Precipitation and Hydrolysis of Metallic Ions

II. Studies on the Solubility of Zirconium Hydroxide in Dilute Solutions and in 1 M NaClO₄

HALKA BILINSKI, MARKO BRANICA and LARS GUNNAR SILLÉN*

*Department of physical chemistry, Institute "Ruder Bošković", Zagreb, Yugoslavia,
Department of inorganic chemistry, Royal Institute of Technology, (KTH),
Stockholm 70, Sweden*

The variation of the solubility of zirconium hydroxide with pH was studied in dilute solution at 20°C and 40°C, and in 1 M NaClO₄ at 20°C, using a tyndallometric method. The results are compared with the scanty and widely diverging literature data. The data could be fitted to a power series which indicated that complexes of charges 0, + 1 and + 4 predominate (in 1 M NaClO₄). For dilute solutions, better agreement was obtained with equations with non-integral powers of h.

The literature contains only few data on the solubility of zirconium hydroxide, and they diverge widely (see Fig. 1 and discussion below). Since too little is known about the species in the solution, measurements at one pH or in a narrow pH range do not suffice to predict the behavior at other pH's. The present investigation was undertaken to study the variation of solubility with pH in as wide a range as possible.

GENERAL EQUATIONS

Let us suppose that zirconium hydroxide is at equilibrium with a number of hydroxido complexes, of the general formula $Zr_q(OH)_{4q-p}{}^{p+}$; they may really contain some water molecules, but this does not change the equilibrium conditions.

The equilibrium condition is then for each species

$$q\,Zr(OH)_4(s) + pH^+ \rightleftharpoons Zr_q(OH)_{4q-p}{}^{p+} + pH_2O \tag{1}$$

$$c_{pq} = [Zr_q(OH)_{4q-p}{}^{p+}] = K_{pq}h^p \tag{2}$$

* The experimental work was carried out in Zagreb, by H.B. and M.B., the computer work in Stockholm by H.B. and L.G.S.

We will write $[H^+] = h$. The total concentration of zirconium is then the sum of the contributions from all these species

$$[Zr]_{\text{total}} = B = \sum_p \sum_q qc_{pq} = \sum_p K_p h^p \tag{3}$$

We have written, for simplicity

$$K_p = \sum_q qK_{pq} \tag{4}$$

So, the coefficient K_p for h^p in the expression for the zirconium solubility contains contributions from all species with the charge $p+$; note that Zr^{4+}, if it exist in appreciable amounts, is treated here as the (4,1) species.

From measurements of B as a function of h we may deduce those p values for which K_p is significantly different from zero and the corresponding coefficients K_p. So, we can derive the values for the total charge of the complex, but not the values for q involved unless we have very accurate measurements of the amount of H^+ consumed; such measurements would have given us $\sum_q K_{pq}$, which might give us together with $\sum_q qK_{pq}$ at least an estimate of the q values connected with each p value.

Hence, from solubility data alone one cannot distinguish between complexes with the same charge. The literature contains many mistakes on this point — where a species was considered as proved because it could explain the data, and it was overlooked that the explanation was not unique.

For the case considered: pure hydroxide precipitate, pure hydroxido complexes, one would then expect $B(h)$ to be a power series with integral powers of h. Non-integer coefficients are, however, also possible, especially if the precipitate is not a pure hydroxide but contains a certain fraction of some anion X^-. The equilibrium will then be:

$$qZr(OH)_{4-x}X_x(s) + (p-qx)H^+ = Zr_q(OH)_{4q-p}^{p+} + qxX^- + (p-qx)H_2O$$
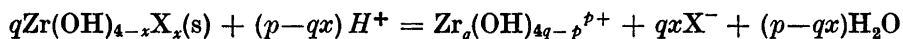
The equilibrium condition will then contain h in the power $(p-qx)$, and also $[X^-]^{qx}$, and different cases arise depending on whether $[X^-]$ is kept reasonably constant or not. As a minor complication, X^- may also enter the complexes.

EARLIER WORK ON Zr(OH)$_4$ SOLUBILITY

In Fig. 1, our own data and earlier published values are plotted for comparison, giving log B as a function of log h (or pH). The authors concerned have often given a value for the solubility product of $Zr(OH)_4$, assuming Zr^{4+} to be the only zirconium species to consider. Since this assumption is not too certain, we may put more weight on the experimental data for log B (log h).

Oka in 1938 [1] studied the precipitation of zirconium hydroxide from nitrate solution at 25°C using a glass-electrode. From a single point he deduced log $K_{s0} = -48.2$.

Britton in his book *Hydrogen ions*,[2] mentions that 0.01 M ZrCl$_4$, when alkali is added, becomes opalescent at pH = 1.86 (18°C). From this single figure, Korenman [3] in 1955 calculated log $K_{s0} = -51.1$. Starik *et al.*[4] in 1957, from radiometric measurements, claimed a very low solubility, $\approx 10^{-11}$ M,
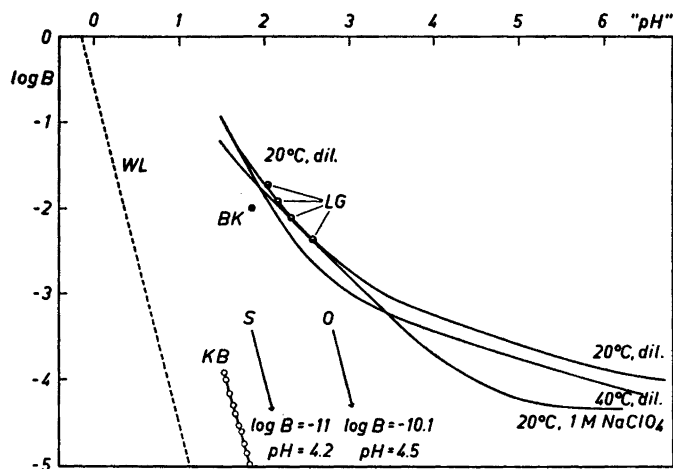
Fig. 1. Solubility B of zirconium hydroxide as a function of "pH". "Best-fit" curves from this paper for 1 M $NaClO_4$ medium at 20°C (Fig. 3), for dilute solutions at 20°C (Fig. 4) and 40°C (Fig. 5) are compared with earlier measurements. LG = Larsen and Gammil,[6] BK = Britton,[2] used by Korenman,[3] KB = Kovalenko and Bagdasarov.[5] The broken line (WL) corresponds to Latimer's [7] estimated solubility product. The single points of Oka [1] (O) and Starik [4] (S) are indicated by arrows since they fall outside the diagram.

at pH ≈ 4.2, which gives log $K_{s0} = -52$. Kovalenko and Bagdasarov [5] in 1961 measured the concentration of zirconium in saturated solutions by photocolorimetry. They estimated log $K_{s0} = -53.96$. Larsen and Gammil [6] in 1950 deduced $K_{s2} = [Zr(OH)_2^{2+}][OH^-]^2 = 10^{-25.5}$, from pH and turbidity measurements.

Latimer [7] estimated the solubility product from calorimetric data and estimated entropies of ions and solids. His value is considerably lower than the others, log $K_{s0} = -57.2$.

Obviously, the data do not fall on a single curve. We shall discuss this more together with our own measurements.

HYDROLYZED SPECIES IN Zr SOLUTIONS

Those who have published work on Zr^{4+} hydrolysis seem to agree that hydroxido complexes are formed, and that these are in general polynuclear. Evidence for a complex $Zr_4(OH)_8(H_2O)_{16}^{8+}$ has been found in crystal structure studies by Clearfield and Vaughan [8] but many formulas have been suggested for the dissolved species. A brief survey of the work is given in Table 2 of the *Tables of Stability Constants.*[9] For q, values 1, 2, 3, 4, 6, and 8 have been suggested, and for the charges, 2+, 3+, 4+, 5+, 6+, and 8+ are suggested by different authors.

EXPERIMENTAL

Reagents. Zirconium hydroxide chloride, $ZrOCl_2(H_2O)_8$, Merck *pro analysi*, was used to make a stock solution, the concentration of which was measured gravimetrically by adding excess NH_3, igniting the precipitate and weighing as ZrO_2.

Potassium hydroxide, Merck *pro analysi*, was used to make a stock solution which was analyzed by titration against HCl which had in its turn been standardized against $Na_2CO_3(s)$.

Sodium perchlorate, *pro analysi*, was made up to a concentrated solution.

Redistilled water was used.

Procedure. The samples were made up in glass tubes by mixing 5 ml of diluted zirconium chloride solution and 5 ml of diluted potassium hydroxide solution. In those cases where 1 M $NaClO_4$ medium was used, the zirconium solution had been made to contain 2 M $NaClO_4$.

Glass tubes were kept in a thermostat bath at 20°C, or 40°C, $\pm$ 0.1°.

24 h after mixing, the "pH" of the solution was measured with a glass electrode against calomel, using a radiometer PHM-4. pH was calibrated against two buffer solutions, of pH 4.01 and 6.99, which were prepared by dissolving buffer solution tablets ('SOLOID' brand N.B.S. Formula, Burroughs Wellcome & Co, England) in 100 ml of distilled water.

The turbidity of the solutions was measured as described earlier [10] using a Zeiss tyndallometer, in connection with a Pulfrich photometer. A green filter at 530 nm was used. The turbidity could be measured at various times. Fig. 2 shows some typical tyndallometric curves for a total concentration of 1.0 mM Zr in the solution: the turbidity at different times (1 min, 10 min, 20 min, 60 min, and 24 h) is plotted as a function of the concentration of potassium hydroxide.

We chose to use the values for 24 h, since our earlier experience with thorium [11] indicated that this time might suffice for equilibration.

In each series of experiments, the total concentration of zirconium was kept constant, and the ratio of added OH/Zr was varied until one could locate within $0.1-0.2$ pH
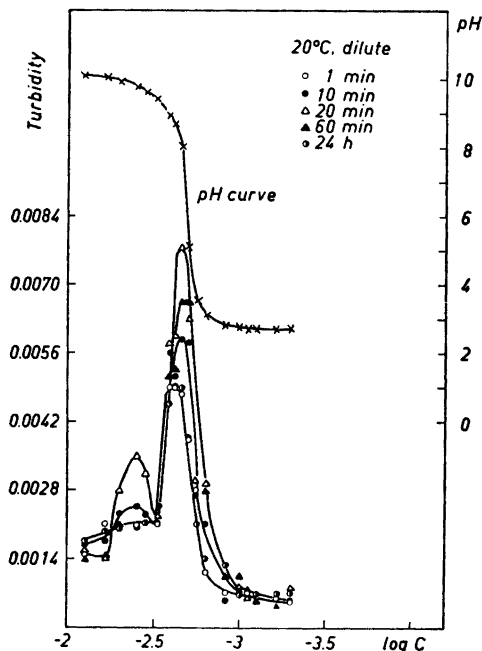

Fig. 2. Typical tyndallometric curve: Equal volumes of 0.002 M $ZrOCl_2$ and 2 *C* M KOH were mixed and the turbidity measured 1, 10, 20, 60 min, and 24 h after mixing.

units pH_{min} and pH_{max} defined as follows: the pH_{min} is the lowest pH at which one could still observe, after 24 h, some turbidity or precipitate, and pH_{max} is the highest pH at which only a clear solution was observed after this time. It may be asked what amount of precipitated zirconium could still escape detection by the tyndallometric method. This is not easy to say since the visibility depends on both concentration and particle size, but we would guess around 10^{-5} M Zr.

Table 1. Precipitation of Zr hydroxide. Data given in order B (total Zr concentration), pH_{min}, pH_{max}.

20°C, 1 M NaClO₄:
3×10^{-5}, 6.22, 6.19; 4×10^{-5}, 5.88, 5.82; 5×10^{-5}, 5.50, 5.32; 6×10^{-5}, 5.50, 5.31; 8×10^{-5}, 4.80, 4.62; 1×10^{-4}, 4.50, 4.32; 1.2×10^{-4}, 4.42, 4.30; 2×10^{-4}, 4.31, 4.11; 2.5×10^{-4}, 4.31, 4.09; 3×10^{-4}, 3.90, 3.70; 5×10^{-4}, 3.61, 3.51; 1×10^{-3}, 3.21, 3.09; 2×10^{-3}, 2.89, 2.82; 3×10^{-3}, 2.69, 2.60; 6×10^{-3}, 2.41, 2.39; 1×10^{-2}, 2.20, 2.15; 1.2×10^{-2}, 2.12, 2.08; 2×10^{-2}, 1.80, 1.75; 3×10^{-2}, 1.72, 1.68; 4×10^{-2}, 1.70, 1.63; 5×10^{-2}, 1.63, 1.48; 6×10^{-2}, 1.57, 1.48;

20°C, dilute:
8×10^{-5}, 7.82, 7.58; 1×10^{-4}, 6.720, 6.51; 1.2×10^{-4}, 6.31, 6.02; 2×10^{-4}, 5.58, 5.31; 4×10^{-4}, 4.101, 3.99; 6×10^{-4}, 3.92, 3.87; 1×10^{-3}, 3.520, 3.430; 1.2×10^{-3}, 3.281, 3.172; 1.6×10^{-3}, 2.980, 2.920; 2.5×10^{-3}, 3.01, 2.920; 3×10^{-3}, 2.781, 2.70; 5×10^{-3}, 2.575, 2.440; 6×10^{-3}, 2.59, 2.54; 8×10^{-3}, 2.338, 2.190; 1×10^{-2}, 2.285, 2.230; 1.2×10^{-2}, 2.180, 2.089; 1.6×10^{-2}, 2.130, 2.070; 2×10^{-2}, 1.951, 1.890; 2.5×10^{-2}, 1.982, 1.878; 3×10^{-2}, 1.830, 1.784; 4×10^{-2}, 1.841, 1.742; 5×10^{-2}, 1.700, 1.630;

40°C, dilute:
6×10^{-5}, 6.68, 6.56; 1×10^{-4}, 5.80, 5.72; 1.2×10^{-4}, 5.54, 5.39; 1.6×10^{-4}, 5.22, 5.07; 2×10^{-4}, 4.93, 4.76; 2.5×10^{-4}, 4.39, 4.22; 3×10^{-4}, 4.06, 3.86; 4×10^{-4}, 3.78; 3.69; 5×10^{-4}, 3.65, 3.55; 6×10^{-4}, 3.44, 3.34; 8×10^{-4}, 3.32, 3.20; 1×10^{-3}, 3.25, 3.12; 1.2×10^{-3}, 3.00, 2.92; 1.6×10^{-3}, 2.68, 2.62; 2.5×10^{-3}, 2.58, 2.50; 4×10^{-3}, 2.39, 2.28; 6×10^{-3}, 2.20, 2.13; 8×10^{-3}, 2.12, 2.05; 1×10^{-2}, 2.120, 2.06; 1.2×10^{-2}, 2.10, 2.08; 1.6×10^{-2}, 1.98, 1.92; 2×10^{-2}, 1.98, 1.94; 3×10^{-2}, 1.82, 1.80; 4×10^{-2}, 1.80, 1.72; 5×10^{-2}, 1.68, 1.62; 6×10^{-2}, 1.71, 1.571; 1×10^{-1}, 1.62, 1.48;

TREATMENT OF DATA

The data are given in a condensed form in Table 1, in the order: B, pH_{min} pH_{max}; B, pH_{min} pH_{max} etc. The data for dilute solutions at 20°C and 40°C, and for 1 M NaClO₄ medium at 20°C are plotted in Figs. 2—4 together with calculated curves to be described presently.

The basis was eqn. (3), $B = \sum_p K_p h^p$. In an earlier work, by some of the authors,[11] we considered only one predominant species at the time, using the rectilinear parts of the curve log B(pH). This time we have considered that several species can be present in the same solution and adjusted the K_p in eqn. (3) using the generalized least-squares program Letagrop.[12,13]

The special block UBBE of Letagrop was modified so that the function to be minimized was the error square sum

$$U = \sum (\log B_{calc} - \log B)^2 \qquad (5)$$

When we tried power series with integer p values, it was found that the combination of terms with h^0, h^1, and h^4 gave the best agreement. For h^2 and h^3, the coefficients were found to be negative or not significantly different

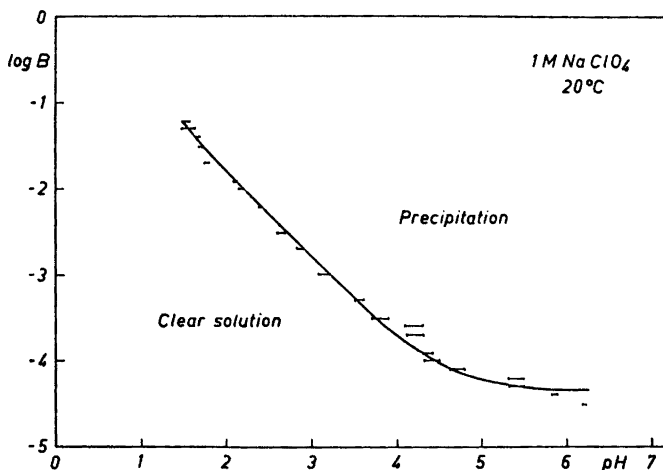*Fig. 3.* Precipitation of $Zr(OH)_4$ at 20°C; pH range *versus* concentration of $ZrOCl_2$; 24 h after mixing, 1 M $NaClO_4$ medium. The solubility curve is calculated from eqn. (6).

from zero. For 1 M $NaClO_4$ medium at 20°C, the following was the "best" equation:

$$[Zr]_{total} = (0.437 \pm 0.055) \times 10^{-4} + (1.58 \pm 0.12)h + (0.63 \pm 1.16) \times 10^4 h^4 \quad (6)$$

These values gave the fit shown in Fig. 3 and $\sigma(\log B) = 0.148$. The deviations given in (6) are $3\sigma(K_p)$. Similarly for dilute solution at 20°C the best fit with an integer power series was found with:
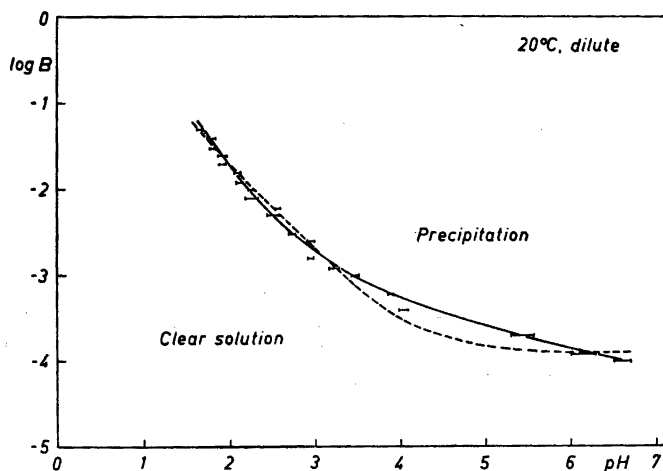

Fig. 4. Precipitation of $Zr(OH)_4$ at 20°C and varying ionic strength, pH range *versus* Zr concentration. The "best fit" curves are indicated by the broken line for eqn. (7) and by the full-drawn line for eqn. (8).

$$B = (1.25 \pm 0.17) \times 10^{-4} + (1.88 \pm 0.15)h + (3.6 \pm 5.4) \times 10^4 h^4 \qquad (7)$$

which gave $\sigma(\log B) = 0.167$.

For 40°C dilute solutions we found:

$$B = (1.23 \pm 0.18) \times 10^{-4} + (1.14 \pm 0.11)h + (11.2 \pm 3.7) \times 10^4 h^4 \qquad (8)$$

which gave $\sigma(\log B) = 0.199$.

The fits are indicated by the broken lines in Figs. 4 and 5. There are systematic deviations in the region with high h (and low B) values. One could get a better fit for dilute solutions by using, instead of $p = 0,1,4$, power series with
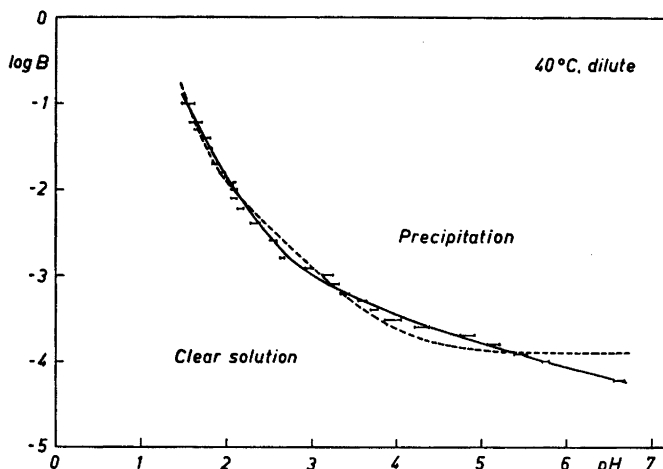

Fig. 5. Precipitation of $Zr(OH)_4$ at 40°C and varying ionic strength. The "best fit" curves are indicated by the broken line for eqn. (9) and by the full-drawn line for eqn. (10).

non-integer coefficients: 0.25 and 0.667 in addition to 1 and 2:

For 20°C

$$B = (4.56 \pm 0.55) \times 10^{-3} h^{0.25} + (1.02 \pm 0.16)h + (68 \pm 18)h^2 \qquad (9)$$

which gave $\sigma(\log B) = 0.123$.

For 40°C:

$$B = (25.9 \pm 3.2) \times 10^{-4} h^{0.25} + (3.7 \pm 3.3) \times 10^{-2} h^{0.667} + (0.9 \pm 3.0) \times 10^{-1} h + (103 \pm 16)h^2 \qquad (10)$$

which gave $\sigma(\log B) = 0.115$.

DISCUSSION

The tyndallometric method is a very suitable experimental method for the determination of a solubility curve in a very broad concentration region. As well as the application shown in this work, tyndallometric measurements can be used for examining the kinetics of precipitation and coagulation.[10,14]

In this way the critical concentrations which have great influence on the formation of the solid phase, and the charge of ions in solution in equilibrium with the solid phase can be determined.

The method itself and the necessary instruments are very simple. In relatively short time much information about the behavior of rather complicated systems can be obtained.

As seen from Fig. 1, the present values agree fairly well with those of Larsen and Gammil,[6] whereas those of Starik[4] and Kovalenko[5] are considerably lower than ours. We can offer no explanation for this fact but feel inclined to believe that the present values are somewhat closer to equilibrium. A possible error in the tyndallometric method is that at very low concentrations, on the order of 10^{-6} M, it is hard to detect a precipitate. This will tend to bend the curve toward a limiting value even if the real concentrations might be lower.

If this view is correct, one might be inclined to put little weight on the values at the lowest concentrations since a precipitate may be observed only at higher concentrations than the equilibrium one. One will then mainly consider the part where the slope $(= 1/p)$ ranges from 1 to $1/4$.

If we assume that the values obtained here correspond to something near to real equilibrium, then eqns. (6—8) can easily be explained by the presence of complexes of charges 0, $+ 1$, and $+ 4$. We must note that the $+ 4$ species need not necessarily be Zr^{4+}, even if it is not unlikely that this ion appears at high enough acidities and low enough total concentrations.

It is harder to explain the apparent non-integer coefficients, 0.25 (1/4) and 0.667 (2/3). The following are the possible explanations:

1. The equilibrium was never attained; one might expect that coagulation and precipitation are quicker in 1 M $NaClO_4$ solution than in the dilute solutions. However, one might also have expected quicker equilibrium at 40°C.

2. The composition of the precipitate was not $Zr(OH)_4(s)$ but it contained also other anions. This would give non-integer coefficients, but it seems surprising that no anions would then enter from 1 M $NaClO_4$.

Table 2. Apparent equilibrium constants; note that Zr species are not unique. Limits and maximum values refer to 3 σ.

	20°C 1 M $NaClO_4$ eqn. (6)	20°C dilute eqns. (7, 9)	40°C dilute eqns. (8, 10)
$K_w^{-1}(H^+ + OH^- \rightleftharpoons H_2O)$ assumed	13.94	14.16	13.53
$*K_{s0}(Zr(OH)_4(s) + 4H^+ \rightleftharpoons Zr^{4+} + 4H_2O)$	$\approx 3.8 (<4.3)$	$\approx 4.6 (<5.0)$ [a]	5.05 ± 0.18 [a]
$*K_{s2}(Zr(OH)_4(s) + 2H^+ \rightleftharpoons Zr(OH)_2^{2+} + 2H_2O)$	—	1.83 ± 0.13 [a]	2.01 ± 0.02 [b]
$*K_{s3}(Zr(OH)_4(s) + H^+ \rightleftharpoons Zr(OH)_3^+ + H_2O)$	0.20 ± 0.04	0.27 ± 0.03 [a]	0.06 ± 0.05 [a]
		0.01 ± 0.08 [b]	$\approx -1 (<-0.5)$ [b]
$K_{s4}(Zr(OH)_4(s) \rightleftharpoons Zr(OH)_4)$	-4.36 ± 0.05	-3.90 ± 0.07 [a]	-3.91 ± 0.07 [a]
$K_{s0}(Zr(OH)_4(s) \rightleftharpoons Zr^{4+} + 4OH^-)$	$\approx -52.0 (<-51.5)$ [a]	$-52.0 (<-51.6)$ [a]	-49.1 ± 0.2 [a]

[a] From eqns. (7, 8) with only integer powers of h.
[b] From eqns. (9, 10) with fractional coefficients.

3. Equilibrium was attained but the lowest B values have come out systematically too high (see above).

If we keept to the integer coefficients, we might explain the results formally by assuming the presence of $Zr(OH)_4^0$, $Zr(OH)_3^+$, Zr^{4+} in the solutions. It should be noted that the same results would, however, be obtained also with polynuclear complexes of the same charges. Assuming the mononuclear species we would obtain the equilibrium constants in Table 2.

One might compare these with K_{s0} values given by various authors. Since, however, these values were usually obtained from only one or few points, we think that the best comparison is made by means of the primary data in Fig. 1.

It should be added that the exact significance of our "pH" values is somewhat dubious especially in 1 M $NaClO_4$ since the liquid junction potential could not be corrected for. However, since $10^{-\text{"pH"}}$, is proportional to $[H^+] = h$, this uncertainty only corresponds to a parallel shift of the "pH" scale, and a constant factor in each equilibrium constant.

REFERENCES

1. Oka, J. *J. Chem. Soc. Japan* **59** (1938) 971.
2. Britton, H. T. S. *Hydrogen ions, e.g.* in 4th Ed., part 2, p. 77, Chapman & Hall, London 1956.
3. Korenman, I. M. *Zh. Obshch. Khim.* **25** (1955) 1859.
4. Starik, I. E., Ratner, A. P., Skul'skii, I. A. and Gavrilov, K. A. *Zh. Neorg. Khim.* **2** (1957) 1175.
5. Kovalenko, P. N. and Bagdasarov, K. N. *Zh. Neorg. Khim.* **6** (1961) 534.
6. Larsen, E. M. and Gammill, A. M. *J. Am. Chem. Soc.* **72** (1950) 3615.
7. Latimer, W. M. *The oxidation state of the elements and their potentials in aqueous solutions*, Prentice Hall, Englewood Cliffs, N. J. 1952.
8. Clearfield, A. and Vaughan, P. A. *Acta Cryst.* **9** (1956) 555.
9. *Stability constants of metal ion complexes* (Sillén, L. G. and Martell, A. E., compilers) *Chem. Soc. Spec. Publ.* **17** (1964).
10. Težak, B., Matijević, E. and Schulz, K. *J. Phys. Colloid Chem.* **1951** 1557.
11. Bilinski, H., Füredi, H., Branica, M. and Težak, B. *Croat. Chem. Acta* **35** (1963) 19 (= Part I).
12. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159.
13. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.
14. Težak, B. *et al. XX Intern. Congr. Pure Appl. Chem. Moscow 1965*, Paper A 81.