solution to produce hydrogen and BF_2NH_2, in accordance with eq. 2

$$BF_3NH_3 + Na \xrightarrow{NH_3} BH_2NH_2 + {}^1/_2H_2 + NaF \quad (2)$$

The stability of BF_3NH_3 in liquid ammonia is in marked contrast to the ammonolytic instability of BCl_3NH_3. The latter compound is so unstable in the presence of ammonia that it has never been isolated; the action of ammonia on BCl_3 invariably produces boron nitrogen compounds with an N/B atomic ratio greater than one.

The X-Ray Pattern of BF_3NH_3.—Laubengayer and Condike[3] first reported spacing and intensity values for BF_3NH_3. Keenan and McDowell[2] reported values which do not agree with those of Laubengayer and Condike. Our spacing and intensity values agree very well with those of Keenan and McDowell. The three sets of data are given in Table II.

Experimental

Preparation and Analysis of BF_3NH_3.—BF_3NH_3 was prepared by the method used by Laubengayer and Condike.[3] Boron trifluoride and ammonia gases were mixed in a resin kettle cooled in an ice-bath. The reaction was allowed to proceed for several hours, after which time the solid salt was scraped out of the kettle and recrystallized from distilled water.

Anal. Calcd. for BF_3NH_3: B, 12.8; NH_3, 20.0; mol. wt., 84. Found: B, 12.8; NH_3, 19.9; mol. wt., 83.

BF_3NH_3 was analyzed for nitrogen by the standard Kjeldahl method. The boron analysis was carried out as follows. The sample was dissolved in water and the solution acidified and allowed to stand for at least one hour at room temperature. The *p*H of an aliquot was then adjusted to 6.3, mannitol was added, and the solution titrated with standard base back to a *p*H of 6.3. If the original solution was not allowed to stand for at least one hour, the results were invariably low. If the titration was taken to *p*H 9, the results invariably were high.

TABLE II

X-RAY DATA FOR BF_3NH_3

Laubengayer and Condike		Keenan and McDowell		This work	
d, Å.	Intensity	*d*, Å.	Intensity	*d*, Å.	Intensity
4.22	S	4.87	M	4.87	M
				4.62	M
3.88	S	4.01	S	4.04	S
3.60	M	3.65	S	3.69	S
3.00	M	3.37	S	3.37	S
2.55	M	2.87	M	2.84	M
2.19	W	2.72	S	2.73	M
		2.45	M	2.44	W
		2.34	M	2.35	W
		2.24	M	2.23	M
		1.97	W	1.97	W
		1.81	M	1.81	M
				1.76	W
		1.65	M	1.65	W

Melting Point, Molecular Weight and X-Ray Data.—The melting point of BF_3NH_3 samples was determined by dropping very small crystals of the sample on the hot stage of a Fisher melting point apparatus and noting the temperature at which they melted within one second after touching the stage. Although this method gives results which are somewhat high, it was found that the values were reproducible within a degree. Laubengayer and Condike obtained a melting point of 163° on a Dennis–Shelton melting point bar.

Molecular weights were determined cryoscopically in water.

The X-ray powder photographs were taken on a North American Philips diffraction unit using filtered Cu K_α radiation.

Acknowledgments.—I am indebted to Mr. Willard M. Johnston for boron and nitrogen analyses, to Mr. Albert F. Biddle for X-ray analyses, to Dr. Russell B. Eaton for much helpful advice, and to the Pigments Department for permission to publish this work.

WILMINGTON, DELAWARE

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[3] A. W. Laubengayer and G. F. Condike, THIS JOURNAL, **70**, 2274 1948).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Equilibria of the Metastable Crystalline Form of Beryllium Hydroxide. Be(OH)₂, in Hydrochloric Acid, Perchloric Acid and Sodium Hydroxide Solutions at 25°

BY R. A. GILBERT[1] AND A. B. GARRETT

RECEIVED APRIL 5, 1956

The solubility of beryllium hydroxide has been determined in dilute acid and base at 25 ± 0.02° and the hydrolysis of beryllium chloride has been measured. The principal equilibria present in these solutions are believed to be the following: $Be(OH)_2(s) + OH^- \rightleftarrows HBeO_2^- + H_2O$, $K_2 = 3.2 \times 10^{-3}$; $Be(OH)_2(s) + 2OH^- \rightleftarrows BeO_2^= + 2H_2O$, $K_3 = 2.0 \times 10^{-3}$ $Be(OH)_2(s) + 2H^+ \rightleftarrows Be^{++} + 2H_2O$, $K_5 = 7.3 \times 10^6$; $x Be(OH)_2(s) + Be^{++} \rightleftarrows Be(OBe)_x{}^{++} + xH_2O$, moles Be^{++}/moles $Be_2O^{++} = 0.60$; $2Be^{++} + H_2O \rightleftarrows Be_2O^{++} + 2H^+$, $K_8 = 1.6 \times 10^{-7}$; $Be(OH)_2(s) \rightleftarrows HBeO_2^- + H^+$, $K_9 = 3.2 \times 10^{-17}$; $Be(OH)_2(s) \rightleftarrows BeO_2^= + 2H^+$, $K_{11} = 2.0 \times 10^{-31}$; $Be(OH)_2(s) \rightleftarrows Be^{++} + 2OH^-$, $K_1 = 7.3 \times 10^{-22}$. The hydrolysis constant given is believed to represent an upper limit in view of the polynuclear ions that are reported to be present.

The purpose of this investigation was to obtain data on the equilibria of the metastable form of crystalline beryllium hydroxide in dilute solutions of sodium hydroxide, hydrochloric acid and perchloric acid. Such data make possible (1) the determination of the character of the ions existing in dilute acid and alkali and (2) the evaluation of the free energies of formation of such ions and the evaluation of the solubility product of the hydroxide.

Many early investigators attempted to determine the exact constitution of precipitated beryllium hydroxide. Haber and Van Oordt[2] showed that the freshly precipitated hydroxide is an amorphous jelly-like material which is transformed with time

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[1] Taken from the dissertation presented by Robert A. Gilbert to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1953.

[2] F. Haber and B. Van Oordt, *Z. anorg. Chem.*, **38**, 377 (1940).

into a much less soluble modification. In later work, Fricke and Humme[3] showed that there are actually two insoluble forms. The first they called a metastable crystalline α-form. This can be changed by months of standing into a more stable β-form which is less soluble in alkali. The β-form can also be prepared by the slow hydrolysis of an alkali beryllate solution or by crystallization of the hydroxide from hot concentrated alkali.

The solubility of beryllium hydroxide in alkaline solution has been studied by Bleyer and Kaufman[4] who determined the solubility of three forms, which they called A, B and C, in potassium hydroxide solutions at 18°, and by Fricke and Humme[4] who measured the solubility of the β form of the hydroxide. However, all these measurements were made in alkali solutions whose initial concentrations were 0.5 molar or greater.

Data are reported here to show the complete record of the behavior of beryllium hydroxide in dilute acid and basic solutions.

Procedure

The general procedure is similar to that used by Garrett and Heiks[5] and by Gayer and Garrett.[6]

Water.—Triply distilled water was used. It was freed of dissolved carbon dioxide by boiling and was then stored under nitrogen.

Sodium Hydroxide Solutions.—Baker and Adamson Reagent sodium hydroxide pellets were dissolved in distilled water; barium hydroxide solution was added in slight excess to precipitate all the carbonate. The solutions were standardized by titrating against standard hydrochloric acid using phenolphthalein as an indicator.

Beryllium Chloride Solutions.—The beryllium solution used for precipitation of beryllium hydroxide was prepared by dissolving 20 g. of fused beryllium (99.5%), obtained from Eimer and Amend, in dilute hydrochloric acid. The resulting clear solution was stored under nitrogen in an all glass preparation train.

To determine the color-concentration standard for the analysis procedure, a standard solution containing 0.85 μg. of beryllium per milliliter was prepared from a stock solution obtained by dissolving a small sample of high purity beryllium in dilute hydrochloric acid. The concentration of the master solution was determined by analysis using the method described in Scott.[7]

The stock solution for the hydrolysis measurements was prepared by carefully dropping distilled beryllium chloride into boiled distilled water in a small closed system such that loss of hydrogen chloride was prevented. The various concentrations were prepared by diluting this solution with boiled distilled water.

Hydrochloric Acid Solutions.—These were prepared from C.P. reagent and standardized by a micro Volhard method using nitrobenzene as the coagulant.

Perchloric Acid Solutions.—These were prepared by dilution from a standardized stock solution initially made from C.P. reagent.

Other Reagents.—An alcoholic solution of Alkanet root was prepared by extracting portions of the powdered root with 95% alcohol until a solution of the desired strength was obtained. All colorimetric solutions were buffered with 0.1 *M* boric acid in 10% glucose.

Beryllium Hydroxide.—It was found that beryllium hydroxide became colloidal when precipitated in dilute solutions and could not be washed without considerable loss. All preparations were made, therefore, by adding strong base to dilute solutions of beryllium chloride made strongly acidic by the addition of C.P. hydrochloric acid.

The freshly precipitated hydroxide was then transferred to a nitrogen-filled washing flask. The mixture was boiled for several minutes and allowed to cool overnight. The hydroxide, which precipitates initially as a gelatinous material, settles out after this treatment as a fine white powder. This powder was washed with hot distilled water until the *p*H of two successive washings remained the same. In addition, a flame test showed the absence of sodium ions.

The powder at this point was found by X-ray analysis to be metastable crystalline (α-form) beryllium hydroxide with a small amount of amorphous material remaining. However, after careful drying of this material, the X-ray data indicated no traces of amorphous material. This high purity crystalline material was used for all the solubility measurements in acid solutions. However, since the transformation from the amorphous to crystalline state takes place rapidly in alkaline solutions, the washed slurry was used to make up base samples.

Equilibrations.—Two 180-ml. samples contained in 200-ml. round-bottom flasks were always prepared at each concentration of acid or alkali. For the concentrated alkali solutions, the insides of the flasks were coated with paraffin and the flasks were sealed with paraffin-filled glass caps.

One series of samples was agitated in a thermostat at 35° for five to seven days, then transferred to the thermostat at 25 ± 0.02° for an additional seven days. A duplicate series of samples was placed directly in the 25° thermostat for seven days. In this way, the equilibrium was approached from supersaturation and undersaturation. Both values checked within limits of experimental error.

Sedimentation.—At the end of the agitation period, the flasks were clamped upright in the 25° thermostat and allowed to sediment for at least seven days.

Removal of Samples.—The flasks were opened and the contents removed under nitrogen pressure through a sintered glass filter into a glass stoppered bottle.

Measurement of Hydrogen Ion Concentration.—As soon as the samples were removed, the *p*H was obtained using a Beckman portable a.c. glass electrode. The meter was standardized with potassium acid phthalate–sodium hydroxide buffer at *p*H 4, with disodium phosphate–monosodium phosphate at *p*H 7 and with boric acid–sodium hydroxide buffer at *p*H 10.

Analysis for Beryllium.—The procedure used was that described by A. L. Underwood.[8] The colorimetric measurements were made with a Lumetron colorimeter, model 400-A, using an extract of Alkanet root to produce the colored complex. With this method, 0.5 to 8 μg. of beryllium could be determined in a 10-ml. sample.

Duplicate aliquots of the solutions obtained after equilibration were taken for analysis. Reproducible values for the solubility were found for each sample. All values were the average of three determinations. The analyses were reproducible to ±1.5%.

The Data

The data are collected in Tables I, II, III and IV. The change in solubility at the neutral point is indicated in Figure 1. The solubility of beryllium hydroxide in water is too low to be measured, so the curves for the acid and hydroxide solubilities were extrapolated to zero $Be(OH)_2$ concentration.

General Equilibria.—In general, the possible equilibria of beryllium hydroxide in neutral, acidic, and alkaline solutions may be:

$$Be(OH)_2(s) \rightleftarrows Be^{++} + 2OH^- \qquad (1)$$

$$Be(OH)_2(s) + OH^- \rightleftarrows HBeO_2^- + H_2O \qquad (2)$$

$$Be(OH)_2(s) + 2OH^- \rightleftarrows BeO_2^= + 2H_2O \qquad (3)$$

$$Be(OH)_2(s) + H^+ \rightleftarrows Be(OH)^+ + H_2O \qquad (4)$$

$$Be(OH)_2(s) + 2H^+ \rightleftarrows Be^{++} + 2H_2O \qquad (5)$$

$$Be^{++} + xBe(OH)_2 \rightleftarrows Be(OBe)_x^{++} + xH_2O \qquad (6)$$

$$Be^{++} + H_2O \rightleftarrows Be(OH)^+ + H^+ \qquad (7)$$

$$2Be^{++} + H_2O \rightleftarrows Be_2O^{++} + 2H^+ \qquad (8)$$

$$Be(OH)_2(s) \rightleftarrows HBeO_2^- + H^+ \qquad (9)$$

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(3) R. Fricke and H. Humme, *Z. anorg. Chem.*, **178**, 400 (1929).

(4) B. Bleyer and S. W. Kaufman, *ibid.*, **82**, 71 (1913).

(5) A. B. Garrett and R. Heiks, THIS JOURNAL, **63**, 562 (1941).

(6) K. H. Gayer and A. B. Garrett, *ibid.*, **71**, 2973 (1949).

(7) W. W. Scott, "Standard Methods of Chemical Analysis," 5th Edition, Volume 1, pp. 139–142.

(8) A. L. Underwood, United States Atomic Energy Commission, Report MDDC 1569.

$$HBeO_2^- \rightleftarrows BeO_2^= + H^+ \qquad (10)$$

$$Be(OH)_2(s) \rightleftarrows BeO_2^= + 2H^+ \qquad (11)$$

Equilibria in Basic Solutions.—Each constant for the basic solubility, when calculated independently for equations 2 and 3, showed a trend indicating that either both reactions determine the solubility of beryllium hydroxide in sodium hydroxide or some additional reaction may be occurring. However, assuming that the increase in solubility can be accounted for by these two reactions we can represent the total solubility as

$$S_{Be(OH)_2} = m_{Be(OH)_2} + K_2 \frac{m_{OH^-} \times \gamma_{OH^-}}{\gamma_{HBeO_2^-}} \times \frac{1}{a_{H_2O}} + K_3 \frac{m^2{}_{OH^-} \times \gamma^2{}_{OH}}{\gamma_{Be_2^=} \times a^2{}_{H_2O}}$$

where

$$K_2 = \frac{m_{HBeO_2^-} \times \gamma_{HBeO_2^-}}{m_{OH^-} \times \gamma_{OH^-}} \times a_{H_2O}$$

$$K_3 = \frac{m_{BeO_2^=} \times \gamma_{BeO_2^=}}{m^2{}_{OH^-} \times \gamma^2{}_{OH^-}} \times a^2{}_{H_2O}$$

At low and moderate ionic strengths, the ratio $\gamma_{OH^-}/\gamma_{HBeO_2^-}$ can be expected to remain near unity. In addition, $\gamma^2{}_{OH^-}/\gamma_{BeO_2^=}$ can be replaced by $\gamma^4{}_{NaOH}/\gamma^3{}_{Na_2BeO_2}$ and $\gamma^3{}_{Na_2BeO_2}$ further replaced by $\gamma^6{}_{NaHBeO_2}$. This follows from the fact that, at low ionic strengths where the Debye–Hückel limiting law is obeyed, the activity coefficient of a 1–2 electrolyte is the square of that of a 1–1 electrolyte at the same ionic strength and that where ions are of nearly the same size as must be true with beryllate and biberyllate ions since they differ only by a proton, this relationship will continue to hold when the limiting law has broken down and terms for the ionic radius are included. This relationship was called to attention by several authors[9] and shown by Walker, Bray and Johnston to hold quite accurately for carbonate and bicarbonate solutions even up to ionic strengths of 2.

Since the solubility of beryllium hydroxide in pure water was below that which could be determined by the method of analysis used (*i.e.*, below 1 × 10^{-7} mole/1000 g. H_2O), it will therefore be neglected in the calculations for K_2 and K_3 and the total solubility equation simplifies to

$$S_{Be(OH)_2} = K_2 \frac{m_{OH^-}}{a_{H_2O}} + K_3 \frac{m^2{}_{OH^-}}{\gamma^2{}_{NaOH}} \times \frac{1}{a^2{}_{H_2O}} \qquad (A)$$

The values of K_2 and K_3 were evaluated from the data by the method of least squares. The method is applicable in this case because the activity of water and the activity coefficient of sodium hydroxide can be considered functions only of the initial molality of the sodium hydroxide since beryllium hydroxide is only slightly soluble in alkali and the initial concentrations of alkali were changed less than one per cent. by solution of the hydroxide. The values for the a_{H_2O} and γ_{NaOH} were obtained from reliable data.[10]

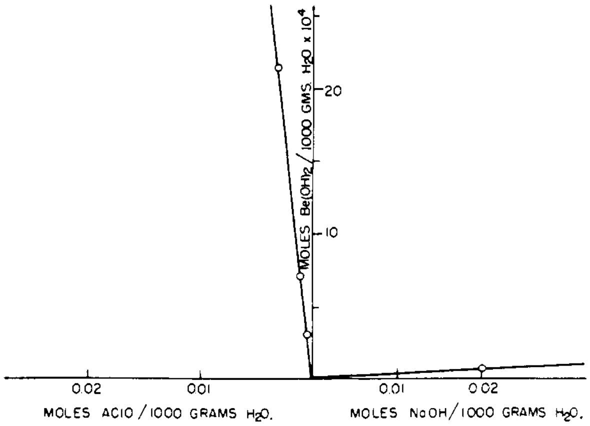

Fig. 1.—The change in solubility of $Be(OH)_2$ at the neutral point.

From the least squares treatment, K_2 was found to be 3.2 × 10^{-3} and K_3 = 2.0 × 10^{-3}. An indication of the limiting values of K_2 and K_3 was obtained by calculating each constant assuming that the opposite reaction did not take place and then plotting, in Fig. 2, these values against the alkali concentration. Extrapolation of the K_2

TABLE I

THE SOLUBILITY OF CRYSTALLINE METASTABLE BERYLLIUM HYDROXIDE IN SOLUTIONS OF SODIUM HYDROXIDE AT 25°

Moles of NaOH/1000 g. H_2O	Moles $Be(OH)_2$/1000 g. H_2O measured	Moles $Be(OH)_2$/1000 g. H_2O calcd. from eq. A
0.0197	7.5 × 10^{-5}	6.32 × 10^{-5}
.0391	1.16 × 10^{-4}	1.28 × 10^{-4}
.0589	1.46 × 10^{-4}	1.97 × 10^{-4}
.0709	1.86 × 10^{-4}	2.40 × 10^{-4}
.0790	2.22 × 10^{-4}	2.70 × 10^{-4}
.0871	3.51 × 10^{-4}	3.00 × 10^{-4}
.0981	2.40 × 10^{-4}	3.43 × 10^{-4}
.1531	6.48 × 10^{-4}	5.69 × 10^{-4}
.2506	1.20 × 10^{-3}	1.04 × 10^{-3}
.3565	1.65 × 10^{-3}	1.65 × 10^{-3}
.4512	2.15 × 10^{-3}	2.28 × 10^{-3}
.7130	4.50 × 10^{-3}	4.46 × 10^{-3}

TABLE II

THE SOLUBILITY OF CRYSTALLINE METASTABLE BERYLLIUM HYDROXIDE IN HYDROCHLORIC AND PERCHLORIC ACIDS AT 25°

Moles acid/1000 g. H_2O	Moles $Be(OH)_2$/1000 g. H_2O
$HClO_4$—0.0005	0.000322
$HClO_4$— .0010	.000695
HCl — .0010	.000708
$HClO_4$— .0030	.00210
HCl — .0030	.00220
$HClO_4$— .0050	.00371
HCl — .0050	.00404
$HClO_4$— .0065	.00510
HCl — .0065	.00510
$HClO_4$— .0080	.00647
HCl — .0080	.00650
$HClO_4$— .0100	.00814
HCl — .0100	.00813
$HClO_4$— .0120	.00982
HCl — .0120	.00967

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[9] A. C. Walker, U. B. Bray and J. Johnston, THIS JOURNAL, **49**, 1235 (1927); H. L. Johnston and L. H. McDowell, *ibid.*, **58**, 2009 (1936).

[10] G. Akerlof and G. Kegeles, *ibid.*, **62**, 620 (1940); H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 560.

TABLE III

EQUILIBRIA OF THE SOLUBILITY OF CRYSTALLINE METASTABLE BERYLLIUM HYDROXIDE IN ACID SOLUTIONS AT 25°

Moles of acid/1000 g. H_2O $\times 10^4$	Activity of H^+ from glass electrode $\times 10^4$	Moles of acid used up in forming Be^{++} $\times 10^4$	Calcd. moles Be^{++} assuming eq. 5 only $\times 10^4$	Total beryllium in soln. (measured) $\times 10^4$	Moles of polymerized beryllium in soln. calcd. as $Be(OBe)^{++}$ $\times 10^4$	Moles of beryllium at equil. as simple ion Be^{++} $\times 10^4$	$\frac{a_{Be^{++}}}{a_{H^{+2}}}$ $\times 10^{-6}$	$K_5 = \frac{\text{moles } Be^{++}}{\text{moles } Be_2O^{++}}$
5.0	0.0478	4.95	2.48	3.22	0.74	1.74	7.6	2.35
10.0	.0617	9.94	4.97	7.02	2.05	2.92	7.7	1.42
30.0	.0981	29.9	14.9	21.5	6.6	8.3	8.6	1.26
50.0	.132	49.9	24.9	38.8	13.9	11.0	6.3	0.79
65.0	.141	64.8	32.4	51.0	18.6	13.8	6.9	0.74
80.0	.155	79.8	39.9	64.8	24.9	15.0	6.3	0.60
100.0	.162	99.8	49.9	81.3	31.4	18.5	7.0	0.59
120.0	.170	119.8	59.9	97.4	5.57	22.4	7.7	0.60

TABLE IV

THE HYDROLYSIS OF BERYLLIUM CHLORIDE AT 25°
ASSUMING $2Be^{++} + H_2O \rightleftharpoons Be_2O^{++} + 2H^+$

Initial concn. of the soln.	a_{H^+}	Concn. of Be^{++} moles/1000 g. H_2O	γ for Be^{++} and Be_2O^{++}	Concn. Be_2O^{++} moles/1000 g. H_2O	$K_8 \times 10^7$ $\frac{a_{Be_2O^{++}} \times a^2_{H^+}}{a^2_{Be_2O^{++}}}$
0.081	1.44×10^{-3}	0.080	0.812	7.9×10^{-4}	3.2
.0505	9.52×10^{-4}	.0494	.828	5.18×10^{-4}	2.3
.0404	7.57×10^{-4}	.0396	.834	4.11×10^{-4}	1.8
.0202	4.78×10^{-4}	.0197	.851	2.57×10^{-4}	1.8
.0101	3.02×10^{-4}	.0098	.864	1.62×10^{-4}	1.8
.0081	2.39×10^{-4}	.0079	.870	1.27×10^{-4}	1.3
.00505	1.66×10^{-4}	.00485	.881	8.83×10^{-5}	1.2
.00202	9.52×10^{-5}	.00193	.900	5.01×10^{-5}	1.4

curve to $m_{NaOH} = 0$ gives a limiting value of $K_2 > 2.5 \times 10^{-3}$ and $<3.5 \times 10^{-3}$ which justifies the value obtained above. A similar extrapolation of the K_3 curve toward $m_{NaOH} = \infty$ shows a limiting value of $K_3 > 1 \times 10^{-3}$ and $<3 \times 10^{-3}$ which again justifies the value obtained above. The graph also shows the lack of constancy of the K's when calculated on this basis and indicates therefore that neither reaction (2) alone nor (3) alone is sufficient to account for the solubility of beryllium hydroxide in sodium hydroxide. The ability to fit the solubility curve with these two equations strongly supports our assumption that in the concentration range investigated these are the reactions that account for the increase in solubility.

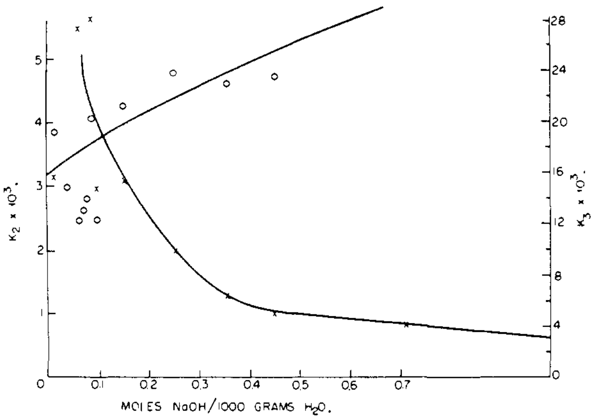

Fig. 2.—Equilibrium constants for equations 2 and 3 plotted as a function of alkali concentration: O, K_2 values; X, K_3 values.

For reaction 2

$$K_2 = 3.2 \times 10^{-3} \text{ and } \Delta F^\circ = 3400 \text{ cal.}$$

and for reaction 3

$$K_3 = 2.0 \times 10^{-3} \text{ and } \Delta F^\circ = 3700 \text{ cal.}$$

The evaluation of the ionization constants for reactions 9 and 11 give

$$K_9 = \frac{K_2 \times K_w}{a_{H_2O}} = 3.2 \times 10^{-17}$$

and

$$K_{11} = \frac{K_3 \times K_w^2}{a^2_{H_2O}} = 2.0 \times 10^{-31}$$

Equilibria in Acid Solutions.—In preliminary experiments using hydrochloric acid, it became apparent that more beryllium was being dissolved than could be explained by the reaction shown by equation 5. To determine whether this additional solubility was due to the formation of soluble complexes involving the chloride ion as a bridge, samples were prepared using hydrochloric and perchloric acid. Kilpatrick and Pokras,[11] in their paper on the acid dissociation of the aquescandium ions pointed out that the large size of the perchlorate ion prevents complexes of this type. If additional beryllium was being carried into solution by this mechanism, the solubility in perchloric acid should be lower than that in hydrochloric acid.

It is immediately apparent from the data in Table II that no chloride bridging occurs since the solubilities in hydrochloric and perchloric acid solubilities agree within the limits of experimental error.

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[11] M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **100**, 85 (1953).

The solubility in acid seems best explained by reactions (5) and (6).

The ability of an aqueous solution of any soluble salt of beryllium to dissolve considerable amounts (up to several molecular proportions) of beryllium oxide or hydroxide is well known[12] and Mattock[13] has made a mathematical analysis of the problem.

It can be seen from Table III that the amounts of beryllium in solution could not be explained by equation 5 alone since more beryllium is in solution than could be dissolved by the initial amount of acid. Furthermore, reaction (4) could explain the high solubility but does not explain the low activity of H^+ obtained from the *p*H measurements at equilibrium.

The calculations in Table III were made in the following manner. The amount of acid remaining at equilibrium was subtracted from the initial concentration to obtain the quantity used up in forming the Be^{++} ion. Making the assumption that the reaction indicated by equation 5 is the initial one, the amount of acid used up was divided by two to obtain the concentration of the Be^{++} ion. This was subtracted from the total beryllium to obtain the additional amount of beryllium in solution. Mattock pointed out that there are a large number of polynuclear species of uncertain composition present in beryllium solutions. In the present study the formation of species of the type (Be)$(BeO)_x^{++}$ or $Be(Be(OH)_2)_x^{++}$ is assumed and the calculations carried out using the simplest case with $x = 1$. Using these assumptions, the moles of Be^{++} and Be_2O^{++} at equilibrium were calculated. A value of K_5 was then calculated for equation 5

$$K_5 = \frac{a_{Be^{++}}}{a^2_{H^+}} = 7.3 \times 10^6$$

$$\Delta F^\circ = -9400 \text{ cal.}$$

From this a value for K_1 may be obtained

$$\begin{aligned} K_1 &= a_{Be^{++}} \times a^2_{OH^-} = K_5 \times K_w^2 \\ &= 7.3 \times 10^6 \times 1 \times 10^{-28} \\ &= 7.3 \times 10^{-22} \end{aligned}$$

These values of K_5 and K_1 are obviously lower limits. More accurate values for both K_5 and K_1 could be obtained if the polynucleation in acid solutions could be predicted quantitatively.

When the ratio of moles Be^{++} to moles Be_2O^{++} at equilibrium is calculated from the data, the ratio decreases and approaches a constant value of 0.60. This means that, using K_5 and this ratio, the amount of beryllium hydroxide dissolved by a given concentration of acid can be calculated if the *p*H of the resulting solution can be obtained.

The Hydrolysis of Beryllium Chloride Solutions.—It was of interest to explore the reactions in hydrolysis although, as was concluded by Mattock, since only the $[H^+]$ parameter is determinable experimentally, the complete analysis of the system is rendered speculative. In view of this conclusion by Mattock, the data obtained in this phase of the investigation were calculated on the basis that the hydrolysis proceeds by reaction 8 postulated by Prytz.[14]

$$K_8 = \frac{a^2_{H^+} \times a_{Be_2O^{++}}}{a^2_{Be^{++}}}$$

In evaluating K_8, the following assumptions were made: 1, the activity coefficients for the Be^{++} and Be_2O^{++} ions are equal. 2. The molar concentration of Be_2O^{++} is one half the molar concentration of H^+. The latter value was obtained from the activities by using the activity coefficients of hydrochloric acid in strontium chloride solutions as given by Harned and Owen.[10]

It can be seen from Table IV that there is a trend in K_8 toward larger values in concentrated solutions but that in the more dilute solutions K_8 does approach constancy.

The average value of K_8 for solutions of 0.0505 molar or less is 1.6×10^{-7} giving

$$\Delta F^\circ = 9300 \text{ cal.}$$

The value of K_8 checks well with those listed by Prytz for beryllium bromide and iodide which were 5.4×10^{-7} and 4.0×10^{-7}, respectively. If the interpretation of Mattock is correct, these values represent the upper limit of the hydrolysis constants.

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COLUMBUS, OHIO

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