recorded. The entire precipitation usually required about 30 minutes. The buret readings were plotted against each other and normally a straight line was obtained which indicated that the same chemical process was occurring throughout the entire precipitation (exceptions to this at high pH will be mentioned later). The slope of the line obtained from the plot of buret readings multiplied by the ratio of the normalities of the alkali and salt solutions yielded the y/x value mentioned above. Thus, the y/x values for basic nickel sulfate, chloride and nitrate were determined at room temperature when the pH of the reacting medium was 8.4, 9.0, 10.0, 11.0, 12.0 and 12.6. Other experiments will also be discussed, but variations from the basic procedure de-

- (1) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2115 (1925).
- (2) H. T. S. Britton, *Endeavour*, **2**, 148 (1943).
- (3) W. Feitknecht, *et al.*, *Helv. Chim. Acta*, **19**, 831 (1936).
- (4) W. Feitknecht, *et al.*, *ibid.*, **22**, 1428 (1939).
- (5) W. Feitknecht, *et al.*, *ibid.*, **23**, 180 (1940).
- (6) A. Berton, *Compt. rend.*, **220**, 693 (1945).
- (7) P. Deschamps, *ibid.*, **226**, 179 (1948).
- (8) M. Geloso and P. Deschamps, *ibid.*, **224**, 1163 (1947).

scribed will be self-evident from the discussion of the results.

Discussion of Limitations of the Method

The composition of the basic salts can be determined precisely by the method indicated above if one knows in addition to the titration buret readings (1) that essentially all the nickel ion is precipitated and (2) that the amount of free alkali (absolute equivalents, not concentration) in the reaction medium is the same after the titration as it was before the titration. A constant pH reading from a glass electrode measuring system throughout the titration indicates approximate constancy of absolute alkalinity. For experiments conducted at low pH and room temperature, this assumption is good, but at higher pH and temperature conditions, limitations appear which lead to errors of increasing magnitude. These errors will be discussed before disclosing experimental results.

a. Dilution Error.—The glass electrode is responsive to hydrogen ion activity and hence to hydroxide ion activity through the hydrolytic equilibrium. If the initial and final hydroxide ion activities are identical, the equivalents of free alkali in the reaction medium are approximately constant. This approximation is better the lower the initial hydroxide ion activity and the smaller the total volume of reagents with respect to the volume of the reaction medium. The error, E , due to the dilution of the reaction medium by the reagents may be expressed in equivalents as

$$E = A_i \left(\frac{V_f - V_i}{V_i} \right)$$

where A_i is the initial number of alkali equivalents in the reaction medium whose initial and final volumes are V_i and V_f , respectively. A_i is larger, the higher the initial pH ; $V_f - V_i$ can be minimized by increasing the volume of the reaction medium and/or by using concentrated titrating solutions. In any case, the dilution error can be calculated and hence is not a true limitation of the method.

b. Salt Error.—The accuracy of the glass electrode is limited at high pH where the potential developed by the glass electrode is influenced by cations other than hydrogen ions—especially by sodium and potassium ions. The resulting error, which is negligible at pH 's less than about 10, is greater the higher the true pH and the higher the activity of the interfering cations. The error also depends on some property of the particular glass electrode membrane since differences in salt error response by two different electrodes in the same solution have been observed.

During the course of a normal titration, the only change in the reaction medium itself is a gradual increase in the concentration of by-product alkali salt (e.g., KCl when $NiCl_2$ solution was added to a KOH medium) which may lead to increasing "salt errors." However, the value of the salt error can be determined in any particular case simply by measuring in a separate titration the equivalents of alkali which must be added to maintain the initial pH reading while a solution of the alkali salt is run into the reaction medium. For reaction mediums consisting of 1.5 l. of 0.017 N KOH at 85° (pH at

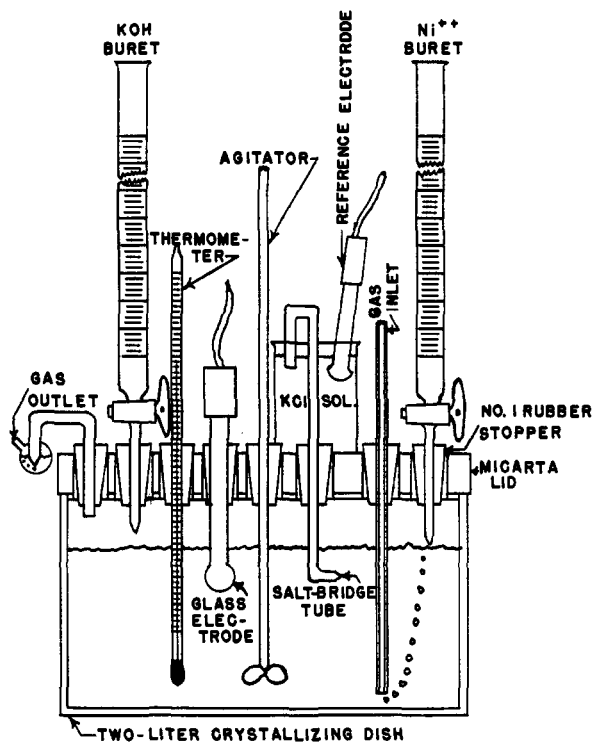


Fig. 1.—Schematic drawing of the apparatus for preparing and determining the composition of basic nickel salts using the method of precipitation at constant pH .

25° , 12.3) salt errors up to 2.5% in the OH/Ni ratio were observed after the addition of 50 ml. of 3.3 N KCl solution. Salt errors always indicate too high hydroxide content in the precipitate.

c. Instrument Error.—The internal constants of the potentiometers used for glass electrode measurement are not absolutely stable. Measurements of the same solution over the course of several hours without recalibration with a standard buffer indicated that pH errors due to the instrument may be as high as ± 0.2 unit. These changes appeared sporadically, so that there was no assurance that they might not occur shortly after calibration. Errors of this magnitude do not seriously concern most users of pH meters and at low pH they do not affect the results of this method. But at high pH , (about 12.5), an error of this type leading to a 0.2 pH unit difference in reading would markedly influence the composition of a precipitate as determined by the procedure described.

d. Reading Error.—At high pH where the electrometric response of the pH meter to a given change in absolute alkalinity is much weaker than at lower pH , reading errors are possible. It is difficult, therefore, to maintain the constant alkalinity required by this method at high pH . A more sensitive galvanometer would, of course, reduce the change of incurring this error. Both the "instrument" and "reading" errors could influence the apparent composition of precipitate in the direction of either more or less hydroxide content.

Results and Discussion

The objective of the first series of experiments was to determine the influence of the pH of the re-

action medium upon the initial composition of basic nickel chloride, nitrate and sulfate precipitated at room temperature. The results are shown in Fig. 2. The composition of the basic chlorides and nitrates, as expressed by OH/Ni equivalent ratios, appears to vary linearly with pH . The curve for the basic sulfate parallels the curve for basic nitrates and chlorides over most of the pH range but bends sharply in the low pH region. Several investigators¹ have reported that under similar conditions the hydroxide content of the basic sulfates is lower than the basic chlorides or nitrates. The curves of Fig. 2 indicate that a pH of about 12.5 to 13 would be required to precipitate a pure nickel hydroxide from nickel chloride or nickel nitrate; but using nickel sulfate a much higher pH would be required.

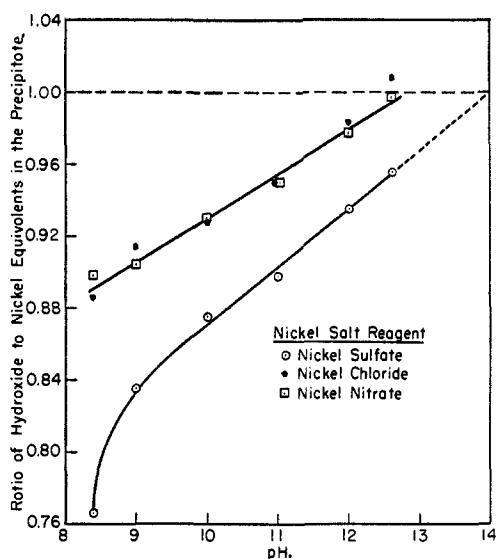


Fig. 2.—The composition of basic nickel salts precipitated at room temperature by the addition of nickel salt solutions to potassium hydroxide solutions of various pH .

The basic nickel salts are metastable in the sense that they are decomposed by the reaction medium so their composition approaches that of nickel hydroxide. The method of precipitation at constant pH would be admirably suited with some refinement to a kinetic study of this transition. Every equivalent of anion (*i.e.*, nitrate, chloride sulfate, etc.) rejected by the precipitate in exchange for a hydroxide ion will, of course, reduce the pH of the medium and require the addition of an equivalent of standard alkali to restore the initial pH .

Some authors have dealt with basic metal salts as if they were in true equilibrium with the reaction medium. A basic nickel sulfate was prepared at room temperature and at pH 9.6 to determine whether evidence for a true equilibrium could be obtained under these conditions. The reaction medium was made 1.5 N with respect to potassium sulfate since high sulfate ion concentration might favor the formation of a stable basic salt. The data, plotted in Fig. 3, indicate that the precipitate changes composition and slowly approaches pure nickel hydroxide as the equilibrium phase.

Without the high concentration of potassium

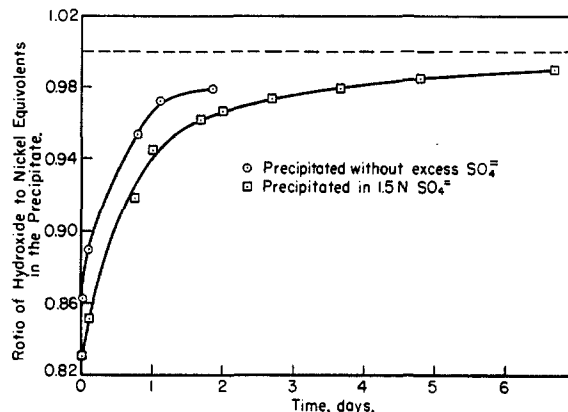


Fig. 3.—The effect of concentration of sulfate ion in the reaction medium on the rate of change of composition of basic nickel sulfate prepared at pH 9.6 and at room temperature.

sulfate in the reaction liquor, the rate of approach to equilibrium was approximately the same; but the composition of the freshly precipitated material was closer to nickel hydroxide. The latter observation is general as indicated by the following experiments. Basic nickel salts were prepared at pH 11 from reaction mediums one normal with respect to the potassium salt having an anion in common with the basic nickel salt:

| Basic nickel salt | Initial salt concn. in rean. medium | Init. OH/Ni eq. ratio in the ppt. |
|-------------------|--|-----------------------------------|
| Sulfate | 1.0 N K ₂ SO ₄ | 0.89 |
| | 0.0 | .90 |
| Chloride | 1.0 N KCl | .93 |
| | 0.0 | .95 |
| Nitrate | 1.0 N KNO ₃ | .93 |
| | 0.0 | .95 |

The rate of conversion of the basic nickel salts to nickel hydroxide is markedly increased at elevated temperature (Fig. 4). Other data illustrating the

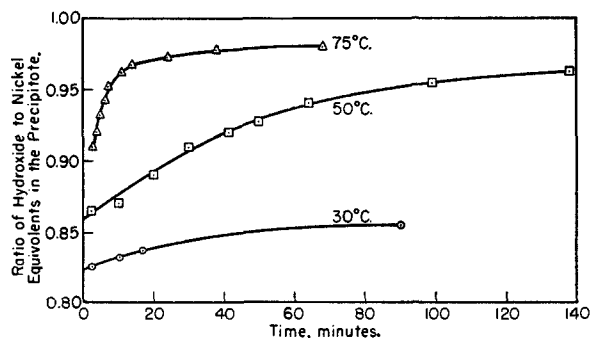


Fig. 4.—The effect of temperature on the rate of change of composition of basic nickel sulfate precipitated at pH 9.

influence of temperature, pH , and potassium "common anion" salt concentration upon the initial basic salt composition and upon its change with time are given in Fig. 5. High potassium chloride concentration (4 N) in the reaction medium reduces the initial OH/Ni equivalent ratios obtained at a given pH , particularly in the temperature range of 45 to 75°; it also influences the extent of change in composition during the first hour of aging.

To avoid the complications associated with the pH concept at elevated temperatures, experiments were run using the same concentration of potassium hydroxide in the initial reaction medium at the different temperatures. They were regarded as being at the same "nominal pH ." For example, at room temperature a 0.00012 N solution of potassium hydroxide had a pH of 9.6. If this solution was heated to 85°, the indicated pH -type reading was generally lower than 9.6. The "nominal pH 9.6" experiments were conducted at high temperatures by using a 0.00012 N potassium hydroxide as reaction medium and heating it to the desired temperature. A steady pH -type reading was then obtained, and this reading, whatever its value, was maintained throughout the subsequent titration.

Results at high temperature, pH , and salt content were probably influenced seriously by the limitations of the method which have been discussed. Actually, some non-linear titration curves were obtained and also OH/Ni equivalent ratios greater than unity. Although the latter is a possibility in the event of partial formation of a nickel-containing anion. This seems unlikely in view of the extremely low solubility of nickel hydroxide in strong alkali at room temperature.⁹

It is interesting to speculate how these metastable materials might form. Minute droplets of nickel salt solution striking the alkaline reaction medium might react at the surface to form a spherical shell coating of nickel hydroxide. Such a coating might impede the diffusion of the anions required to convert the unreacted nickel salt in the interior of the

(9) K. Gayer and A. B. Garrett, *THIS JOURNAL*, **71**, 2973 (1949).

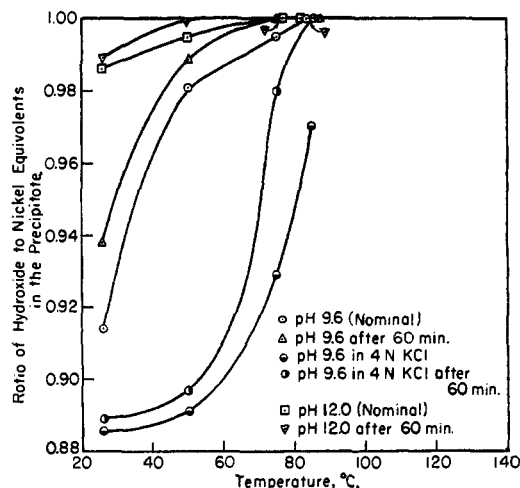


Fig. 5.—The composition of basic nickel chlorides as a function of pH , temperature, time and concentration of chloride ion in the reaction medium.

particles to nickel hydroxide. Weak forces might also exist further stabilizing the interior of the "clump" of precipitate. These may be the forces which slowly develop the crystallinity observed by Feitknecht in precipitates stored in a medium containing a chemical deficiency of hydroxide ion.^{3,5} Actually no simple picture gives an explanation of all of the experimental findings even in a qualitative way. A more comprehensive experimental application of this method with a more refined measuring apparatus would undoubtedly lead to a better understanding of these interesting basic salts.

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Condensed Gas Calorimetry. III. Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressures and Entropy of Diborane between 13°K. and the Boiling Point (180.32°K.)¹

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Heat capacity measurements have been carried out on high purity diborane from 14–177°K. Vapor pressures of the liquid were also measured for the temperature range 112–176°K. The triple point was determined as 108.30°K. and the normal boiling point 180.32°K. Heats of fusion and of vaporization were determined as 1069.0 and 3412 cal., respectively. A less accurate value for the latter, 3422 cal./mole, was computed from the measured vapor pressures. Entropy and heat contents of the gas at the normal boiling points were found to be 49.43 ± 0.10 e.u. and 6520 cal./mole, respectively.

Introduction

Considerable interest, both practical and theoretical, has been evident recently in the physical and thermal properties of the hydrides of boron. The lack of adequate thermodynamic data on these compounds has hampered research and technical development. With these things in mind, the authors have undertaken a program of obtaining adequate thermodynamic data on several of the more important members of the boron hydride family.

This paper deals with the simplest member of the series, diborane. With the exception of gaseous

heat capacities by Stitt² and the vapor pressure by Stock,³ very few precise low temperature thermochemical data have been obtained on this compound.

There is, however, a considerable volume of literature dealing with proposed structures for diborane, based on interpolation of infrared and Raman spectra. From the entropy of diborane at its boiling point it is possible to make a check against proposed structures, based on various interpretations of spectroscopic data. Comparison of computed entropies with that obtained in this research,

(1) This work was supported in part by The Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) F. Stitt, *J. Chem. Phys.*, **9**, 780 (1941).

(3) A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).