

Studies on the Hydrolysis of Metal Ions. 52. A Recalculation of emf Data on Beryllium Hydrolysis

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We shall write, as usual, β_{pq} for the equilibrium constant of $p \text{H}_2\text{O} + q \text{Be}^{2+} \rightleftharpoons \text{Be}_q(\text{OH})_p^{(2q-p)+} + p \text{H}^+$, and denote the complex by (p,q) .

All those who have made quantitative studies on the hydrolysis of the ion Be^{2+} agree that one of the main products is a polynuclear ion of composition $(\text{BeOH})_n^{n+}$ thus a (n,n) complex. However, several values for n have been proposed. Around 1930 Prytz,¹ who made a very good emf study for that time, assumed the (2,2) complex without discussing other possibilities. On the other hand, Souchay and coworkers from freezing-point and glass electrode data concluded that the (4,4) complex predominates. Kakihana and

Sillén,³ by an emf study in 3 M $(\text{Na})\text{ClO}_4$ medium at 25°C and total Be concentration B varying from 0.001 to 0.049 M, came to the conclusion that the main complex is (3,3), but that there are also appreciable amounts of (1,2) and (2,1). Carell and Olin⁴ studied beryllium hydrolysis in the same medium but with a higher range of total Be concentrations, $B = 0.040$ to 1.0 M; the experimental methods had been improved somewhat in the meantime. Their analysis of the data confirmed the two complexes (3,3) and (1,2), indicated by Kakihana and Sillén; in the range of high B , the (2,1) complex could not be expected to be important.

Earlier methods of equilibrium analysis usually had to be content with finding the two or three most important species, using, for instance, curve-fitting and projection maps. By means of LETAGROP — a generalized least-squares method — it is now possible to test and refine hypotheses involving a greater number of complexes. The work is speeded up in a recent version, LETAGROP VRID with MIKO,⁵ where the computer eliminates automatically complexes that would otherwise have got negative formation constants at the "best fit". We thought it would be interesting to check combinations of all the complexes

Table 1.

	Data 1	Data 2	Data 3
$10^7 \beta_{11} =$	(-2.4 ± 3.4)	(-36.2 ± 8.5)	—
$10^{11} \beta_{21} =$	1.28 ± 0.11	15.5 ± 6.2	1.36 ± 0.04
$10^4 \beta_{12} =$	6.51 ± 0.83	6.728 ± 0.066	5.99 ± 0.14
$10^8 \beta_{22} =$	(-1.1 ± 0.8)	(-2.1 ± 0.9)	—
$10^9 \beta_{33} =$	2.03 ± 0.11	2.068 ± 0.013	2.168 ± 0.011
$10^{12} \beta_{44} =$	1.6 ± 0.9	(-0.22 ± 0.19)	(-0.56 ± 0.19)

Table 2.

	$\log \beta_{33}$	$\log \beta_{12}$	$\log \beta_{21}$
From data 3 by LETAGROP	-8.664 ± 0.007	-3.22 ± 0.03	-10.87 ± 0.04
Kakihana and Sillén ³	-8.66 ± 0.03	-3.24 ± 0.02	-10.9 ± 0.2
Carell and Olin ⁴	-8.66 ± 0.03	-3.22 ± 0.05	—

proposed (1,1), (1,2), (2,2), (3,3), and (4,4), to see whether a better fit could be obtained by assuming other complexes than those proposed earlier from this laboratory.

We used three combinations of data: (1) all data (78 points) of Ref.³, $B \approx 0.001$ to 0.049 M. (2) 122 points selected at random from Ref.⁴, $B \approx 0.040$ to 1.0. (3) Data as in 1 + 2, except for 42 points from the two highest B values and two points from Ref.³ which had very high deviations, thus 156 points with $B \approx 0.001$ to 0.318 M.

The results are given in Table 1; the limits given are the standard deviations $\sigma(\beta)$. "Minus" β_{pq} -values were set = 0 in calculating the final set.⁵

These calculations thus confirm the existence of the three main complexes suggested by earlier work from this laboratory; the (4,4) and (2,2) complexes are not supported by the present data, even as minor products.

Obviously "data 1" (low B) are less sensitive to (4,4), and "data 2" (high B) to (2,1) and (1,1). Using "data 3" and giving, as usual, 3σ , and logarithms,⁶ we obtained the results given in Table 2.

From the 3σ limits we estimate as a maximum value, $\log \beta_{11} < -6.1$.

Again, we find that our earlier graphical methods gave practically the same result as the computer refinement by LETAGROP.

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Processes Regulating the Oxidation State of the System (Air + Sea + Sediments) in Past and Present

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From present theories of planet formation it seems likely that there was little or no oxygen in the original atmosphere of the Earth. Oxygen is formed by biological photosynthesis and by photochemical splitting of H_2O ; it is consumed by biological oxidation, and by some inorganic processes such as weathering of sulfides and oxidation of Fe(II). As estimated by Goldschmidt,¹ the free O_2 (0.027 mole) and the O_2 buried in Fe(III) (0.030 to 0.065 mole) are roughly equivalent to the carbon (0.06 to 0.08 mole) that has been buried and thus withdrawn from circulation. Goldschmidt's figures have been recalculated here to the unit mole per liter of sea water.

One may ask whether $p(O_2)$ is still increasing slowly, or whether it is fixed around 0.21 atm (its present value) by some equilibrium or steady-state mechanism. For instance, Redfield² has suggested a regulating biological mechanism involving the oxidation of organic matter with SO_4^{2-} in regions deficient in O_2 on the ocean floor.

From Goldschmidt's figures¹ one may calculate that (1 l seawater + 0.6 kg sediments + 3 l H_2O) have been formed by the reaction of (0.6 kg primary rock and \approx 1 kg volatiles), containing 54.90 mole H_2O , 16.06 SiO_2 , 1.85 $Al(OH)_3$, 0.55 HCl, 0.47 NaOH, 0.56 $Ca(OH)_2$, 0.53 Mg $(OH)_2$, 0.41 KOH, 0.55 CO_2 , 0.03 O_2 , 0.55 Fe, 0.06 Ti, 0.07 S, 0.03 F, 0.02 P, 0.01 Mn and 0.10 N_2 .

Some time ago, the author^{3,4} made an attempt to compare the system (sea + sediments + air) with a model in which the components were allowed to reach equilibrium. In this way, the pH (\approx 8.1) and the concentrations of the major ions in seawater may be explained as a result of equilibria with various aluminosilicates and SiO_2 .

The small amounts of carbonate in seawater, and of CO_2 in air roughly correspond to equilibrium with solid $CaCO_3$ at around 5°C.