COMPOSITION OF SLIGHTLY SOLUBLE COMPOUNDS PRECIPITATED BY BASES FROM NICKEL SALT SOLUTIONS IN THE PRESENCE OF BORIC ACID

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The addition of bases to salt solutions of many metals produces slightly soluble hydroxides or more complex compounds.

The composition of these slightly soluble compounds and the standard isobaric potentials at which they form may be computed by the measurement of pH (in equilibrium with the solid phase), as a function of the activity of metal salts in solution [1,2].

Complex slightly soluble compounds may be formed from a metal hydrate and the salt of the same metal ($x[Me_bA_d] \cdot y[Me(OH)_n]$), or may contain molecules of foreign compounds (if the latter are present in the solution.).

Obviously, only the first type of slightly soluble compounds may be formed in pure sulfate solutions: their compositions and standard isobaric potentials have been computed in accordance with the general formula:

$$pH = \frac{\Delta Z^0_{basic}}{2.3nyRT} - \frac{y + bx + dx}{ny} \log a_{\pm} - \frac{1}{ny} \log \frac{b^{(y+bx)}\, d^{dx}}{\left(\frac{b}{b+d}\right)^{b} \left(\frac{d}{b+d}\right)^{d}}^{y+bx+dx} - \log K_W, \qquad (1)$$

where ΔZ^0_{basic} is the standard isobaric potential at which the basic salt begins to form, $a_{\pm}$ is the activity of the metal salt in solution, and K_W is the ion product of the water.

Study of the formation of slightly soluble compounds consisting of metal hydrates and molecules of foreign substances in solutions is also of interest, however.

Rotinyan and Zeldes [3,4] directed attention, a few years ago, to the fact that the addition of boric acid to nickel salt solutions resulted, upon titration with alkali, in the reduction of pH at the beginning of the formation of the solid phase.

At that time no explanation was found for this phenomenon, but after Keshan and his associates [5] discovered the existence of an entire series of slightly soluble metal borates, it became possible to relate the reduction in pH at the beginning of the appearance of the solid phase to the formation of boron-nickel compounds of lower solubility than that of pure nickel hydroxide. Thereupon it was decided to subject the problem of boron-nickel compound formation to more detailed investigation.

The foregoing certainly contradicts the very widespread opinion which holds the role of boric acid in a nickel electrolyte to be limited merely to the buffering properties of boric acid as a weak electrolyte [6]. It was therefore necessary to begin by independently demonstrating this view to be incorrect. This was confirmed by the potentiometric titration curves of boric acid and nickel sulfate solutions and mixtures thereof. Experience has shown the buffer branches of potentiometric titration curves of pure boric acid and nickel sulfate solutions to appear at much higher pH than in solutions containing a mixture of nickel sulfate and boric acid.

This difference in the curves cannot be explained other than by the assumption that the composition of the solid phase is qualitatively different in the presence of boric acid than when it is absent from the solution.

If, in the general case, the composition of the solid phase be represented by the formula $xNiSO_4 \cdot yNi(OH)_2 \cdot zH_3BO_3$ and if it be considered that this compound is in equilibrium with the solution*, i.e.,

* We are considering only the first stage dissociation of boric acid.

$$zH^+ + zH_2BO_3' + (x + y)\,Ni^{++} + 2yOH' + xSO_4'' \rightleftarrows xNiSO_4 \cdot yNi(OH)_2 \cdot zH_3BO_3, \quad (2)$$

the following may be written:

$$z\Delta Z_6^0 + RT\ln a_{H+}^z + z\Delta Z_7^0 + RT\ln a_{H_2BO_3'}^z + (x + y)\Delta Z_2^0 + RT\ln a_{Ni^{++}}^{(x+y)} + 2y\Delta Z_3^0 + RT\ln a_{OH'}^{2y} + x\Delta Z_4^0 +$$

$$+ RT\ln a_{SO_4''}^x = \Delta Z_5^0. \quad (3)$$

In Equation (3) the activity of the solid phase is as usual taken as unity. ΔZ_2^0, ΔZ_3^0, ΔZ_4^0, ΔZ_6^0, ΔZ_7^0 and ΔZ_5^0 represent the standard isobaric potentials at which Ni^{++}, OH', SO_4'', H^+, H_2BO_3' and the slightly soluble compounds are formed.

As

$$K_{H_3BO_3} = \frac{a_H + a_{H_2BO_3'}}{a_{H_3BO_3}} \quad (4)$$

and

$$a_{OH'} = \frac{K_W}{a_{H^+}}, \quad (5)$$

therefore

$$z\Delta Z_6^0 + z\Delta Z_7^0 + RT\ln K_{H_3BO_3}^z + RT\ln a_{H_3BO_3}^z + (x + y)\Delta Z_2^0 + RT\ln a_{Ni^{++}}^{x+y} + 2y\Delta Z_3^0 + RT\ln K_W^{2y} - RT\ln a_{H^+}^{2y} + x\Delta Z_4^0 +$$

$$+ RT\ln a_{SO_4''}^x = \Delta Z_5^0 \quad (6)$$

or

$$pH = \frac{\Delta Z_5^0 - (x + y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0}{2.3 \cdot 2yRT} - \frac{z}{2y}\log a_{H_3BO_3} - \frac{1}{2y}\log a_{Ni^{++}}^{(x+y)} a_{SO_4''}^w - \log K_W - \frac{z}{2y}\log K_{H_3BO_3}. \quad (7)$$

As

$$\Delta Z_5^0 - (x + y)\Delta Z_2^0 - 2y\Delta Z_3^0 - x\Delta Z_4^0 - z\Delta Z_6^0 - z\Delta Z_7^0 = \Delta Z_{st}^0 \quad (8)$$

Z^0 is the standard isobaric potential of reaction (2), $a = m\gamma$, $m_{SO_4''} = m_{Ni^{++}} = m_c$ (m=the molality of the salts and ions; γ = the coefficient of activity), equation (7) may be rewritten as follows:

$$pH = \frac{\Delta Z^0_{st}}{2.3 \cdot 2yRT} - \frac{z}{2y}\log a_{H_3BO_3} - \frac{2x + y}{2y}\log a_+ - \log K_W - \frac{z}{2y}\log K_{H_3BO_3}. \quad (9)$$

Equation (9) was derived for a particular case; however, it may be worked out without difficulty in a general form applicable to complex slightly soluble compounds, regardless of composition. It differs from formula (1) not only in the presence of supplementary constants, but in the presence of the pH ratio to concentration of the second component of the solution – boric acid.

We conducted experiments of this type at 10 and 50°. Determination of pH, in equilibrium with the solid phase, was by potentiometric titration [3], subsequent to prior determination that slightly soluble compounds in equilibrium are not formed in this situation. This was confirmed by the fact that the pH values for the moment of formation of the solid phase and the equivalent pH values we obtained by the Gromov method, coincided.

Tables 1 and 2 show the results of our experiments. Boric acid activity is always equated to concentration. The data in Tables 1 and 2 were used to plot the pH–log a_+ and pH–log $C_{H_3BO_3}$ (Figs. 1 and 2).

These figures show that $\frac{2x + y}{2y} = 0.5$ and $\frac{z}{2y} = 1$.

The former equation gives $x = 0$ and a minimum integer value, $y = 1$.

Combination of the two equations gives $z = 2$. Consequently, the composition of the solid phase is $Ni(OH)_2 \cdot 2H_3BO_3$. It is interesting to note that this formula corresponds to that of the slightly soluble nickel diborate $NiB_2O_4 \cdot xH_2O$ [5].

TABLE 1

Ratio of pH at Moment of Solid Phase Formation to Activity of Nickel Sulfate in Solution (Concentration H_3BO_3 20 g/l)

Nickel concentration				pH	
(g/l)	(M)	$\gamma_{\pm}$	$a_{\pm}$	20°	50°
0.5	0.008	0.425	0.00361	5.22	4.75
1.0	0.017	0.340	0.00578	5.18	4.64
5.0	0.085	0.180	0.01534	4.94	4.44
10	0.170	0.120	0.02045	4.92	4.35
20	0.341	0.075	0.02556	4.88	4.24
30	0.515	0.065	0.03345	4.82	4.26
40	0.681	0.055	0.03748	4.76	4.22
50	0.852	0.050	0.04259	4.64	4.12
60	1.022	0.045	0.04600	4.60	4.04

TABLE 2

Ratio of pH at Moment of Solid Phase Formation to Concentration of Boric Acid in Solution (Concentration Ni 30 g/l)

H_3BO_3 concentration		pH	
(g/l)	(M)	20°	50°
2	0.032	5.66	5.06
4	0.064	5.48	4.82
8	0.128	5.18	4.54
12	0.192	4.96	4.36
20	0.323	–	4.20
25	0.404	4.50	4.06
35	0.566	4.44	3.88
45	0.727	4.26	3.73
55	0.889	–	3.60

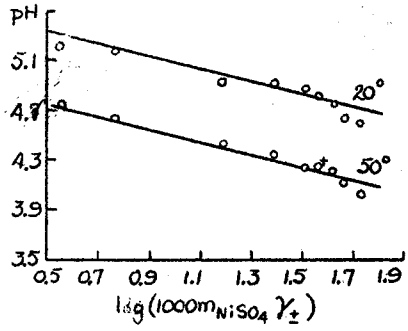

Fig. 1. Ratio of pH to logarithm of nickel sulfate activity (at 20 and 50° and at a constant concentration of boric acid, 20 g/l). The cross represents data from source [3].

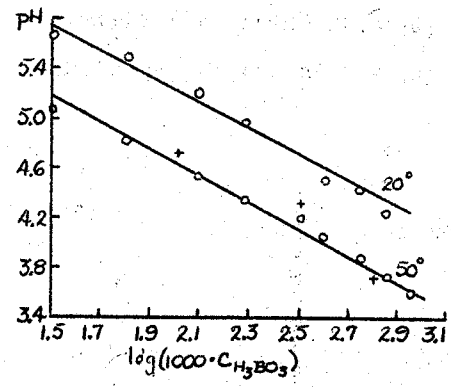

Fig. 2. Ratio of pH to logarithm of boric acid concentration (at 20 and 50° and a constant nickel sulfate concentration, 0.514 M.).

As the solid phase formed is in equilibrium with the solution, the standard isobaric potential of nickel diborate anhydride formation may be computed.

The first series of measurements at 20° provided a value of −55.0 Cal/mole, and the second −54.0 Cal/mole. As the standard isobaric potential of nickel hydroxide formation is −18.9 Cal/mole [1], the standard isobaric potential of association (ΔZ_n^0) of two boric acid moles to one of nickel hydroxide would be −36.1 Cal.

This magnitude is greater than ΔZ_n^0 when nickel sulfate associates with nickel hydrate to form $3NiSO_4 \cdot 4Ni(OH)_2$ (−20.4 Cal [2]), so that when boric acid is present and there is a gradual precipitation of nickel hydroxide, it is nickel diborate that forms to begin with, and not the basic salt.

As may readily be seen from Figs. 1 and 2, the angle coefficients of the straightlines pH-log $a_{\pm}$ do not change with change from 20 to 50°.

This makes it possible to contend that the composition of a slightly soluble compound does not vary with rising temperature. The pH temperature coefficient at the beginning of formation of the solid phase in these experiments is 0.2 pH unit per 10°, which is somewhat lower than previous measurement of this magnitude (0.26 pH unit per 10° [3]).

SUMMARY

1. Potentiometric titration was used to study the composition of the solid phase at the moment of the beginning of its formation, when nickel was precipitated by a base from mixed solutions of nickel sulfate and boric acid.

2. It has been shown that in the entire concentration interval studied, the solid phase, in equilibrium with the solution, consists of nickel diborate $Ni(OH)_2 \cdot 2H_3BO_3$. Basic nickel salts in pseudo equilibrium do not form in the presence of boric acid.

3. Computations of the standard isobaric potentials of nickel diborate formation from ions and from nickel hydroxide and boric acid have been made, and it was demonstrated that the first compound to be formed must be nickel diborate, and not the basic nickel salt.

4. Elevation of temperature to 50° did not change the composition of the solid phase precipitated.

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* T.p. = C.B. Translation pagination.