

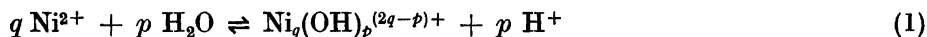
Studies on the Hydrolysis of Metal Ions

54. The Nickel Ion, Ni^{2+} , in 3 M (Na)ClO₄ MediumKIM ALEKSANDROVIČ BURKOV, LUKA STOJANOVIČ LILIČ
and LARS GUNNAR SILLÉN**Departments of inorganic chemistry, the State University (LGU), Leningrad, SSSR;
Royal Institute of Technology (KTH), Stockholm 70, Sweden*

The hydrolysis of the nickel ion, Ni^{2+} , was studied at 25°C in the medium, 3 M (Na)ClO₄. The reactions are written as: $q \text{Ni}^{2+} + p \text{H}_2\text{O} \rightleftharpoons \text{Ni}_q(\text{OH})_p^{(2q-p)+} + p \text{H}^+$, equilibrium constant β_{pq} . $[\text{H}^+] = h$ was measured with a glass electrode. $B = [\text{Ni}]_{\text{total}}$ was varied from 0.1 M to 0.8 M. The hydrolysis begins to be measureable around $\log h = -6$ but a precipitate appears at Z (OH^- bound per Ni^{2+}) as low as ≈ 0.018 .

The data were treated by the self-medium principle and by various graphical methods, *e.g.* Ref.² which all indicated the main complex (4,4). Deviations can largely be ascribed to small analytical errors, but may also indicate some minor complex, if so probably (1,1) or (1,2). The data were treated with a recent version of LETA-GROP³⁻⁵ with independent adjustment of analytical errors. The "best" combination was found to be $\log \beta_{44} = -27.37 \pm 0.02$, $\log \beta_{13} \approx -10 (< -9.5)$ (error limits = 3 σ). Other complexes tried came out with negative constants and were thus rejected by the computer; upper limits for their values (3 σ range) are given in eqn. (24).

The nickel ion, Ni^{2+} , is hydrolyzed weakly in aqueous solution. We may write each soluble hydrolysis product in the general form $\text{Ni}_q(\text{OH})_p^{(2q-p)+}$, and call it the (p,q) species (complex) for short, and we may define an equilibrium constant β_{pq} for each reaction



(In the IUPAC tables of stability constants,²⁵ the present β_{pq} is denoted by $^*\beta_{pq}$). If c_{pq} is the concentration of the (p,q) complex, $b = [\text{Ni}^{2+}]$ and $h = [\text{H}^+]$, then we have

$$c_{pq} = \beta_{pq} h^{-p} b^q \quad (2)$$

* The experimental part of the present work was carried out at Leningrad University by KAB together with LSL. The computer treatment was carried out in Stockholm, by KAB and LGS together.

The first authors who studied the hydrolysis of Ni^{2+} measured pH in solutions of "pure" Ni salts. Using a hydrogen electrode at 25°C, Denham⁶ found evidence for the (1,1) complex, NiOH^+ , or possibly the (2,1) complex, $\text{Ni}(\text{OH})_2$. He gave the values, for NiSO_4 solutions, $\log \beta_{11} = -8.3$ (or $\log \beta_{21} = -12.96$) and for NiCl_2 solutions $\log \beta_{11} = -6.5$. In 1913, Kullgren⁷ deduced by kinetic methods $\log \beta_{11} = -8.6$ for dilute solutions at 100°C.

From the distribution measurements of Löfman,⁸ Jellinek⁹ deduced $\log \beta_{11} \approx -9.3$ for nickel acetate solutions. Other values for $\log \beta_{11}$ (symbols for medium and method are those used in Stability Constants²⁵): -10.64 (0 corr, 25°, gl, Gayer and Woontner¹⁰ 1952); -9.4 (0.1 (KCl), 30°C, gl, Chaberek *et al.*¹¹ 1952); -9.49 to -9.23 (25°, E, con, Ksandr and Heitmanek¹² 1952); ≈ -9 (gl, temperature?, Schwab and Polydoropoulos¹³ 1953); -8.94 (0 corr, 20°, gl, Čuta *et al.*¹⁴ 1956); -10.92 (0 corr, 25°C, gl, Achenza¹⁵ 1959). The difference between the values may, among other things, indicate the high influence of impurities.

There is some indication of slow reactions. Čuta *et al.*¹⁴ and Vepřek-Šiška¹⁶ have suggested that the slowly formed product is a polynuclear complex, for instance $\text{Ni}_2(\text{OH})_2^{2+}$, but give no equilibrium constants for it. Achenza¹⁵ suggests the (2,1) complex, $\text{Ni}(\text{OH})_2$, with $\beta_{21} \approx -15$.

SYMBOLS

B = total concentration of Ni(II); $b = [\text{Ni}^{2+}]$, concentration of free nickel ions in solution; H = analytical excess of hydrogen ions in the solution, negative in hydrolyzed solutions; $h = [\text{H}^+]$, equilibrium concentration of hydrogen ions; p = number of OH^- groups in (p,q) complex; q = number of Ni atoms in (p,q) complex; $K_p = \Sigma B^q \beta_{pq}$, total apparent equilibrium constant for complexes with p ligands; Z = average number of OH^- bound per nickel atom in the solution; β_{pq} = equilibrium constant defined by (2) and (1).

EXPERIMENTAL

In the present work, the hydrolysis of Ni^{2+} was studied by means of emf titrations at 25°C with the medium 3 M (Na)ClO₄. The reactions could be followed by measuring h by means of a glass electrode.

Preliminary experiments had shown that the hydrolysis begins around pH = 6–7 (depending on B), and that a precipitate is formed already at values for Z between 0.015 and 0.02. As has been stressed by Biedermann and Ciavatta¹⁷ the purity of the reagents is very important in studies of the hydrolysis of metal ions at pH > 5 and low Z values.

Reagents

Sodium perchlorate was prepared by dissolving sodium carbonate in HClO_4 , both of the best quality (*chim. čist.*, corresponding to analytical grade). The NaClO_4 was recrystallized three times, and the stock solution was analyzed in two ways, by ion exchange, and by evaporating a known volume to dryness and constant weight.

Nickel perchlorate was prepared by dissolving nickel carbonate in HClO_4 , and recrystallized a few times. Total nickel, B , in the solutions was determined in two ways, by means of dimethylglyoxime,¹⁸ and by titration with trilon B.¹⁹ The concentration of ClO_4^- was determined by ion exchange.²⁰ A known volume of nickel perchlorate solu-

tion was sent through the H^+ form of the cation exchanger KU-2, after which the eluate was titrated with NaOH. A rough value for the original H^+ excess, H , was obtained from $H = [ClO_4^-] - 2B$. Afterwards, H in the various Ni^{2+} solutions was determined more accurately by Olin's improved version²¹ of Gran's method.²²

Sodium hydroxide was taken from a *chim. čist.* preparation, a concentrated solution was prepared, and carbonate removed in the usual way. After dilution, the concentration of OH^- was determined by titration, using potassium biphthalate and oxalic acid as standard substances.²³

Perchloric acid., also *chim. čist.*, was diluted. The concentration of the stock solutions was determined by titration with NaOH.

Apparatus

The equilibrium value for $[H^+] = h$ was determined using the cell
 $-Hg, Hg_2Cl_2/4 M NaCl/3 M NaClO_4/equilibrium\ solution/glass\ electrode +$ (I)

The salt bridge was of the "Wilhelm" type, described by Forsling, Hietanen and Sillén.²⁴ The cell with the titration vessel was kept in an oil thermostat at $25.0 \pm 0.1^\circ C$. The oil thermostat and the burets with NaOH and Ni solutions were kept in an air thermostat at $\approx 25^\circ C$. During the experiments, argon was bubbled through the solution for stirring, and for keeping an inert atmosphere. The argon had previously been bubbled through solutions of NaOH, distilled water, and 3 M $NaClO_4$, to get the right H_2O pressure. It contained 0.02 % O_2 , which was not considered important in the present case.

The emf of cell (I) was measured to within ± 0.1 mV by means of a high-capacity potentiometer for constant current, PPTV-1, a milliammeter of type M 198, and an amplifier with the electrometric valve 6Ž1Ž. The apparatus was set up as described in Ref. 26, using a standard Weston cell.

In general, E had reached a constant value 15–20 minutes after each addition from the burets.

ON THE CHOICE OF METHOD

The hydrolysis of Ni^{2+} is one of those unfavorable cases, like Cd^{2+} and La^{3+} (Refs. 27, 17), where the cation is a very weak acid and moreover the hydroxide or a hydroxide salt precipitates already at a very low value for Z . This means that the solutions to be studied have a low buffer capacity. In the present case, the total concentration, B , that could be used was limited by the experimental accuracy to values from 0.1 M and upward. The upper limit 0.8 M was set by the solubility of $Ni(ClO_4)_2$ and the method chosen.

The hydrolysis of Ni^{2+} was studied at $25^\circ C$ and the total concentrations $B = 0.1, 0.2, 0.4, 0.6,$ and 0.8 M. By the addition of $NaClO_4$, we kept $[ClO_4^-] = 3$ M, thus the medium was 3 M $(Na)ClO_4$.

In each experiment (titration) at constant B , the initial solution was acidic. The acidity was decreased by adding equal volumes of NaOH solution, and of nickel solution of concentration $2B$ so that B did not change. The ionic medium, 3 M $(Na)ClO_4$, was the same in all solutions.

Since it was feared that the activity factors might be different for different B values, when a large part of the medium ions Na^+ had been replaced by Ni^{2+} , the data were at first treated by the self-medium method.¹ For each value for B , the ionic medium changed very little during an experiment, since the experiment ended at $Z \approx 0.018$ when the precipitate appeared. So, the assumption of constant activity factors for constant B is a very reasonable one. At the end, it came out that the activity factors could also be approximately treated as being the same for all B values.

In the following we can thus use concentrations instead of activities, at least for each B separately. The emf of the cell (I) will be assumed to follow the equation:

$$E = E_0 + 59.15 \log h + E_j \quad (3)$$

In this equation, E_0 is a constant, at least for each B , and E_j is the liquid-junction potential at the junction: 3 M NaClO₄/equilibrium solution. We can expect E_j to be mainly a function of $[H^+] = h$; Biedermann and Sillén²⁸ found $E_j = -16.7 h = -j\bar{h}$, mV, but there may be an extra term for deviations of the glass electrode with varying h . The constants j and E_0 can be determined by measurements in acidic solutions. At any rate, E_j is completely negligible in the hydrolyzed solutions at pH \approx 6.7.

In the first part of a titration, with $\log h = -2$ to -3 , the hydrolysis of Ni²⁺ could be neglected; from this part, we could calculate accurately both E_0 and H_0 , the excess of H⁺ in the original nickel solution.

When E_0 and E_j were known, one could calculate the free concentration $[H^+] = h$ for each point from E , using eqn. (3).

Now that also B and H were known, from analysis, we could calculate

$$Z = (h - H)/B \quad (4)$$

which is the average number of OH bound per Ni, or the average number of H⁺ set free per Ni. These data and calculations thus gave a series of sets of data $Z(\log h)_B$, which were used as the basis for the following calculations of the formulas of the complexes, and their formation constants.

As an example, the experimental data for an emf-titration at $B = 0.200$ M are given in Table 1. The experiment started with $v_0 = 50$ ml solution S_0 in

Table 1. Details from potentiometric measurements with $B = 0.20$ M. Solutions:

S_0 ($v_0 = 50$ ml): $B = 0.20$ M; $[H^+] = H_0 = 0.00458$ M, 3 M (Na)ClO₄
 S_1 (v ml): $B = 0.40$ M; $[H^+] = H_S = 0.00916$ M, 6 M (Na)ClO₄
 T_1 (v_1 ml): 0.01857 M NaOH, $H = H_1 = -0.01857$ M
 T_2 (v_2 ml): 0.09635 M NaOH, $H = H_1 = -0.09635$ M

1a: determination of E_0 (mM scale)

| v | v_1 | E mV | $10^3 H$ | E_0 mV |
|-----|-------|--------|----------|----------|
| 0 | 0 | 346.1 | 4.58 | 307.0 |
| 1 | 1 | 344.3 | 4.22 | 307.3 |
| 2 | 2 | 342.2 | 3.89 | 307.3 |
| 3 | 3 | 340.0 | 3.58 | 307.2 |
| 5 | 5 | 335.6 | 3.03 | 307.2 |
| 6 | 6 | 333.5 | 2.78 | 307.2 |
| 7 | 7 | 331.2 | 2.55 | 307.2 |
| 8 | 8 | 322.0 | 2.33 | 307.3 |
| 10 | 10 | 324.2 | 1.93 | 307.3 |
| 12 | 12 | 319.0 | 1.57 | 307.4 |

$$E_0 = 307.2 \pm 0.1 \text{ mV}$$

the equilibrium vessel (composition see table). After this, we added stepwise equal volumes, v , of NaOH solution T_1 and Ni solution S_1 . In this way, the total concentration of Ni, and of perchlorate, were kept constant.

In the first part of the titration, Table 1a, the excess H^+ concentration was calculated from the equation

$$H = (v_0H_0 + v_1H_1 + vH_s)/(v_0 + v + v_1) \quad (5)$$

The values for H in S_0 and S_1 , $H_0 = 0.00458$ M and $H_s = 0.00916$ M, were determined by the method described by Olin,²¹ which is an improvement of Gran's method²² for this special case. Table 1a gives, for each point, v , E , H , and the value for E_0 calculated from eqn. (3). The constancy of $E_0 = 307.2 \pm 0.1$ mV is an additional support of the accuracy of the value determined for H_0 . If the value for H_0 is changed by only, say, 0.05 mM, E_0 is found to change perceptibly from point to point.

Table 1b gives the data for the second part of the titration. At the end, a more concentrated NaOH solution was added, T_2 . Table 1b also gives $\log h$ and the values for Z , calculated from the data.

Table 1 cont.

1b:

| v | v_1 | v_2 | E mV | $-\log h$ | $Z \times 10^4$ |
|------|-------|-------|--------|-----------|-----------------|
| 1.2 | | 1.2 | 260.1 | | |
| 1.0 | | | 224.4 | | |
| 1.2 | 1.0 | | 210.1 | | |
| 1.5 | 1.5 | | 172.2 | | |
| 1.6 | 1.6 | | 156.5 | 5.547 | 2.4 |
| 1.7 | 1.7 | | 123.4 | 6.110 | 2.9 |
| 1.8 | 1.8 | | 119.4 | 6.174 | 3.5 |
| 1.9 | 1.9 | | 116.3 | 6.227 | 4.0 |
| 2.0 | 2.0 | | 112.7 | 6.288 | 4.6 |
| 2.2 | 2.2 | | 110.5 | 6.325 | 5.8 |
| 2.5 | 2.5 | | 106.9 | 6.386 | 7.4 |
| 2.9 | 2.9 | | 104.3 | 6.429 | 9.6 |
| 3.2 | 3.2 | | 102.7 | 6.457 | 11.3 |
| 4.0 | 4.0 | | 101.6 | 6.475 | 15.5 |
| 5.0 | 5.0 | | 99.3 | 6.514 | 20.6 |
| 6.0 | 6.0 | | 97.5 | 6.545 | 25.5 |
| 7.0 | 7.0 | | 96.3 | 6.565 | 30.1 |
| 8.5 | 8.5 | | 95.4 | 6.580 | 36.7 |
| 9.5 | 9.5 | | 94.4 | 6.597 | 40.8 |
| 10.5 | 10.5 | | 93.7 | 6.609 | 44.9 |
| 12.0 | 12.0 | | 92.1 | 6.619 | 50.5 |
| 12.2 | | 0.2 | 91.4 | 6.648 | 58.9 |
| 12.5 | | 0.5 | 89.7 | 6.676 | 71.5 |
| 12.8 | | 0.8 | 88.7 | 6.693 | 83.9 |
| 13.1 | | 1.1 | 87.5 | 6.714 | 96.2 |
| 13.4 | | 1.4 | 86.9 | 6.724 | 108.3 |
| 13.7 | | 1.7 | 86.4 | 6.732 | 120.3 |
| 14.0 | | 2.0 | 85.7 | 6.744 | 132.7 |
| 14.8 | | 2.8 | 85.1 | 6.754 | 163.0 |

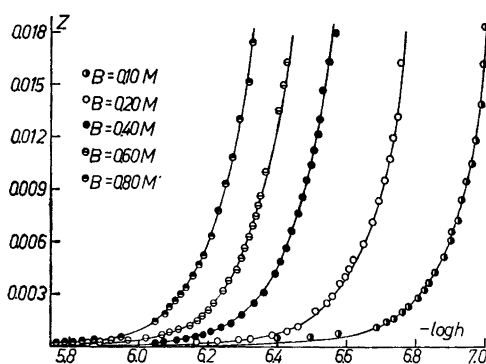


Fig. 1. Nickel hydrolysis, data $Z(\log h)_B$. The circles are the experimental points for various total concentrations B . The curves were calculated, assuming $\log \beta_{12} = -9.96$ and $\log \beta_{44} = -27.37$.

Table 2. Nickel hydrolysis. All experimental data, in the form: $-\log h$, $10^4 Z$, and $10^4 (Z_{\text{calc}} - Z_{\text{exp}})$. In calculating Z_{calc} we used $\log \beta_{44} = -27.37$, $\log \beta_{12} = -9.96$, and the δZ values in the next to the last line of Table 4i.

$B = 0.100 \text{ M}$; 5.907, 4.6, -6; 6.401, 5.6, -6; 6.496, 6.6, -6; 6.578, 8.8, -6; 6.639, 10.8, -6; 6.689, 11.9, -3; 6.693, 12.9, -4; 6.739, 17.0, -3; 6.781, 23.0, -2; 6.812, 27.9, +1; 6.842, 37.3, +1; 6.859, 42.8, +2; 6.881, 51.6, +3; 6.905, 61.8, +6; 6.925, 72.3, +9; 6.935, 84.4, +4; 6.951, 95.1, +7; 6.965, 105.2, +11; 6.974, 117.9, +8; 6.991, 139.9, +6; 6.998, 161.7, -7; 7.013, 183.3, -7;

$B = 0.200 \text{ M}$; 5.547, 2.4, +3; 6.110, 2.9, +3; 6.174, 3.5, +3; 6.227, 4.1, +3; 6.287, 4.6, +3; 6.325, 5.8, +3; 6.386, 7.4, +4; 6.429, 9.6, +4; 6.458, 11.3, +4; 6.475, 15.5, +2; 6.514, 20.6, +1; 6.545, 25.5, +1; 6.565, 30.1, +1; 6.580, 36.7, -2; 6.597, 40.8, -2; 6.609, 44.8, -2; 6.619, 50.5, -4; 6.648, 58.9, -1; 6.676, 71.5, +2; 6.693, 83.9, +0; 6.714, 96.2, +4; 6.724, 108.3, +0; 6.732, 120.3, -4; 6.744, 132.7, -4; 6.754, 163.0, -23;

$B = 0.400 \text{ M}$; 6.075, 3.7, +0; 6.101, 4.3, +1; 6.115, 4.8, +0; 6.141, 5.6, +0; 6.189, 7.8, +1; 6.242, 11.5, +1; 6.266, 13.6, +1; 6.283, 16.2, +1; 6.301, 18.3, +1; 6.315, 18.8, +3; 6.335, 25.3, +1; 6.367, 31.6, +2; 6.396, 41.9, +1; 6.426, 56.1, -0; 6.443, 66.1, -1; 6.460, 75.8, -1; 6.472, 85.3, -2; 6.484, 94.7, -2; 6.497, 103.8, -0; 6.506, 112.8, -1; 6.516, 121.7, +0; 6.521, 130.4, -3; 6.528, 147.3, -12; 6.548, 163.4, -3; 6.568, 179.4, +11;

$B = 0.600 \text{ M}$; 5.645, 1.8, -4; 5.775, 1.9, -3; 5.801, 2.1, -3; 5.856, 2.4, -3; 5.924, 3.4, -3; 5.972, 4.2, -3; 6.004, 5.2, -3; 6.071, 7.7, -2; 6.151, 12.2, +1; 6.171, 14.3, +2; 6.201, 21.1, +1; 6.221, 25.2, +1; 6.245, 32.1, +1; 6.284, 44.0, +4; 6.296, 50.5, +3; 6.318, 63.1, +2; 6.328, 69.2, +2; 6.338, 75.2, +3; 6.345, 81.1, +2; 6.354, 86.9, +4; 6.364, 98.2, +1; 6.372, 108.9, -3; 6.379, 119.6, -6; 6.397, 134.7, -2; 6.408, 149.2, -3; 6.429, 162.8, +13;

$B = 0.800 \text{ M}$; 5.709, 1.9, +2; 5.749, 2.2, +2; 5.792, 2.8, +2; 5.842, 3.7, +2; 5.854, 3.9, +2; 5.949, 5.8, +3; 6.052, 14.9, +3; 6.079, 19.9, +2; 6.087, 23.7, -1; 6.109, 27.3, -0; 6.123, 30.9, -0; 6.137, 34.5, -0; 6.157, 41.5, -1; 6.174, 47.2, -1; 6.187, 52.8, -1; 6.209, 63.5, -1; 6.231, 78.6, -4; 6.248, 93.6, -7; 6.272, 108.5, -3; 6.294, 130.6, -3; 6.319, 152.3, +5; 6.331, 173.9, +1;

The complete data for all five B values, are given in Table 2 and Fig. 1 in the form $Z(\log h)_B$.

ANALYSIS OF DATA

In order to deduce the sets (p, q, β_{pq}) for the complexes formed we treated the data $Z(\log h, B)$ as follows. First, the data for each value of B were analyzed separately by several graphical methods. It then came out that the main complex is (4,4) and the same formation constant $\beta_{4,4}$ was found for different B , within the experimental errors. It was then thought worth-while to treat all the data for different B values simultaneously with the generalized least-squares computer program LETAGROP, in order to find the "best" value for the average β_{44} in the interval and to seek for evidence for other complexes.

Self-medium method. From the earlier definitions (1, 2, 4) and the material balance it follows for B , and for BZ (the amount of OH bound to Ni per liter):

$$B = b + \Sigma \Sigma qc_{pq} = b + \Sigma \Sigma q\beta_{pq}h^{-p}b^q \quad (6)$$

$$BZ = h - H = \Sigma \Sigma pc_{pq} = \Sigma \Sigma p\beta_{pq}h^{-p}b^q \quad (7)$$

In the present case Z is so small (< 0.018) that we can set $b \approx B$, which gives

$$BZ = \Sigma p\beta_{pq}h^{-p}B^q \quad (8)$$

$$\text{where } K_p(B) = \Sigma q\beta_{pq}B^q \quad (8a)$$

Various graphical methods were used in order to determine p and K_p from the data $Z(\log h)_B$. Most of the necessary calculations were made by means of a high-speed computer.

The predominating complex. Let us first assume that only complexes with one value for $p = P$ are formed, with one or more values for q . In this case (8) gives

$$BZ = PK_P h^{-P} = \Sigma q P \beta_{Pq} B^q h^{-P} \quad (9)$$

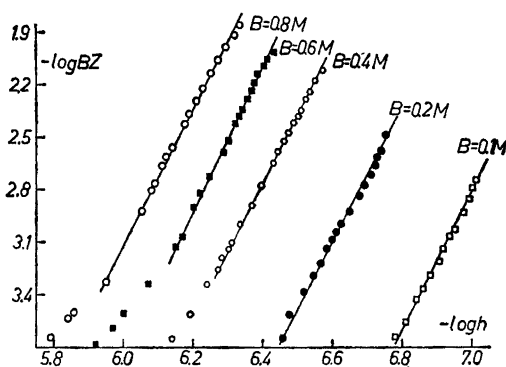


Fig. 2. Diagram $-\log(BZ)$ versus $-\log h$. Circles etc. = experimental points: Straight lines, with slope ≈ 4 , were fitted to upper part of points.

(1) We may transform (9) as follows

$$\log (BZ) = \log P + \log K_p - P \log h = \text{constant} - P \log h \quad (10)$$

Fig. 2 gives a plot of $\log (BZ)$ versus $(-\log h)$, for various B values. In their upper parts all curves approximate to straight lines. The slopes were 3.88, 3.81, 3.85, 3.89, and 3.81, which corresponds to a complex with $P = 4$. From the position of each curve, for instance from an intercept with $\log (BZ) = -3.0$, we obtained K_4 using equation (10). Assuming that there is one predominating complex (4, Q) we plotted $(\log K_4 - Q \log B)$ versus B for various values for Q . A horizontal line was obtained only with $Q = 4$ (Fig. 3), and we find

$$\log K_4 - 4 \log B = \log \beta_{44} = -27.35 \pm 0.07 \quad (10a)$$

Thus, (4,4) would be the predominating complex.

The deviations in the lower part of the curves in Fig. 2 may either be due to small analytical errors — this part is very sensitive to small errors in Z — or to some additional complex being present.

(2) We may transform (9) in another way; assuming only one complex (P, Q)

$$\log h = P^{-1} (\log \beta_{PQ} + \log P - \log Z) + P^{-1} (Q - 1) \log B \quad (11)$$

If $\log h$ is plotted versus $\log B$ for a constant value for Z , one should thus obtain a straight line of slope $(Q - 1)P^{-1}$. Fig. 4 shows such a plot for $Z =$ from

Fig. 3. Diagram, $(\log K_4 - Q \log B)$ versus B for $Q = 3, 4,$ and 5 . Only for $Q = 4$, a constant value is obtained. Straight line: $\log K_4 - 4 \log B = \log \beta_{44} = -27.35 (\pm 0.07)$.

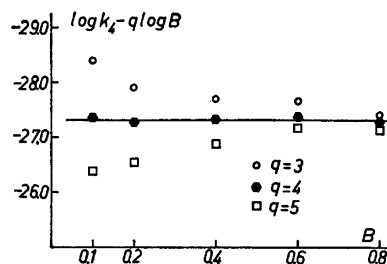
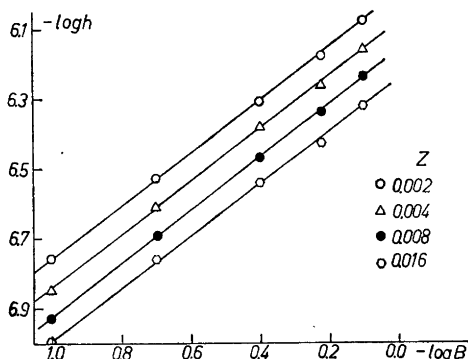


Fig. 4. Diagram $-\log h (-\log B)_z$, $Z = 0.002$ through 0.016 . Straight lines of slope 0.75, calculated with $\log \beta_{44} \approx -27.39$.



0.002 to 0.016. The slope comes out as 0.75 ± 0.01 which means that $Q = 4$ if $P = 4$. Using eqn. (11) we found $\log \beta_{44} = -27.39$.

(3) The curves $Z(\log h)_B$ were also compared with normalized curves $Z(\log u)$ calculated without the approximation $b \approx B$. If only one complex is formed, we have

$$B = b + Qc_{PQ}; BZ = Pc_{PQ}; c_{PQ} = \beta_{PQ}h^{-P}b^Q \quad (12)$$

We may eliminate $b = B(1-QP^{-1}Z)$ and then find, introducing the auxiliary variable u

$$u^{-P} = Z(1-ZQP^{-1})^{-Q} \quad (15)$$

$$u^{-P} = h^{-P}P\beta_{PQ}B^{Q-1} \quad (15a)$$

$$\log u = \log h - P^{-1} \log (P\beta_{PQ}B^{Q-1}) \quad (16)$$

For various combinations (P, Q) we calculated the plot $Z(\log u)$ by using (15). A reasonable agreement was found with the curve $Z(\log h)_B$ only for $P = 4$, and a good agreement with $P = 4$ and $Q = 4$. As earlier there were deviations in the lower part of the curves which might either be ascribed to analytical errors (shifts along the Z axis), or to some other complex being present.

From the upper part of the curves, we may derive $\log \beta_{44} = -27.35 \pm 0.05$.

Minor complexes. The previous calculations have indicated that the main complex is $\text{Ni}_4(\text{OH})_4^{4+}$, and that there are deviations at small values for Z which may be due either to other complexes with lower values for p and q or to small analytical errors, or both. To start with the first explanation we have assumed that, besides complexes with $P = 4$, there are also some with $p = p'$, and that there is only one value for p' . From (8) we then find

$$BZ = p'h^{-p'} K_{p'} + 4h^{-4} K_4 \quad (17)$$

or

$$BZh^{p'} = p'K_{p'} + 4K_4h^{p'-4} \quad (17a)$$

Plotting experimental data $BZh^{p'}$ versus $h^{p'-4}$ straight lines were found with $p' = 1$ but not with higher p' . Figs. 5a and 5b give an example, for $B = 0.2$ M. The calculated homoligandic constants K_1 are given in Table 3. The

Table 3. Homoligandic constant, K_1 for $B = 0.1$ through 0.8 M. 1) Calculated from straight line in graph like Fig. 5a, using eqn. (17a). 2) From experimental data, using normalized curves (18, 19).

| B | 1) $\log K_1$ from linear graph | 2) $\log K_1$ from normalized curves |
|-----|---------------------------------|--------------------------------------|
| 0.1 | 11.00 | 11.01 |
| 0.2 | 10.40 | 10.53 |
| 0.4 | 10.22 | 10.31 |
| 0.6 | 9.92 | 9.80 |
| 0.8 | 9.70 | 9.67 |

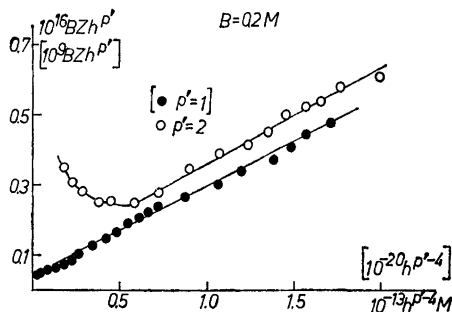


Fig. 5. Plot of $BZh^{p'}$ versus $h^{(p'-4)}$, for $p' = 1$ and $p' = 2$. A straight line is obtained only for $p' = 1$.

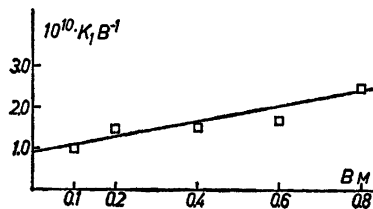


Fig. 6. Plot of $K_1 B^{-1}$ versus B . Straight line drawn assuming $\beta_{11} = 0.9 \times 10^{-10}$, $\beta_{12} = 1.9 \times 10^{-10}$.

values for K_4 are not given; they coincide within the experimental errors with the values earlier obtained from eqn. (10a).

K_1 could also be determined by means of normalized functions.² With $p' = 1$ we may write (17) in the form

$$\log (BZh^4) = \log (4K_4) + \log (1 + (K_1/4K_4)h^3) \tag{18}$$

which may be normalized as follows

$$y = \log (1 + x^3) \tag{19}$$

The data $[\log (BZh^4)] (\log h)_B$ were compared with the normalized curve $y(\log x)$ from (19) and the K_1 so obtained are also given in Table 3.

In Fig. 6, $K_1 B^{-1}$ is plotted versus B . In such a diagram, according to (8a)

$$K_1 B^{-1} = \beta_{11} + \beta_{12} B + \beta_{13} B^2 + \dots \tag{8b}$$

The straight line in the diagram would correspond to $\beta_{11} = 0.9 \times 10^{-10}$, $\beta_{12} = 1.9 \times 10^{-10}$. However, this procedure is uncertain: the fit with a straight line is not too good and small analytical errors may have a large influence. The analytical errors might have been introduced as a vertical shift in normalized curves $Z(\log h)$; instead we estimated them by means of LETAGROP, as will be described.

Treatment by LETAGROP. The graphical treatment thus indicated strongly that (4,4) is the main complex. At the lowest values for Z there were small deviations which might be due to the presence of some minor species, if so, probably (1,2) or (1,1). However, small systematic errors in Z might also cause deviations in the same range; this possibility must be considered in the final refinement, as well as certain other complexes such as (2,2), (2,1), and (3,3).

The experimental data were now treated by means of a recent edition of LETAGROP,³⁻⁵ a computer program designed to find the minimum for a function of a number of unknown constants, k_1, k_2, \dots . In the present case we tried to find the equilibrium constants, and systematic errors δZ that minimized the error square sum:

$$U = \Sigma (Z_{\text{exp}} - Z_{\text{calc}})^2 \tag{20}$$

Thus, no weighing of the points was made. On the other hand, what corresponds to weighing is made by the distribution of the experimental points over the various ranges of B and $\log h$. The idea that the random spread in Z is approximately equal for all points, seems reasonable in view of the experimental arrangement.

We obtained Z_{calc} as follows. B and h being known for each point, b can be eliminated from the equations

$$B = b + \Sigma \beta_{pq} h^{-pb^q}; \quad BZ = \Sigma p \beta_{pq} h^{-pb^q} \quad (6,7)$$

which gives a value for Z . In addition we assumed that in each series ("titration") there is a constant error, δZ , which may be due to, for instance, the presence of carbonate or to small errors in the determination of H for the first solution. Adding δZ we get

$$Z_{\text{calc}} = Z \text{ (from eqns. 6 and 7) } + \delta Z \quad (21)$$

It was decided that these systematic errors δZ should be treated as unknown constants.

The β_{pq} then correspond to the "common constants" (k) and δZ is a "group constant" (ks) is the LETAGROP program as described in Refs.⁴⁻⁵ By the way, the detailed program given in Ref. 5 is designed exactly for this type of problem ("the Z problem").

The program, which includes the operation MIKO, operates as follows. If one assumes a certain set of complexes, the computer finds the "best" values for the constants, which means the values that give the lowest value for U that is possible with the added condition that no equilibrium constant may be negative; if the first minimum found would imply a negative value for a certain equilibrium constant, this constant is set as zero, and a new minimum is calculated using only the other constants. If necessary this operation may be repeated. The computer also finds the standard deviations for the constants.

Nickel hydrolysis was used as a testing case in the development of the new program with MIKO since there were relatively few complexes so that one could easily add a number of "impossible" ones without needing excessive computer time. Exactly for this reason, the progress of the calculations cannot be shown as a short logical sequence, as can be done for systems treated now that the program has been made to work reliably.

The results are summarized in Table 4. The deviations given in this table are σ , the standard deviation calculated by LETAGROP, whereas in the final results we give 3σ . If β or δZ values are given without error limits, they were not varied in the "shot" considered.

Table 4 is divided into a number of sections. Each section shows how a certain combination of complexes was treated by the computer. The first line is the starting value, and usually there is just one "shot" between two lines, sometimes several. More combinations were tried than those shown here, and the order really followed was not always the one given in the table.

For each combination of complexes we have usually tried both to assume the systematic errors, $ks = \delta Z$, to be = 0, and to let them be variable parameters to be determined.

Table 4a shows an attempt to fit assuming only one complex (4,4). Table 4b and 4c are combinations of (1,1) + (4,4) with (2,1) or (2,2): the two first complexes remain but the latter two are thrown out by MIKO since their equilibrium constants come out negative at the minimum. Table 4d shows an attempt to refine the k_s assuming only (1,1) and (4,4).

In Tables 4e, 4f and 4g, the combination (4,4) + (1,2) is seen to strike out (1,1), (3,3), (2,1) and (3,2).

Table 4h and 4i finally show attempts to refine the constants for the combination (1,2) + (4,4).

The last line of Table 4i gives the results of a continued calculation, varying the β_{12} , β_{44} and δZ simultaneously. It gave the same β_{44} and a still lower value for $\log \beta_{12}$.

Let us first note that the values for $k_s = \delta Z$ obtained by LETAGROP are of the order of 0.0001 to 0.0006, which is not unreasonable; it means at any rate that the analytical accuracy was fairly good.

If we start by assuming only the (4,4) species and no analytical errors (Table 4a) the error square sum comes out as $U = 0.367 \times 10^{-4}$. Adding the complex (1,2) but assuming all the $\delta Z = 0$ (Table 4h) brings U down to $U = 0.340 \times 10^{-4}$, whereas adjusting the δZ (but not adding a new complex,

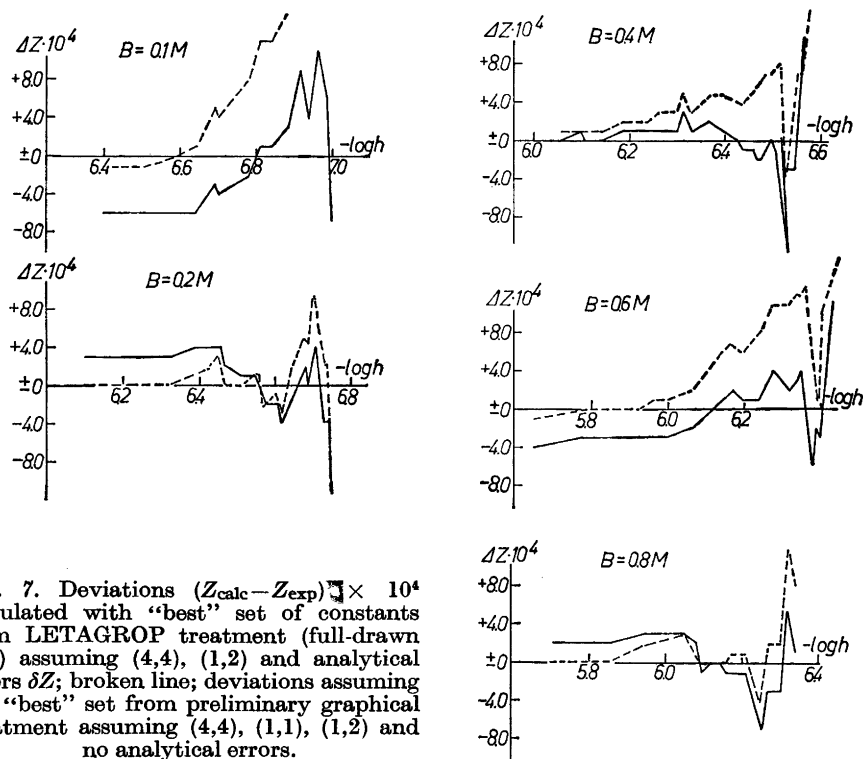


Fig. 7. Deviations $(Z_{\text{calc}} - Z_{\text{exp}}) \times 10^4$ calculated with "best" set of constants from LETAGROP treatment (full-drawn line) assuming (4,4), (1,2) and analytical errors δZ ; broken line; deviations assuming the "best" set from preliminary graphical treatment assuming (4,4), (1,1), (1,2) and no analytical errors.

Table 4. Results of LETAGROP treatment.
4,4 - 4,4

| | $10^3 k_{s1}$ | $10^3 k_{s2}$ | $10^3 k_{s3}$ | $10^3 k_{s4}$ | $10^3 k_{s5}$ | $10^4 U$ | $10^{27} \beta_{44}$ | |
|----|--|--------------------------------------|--------------------------------------|--|--------------------------------------|---------------------------------------|--|--|
| 4a | 0 { -0.41 ± 0.10 } » | 0 { 0.61 ± 0.10 } » | 0 { 0.19 ± 0.07 } » | 0 { -0.18 ± 0.07 } » | 0 { 0.35 ± 0.06 } » | 0.369 0.367 » | 0.428 0.431 ± 0.003 » | |
| 4b | 0 { -0.25 ± 0.13 } » | 0 { 0.55 ± 0.10 } » | 0 { 0.13 ± 0.07 } » | 0 { -0.23 ± 0.08 } » | 0 { 0.30 ± 0.06 } » | 4.810 0.367 0.367 0.366 » | 0.447 0.428 ± 0.005 0.429 ± 0.005 » | $10^{16} \beta_{21}$ 0.12 0 » $10^9 \beta_{11}$ 0.30 0.10 0.11 ± 0.02 0.11 ± 0.02 » |
| 4c | 0 { -0.25 ± 0.13 } » | 0 { 0.55 ± 0.10 } » | 0 { 0.13 ± 0.07 } » | 0 { -0.23 ± 0.08 } » | 0 { 0.30 ± 0.06 } » | 0.236 » | 0.426 ± 0.004 » | $10^{15} \beta_{22}$ 0 » $10^9 \beta_{11}$ 0.30 0.01 ± 0.02 0.01 ± 0.02 » |
| 4d | -0.25 » { -0.20 ± 0.13 } » | 0.55 » { 0.57 ± 0.10 } » | 0.13 » { 0.17 ± 0.07 } » | -0.23 » { -0.20 ± 0.08 } » | 0.30 » { 0.33 ± 0.06 } » | 0.240 0.236 » | 0.429 0.426 ± 0.004 » | $10^{15} \beta_{22}$ 0.12 0 » $10^{10} \beta_{11}$ 0.15 0.09 ± 0.17 » |
| | | | | | | 0.236 » | 0.426 ± 0.004 » | $10^{15} \beta_{22}$ 0 » $10^9 \beta_{11}$ 0.01 ± 0.02 0.01 ± 0.02 » |

Table 4a) makes $U = 0.231 \times 10^{-4}$. By using both β_{12} and δZ one finally obtains $U = 0.227 \times 10^{-4}$. (End of Table 4i). Obviously, by far the greatest improvement was that from introducing the δZ .

The conclusion we may draw from these calculations is that in all likelihood the main product is the (4,4) complex $\text{Ni}_4(\text{OH})_4^{4+}$ and that the deviations observed are to a large part due to small analytical errors. We find for β_{44} (3σ limits):

$$\beta_{44} = (0.423 \pm 0.015) \times 10^{-27}, \log \beta_{44} = -27.37 \pm 0.02 \quad (22)$$

If another complex is of importance, our data would suggest the (1,2) complex, $\text{Ni}_2\text{OH}^{3+}$, with (3σ limits)

$$\log \beta_{12} \approx -10 (\leq -9.5) \quad (23)$$

Obviously, the support for the (1,2) species is not very strong. Still smaller is, however, the support for the other minor species suggested (here again we give 3σ as limits):

$$\begin{aligned} \beta_{11} &= (-0.12 \pm 0.55) \times 10^{-10}; \beta_{33} = (-0.21 \pm 0.84) \times 10^{-22}; \\ \beta_{23} &= (-0.31 \pm 0.15) \times 10^{-16}; \beta_{32} = (-0.26 \pm 2.24) \times 10^{-24} \text{ etc.} \end{aligned} \quad (24)$$

From such results one may estimate maximum values (at various levels of confidence) for the formation constants, but really the data give no support whatsoever for their existence. This does not mean that they may not exist, within the limits given, and evidence for them could perhaps be found by other methods, or by increasing the experimental accuracy and extending the range of concentrations.

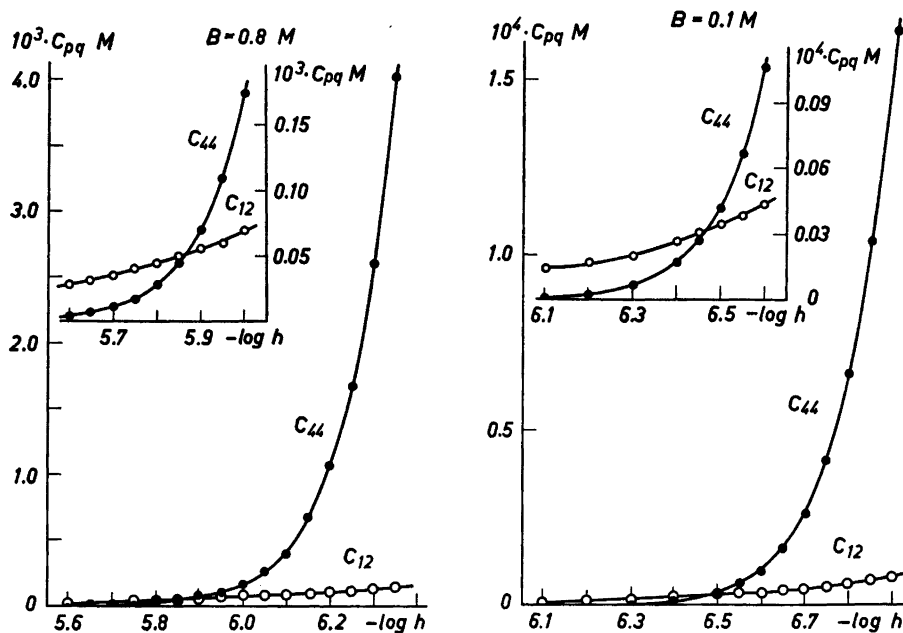


Fig. 8. Concentrations of (4,4) and (1,2) species for total Ni concentrations a) $B = 0.8$ and b) 0.1 M Ni^{2+} , assuming $\log \beta_{44} = -27.37$, $\log \beta_{12} = -9.96$.

In Table 2, the last figure for each experimental point gives the value for $10^4 (Z_{\text{calc}} - Z_{\text{exp}})$, obtained using the values for β_{44} , β_{12} , and δZ obtained in next to the last line of Table 4i. The errors are also visualized in Fig. 7. The full-drawn line gives the deviations in the Z calculated with the "best" values, and the broken line gives the deviations obtained assuming a combination of β_{11} , β_{12} , and β_{44} and with no analytical errors ("best result" from the preliminary graphical treatment). As seen already from the table, the error square sum is considerably larger for the latter mechanism (broken lines).

Fig. 8 gives the concentrations of the (1,2) and (4,4) species assuming $\log \beta_{44} = -27.37$, and $\log \beta_{12} = -9.96$. It seems that the (1,2) species would be of importance only at the lowest degrees of hydrolysis; as mentioned, the exact value for the β_{12} is uncertain.

In Fig. 1, the full-drawn curves are also calculated assuming the same set of constants and δZ values. However, the deviations are so small that they are best seen in Table 2.

The present results may indicate the importance of not forgetting the unavoidable small analytical errors, which may have practically the same effect as an additional minor species. It is desirable, whenever possible, that the analytical errors are also treated as unknown constants to be determined. If this had not been done here, misleading conclusions would have resulted.

We wish to thank Professor S. A. Ščukarev, LGU, for the interest he has shown in this work, and Dr. Georg Biedermann for valuable discussions. Dr. Phyllis Brauner kindly corrected the English of the manuscript.

We would also like to thank many of our other friends in Stockholm, especially Drs. Nils Ingri and Hitoshi Ohtaki for a pleasant cooperation and much practical aid in the computer work in Stockholm. Statskontoret (Dataavdelningen) has given us free computing time at the computers Besk and Facit in Stockholm and Univac (in Oslo).

REFERENCES

1. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **13** (1959) 533.
2. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 186.
3. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159; Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 173.
4. Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1085.
5. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
6. Denham, H. G. *J. Chem. Soc.* **93** (1908) 41.
7. Kullgren, C. *Z. physik. Chem.* **85** (1913) 466.
8. Löfman, N. *Z. anorg. Chem.* **107** (1919) 241.
9. Jellinek, K. *Lehrbuch der physikalischen Chemie*, 2nd Ed. Stuttgart 1933, IV, p. 62.
10. Gayer, K. H. and Woontner, L. *J. Am. Chem. Soc.* **74** (1952) 1436.
11. Chaberek, S., Jr., Courtney, R. C. and Martell, A. E. *J. Am. Chem. Soc.* **74** (1952) 5057.
12. Ksandr, Z. and Hejtmánek, M. *Sborník I. Celostátní Pracovní Konf. anal. Chemiků* (1952) 42; *Chem. Abstr.* (1956) 3150.
13. Schwab, G. M. and Polydoropoulos, K. *Z. anorg. Chem.* **274** (1953) 234.
14. Čůta, F., Ksandr, Z. and Hejtmánek, M. *Chem. Listy.* **50** (1956) 1064; *Collection Czech. Chem. Commun.* **21** (1956) 1388.
15. Achenza, F. *Ann. Chim.* (Rome) **49** (1959) 624, 848.
16. Vepřek-Šiška, J. *Collection Czech. Chem. Commun.* **20** (1955) 1018.
17. Biedermann, G. and Ciavatta L. *Acta Chem. Scand.* **15** (1961) 1347.

18. Tredvell, F. and Goll, V. (Treadwell and Hall). *Kurs analitičeskoj chimii*, t II ONTI 1935.
19. Pršibil, R. (Přibil), *Kompleksny v chimičeskom analize*, I I L, Moskva 1960.
20. Samuelson, O. *Primenenie ionnogo obmena v analitičeskoj chimii*, I I L, M 1955.
21. Olin, Å. *Acta Chem. Scand.* **14** (1960) 126.
22. Gran, G. *Analyst* **77** (1952) 661.
23. Kol'tgof (Kolthoff), I. M. and Stenger, V. A. *Obemnyi analiz t II*, Goschimizdat 1952.
24. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 901.
25. *Stability constants. (Inorganic ligands)* First edition; Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Chem. Soc. Spec. Publ. No. 7* (1958); Second edition, Sillén, L. G. and Martell, A. E. *Chem. Soc. Spec. Publ. No. 17* (1964).
26. Nikol'skii, B. P. (Ed.) *Sbornik praktičeskich rabot po fizičeskoj chimii*, v. 1. I L U 1956.
27. Biedermann, G. and Ciavatta, L. *Acta Chem. Scand.* **16** (1962) 2221.
28. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.

Received September 3, 1964.