iron(III) systems. The increased activation energy for the chromium(III) reactions reflects the loss of a substantial amount of crystal field stabilization energy in forming the transition state in the d^3 system. This loss is somewhat smaller for an S_N1 than for an S_N2 mechanism. It is noteworthy that the entropies of activation for the chromium(III) reactions are also more positive than the entropies of activation for the vanadium(III) reactions. However, because of the importance of crystal field effects in the chromium(III) reactions, comparisons between the chromium(III) and vanadium(III) systems may be less valid than comparisons between the iron(III) and vanadium(III) systems.

The conclusion that the vanadium(III) reaction is predominantly S_N2 in character is consistent with the decreased importance of the inverse acid path in the vanadium(III) system.[17] The inverse acid path in the iron(III) system has been interpreted in terms of the conjugate base mechanism

$$Fe(H_2O)_5X^{2+} \rightleftharpoons Fe(H_2O)_4(OH)X^+ + H^+ \qquad (9)$$

$$Fe(H_2O)_4(OH)X^+ + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+} + X^- \qquad (10)$$
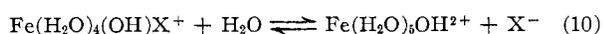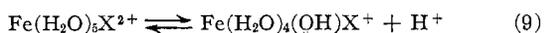
in which the five-coordinated intermediate $Fe(H_2O)_4$-OH^{2+} is stabilized through π bonding of the hydroxide group. A similar five-coordinated intermediate could

also be formed in the vanadium(III) system. Since the activation parameters for the inverse acid path are not known, it is not profitable to speculate whether such an intermediate is indeed formed in the vanadium-(III) reaction. On the other hand, if an S_N2 mechanism also operates in the inverse acid path, then the results obtained in the present study suggest that the seven-coordinated transition state formed by the addition of thiocyanate to $V(H_2O)_5OH^{2+}$ is not much more stable (and may well be much less stable) than the one formed by the addition of thiocyanate to $V(H_2O)_6^{3+}$. In any event the S_N2 mechanism appears to provide such a favorable pathway for the acid-independent reaction that this reaction effectively masks the contribution of the inverse acid path.[18]

Finally, S_N2 mechanisms have recently been proposed for the reactions of CH_3HgOH and of UO_2^{2+} with various anions.[19,20] In both cases no contribution from an acid-dependent pathway was discerned within the experimental error of the measurements. More significantly, however, the rate constants for complex formation depended upon the nature of the incoming ligand. Additional work on the substitution reactions of $V(H_2O)_6^{3+}$ is planned in order to determine the ligand dependence of the rate constants.

(17) Whereas the rate of formation of $VNCS^{2+}$ is independent of the hydrogen ion concentration in the range 0.025–1.0 M, the rates of formation of $FeNCS^{2+}$ and $CrNCS^{2+}$ increase by factors of 5 and 1.2, respectively, when the hydrogen ion concentration is decreased from 0.40 to 0.025 M at 25.0°. However, in comparing these rate constant variations, it should be remembered that the hydrolysis constants of $V(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ are similar and are about ten times larger than the hydrolysis constant of $Cr(H_2O)_6^{3+}$ at 25.0°.

(18) The above argument assumes that the hydrolysis constants of V-$(H_2O)_5NCS^{2+}$ and $Fe(H_2O)_5NCS^{2+}$ have similar values. Since the hydrolysis constants of $V(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ are not very different, there is no reason to believe that the hydrolysis constants of their thiocyanate complexes will not be similar.

(19) M. Eigen, G. Geier, and W. Kruse in "Essays in Coordination Chemistry," W. Schneider, G. Anderegg, and R. Gut, Ed., Birkhäuser Verlag, Basel, Switzerland, 1964, pp 164–178.

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The Hydrolysis of Beryllium(II) in 1 *m* NaCl

BY R. E. MESMER AND C. F. BAES, JR.

The hydrolysis of beryllium(II) in 1 *m* NaCl was measured at 0, 25, and 60° to establish better the reactions which occur and their temperature coefficients. Potentiometric measurements were made with hydrogen electrodes at 0 and 60° and with a quinhydrone electrode at 25°. The beryllium concentration was varied in the range 0.002–0.05 *m* and the pH was varied in the range 2–7. The results at low $\bar{n}$, the hydroxyl number, are consistent with previous work suggesting the formation of $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$. The third species previously proposed to account for data in nearly neutral solutions, $Be(OH)_2$, is incorrect. By computer analysis of the data at three temperatures, the most probable third species is $Be_5(OH)_7^{3+}$ which gives a slightly better fit than $Be_6(OH)_8^{4+}$. With careful consideration of the experimental error and the weighting of the data, there was no justification for adding more species to the scheme. The $-\log Q$ values for the most probable scheme are: 0°, (2, 1) 3.64, (3, 3) 10.08, (5, 7) 28.66; 25°, (2, 1) 3.43, (3, 3) 8.91, (5, 7) 25.33; and 60°, (2, 1) 2.93, (3, 3) 7.67, (5, 7) 22.11, where the numbers in parentheses are the subscripts (x, y) for the species $Be_x(OH)_y^{(2x-y)+}$ formed in the reaction $xBe^{2+} + yH_2O = Be_x(OH)_y^{(2x-y)+} + yH^+$. The $\Delta H°$ values at 25° for the formation of these species in the order of increasing polynuclearity are 5.0, 16.0, and 45.3 kcal/mole and the respective $\Delta S°$ values are 1.4, 15.3, and 35.2 eu. Relationships among the $\Delta H°$ and among the $\Delta S°$ terms for the polynuclear hydrolysis products of several different metal ions are discussed.

Introduction

The beryllium(II) ion is the lightest and smallest ion to produce polynuclear hydrolysis products—$(M_x$-$(OH)_y^{(2x-y)+}$—in aqueous solutions. The unhydrolyzed

ion is known to be tetrahedrally hydrated in water,[1] as would be expected from its uniquely small size, and

(1) D. N. Fiat and R. E. Connick, *J. Chem. Phys.*, **39**, 1349 (1963); M. Alei and J. A. Jackson, *ibid.*, **41**, 3402 (1964).

because of this small coordination number, relatively uncomplicated hydrolysis behavior might be expected.

The extensive measurements of Kakihana and Sillén[2] in 3 M NaClO$_4$ led them to propose a simple series of three hydrolysis products: Be$_2$(OH)$^{3+}$, Be$_3$(OH)$_3^{3+}$, and Be(OH)$_2$. While a later reexamination[3] of this data by computer analysis suggested that small amounts of Be(OH)$^+$ might be formed, their results seem clearly to rule out many of the other species which have been proposed over the years. The most noteworthy of these are: Be$_2$(OH)$_2^{2+}$,[4-6] Be$_4$(OH)$_4^{4+}$,[7,8] and Be-(OBe)$_4^{2+}$.[9] Employing the self-medium method at high concentrations of beryllium, Carell and Olin[10] confirmed the existence of Be$_2$(OH)$^{3+}$ and Be$_3$(OH)$_3^{3+}$. Bertin, *et al.*,[11] reached the same conclusion as Kakihana and Sillén on the basis of another potentiometric study.

There are several arguments which suggest, however, that the most basic hydrolysis product proposed by Kakihana and Sillén, Be(OH)$_2$, is incorrect: (1) When the equilibrium for the formation of this hydrolysis product

$$Be^{2+} + 2H_2O \rightleftharpoons Be(OH)_2(soln) + 2H^+; \quad Q_{1,2} = 1.2 \times 10^{-11}$$
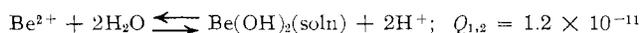
is combined with the following solubility equilibrium for α-Be(OH)$_2$[12]

$$\alpha\text{-Be(OH)}_2 + 2H^+ \rightleftharpoons Be^{2+} + 2H_2O; \quad Q_s = 7.2 \times 10^6$$
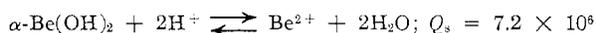
one obtains the concentration of the neutral hydrolysis product in solution which should be at equilibrium with the solid hydroxide

$$\alpha\text{-Be(OH)}_2 \rightleftharpoons Be(OH)_2(soln); \quad Q = Q_{1,2}Q_s = 0.9 \times 10^{-4} \; m$$
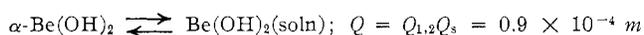
This concentration (9×10^{-5} m)—which should not be greatly dependent on pH or on the ionic medium—greatly exceeds the solubility observed for α-Be(OH)$_2$ in neutral water ($<10^{-7}$ m[12]). To be consistent with the reported solubility behavior of beryllium hydroxide, the stability quotient ($Q_{1,2}$) of the hydrolysis product, Be(OH)$_2$, in solution must be lowered three orders of magnitude or more below the value reported by Kakihana and Sillén. (2) The ionic charge on the most basic species was observed in critical coagulation studies[13] to be greater than $+2$ and probably equal to $+3$. (3) No other case is known wherein a metal ion hydrolyzes to produce a series of polynuclear hydroxide complexes followed by a more basic mononuclear species.

These considerations have led us to reinvestigate the hydrolysis behavior of beryllium by potentiometry using the precision techniques developed at this labora-

tory, *i.e.*, the use of high-quality electrometers in potentiometric measurements to obtain a continuous signal for recording and the use of computer analysis for data reduction. Since measurements at several temperatures have contributed greatly to the definition of the composition of the species formed by hydrolysis in the UO$_2^{2+}$ [14] and Th^{4+} [15] systems and, as well, have yielded the thermodynamic quantities for the hydrolysis reactions, this approach has also been extended to the beryllium system.

Experimental Section

Reagents.—All beryllium solutions were prepared from very high purity beryllium hydroxide prepared by an exhaustive solvent-extraction procedure.[16] The detectable metallic impurities totaled less than 5 ppm. An upper limit set for titratable organic impurities was less than 0.3 mole % of the beryllium. The beryllium content of the hydroxide was determined from the ignition loss at 1100°. The hydroxide was dissolved in a slight excess of HCl, and the free acid composition was determined by the method previously described;[17] *i.e.*, the initial free acidity in a titration experiment was adjusted to give $h = m_H$ in regions of acidity where no hydrolysis occurs, where m_H is the calculated acidity in the absence of hydrolysis and h is the potentiometrically measured free hydrogen ion concentration. We estimate that in the range 0.02–0.001 m the free acidity was determined to about 1% by this method. This corresponds to an error of less than about 0.01 in $\bar{n}$.

Baker and Adamson sodium chloride was recrystallized from aqueous solution by evaporation of the solvent to recover about half of the salt. The pH of a saturated solution was adjusted to 3 in a polyethylene vessel, and purging with N$_2$ was continued during the evaporation. Recrystallization was required to reduce the protolytic impurities to less than 10^{-5} m. Stock solutions of sodium chloride were made up with deionized, distilled water and acidified for removal of CO$_2$ by N$_2$ purging and then neutralized with CO$_2$-free base to pH 7. Stock solutions of NaOH were prepared from Fisher Certified NaOH containing less than 0.2 mole % Na$_2$CO$_3$. All NaOH solutions were stored in polyethylene-lined or paraffin-lined vessels.

All solutions were made up by weight, and concentrations are expressed in molality.

High-purity hydrogen ($>99.5\%$) was further purified by passage through a Serfass hydrogen purifier, Model C-15D. The unit is capable of producing hydrogen containing less than 10 ppb impurities. Nitrogen was purified by passage through 50% NaOH solution before saturating with water vapor from 1 m NaCl solution.

Eastman quinhydrone was recrystallized from deionized, oxygen-free water and dried over NaOH pellets. The calomel electrode was made up from the element of a Leeds and Northrup standard 1119-31 calomel reference electrode.

Potentiometric Cells.—The potentiometric circuit as previously described[14] consisted primarily of a vibrating-reed electrometer and a precision potentiometer in series with the chemical cells. The cell temperature was maintained at 25.0 and 60.0° ($\pm 0.02°$) and at 0° ($\pm 0.05°$). The hydrogen electrode concentration cells employed at both 60.0 and at 0° were

$$\text{Pt, H}_2 \left| \begin{array}{l} \text{NaCl, } (1 - a - 2b) \; m \\ \text{HCl, } a \; m \\ \text{BeCl}_2, \; b \; m \end{array} \right| \left| \begin{array}{l} \text{NaCl, } (1 - c) \; m \\ \text{HCl, } c \; m \end{array} \right| \text{H}_2, \text{ Pt}$$
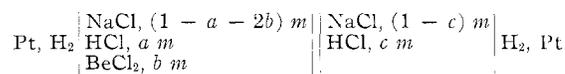
The HCl concentration in the half-cell on the right remained constant throughout one experiment while a titration with HCl

(2) H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, **10**, 985 (1956).

(3) S. Hietanen and L. G. Sillén, *ibid.*, **18**, 1015 (1964).

(4) M. Prytz, *Z. Anorg. Allgem. Chem.*, **180**, 355 (1929); **197**, 103 (1931); **231**, 238 (1937).

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(11) F. Bertin, G. Thomas, and J. C. Merlin, *Compt. Rend.*, **260**, 1670 (1965).

(12) R. A. Gilbert and A. B. Garrett, *J. Am. Chem. Soc.*, **78**, 5501 (1956); P. Schindler and A. B. Garrett, *Helv. Chim. Acta*, **43**, 2176 (1960).

(13) E. Matijevic, *J. Colloid Sci.*, **20**, 322 (1965).

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(15) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, *ibid.*, **4**, 518 (1965).

(16) C. E. L. Bamberger, H. F. McDuffie, and C. F. Baes, Jr., *Nucl. Sci. Eng.*, **22**, 14 (1965).

(17) C. F. Baes, Jr., *Inorg. Chem.*, **4**, 588 (1965).

or NaOH solutions was conducted on the left. Platinized platinum electrodes were placed in both compartments and hydrogen from a common source was bubbled through each. The hydrogen was presaturated with water vapor from a 1 m NaCl solution held at the same temperature as the cell. Agitation in the constant-potential cell was provided by the bubbling gas and in the titration compartment by a magnetic stirrer.

The electrode system employed at 25.0° was

$$\text{Pt} \begin{vmatrix} \text{NaCl}, (1 - a - 2b) \, m \\ \text{HCl}, a \, m \\ \text{BeCl}_2, b \, m \\ \text{quinhydrone, } 0.003 \, m \end{vmatrix} \begin{vmatrix} \text{NaCl}, 1 \, m \end{vmatrix} \begin{vmatrix} \text{Hg}_2\text{Cl}_2, \text{Hg} \end{vmatrix}$$
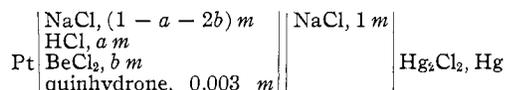
Quinhydrone at concentrations up to 0.006 m had no effect on the cell potential in the presence of 0.04 m beryllium. The absence of the interaction of either quinone or hydroquinone with the beryllium ion, which was demonstrated in this way, is in agreement with the findings of Kakihana and Sillén.[2] A minor correction was applied to potentials recorded using this cell to correct for a small slow drift (0.06 mv/hr). The source of this drift was not identified but it is believed to result from a slow chlorination of quinone.[18] Measurements with this electrode system were made in a pH range where no error is introduced through the acidity of hydroquinone.

The liquid junction employed in all cells in this study was the standard glass salt-bridge tube 1119-31-B manufactured by Leeds and Northrup. It consists of a cracked-glass bead imbedded in the tip of a Pyrex tube. This liquid junction was chosen because of its negligible leak rate—0.001 g of H_2O/cm head of water hr^{-1}.

Equilibrium Measurements.—The hydrolysis reactions occurred slowly under some of the experimental conditions. At temperatures of 25° and lower, equilibration times of several minutes to several hours were encountered. Highly precise measurements could not be expected using glass electrodes since corrections for the drift in asymmetry potential by the usual extrapolation cannot be made under these conditions. Both the quinhydrone and hydrogen electrodes, however, do have the necessary stability of potential.

Unusual kinetic behavior was most apparent at 0° but was also observed at 25°. At 60° the reactions were complete in 10–20 min. Three distinct phenomena could be observed by the recorded potential in three general regions of $\bar{n}$ (average number of hydroxides bound per beryllium) after additions of base to the acidic solutions of the metal ion: (1) At low values of $\bar{n}$ the equilibrium acidity was attained slowly from the direction of high acid concentration. (2) At $\bar{n} \simeq 0.5$ the pH rose sharply, then decreased more slowly, and passed through a minimum before equilibrium was attained, again from the direction of higher acidity. The over-all equilibration time was minimal in this vicinity of $\bar{n}$. (3) At $\bar{n} \simeq 1.0$ the pH rose slowly until the equilibrium pH was attained.

The point of initial precipitation at $\bar{n} \simeq 1.1$ was clearly evident from the recorded potential. When precipitation occurred the cell potential began drifting toward greater acidity and no steady value was obtained even after several hours. This behavior was found to be a reliable measure of the onset of precipitation based on experiments in relatively concentrated solutions in which precipitation of only a few per cent of the total beryllium was easily detectable by visual observation.

In order to demonstrate that equilibrium was achieved over the entire range of $\bar{n}$ studied, titrations of prehydrolyzed solutions were also conducted. The consistency of data taken with both increasing and decreasing $\bar{n}$ is evidence of equilibrium.

Results

Acidity Measurements.—Observed changes in potential, ΔE, accompanying incremental additions of titrant are related to the free acidity, h, as

$$\Delta E = (RT/\mathfrak{F}) \ln (h_r/h) - \sum(D_i(m_{i,r} - m_i)) \quad (1)$$

where m_i represents the concentration of each ion present and $m_{i,r}$ denotes these values at the reference point in a titration, *i.e.*, at the start or at the end. D_i is the liquid junction potential coefficient for each ion as calculated from the Henderson equation as expressed for a constant ionic medium[17]

$$D_i = RT\lambda_i/Z_i\mathfrak{F}\sum(m_i\lambda_i) \quad (2)$$

where Z is the charge on the ion and λ is the limiting equivalent conductance.

To demonstrate the validity of eq 1 and the Henderson equation for calculating liquid junction potential coefficients for these cells, the terms $(D_{H^+} - D_{Na^+})$ were measured by titrations in the absence of beryllium ions at each temperature. The results were compared with values calculated from the Henderson equation using limiting conductance data given by Robinson and Stokes.[19] Measured values of $(D_{H^+} - D_{Na^+})$ at 0, 25, and 60° were 69, 61, and 51 mv m^{-1} and calculated values were 67, 63, and 49 mv m^{-1}, respectively. These results indicate that the calculated values are not in error by more than a few mv m^{-1} units which leads to very small errors in h or in $\bar{n}$ even at the highest acidities used in these measurements.

Hydrolysis data covering a range of beryllium concentrations from about 0.05 to 0.002 m and pH from about 2 to 7 are given in Table I. The average number of hydroxides bound per beryllium ion in solution, $\bar{n}$, is calculated from $(h - m_H)/m_b$, where m_b is the total beryllium concentration. Titrations in the directions of increasing $\bar{n}$ and decreasing $\bar{n}$ are included. All the data listed are equilibrium data as indicated by the constant cell potentials obtained and the reproducibility in reverse titrations.

The results obtained in experiments with increasing $\bar{n}$ are illustrated in Figure 1 for the three temperatures. The curves are approximately parallel over much of the range. The beryllium concentrations investigated at 0° were slightly higher than at the higher temperatures. This was necessitated by the very slow hydrolysis rates in dilute solutions. The beryllium ion concentration decreases in each case as $\bar{n}$ increases as a result of dilution. Constancy of the metal ion concentration is not required in the method of data treatment employed to derive equilibrium quotients.

In agreement with earlier results[14,15] on UO_2^{2+} and Th^{4+} hydrolysis studies, the pH at which hydrolysis begins at a given metal ion concentration decreases with temperature. However, in this case, the $\bar{n}$ at which precipitation begins is relatively constant while the pH at which precipitation begins decreases with temperature.

Data Analysis.—The computer program originally employed by Rush, Johnson, and Kraus[20] was used to analyze the beryllium hydrolysis data to derive the most probable scheme of hydrolysis products, *i.e.*, the scheme containing the lowest number of species which

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(19) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1965, p 465.

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TABLE I
BERYLLIUM(II) HYDROLYSIS RESULTS IN 1 m NaCl

$m_b \times 10^3$	$-\log h$	$\bar{n}$	$m_b \times 10^3$	$-\log h$	$\bar{n}$	$m_b \times 10^3$	$-\log h$	$\bar{n}$	$m_b \times 10^3$	$-\log h$	$\bar{n}$
0°						**25°**					
94.11	3.364	.055	35.21	4.927	.815[a]	45.43	2.431	.0012	5.377	5.250	.910
91.67	3.667	.166	34.87	4.863	.788	44.88	2.705	.0019	5.331	5.413	.954
88.49	3.895	.321	34.22	4.754	.733	44.41	2.983	.015	5.289	5.586	.993
84.99	4.134	.506	34.10	4.640	.663	43.97	3.173	.038	5.241	5.788	1.039
81.16	4.480	.727	32.68	4.546	.597	43.46	3.351	.074	5.189	5.962	1.090
78.27	5.0355	.908	31.73	4.435	.507	42.85	3.431	.115			
76.59	5.789	1.019	30.66	4.314	.399	42.13	3.535	.169	2.420	3.589	.0008
			29.76	4.205	.301	41.18	3.647	.244	2.365	4.054	.037
58.60	3.315	.026	28.75	4.058	.186	40.28	3.747	.320	2.332	4.243	.092
55.96	3.764	.133	27.72	3.768	.061	39.27	3.859	.409	2.301	4.359	.150
53.68	3.945	.237				37.93	4.020	.534	2.255	4.496	.244
50.74	4.147	.387	17.99	6.336	1.077[a]	36.06	4.326	.725	2.203	4.638	.358
47.75	4.374	.558	17.70	5.884	.987	34.48	4.808	.902	2.145	4.796	.489
44.80	4.694	.749	17.47	5.457	.914	33.33	5.499	1.044	2.098	4.947	.604
42.75	5.126	.898	17.18	5.136	.819				2.053	5.125	.717
41.65	5.641	.983	16.86	4.907	.709	21.11	2.906	.0014	2.010	5.365	.832
40.58	6.094	1.071	16.53	4.732	.592	20.94	3.297	.022	1.989	5.529	.890
			16.23	4.597	.481	20.81	3.482	.054	1.971	5.696	.940
27.72	4.053	.180	15.91	4.460	.360	20.51	3.714	.148	1.952	5.891	.994
26.97	4.280	.320	15.51	4.261	.200	20.16	3.885	.263	1.940	6.023	1.030
26.08	4.462	.494				19.94	3.977	.340	1.930	6.097	1.061
25.50	4.633	.616	9.548	3.087	.017	19.57	4.138	.472			
24.97	4.823	.732	9.267	3.940	.028	19.23	4.300	.596	17.68	5.561	1.025[a]
24.43	5.165	.854	8.901	4.318	.139	18.91	4.499	.720	17.40	5.120	.934
23.96	5.678	.965	8.481	4.539	.286	18.62	4.764	.837	17.13	4.802	.844
23.70	6.082	1.029	8.023	4.764	.464	18.29	5.300	.969	16.61	4.448	.665
23.41	6.304	1.101	7.618	5.009	.640	18.14	5.612	1.033	16.24	4.271	.531
			7.303	5.301	.790	17.96	5.750	1.112	15.87	4.114	.392
4.918	4.492	.117	7.026	5.819	.934				15.62	4.003	.293
4.197	5.051	.500				6.871	2.928	.0026	15.29	3.829	.160
3.910	5.341	.693	23.32	5.580	.960[a]	6.737	3.186	.0052	14.92	3.353	.020
3.702	5.703	.852	22.74	5.120	.853	6.597	3.638	.027			
3.589	6.087	.946	22.12	4.849	.731	6.489	3.885	.079	5.099	5.630	.998[a]
3.517	6.438	1.010	21.32	4.605	.564	6.346	4.070	.166	5.011	5.277	.910
3.420	6.697	1.099	19.96	4.244	.248	6.207	4.200	.256	4.923	5.040	.819
						6.075	4.312	.347	4.759	4.744	.640
60°						5.827	4.530	.531	4.680	4.631	.549
						5.655	4.719	.669	4.553	4.461	.397
						5.546	4.877	.761	4.480	4.359	.308
18.00	5.140	1.084[a]	4.752	4.640	.823	5.445	5.071	.849	4.411	4.248	.220
17.87	5.020	1.043	4.710	4.778	.872						
17.74	4.876	1.002	4.661	4.955	.930						
17.60	4.719	.961	4.620	5.124	.980	**60°**					
17.36	4.459	.883	4.583	5.274	1.026						
16.95	4.149	.745	4.542	5.416	1.078	38.64	2.339	.0072	18.16	2.590	.0014
16.53	3.934	.602				37.82	2.669	.023	17.89	2.996	.035
16.14	3.769	.461	2.265	3.054	.0037	37.46	2.822	.042	17.74	3.189	.077
15.76	3.611	.318	2.180	3.343	.014	37.01	2.970	.076	17.56	3.354	.149
15.37	3.419	.165	2.096	3.799	.085	36.39	3.116	.133	17.40	3.461	.217
14.81	2.764	.013	2.069	3.922	.138	35.75	3.230	.196	17.18	3.586	.314
			2.039	4.031	.202	34.98	3.346	.278	16.99	3.690	.402
5.642	3.285	.024	2.007	4.137	.279	34.20	3.458	.366	16.76	3.818	.509
5.516	3.564	.090	1.984	4.213	.341	33.36	3.570	.457	16.58	3.930	.597
5.469	3.638	.124	1.943	4.341	.450	32.62	3.702	.560	16.46	4.021	.660
5.373	3.765	.201	1.908	4.460	.550	31.89	3.840	.655	16.31	4.146	.737
5.257	3.898	.302	1.880	4.570	.633	31.29	3.980	.737	16.15	4.313	.819
5.167	3.999	.386	1.853	4.693	.716	30.86	4.105	.798	16.02	4.487	.886
5.073	4.108	.478	1.822	4.861	.812	30.47	4.246	.855	15.91	4.665	.940
4.987	4.220	.565	1.798	5.036	.893	30.16	4.389	.902	15.77	4.976	1.023
4.898	4.353	.660	1.778	5.216	.961	29.89	4.540	.943	15.70	5.111	1.064
4.804	4.532	.763	1.758	5.420	1.030	29.58	4.735	.991	15.62	5.224	1.105
			1.739	5.597	1.098	29.26	4.937	1.043			
						28.95	5.088	1.094			

[a] Titrations of prehydrolyzed beryllium solutions with acid; all other titrations are of unhydrolyzed beryllium solutions with base.

suffice to account for all of the data within the limits of the estimated error.

Formation quotients $Q_{x,y}$, represent equilibria of the type

$$x\text{Be}^{2+} + y\text{H}_2\text{O} = \text{Be}_x(\text{OH})_y^{(2x-y)+} + y\text{H}^+$$
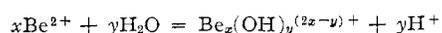
and are expressed as

$$Q_{x,y} = \frac{[\text{Be}_x(\text{OH})_y^{(2x-y)+}][\text{H}^+]^y}{[\text{Be}^{2+}]^x} = b_{x,y}h^y/b^x \qquad (3)$$

where b refers to the free beryllium ion concentration and $b_{x,y}$ to the concentration of the hydrolysis product.
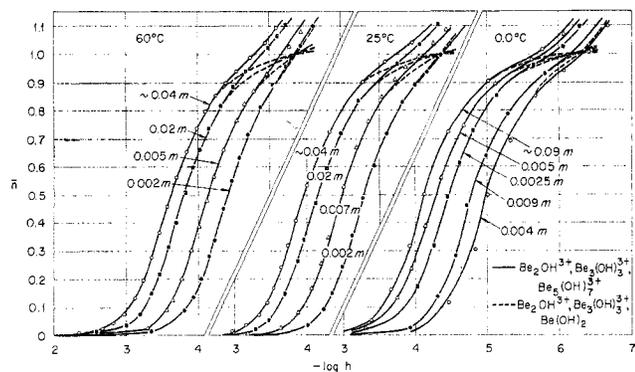
Figure 1.—Hydrolysis data for Be^{2+} in 1 m NaCl from 0 to 60°; hydrogen electrode data are at 0 and 60° and quinhydrone data are at 25°. The numbers refer to m_b which decreases with increasing $\bar{n}$ as a result of dilution. The solid and dashed curves were calculated for the schemes indicated in the legend (the curves superimpose below $\bar{n} \simeq 0.9$).

The value for b is computed for each data point by successive approximations from the material balance expression corresponding to the assumed hydrolysis scheme

$$m_b = b + \sum x Q_{x,y}(b^x/h^y) \qquad (4)$$

and the hydroxyl number, $\bar{n}$, is calculated from the expression

$$\bar{n}_c = \sum y Q_{x,y}(b^x/h^y)/m_b \qquad (5)$$

where m_b is the total beryllium concentration. Finally, as a measure of the agreement of $\bar{n}_c$ (calculated) with $\bar{n}_o$ (observed), the agreement factor is

$$\sigma(\bar{n}) = \sqrt{\sum W(\bar{n}_o - \bar{n}_c)^2/(N_o - N_v)} \qquad (6)$$

where N_o is the number of observations, N_v is the number of parameters varied in the calculation, and W is a weighting factor (see Appendix for discussion of this quantity).

The formation quotients, their standard deviations, and the agreement factors serve to characterize a given scheme of hydrolysis products (see Figures 2–4 and Tables II and III).

TABLE II

AGREEMENT FACTORS FOR THE SCHEMES
$(Be_x(OH)_y^{(2x-y)+}-Be_3(OH)_3^{3+})$ WHERE $\bar{n} < 0.5$
(VALUES GIVEN ARE $\sigma(\bar{n}) \times 10^3$)

	This work			Ref 2	Ref 10[a]
x, y	0°	25°	60°	25°	25°
1, 1	17	11	8	13	26
2, 1	8	6	8	10	2
3, 1	15	9	9	11	13
3, 2	9	8	13	12	14
2, 2	17	10	8	13	26

[a] Self-medium method at high beryllium concentration and low $\bar{n}$.

Discussion

The minimum agreement factor, $\sigma(\bar{n})$, is significant when the proposed hydrolysis scheme fits the experimental data within the estimated experimental error and particularly when no simpler scheme—one con-
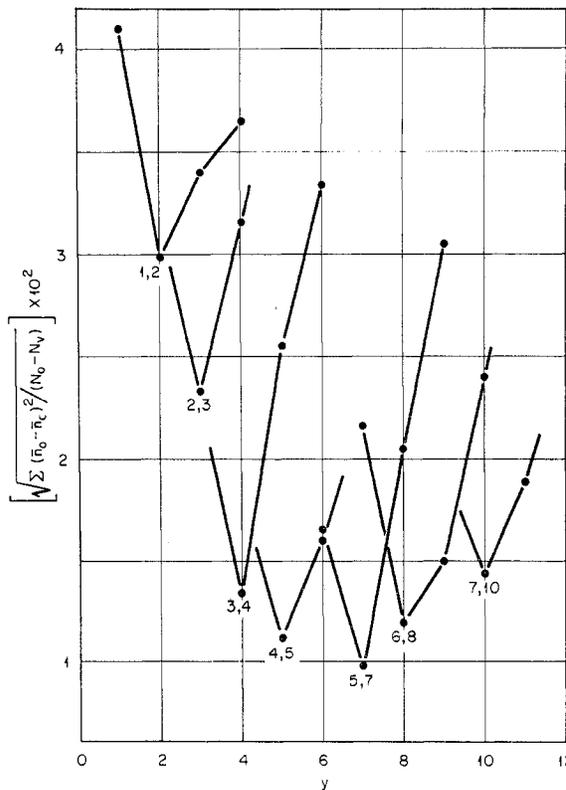
Figure 2.—Agreement factors for three-species hydrolysis schemes in the array $Be_2(OH)^{3+}-Be_3(OH)_3^{3+}-Be_x(OH)_y^{(2x-y)+}$ calculated from data at 60°. The x, y values are indicated at the minimum of each "curve." (Solid lines only serve to indicate the set of points with the same x.)

sisting of fewer species—suffices to explain the data. The possibility that the correct scheme consists of a large number of species when a small number of species will account for the data appears to be remote although conceivable. For this reason it seems obvious that one has little justification for introducing additional species into a proposed scheme which already fits the data within the estimated limits of error.

Two-Species Schemes.—Upon examination of the hydrolysis behavior in Figure 1 certain features immediately aid in selecting possible hydrolysis products. The inflection in the $\bar{n}$ *vs.* $-\log h$ curves at $\bar{n} \simeq 0.95$ requires that at least two species be included in any proposed scheme. Because $\bar{n}$ values of *ca.* 1.1 are attained before precipitation begins, at least one species present has a y/x ratio of greater than unity. Also, plots of $\log \bar{n}$ *vs.* $\log h$ indicate that the number of hydroxides (y) in at least one of the species is less than 3. On the basis of these restrictions a large number of two-species schemes were examined including all reasonable possibilities with x between 1 and 4 and y between 1 and 5. Of the 32 schemes tested none was found which fit the data within the experimental error and was free of large systematic errors. Results of these calculations—formation quotients, standard errors, and agreement factors—are available to those interested.[21]
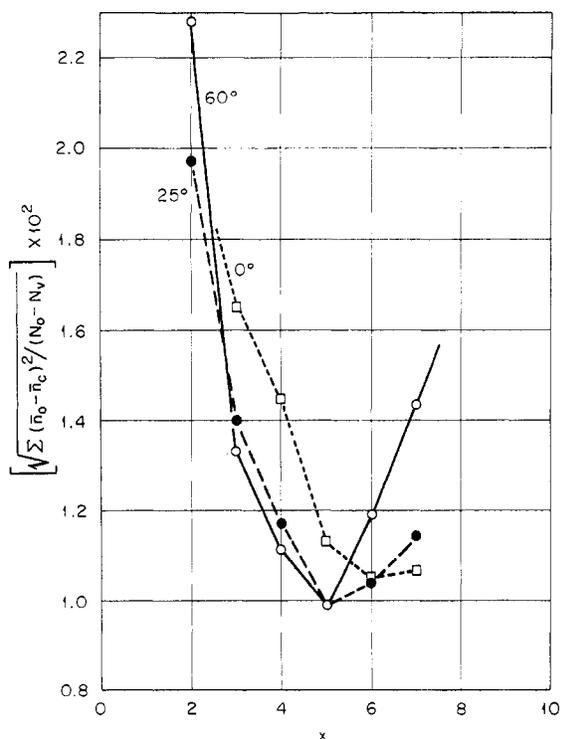
Figure 3.—Agreement factors for three-species schemes as a function of x where the x, y values for each point correspond to a minimum such as in Figure 2.
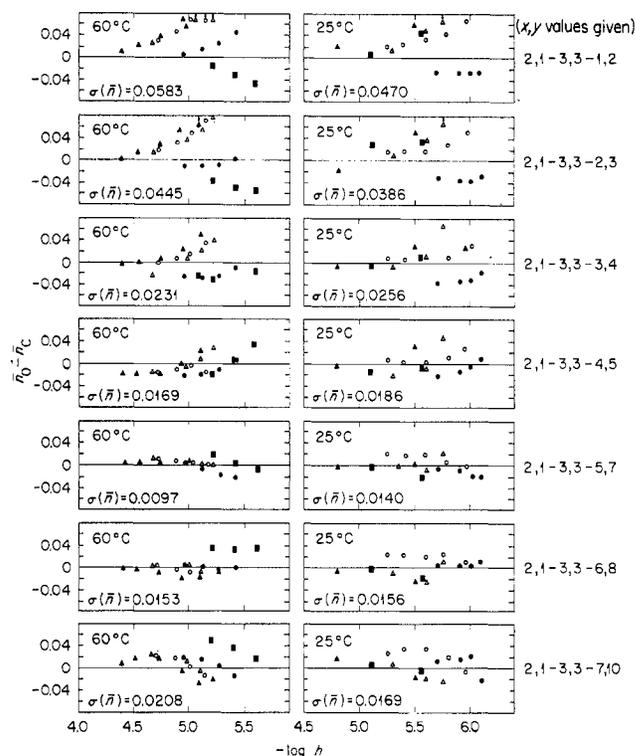
Figure 4.—Deviation plots for $\bar{n} > 0.9$ at 60 and 25°. Hydrolysis schemes are indicated at the right.

TABLE III

FORMATION QUOTIENTS FOR BERYLLIUM(II) HYDROLYSIS PRODUCTS IN 1 m NaCl

Temp, °C	2, 1	3, 3	5, 7	6, 8	$\sigma(\bar{n})$
			$-\text{Log } Q_{x,y}$		
			Scheme I		
0	3.64 ± 0.05	10.081 ± 0.009	28.66 ± 0.04	...	0.0113
25	3.43 ± 0.07	8.908 ± 0.007	25.33 ± 0.03	...	0.0099
60	2.93 ± 0.06	7.665 ± 0.007	22.11 ± 0.02	...	0.0099
			Scheme II		
0	3.64 ± 0.05	10.081 ± 0.008	...	31.15 ± 0.04	0.0105
25	3.42 ± 0.07	8.907 ± 0.007	...	27.46 ± 0.03	0.0104
60	2.91 ± 0.07	7.664 ± 0.008	...	23.73 ± 0.03	0.0119

Three-Species Schemes.—Based on the observations of a majority of the earlier investigators, Be_3-$(OH)_3{}^{3+}$ was selected as one of the species to be in-included in the first schemes to be tested. Of course, this selection must be substantiated by the data; *i.e.*, schemes containing this species must fit the experimental data within the limits of error.

A relatively large region of $\bar{n}$ was found (between 0 and 0.5) for which only two species give an excellent fit for the data of Table I. Calculated agreement factors for schemes containing several different species paired with $Be_3(OH)_3{}^{3+}$ are summarized in Table II for data from Table I and the data from ref 2 and 4 where $\bar{n}$ is less than 0.50. The maximum value considered for y was 2 since the plots of log $\bar{n}$ *vs.* log h indicate that the number of hydroxides in one species must be less than 3.

The data of Carell and Olin[10] obtained at high concentrations of beryllium at 25° are the most sensitive to the formula for the first species as expected and our

data at 60° are the least sensitive since the contribution of that species is low at this temperature and at these low concentrations of beryllium ion. That the Be_2-$(OH)^{3+}$ species is the best choice of those paired with $Be_3(OH)_3{}^{3+}$ is clearly evident from the data in Table II.

To arrive at the best three-species scheme for representing all of the data up to $\bar{n} = 1.1$, the following array of hydrolysis schemes was examined where x and y were allowed to vary from 1 to 7 and 1 to 11, respectively: $Be_2(OH)^{3+}$, $Be_3(OH)_3{}^{3+}$, $Be_x(OH)_y{}^{(2x-y)+}$. Figure 2 illustrates $\sigma(\bar{n})$ data at 60° for schemes where each connected set of points pertains to a series with a constant value for x and changing values of y for the third species (the lines have no significance except to tie together the points of a given series). A minimum occurs in each series at a particular species and the lowest minimum occurs for the scheme containing Be_5-$(OH)_7{}^{3+}$ as the third species.

Such calculations for data at all three temperatures are summarized in Figure 3 where only the minimum

for each value of x is plotted (y takes the value occurring at this minimum value of x as shown in Figure 2). The value of y producing the minimum for a given value of x was the same at all three temperatures. The reproducibility of the over-all minimum is indicated in Figure 3. The 25 and 60° data concur on the (5, 7) species (in this notation only the x and y values are given to represent the species) while the 0° data give a slightly lower minimum for the (6, 8) species. Based on the observed sluggishness of equilibria at 0° we consider our data at the higher temperatures to be a more reliable indicator of the composition of this species. On this basis the most probable composition of the third species is $Be_5(OH)_7^{3+}$ although the improvement of the fit to the data over the scheme containing $Be_6(OH)_8^{4+}$ is not great.

Another useful aid in selecting the most probable hydrolysis scheme is to observe the scatter of data on deviation plots of $\bar{n}_o - \bar{n}_c$ such as shown in Figure 4. For this purpose only the data above $\bar{n} = 0.9$ from Table I are shown (the region of existence of measurable amounts of the third species). To obtain these results the values for $Q_{2,1}$ and $Q_{3,3}$ were fixed by the data at $\bar{n} < 0.5$ and the value for $Q_{x,y}$ was computed by least squares from the data in the higher region of $\bar{n}$ where the species $Be_x(OH)_y^{(2x-y)+}$ is significant. Qualitatively similar results are obtained allowing all three formation quotients to vary, but, by fixing the values of $Q_{2,1}$ and $Q_{3,3}$ as indicated above, partial compensation for incorrect species made through small changes of $Q_{2,1}$ and $Q_{3,3}$ is excluded. Systematic errors are clearly minimized at 60° for the scheme containing the (5, 7) species, and the over-all scatter is minimal at both 60 and 25° for this species. From this point of view the (6, 8) species is again a slightly poorer choice.

It should be pointed out that the limitation here in defining the composition of the last species is not inherent in either the technique or the errors in the data but in the accessible range of $\bar{n}$ available to investigation before precipitation begins.

The solid lines in Figure 1 were drawn for the scheme $Be_2(OH)^{3+}-Be_3(OH)_3^{3+}-Be_5(OH)_7^{3+}$ and the dashed curves for the scheme originally proposed by Kakihana and Sillén[2] ($Be_2(OH)^{3+}-Be_3(OH)_3^{3+}-Be(OH)_2$). The two schemes superimpose at lower values of $\bar{n}$ as expected and diverge above $\bar{n} \simeq 0.9$. The latter scheme predicts a point of intersection for curves of different beryllium ion concentration and this is clearly absent from our data. In our analysis of the data of Kakihana and Sillén the best fit was obtained with the (3, 4) species in place of the (1, 2) species. The significance of this observation is, however, doubtful because of the sparsity of data in this region of $\bar{n}$ and because of the difficulty of obtaining equilibrium expressed by the authors. Likewise, it is not known whether corrections were applied to their data for the formation of bicarbonate in titrations with carbonate at pH in excess of 4.5. Representations of the data of Bertin, *et al.*,[11] are, however, in agreement with our data in this region of high $\bar{n}$ although these authors interpreted

their data in terms of the scheme $Be_2(OH)^{3+}-Be_3(OH)_3^{3+}-Be(OH)_2$ in spite of the inconsistency.

Distribution of Species.—The formation quotients are listed in Table III for the two most probable schemes: Scheme I: $x, y = 2, 1$; $3, 3$; $5, 7$. Scheme II: $x, y = 2, 1$; $3, 3$; $6, 8$. The results for all other three-species schemes tested are filed with the ADI.[21] The excellent precision with which the log $Q_{3,3}$ values for the principal species are determined is indicated by the standard error, 0.007–0.009, at the three temperatures.

None of the previously reported formation quotients is exactly comparable to these results since they were determined in different media. The results of Kakihana and Sillén at 25° in 3 M $NaClO_4$ for log $Q_{2,1}$ and log $Q_{3,3}$ are −3.22 and −8.66. In comparison with Table III the relatively small differences could well be caused by differences in activity coefficients and/or differences in counterion binding in the perchlorate and chloride media; *e.g.*, to explain centrifugation results in a study of the Bi(III) hydrolysis it was necessary to postulate that two of the weakly complexing perchlorate anions were bound to the Bi(III) hexanuclear hydrolysis product.[22]

On the other hand, in a careful potentiometric study of Pb(II) hydrolysis in 1960, Olin[23] found larger differences in formation quotients for 0.3 and 3.0 M $NaClO_4$. The $-\log Q_{x,y}$ values for the species (x, y) in 3.0 M $NaClO_4$ were: (1, 1) 7.9, (4, 4) 19.25, (3, 4) 22.87, and (6, 8) 42.14. The corresponding values in 0.3 M $NaClO_4$ were: (1, 1) 7.8, (4, 4) 19.90, (3, 4) 23.35, and (6, 8) 42.66. These differences in $-\log Q_{x,y}$ of *ca.* 0.5 unit found for the polynuclear complexes were not discussed. The differences are probably due to the factors mentioned above and are slightly greater than those found for beryllium hydrolysis products in the chloride and perchlorate media. Presently there is no direct method for isolating activity coefficient and counterion binding effects in such studies, but some investigators have attempted to estimate the exceptionally weak complexing in the beryllium(II) chloride system.[24]

The distributions of species calculated for scheme I of Table III in solutions at 0 and 60° and at total beryllium concentrations of 0.1 and 0.001 m are represented in Figure 5. The dominance of the trinuclear species in the accessible pH region (below the point where precipitation begins) is apparent in every case. There is a general shift toward more hydrolysis at a given pH at high temperatures and high beryllium concentrations. The amount of the dinuclear species remains below 14% and the maximum amount of the pentanuclear species is about 35% under these conditions. The dominance of the trinuclear species is greatest at 0° at the highest beryllium concentration (95% at the

(22) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).

(23) A. Olin, *Acta Chem. Scand.*, **14**, 126 (1960).

(24) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, pp 39–84.
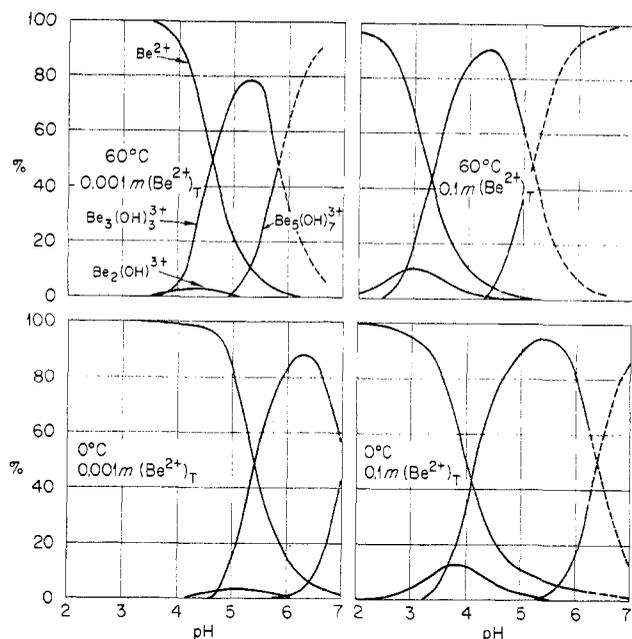
Figure 5.—Calculated distribution of beryllium among the three species of scheme I. Dashed lines represent regions where precipitation occurs.

maximum) and it is least at 60° in the more dilute solution (78% at the maximum).

Thermodynamic Parameters.—The quotients of Table III were used to compute the thermodynamic parameters for the most probable scheme of hydrolysis products, scheme I. The results summarized in Table IV show that $\Delta H°$ and $\Delta S°$ increase regularly with polynuclearity of the complexes. The calorimetric data of Carell and Olin[25] are also listed for comparison (in parentheses). Although calorimetric techniques are in principle a more precise means for measurement of heats of reaction than temperature coefficient data, here both methods are limited by the accuracy with which the equilibria are known and their constants determined. The uncertainties for the heats and entropies are assessed at about 0.5 kcal/mole and about 1–2 eu, respectively. The standard states are, of course, hypothetical 1 m solutions in 1 m NaCl as the solvent. The $\Delta G_f°_{298}$ values for the hydrolysis products were calculated from $\Delta G_f°_{298}$ for Be^{2+} (91.0 kcal/mole) reported by Bear and Turnball[26] and $\Delta G°$ for the ionization of water from ref 27.

All of the thermodynamic data presently available for polynuclear complexes are summarized in Table V for the reaction $xM^{n+} + yOH^- = M_x(OH)_y^{(nx-y)+}$. Here the hypothetical unit mole fraction standard state has been chosen as most appropriate for the correlation of entropies of reaction; the heats of reaction are unaffected by this change in standard state. In every instance the formation of the complex is favored both by the ΔH term (negative enthalpy) and by the ΔS term (positive entropy). The enthalpy term derives from the new M–OH–M bridges formed; probably

(25) B. Carell and A. Olin, *Acta Chem. Scand.*, **16**, 2357 (1962).
(26) I. J. Bear and A. G. Turnball, *J. Phys. Chem.*, **69**, 2828 (1965).
(27) F. D. Rossini, *et al.*, U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

TABLE IV
CALCULATED THERMODYNAMIC QUANTITIES
FOR THE HYDROLYSIS REACTIONS AT 25°
$xBe^{2+} + yH_2O = Be_x(OH)_y^{(2x-y)+} + yH^+$

Species	$\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, eu	$\Delta G_f°$, kcal
$Be_2(OH)^{3+}$	4.5	5.0	1.4	−234.0
		$(4.4)^a$	(0.2)	
$Be_3(OH)_3^{3+}$	12.2	16.0	15.3	−430.6
		(15.2)	(11.3)	
$Be_5(OH)_7^{3+}$	34.8	45.3	35.2	−816.5

^{a} Data in parentheses from B. Carell and A. Olin, *Acta Chem. Scand.*, **16**, 2357 (1962).

most of the hydroxides are present in these structures as bridges rather than M–OH bonds. The average $\Delta H°$ per hydroxide in these hydrolysis species, $\Delta H°/y$, is found to remain surprisingly constant throughout these six widely different systems, i.e., -7.6 ± 1.6 kcal per hydroxide in the complex. This is slightly more than half the value for the heat of neutralization of water, a somewhat analogous reaction involving the hydrogen ion.

The average entropy, $\Delta S°_{mf}/y$, shows more variation, 36 ± 10 eu. This might be expected since the analogous ionization reactions for oxyacids are related to ΔZ^2, the difference in the sums of the squares of the ionic charges of the products and reactants after correction for symmetry differences.[28] In the case of hydrolysis reactions, one does not know the structure of the complexes and cannot make a meaningful symmetry correction; likewise the actual charge on the complex is probably not the formal charge as written in Table V since some amount of counterion binding is likely. No correlation with ΔZ^2 exists.

However, a correlation can be made with Z^2 for the unhydrolyzed cation in which

$$\frac{\Delta S°_{mf}}{y} = 28 + 1.0Z^2 \qquad (7)$$

with an average deviation of 3.0 eu for $\Delta S°_{mf}/y$ and a maximum deviation of 5.6 eu. This correlation probably indicates a real dependence on the ionic charge. With the different ionic media involved in the tabulated data better agreement would be considered fortuitous. The contribution of the entropy change to the stability of the complex must derive from the changes in hydration in going from the simple ions to the hydroxide complexes.

The structure for $Pb_4(OH)_4^{4+}$, the dominant species in that system, has been shown[29] to exhibit a very symmetrical tetrahedral cage structure. The similarity of the ΔS values for the hydrolysis reactions in Table V, after correction for ionic charge and the number of hydroxides in the complexes, suggests that compact structures such as were found for $Pb_4(OH)_4^{4+}$ are quite common. Investigators have been quick to propose ring and cage structures in the past to account for the unique occurrence of few species and seemingly with justification.

(28) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959).
(29) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **89**, 45 (1967); O. E. Esval, Thesis, University of North Carolina, 1962.

TABLE V

SUMMARY OF THERMODYNAMIC DATA AT 25° ON POLYNUCLEAR HYDROLYSIS PRODUCTS FOR THE FORMATION REACTION

$$x M^{n+} + y OH^- = M_x(OH)_y^{(nx-y)+}$$

Species	$\Delta H°$, kcal	$\Delta S°_{mf}$,[a] eu	$\Delta H°/y$, kcal	$\Delta S°_{mf}/y$, eu	Medium	Ref[b]
$Fe_2(OH)_2^{4+}$	−18.4	76.4	−9.2	38.2	3 M NaClO₄	24[b] (62 Sa/63 Sa)
$Fe_3(OH)_4^{5+}$	−36.0	161.1	−9.0	40.3	3 M NaClO₄	24 (62 Sa/63 Sa)
$In_2(OH)_2^{4+}$	−16.6	70.9	−8.3	35.5	3 M NaClO₄	24 (61 Sa+56 Bd)
$Pb_4(OH)_4^{4+}$	−33.5	108.5	−8.4	27.1	3 M NaClO₄	24 (62C)
$Pb_3(OH)_4^{2+}$	−27.1	105.3	−6.8	26.3	3 M NaClO₄	24 (62C)
$Pb_6(OH)_8^{4+}$	−57.8	222.6	−7.2	27.8	3 M NaClO₄	24 (62C)
$Be_2(OH)^{3+}$	−8.4	36.7	−8.4	36.7	1 m NaCl	This work
$Be_3(OH)_3^{3+}$	−24.2	113.2	−8.1	37.7	1 m NaCl	This work
$Be_5(OH)_7^{3+}$	−48.5	258.2	−6.9	36.9	1 m NaCl	This work
$Th_2(OH)_2^{6+}$	−12.0	91.0	−6.0	45.5	1 m NaClO₄	15
$Th_4(OH)_8^{8+}$	−49.5	348.8	−6.2	43.6	1 m NaClO₄	15
$Th_6(OH)_{15}^{9+}$	−89.5	644.7	−6.0	43.0	1 m NaClO₄	15
$(UO_2)_2(OH)_2^{2+}$	−16.8	69.6	−8.4	34.8	0.5 m KNO₃	14
$(UO_2)_3(OH)_5^+$	−42.0	162.2	−8.4	32.4	0.5 m KNO₃	14

[a] Standard states changed to hypothetical unit mole fraction $(\Delta S°_{mf})$ from either unit molal $(\Delta S°)$ or unit molar $(\Delta S°_M)$ by: $\Delta S°_{mf} = \Delta S° + R(x + y - 1) \ln (55.51 + 2m_I)$ and $\Delta S°_{mf} = \Delta S°_M + R(x + y - 1) \ln (41.1)$, where m_I is the molar concentration of electrolyte. [b] References given by ref 24 in parentheses.

Appendix

The usual practice in the treatment of hydrolysis data in the past[14,15,30] has been to weight the data equally on the assumption that no significant bias is introduced by this approximation. The results described previously in this paper were calculated using equal weights ($W = 1$). A more rigorous way to weight such data would be according to the reciprocal of the estimated standard error for F, the function minimized; e.g., if

$$F = \bar{n}_o - \bar{n}_c \tag{8}$$

then W in eq 6 becomes

$$W = 1/\sigma^2(F) \tag{9}$$

when $\sigma^2(F)$ is the variance of the function F. A similar approach was recently taken by Schaefer[31] in evaluating equilibria for acetylacetone complexes with V^{2+} ion, although a somewhat different function was minimized in that case.

From propagation of error theory[32]

$$\sigma^2(F) = \left(\frac{\partial F}{\partial m_H}\right)^2_{h,m_b} \sigma^2(m_H) + \left(\frac{\partial F}{\partial h}\right)^2_{m_H,m_b} \sigma^2(h) + \left(\frac{\partial F}{\partial m_b}\right)^2_{h,m_H} \sigma^2(m_b) \tag{10}$$

(30) L. G. Sillén in "Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964," Akademiai Kiado, Budapest, 1965, pp 127–148.
(31) W. P. Schaefer, *Inorg. Chem.*, **4**, 642 (1965).

where m_H, h, and m_b are the variables from which F is calculated using eq 4, 5, and 8. This reduces to the expression[33]

$$\sigma^2(F) = \frac{\sigma^2(m_H)}{m_b^2} + \left[\frac{1}{m_b^2} - \frac{2}{m_b}\left(\frac{\partial \bar{n}_c}{\partial h}\right)_{m_b} + \left(\frac{\partial \bar{n}_c}{\partial h}\right)^2_{m_b}\right]\sigma^2(h) + \left[\frac{\bar{n}_o^2}{m_b^2} + \frac{2\bar{n}_o}{m_b}\left(\frac{\partial \bar{n}_c}{\partial m_b}\right)_h + \left(\frac{\partial \bar{n}_c}{\partial m_b}\right)^2_h\right]\sigma^2(m_b) \tag{11}$$

Attempts were made to estimate both random and systematic errors in the data. However, some of the more subtle errors such as changes in activity coefficients and liquid junction potential errors were not included. Under the conditions of these experiments these are expected to be small. The variation in liquid junction potential during a given run was *ca.* 0.5 mv and the error is believed to be well below 0.1 mv, or less than 0.4% in h—approximately the random scatter in the data. The errors caused by activity coefficient variations may be estimated from data on the $\gamma_\pm$ of $BaCl_2$ in HCl.[22] Over the composition range 0 m $BaCl_2$–1 m HCl to 0.02 m $BaCl_2$–0.96 m HCl, $\gamma_\pm$ for $BaCl_2$ decreases only 0.7% and $\gamma_\pm$ for HCl decreases only 0.5%. We would expect $BaCl_2$ to approximate $BeCl_2$ satisfactorily indicating that activity coefficient changes should indeed be small.

The partial derivatives $(\partial \bar{n}_c/\partial h)_{m_b}$ and $(\partial \bar{n}_c/\partial m_b)_h$ in eq 11 are estimated from the experimental data $(\partial \bar{n}_o/\partial h)_{m_b}$ and $(\partial \bar{n}_o/\partial m_b)_h$, since $\bar{n}_o$ is approximately equal to $\bar{n}_c$ in the case where a close fit of the data is attained.

(32) H. D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 96–101.
(33) Using eq 4, 5, and 8 the partial derivatives can be evaluated as

$$\left(\frac{\partial F}{\partial m_H}\right)_{h,mb} = -\frac{1}{m_b}$$
$$\left(\frac{\partial F}{\partial m_b}\right)_{h,mH} = -\frac{\bar{n}_o}{m_b} - \left(\frac{\partial \bar{n}_o}{\partial m_b}\right)_h$$
$$\left(\frac{\partial F}{\partial h}\right)_{mb,mH} = \frac{1}{m_b} - \left(\frac{\partial \bar{n}_c}{\partial h}\right)_{mb}$$

since $\bar{n}_c$ is a function of only m_b and h.

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The values for $\sigma(m_H)$, $\sigma(h)$, and $\sigma(m_b)$ are obtained from the observables by application of the propagation of error principle. An analysis of this kind was made on selected data at 60° covering the range of $\bar{n}$ and m_b. In a given run $\sigma^2(F)$ was found to vary no more than 50% in going from an $\bar{n}$ of 0.1 to 1.0 and it was found in different runs to depend largely on the ratio $m_{H,0}/m_b$ (initial free acidity to the total beryllium concentration) which varied between about 0.5 and 1.3. The following expression represents this dependence

$$\sigma(F) = 0.00125 + 0.0075(m_{H,0}/m_b) \qquad (12)$$

Equation 12 was used to weight all of the data at 60 and 25° and the calculation for the best scheme for each value of x in Figure 3 was repeated. Essentially the same relative relationship between schemes was obtained as is shown in Figure 3. The agreement factor calculated using W from eq 9 indicates the agree-ment within some number of units of standard error. For scheme I (Table III) the agreement factor at 60° was 1.1 and at 25°, using the same estimates of error, it was 2.1. This probably indicates that the error at 25° was underestimated. Nevertheless, agreement within a factor of 2 of the estimated error (0.01 unit in $\bar{n}$) is considered good and, therefore, one has no justi-fication for adding additional complexes to the three-species schemes to attempt further minimization of F.

Formation quotients calculated from weighted data at these two temperatures did not differ from the pre-vious values by more than σ in most cases and never by more than 2σ. Thus, the approximation of equal weighting, which is generally made, is found to lead to very minor errors in this case and probably need be examined in detail only in cases where marginal effects might be expected to alter conclusions from the data.

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Raman Study of Chloride and Bromide Complexes of Bismuth(III)[1]

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Raman intensity measurements were made on aqueous solutions containing various ratios of chloride to bismuth. The species $BiCl_4^-$, $BiCl_5^{2-}$, and $BiCl_6^{3-}$ were identified, and their frequencies were determined. In addition, species containing three, two, and possibly one Cl^- per Bi(III) were found. Experiments with bismuth bromide solutions showed that $BiBr_6^{3-}$ is the highest species formed, and not $BiBr_8^{5-}$ as previously postulated. Raman spectra of crystalline solids containing $BiCl_4^-$, $BiCl_5^{2-}$, $BiCl_6^{3-}$, and $BiBr_6^{3-}$ were recorded for comparison. No evidence was found for either hydrolytic hydroxide bridging or halide bridging in solution. A weak polarized band at *ca.* 390 cm^{-1} can be assigned to the symmetric bismuth–water stretching motion. The ClO_4^- ν_3 band at 1120 cm^{-1} reveals a shoulder at 1040 cm^{-1} in dilute bismuth perchlorate solutions. This might be assigned to a BiO^+ species with considerable uncertainty. Structural considerations are pre-sented for all of the complex bismuth halide species identified.

Introduction

Aqueous bismuth(III) chloride and bromide com-plexes have been the subject of considerable investi-gation during the past 10 years. From spectrophoto-metric studies, Newman and Hume[3] established the existence of species $BiCl_n^{3-n}$, where $n = 1–5$. Ahrland and Grenthe[4] found potentiometrically that n assumes values 1–6 for both $BiCl_n^{3-n}$ and $BiBr_n^{3-n}$ and that the fifth complex has an exceptionally wide range of exist-ence. Haight and co-workers[5] have more recently used solubility methods to investigate the bismuth bromide system and the high-ligand-number region of the chloride system. They found $n = 1, 2, 4, 6,$ and 8 for $BiBr_n^{3-n}$ and $n = 4$ and 6 for the two $BiCl_n^{3-n}$ species involved in the highest equilibrium in chloride solutions. Their data indicate that complex species with $n = 3$ or 5 are either absent or present only in extremely low concentration, in conflict with the results of the previous workers. The possibility of eight co-ordination in the highest bromide complex is a further subject for debate. It was with the objects in mind of resolving these questions and extending the current state of knowledge to more concentrated solutions that the present Raman study was initiated.

Compared with most other common techniques used for the characterization of aqueous complex ions, Raman spectroscopy is considerably more direct and reliable. By both treating solution spectra as quan-titatively as possible and using spectra of the appropri-ate solids for comparison, it is possible to determine the stoichiometry and structure of the predominant solution species. Where such studies have been con-ducted in other halide systems, it has frequently been

(1) Sponsored by a research grant from the Office of Saline Water, U. S. Department of the Interior.
(2) Financially supported by a National Science Foundation Predoctoral Fellowship, 1966–1967.
(3) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4576 (1957).
(4) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).
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