an equimolar mixture of Th + ThO$_2$ showed, at 1850°, the almost complete disappearance of the ThO$_2$ and Th diffraction lines and the appearance of a new set of diffraction lines. On cooling this new set of diffraction lines disappeared and the Th and ThO$_2$ pattern reappeared. The new diffraction lines could be indexed with a face-centered cubic pattern with a_0 = 4.31 Å. Interplanar distances are given in Table III. This new diffraction pattern is that

TABLE III

X-RAY DIFFRACTION LINES OF ThO AT 1850°

(a_0 = 4.31 Å.)

sin$^2\theta$	d in Å.	Indices h,k,l
0.0967	2.47	1,1,1
.1280	2.14	2,0,0
.2540	1.52	2,2,0
.3491	1.30	3,1,1
.3785	1.25	2,2,2
.5238	1.06	4,0,0
.6229	0.974	3,3,1

of thorium monoxide, indicating that above 1850° the reaction ThO$_2$(s) + Th(l) $\rightleftarrows$ 2ThO(s) goes to the right.

Conclusion.—We can now answer the last question, what happens on a thoriated filament, when it is activated at 2600°K., then cooled to 1800–1900°K. At 2600°K. some of the ThO$_2$ dissociates to gaseous and solid ThO, which disproportionates to Th and ThO$_2$ on cooling to 1900°K. For the heat of reduction of ThO$_2$, Langmuir[2] gave 138 kcal. The heat of formation of ThO$_2$ from Th and O$_2$ is 293 kcal.[14] Thus the value of 138 kcal. is very probable for the reaction

$$ThO_2(s) \longrightarrow ThO(s) + {}^1\!/_2 O_2(g)$$

Acknowledgment.—We wish to thank Robert W. Mattox and David P. Dingledy, who helped with the vapor-pressure measurements.

(14) E. J. Huber, C. E. Holley, Jr., and E. H. Meierkord, THIS JOURNAL, **74**, 3406 (1952).

COLUMBUS, OHIO

The Hydrolysis and Aggregation of the Beryllium Ion
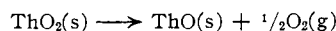
BY G. MATTOCK[1]

The complexity of aqueous solutions of beryllium is shown by a discussion of previous work, and the system is examined experimentally by means of the glass electrode in perchlorate medium. Use of a general expression involving all possible ion species (neglecting any perchlorate complex formation) enables calculation of the following constants from the pH data: [BeOH$^+$][H$^+$]/[Be^{2+}] = (0.3 ± 0.1) × 10^{-6}; [Be$_2$OH^{3+}][H$^+$]/[Be^{2+}]^2 = (0.31 ± 0.06) × 10^{-3}; in a 1.0 molar perchlorate medium at 25 + 0.02°. The pH characteristics of the system are discussed in terms of a number of possible combinations of polynuclear species, and it is concluded that description by means of only a few ionic types is incomplete. It is shown that a large number of different ionic species of increasing polynuclear complexity co-exist in hydrolyzed solutions of beryllium.

It has long been known that beryllium ions are hydrolyzed and aggregated in aqueous solution. Thus Britton,[2] in 1925, considered that beryllium salt solutions are colloidal in nature, while shortly afterwards Sidgwick and Lewis[3] suggested the existence of [Be(OBe)$_4$]$^{2+}$ aggregates. Milda Prytz[4] inferred that addition of sodium hydroxide to BeSO$_4$ and BeCl$_2$ causes stagewise hydrolysis, with formation of BeOH$^+$ and Be$_2$O^{2+}. Assuming that the predominant hydrolysis reaction is one involving condensation to Be$_2$O^{2+}, she obtained average values for [Be$_2$O^{2+}][H$^+$]^2/[Be^{2+}]^2 of 5.9 × 10^{-7} and 4.4 × 10^{-7} for bromide and iodide solutions respectively.[5]

J. Bjerrum[6] examined the hydrolysis in ammonium nitrate–ammonia buffers, and explained the variation in Prytz's constants with metal ion concentration as being due to the presence of a Be$_2$OH^{3+} ion. Prytz's assumption of dimerization being the only reaction at the point of half-neutralization to the BeOH$^+$ turning point (from which region the

data were drawn) is rather arbitrary, however, and Bjerrum[6] mentions the possibility of a trinuclear species. On the other hand, Schaal and Faucherre[7] postulate a [Be$_4$O$_2$]$^{4+}$ (or [Be$_4$(OH)$_4$]$^{4+}$) ion as being involving in the hydrolysis.

Recently the ion exchange of beryllium perchlorate solutions was studied[8] by means of radioactive tracers. At an ionic strength of 0.1 and a temperature of 37°, polymerization of beryllium was observed in 10^{-5} molar solutions at a pH 4.5. At pH 5.5 the solutions were colloidal. The effect of time, pH, electrolytes, solvents and stirring on the coagulation of carrier-free Be^8 at 10^{-9} molar concentrations in dilute nitric acid have also been studied.[9]

This survey of the literature shows that beryllium ions readily hydrolyze in solution and form condensed species containing more than one beryllium atom. It appears that as the concentration of beryllium increases and the acidity decreases, these condensation products increase in size to become colloidal and finally to precipitate. Apart from the work of Prytz, no quantitative idea of the tendencies to hydrolyze and aggregate is available, however, and it was considered worthwhile to ob-

(1) Present address: Chemistry Department A. Technical University of Denmark, Copenhagen, Denmark.

(2) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2120 (1925).

(3) N. V. Sidgwick and N. B. Lewis, *ibid.*, **128**, 1287 (1926).

(4) M. Prytz, *Z. anorg. Chem.*, **180**, 355 (1929); see also *ibid.*, **231**, 238 (1937); W. Henkeshoven and A. Winkel, *ibid.*, **213**, 1 (1933).

(5) M. Prytz, *ibid.*, **197**, 103 (1931).

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941, p. 176.

(7) R. Schaal and J. Faucherre, *Bull. soc. chim., France*, **14**, 927 (1947); see also M. Teyssèdre and P. Souchay, *ibid.*, **18**, 945 (1951).

(8) I. Feldman and J. R. Havill, THIS JOURNAL, **74**, 2337 (1952).

(9) G. K. Schweitzer and J. W. Nehls, *ibid.*, **75**, 4354 (1953).

tain such information. For reasons of mathematical complexity made clear in the Discussion, the equilibrium data obtained were limited to the simplest species.

Experimental

Analytical grade chemicals were used throughout wherever possible. The stock beryllium solution was prepared from Fisher and Amend C.P. beryllium nitrate. To the nitrate solution freshly filtered dilute ammonia was carefully added, and the middle fraction of the precipitate collected. After washing thoroughly by decantation with 1% sodium perchlorate, the hydrous oxide was redissolved in dilute perchloric acid, and the process of precipitation, washing, and dissolution repeated. After 3 such treatments, the final precipitate was washed well with freshly distilled water (used throughout), and dissolved in a known quantity of perchloric acid. The solution gave negative results for iron by the thiocyanate test and aluminum by the sensitive oxine test of Gentry and Sherrington.[10] The total beryllium concentration was determined in the usual way by precipitation with freshly filtered ammonia, washing the precipitate with 1% ammonium nitrate solution, and ignition to BeO. The pH of the stock solution was about 1; identical experimental results were subsequently obtained using fresh or old solutions, indicating that the depolymerization process of solution in acid was effected very rapidly. Moreover, under these pH conditions, the beryllium is present entirely as Be^{2+} (hydrolysis does not commence until around pH 2.6).[8]

The solutions used in all the experiments were at a constant ionic strength of $[ClO_4^-] = 1.0$ molar, this being achieved by suitable additions of sodium perchlorate solution, prepared from recrystallized G. F. Smith $NaClO_4 \cdot H_2O$. No chloride could be detected in the perchlorate. All measurements were made at 25 ± 0.02. A Beckman model G pH meter and glass electrode assembly were employed to determine the pH to ± 0.01 unit; in high pH regions (>10) an alkali-resistant glass electrode was used. From these pH measurements the hydrogen ion concentration was calculated from the definition $pH = -\log [H^+]$ (the standardizing solutions being 1.0 M in perchlorate). The results are thus referred to an ionic strength 1.0 in perchlorate. Changes in activity coefficients due to replacement of hydrogen ions by sodium ions were negligible, since in the experimental region actually used for calculation of the results (see below) this replacement was quite small.

It was found, in accordance with the experience of previous workers,[11] that potassium chloride could not be used

NaOH (arbitrary scale).

Fig. 1.—Characteristics of the beryllium titration curve: (a) "blank" acid (HClO₄) titration; (b) beryllium titration (broken lines represent initial characteristics, before aging).

(10) C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 432 (1946).

(11) H. M. Hershenson, M. E. Smith and D. A. Hume, This Journal, **75**, 507 (1953).

in the cell liquid junction, owing to precipitation of $KClO_4$ causing irregularities. Accordingly, a bridge containing M ammonium nitrate in a 2% agar gel was employed throughout: this was found to be completely satisfactory.

It was necessary to know the free acid concentration of the beryllium solutions. After experimental trial of methods that had previously been adopted by other workers in similar situations,[12] a more satisfactory approach was found. The experimental technique used involved the construction of an alkali titration curve of the beryllium (see below). Perchloric acid solutions, at $[ClO_4^-] = 1.0$, were prepared, and their titration curves obtained in a similar fashion. By a method of trial and error the blank acid solution which gave the curve closest to the beryllium curve up to about pH 2-2.5 was found, and its complete curve used for comparison calculations with that of the corresponding beryllium solution.

The pH of the beryllium solutions was varied by addition of carbonate-free sodium hydroxide (stored under soda lime). The "static" titration technique was adopted: to a fixed volume of stock beryllium solution, appropriate quantities of sodium perchlorate and water were added, followed by the required quantity of sodium hydroxide to give a total volume of 100 ml. This solution (the constituents of which were previously at about 25°) was immediately transferred to the thermostat, and pH readings taken at definite time intervals after temperature equilibrium had been established ($\sim$ 15 min.). A titration curve at a given beryllium concentration was then constructed from the equilibrium pH values of a series of such solutions.

Results

The general shape of a typical beryllium titration curve is shown in Fig. 1, illustrating its step-like character. The first step is due to neutralization of the "free acid" in the solution. Equilibrium was established before measurement in solutions up to the second step (which would presumably theoretically correspond to complete formation of BeOH⁺), but after this stage complete equilibrium was only attained after a period of about two months. During this time, the pH dropped slowly; that this was not due to carbon dioxide absorption was shown by storing some samples under soda lime. No difference in the equilibrium value was observed between those solutions which had been protected from carbon dioxide and those which had not. Precipitation occurred between the second and third steps, but the treatment did not require data from this region. Beyond the third step, presumably corresponding to theoretical formation of $Be(OH)_2$, it was found extremely difficult to obtain reproducible results, due, possibly, to the large pH changes which occurred on small additions of alkali. Elsewhere, reproducibility was readily achieved.

Treatment of Data.—The apparent complexity of beryllium solutions[2-9] underlines the need for analysis in the most general way, without neglecting any possible ion species. A suitable treatment is that of Ahrland,[12b] and this has been applied to the present data.

The possible metal hydroxyl ion complexes in an aqueous solution of metal ion M where no other anion complex formation occurs may be written

$$\begin{aligned} MOH, \quad & M(OH)_2, \quad \ldots\ldots\ldots M(OH)_n \ldots \\ M_2OH, \quad & M_2(OH)_2, \quad \ldots\ldots\ldots M_2(OH)_n \ldots \\ & M_3(OH)_2, \quad \ldots\ldots\ldots M_3(OH)_n \ldots \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ & \qquad\qquad\qquad M_m(OH)_n \end{aligned}$$

(12) (a) C. Brosset, *Acta. Chem. Scand.*, **6**, 912 (1952); (b) S. Ahrland, *ibid.*, **3**, 374 (1949).

Species such as $M_mO_p(OH)_q$ and $M_m(OH)_{2p+q=n}$ are thermodynamically indistinguishable in aqueous solutions.

An average ligand number $\bar{n}$ may be defined after Bjerrum[13] as

$$\bar{n} = [OH^-] \text{ bound/total metal concn.}$$

In the present case this becomes

$$\bar{n} = \frac{\{[BeOH^+] + 2[Be(OH)_2] + \ldots\} + \{[Be_2OH^{3+}] + 2[Be_2(OH)_2^{2+}] + \ldots\} + \cdots}{[Br^{2+}] + \{[BeOH^+] + [Be(OH)_2] + \ldots\} + 2\{[Be_2OH^{3+}] + [Be_2(OH)_2^{2+}] + \ldots\} + \cdots} \quad (1)$$

if it is assumed that perchlorate ion does not form complexes with beryllium. Defining also a set of acid dissociation constants[14] $\kappa_n^{(m)}$, at the constant ionic strength used, by

$$[Be_m(OH)_n^{(2m - n)+}] = \kappa_n^{(m)} \times \frac{[Be^{2+}]^m}{[H^+]^n}$$

and substituting into (1) gives

$$\bar{n}[H^+] = \frac{\left\{\kappa_1' + \frac{2\kappa_2'}{[H^+]} + \ldots\right\} + [Be^{2+}]\left\{\kappa_1'' + \frac{2\kappa_2''}{[H^+]} + \ldots\right\} + \cdots}{1 + \left\{\frac{\kappa_1'}{[H^+]} + \frac{\kappa_2'}{[H^+]^2} + \ldots\right\} + 2[Be^{2+}]\left\{\frac{\kappa_1''}{[H^+]} + \frac{\kappa^{2''}}{[H^+]^2} + \ldots\right\} + \cdots} \quad (2)$$

Now as $[H^+] \rightarrow \infty$, $n \rightarrow 0$ and $[Be^{2+}] \rightarrow C_{Be}$ (the total beryllium concentration), while the product $\bar{n}[H^+]$ tends toward a limit, given by

$$\underset{1/[H^+]\rightarrow 0}{Lt} \bar{n}[H^+] = (\bar{n}[H^+])_0 = \kappa_1' + \kappa_1'' C_{Be} \quad (3)$$

By plotting $\bar{n}[H]$ against $1/[H^+]$, and extrapolating to $1/[H^+] = 0$, it is possible to find different values of $(\bar{n}[H^+])_0$ for different C_{Be} values. These, plotted against C_M, give a value of $\kappa_1' = (\bar{n}[H^+])_0$ when $C_{Be} = 0$. Further, the slope of $(\bar{n}[H^+])_0$ against C_{Be} at $C_{Be} = 0$ is equal to κ_1''.

This method was used by Ahrland to evaluate κ_1' and κ_1'' for the uranyl system. It may be noted in passing that he did not obtain a straight line, as would be expected from (3). This was almost certainly due to his $(\bar{n}[H^+])_0$ values being somewhat incorrect: an arbitrary line parallel to the $1/[H^+]$ axis was drawn from a convenient maximum on the plot to $1/[H^+] = 0$. This is unjustifiable theoretically, for if the general form of (2) is differentiated with respect to $1/[H^+]$, the slope at $1/[H^+] = 0$ is given by the expression

$$\underset{1/[H^+]\rightarrow 0}{Lt} \frac{d(\bar{n}[H^+])}{d(1/[H^+])} = \frac{2\kappa_2' + 3\kappa_1'\kappa_2' + C_M(2\kappa_2'' + 2\kappa_1''\kappa_2') + C_M{}^2(2\kappa_3'' + 3\kappa_1''\kappa_2' - \kappa_2''\kappa_1')}{(1 + \kappa_1' + 2C_M\kappa_1'')^2}$$

which in general is not equal to zero, although Ahrland's extrapolation implies that it is. It is in some ways fortuitous, therefore, that his values are not greatly different from those obtained from more careful extrapolations.

Application of equation 3 to the present data on beryllium is shown in Figs. 2 and 3. In order to facilitate the extrapolation of the plot of $\bar{n}[H^+]$ against $1/[H^+]$ to $1/[H^+] = 0$ (Fig. 3), $\bar{n}$ was first plotted against $1/[H^+]$ for different values of C_{Be} (Fig. 2), and these curves extrapolated to the origin (since $\bar{n} = 0$ when $1/[H^+] = 0$). $\bar{n}$ values corresponding to $1/[H^+]$ values in an experimentally difficult region near the origin were thus ob-

(13) Reference 5, p. 21.

(14) The convenient terminology of the Swedish school is adopted here. See, e.g., S. Ahrland, ref. 12b, and succeeding papers in that series.

tained for use in Fig. 3. The straight line plot of $(\bar{n}[H^+])_0$ against C_{Be} (equation 3) gave the following data

$$\kappa_1' = \frac{[BeOH^+][H^+]}{[Be^{2+}]} = (0.3 \pm 0.1) \times 10^{-6}$$

$$\kappa_1'' = \frac{[Be_2OH^{3+}][H^+]}{[Be^{2+}]^2} = (0.31 \pm 0.06) \times 10^{-3}$$

These figures indicate that the concentration of monomeric beryllium hydrolysis products is always very low in aqueous beryllium solutions.

The degree of accuracy of the results is limited by the use of data in an experimentally uncertain region, and it was considered desirable to check them further. This is feasible for κ_1'. Rearrangement of (2) gives

$$\begin{aligned}
\bar{n}[H^+] = &\left\{(1 - \bar{n})\kappa_1' + \right. \\
&\frac{(2 - \bar{n})}{[H^+]}\kappa_2' + \ldots\right\} + \\
&[Be^{2+}]\left\{(1 - 2\bar{n})\kappa_1'' + \right. \\
&\frac{2(1 - \bar{n})}{[H^+]}\kappa_2'' + \ldots\right\} + \cdots
\end{aligned}$$

At $C_{Be} = 0$, $[Be^{2+}] = 0$, so that

$$\underset{C_{Be}\rightarrow 0}{Lt} \bar{n}[H^+] = (\bar{n}[H^+] c_{Be = 0} = (1 - \bar{n})\kappa_1' +$$

$$\frac{2 - \bar{n}}{([H^+])c_{Be = 0}}\kappa_2' + \ldots \quad (4)$$

$(\bar{n}[H^+])C_{Be} = 0$ and $([H^+])C_{Be} = 0 (= (\bar{n}[H^+]) \cdot C_{Be} = 0/\bar{n})$ were obtained by plotting $\bar{n}[H^+]$ against C_{Be} for given $\bar{n}$ values (Fig. 4), thus giving the required number of simultaneous equations representing (4) in terms of κ_1', κ_2', etc. In this case, only κ_1' was needed to correlate the data up to $\bar{n} = 0.5$. The values of κ_1' thus found (Table I) were in good agreement with that obtained above.

TABLE I

κ_1' VALUES OBTAINED FROM APPLICATION OF EQUATION 4

$\bar{n}$	0.1	0.2	0.4	0.5
$\kappa_1' \times 10^6$	0.4 ± 0.2	0.3 ± 0.2	0.4 ± 0.2	0.4 ± 0.2

Further analysis of the system is difficult, owing to the lack of knowledge of the $[Be^{2+}]$ parameter. A number of attempts were made to account for the pH data up to the precipitation region, assuming various possible species, with the following results.

(a) Be^{2+}, $BeOH^+$, Be_2OH^{3+}.—Successful in explaining data at low values of $\bar{n}$, but obviously not representative of the whole range.

(b) Be^{2+}, $BeOH^+$, Be_2OH^{3+} and any one or several of $Be_n(OH)_n{}^{n+}$, where $n > 1$ (cf. $Be_2(OH)_2{}^{2+5}$ and $Be_4(OH)_4{}^{4+7}$).—The calculated values of $\bar{n}$ increased far more rapidly with pH than the observed values.

(c) Be^{2+}, $BeOH^+$, Be_2OH^{3+}, $Be_3(OH)_2{}^{4+}$.—Partially successful assuming

$$\kappa_3'' = \frac{[Be_3(OH)_2{}^{4+}][H^+]^2}{[Be^{2+}]^3} \approx 0.5 \times 10^{-5}$$

but the calculated values of $\bar{n}$ did not increase with pH as rapidly as the observed values.

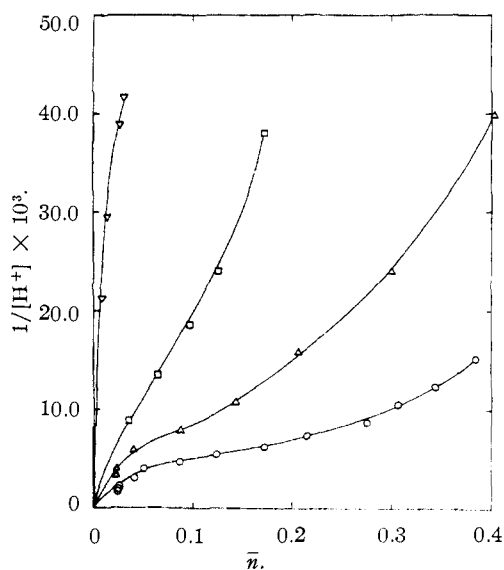Fig. 2.—Graphical estimation of $\bar{n}$ at low $1/[H^+]$ values; total Be concentrations in mole/l.: O, 3.00×10^{-2}; △, 1.50×10^{-2}; □, 0.75×10^{-2}; ▽, 0.10×10^{-2}.
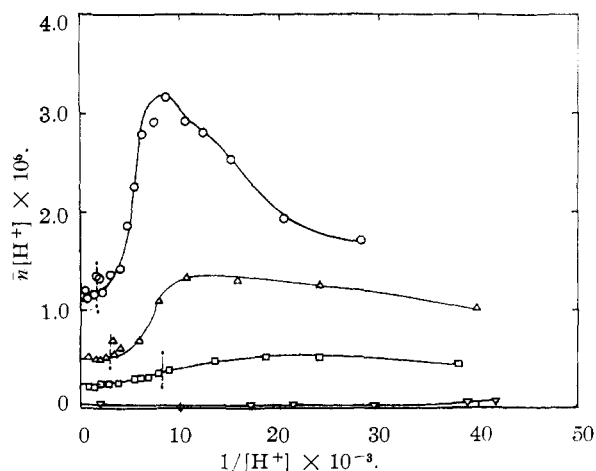
Fig. 3.—Determination of $(\bar{n}[H^+])_0$; total Be concentrations in mole/l.: O, 3.00×10^{-2}; △, 1.500×10^{-2}; □, 0.75×10^{-2}; ▽, 0.10×10^{-2}. Points to the left of the broken lines were estimated from Figure 2.

(d) Be^{2+}, $BeOH^+$, Be_2OH^{3+}, $Be_2(OH)_2^{2+}$, $Be_3(OH)_2^{4+}$.—The complexity of the expressions only justified qualitative inferences. These were that, assuming $\kappa_3'' = 0.5 \times 10^{-5}$, it was not possible to obtain a reasonably constant value of $\kappa_2'' = [Be_2(OH)_2^{2+}][H^+]^2/[Be^{2+}]^2$ from the data.

(e) Since the postulation of a few species could not adequately describe the behavior of the system, the presence of an infinite number of polynuclear species of increasing complexity was considered (cf. Granér and Sillén's treatment of Bi^{3+} hydrolysis[15]): Be^{2+}, $BeOH^+$, Be_2OH^{3+}, $Be_3(OH)_2^{4+}$, $Be_4(OH)_3^{5+}$, ... In order to treat this mathematically, two simplifying assumptions were necessary.

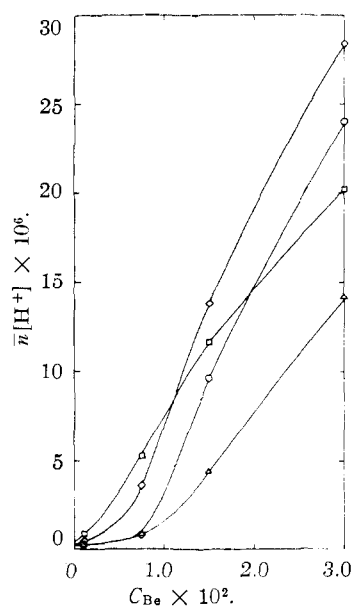(15) F. Granér and L. G. Sillén, Acta Chem. Scand., 1, 631 (1947).

Fig. 4.—Determination of $\kappa_1' = (\bar{n}[H^+])_0$ at $C_{Be} = 0$ in support of the results of Table I. Curves at constant $\bar{n}$: □, 0.1; ◇, 0.2; O, 0.4; △, 0.5.

Thus $[BeOH^+]$ was neglected, since it is always small compared with $[Be_2OH^{3+}]$, and it was assumed that

$$\frac{[BeOH^{3+}]}{[Be^{2+}][BeOH^+]} = \frac{[Be_3(OH)_2^{4+}]}{[Be_2OH^{3+}][BeOH^+]} = \frac{[Be_4(OH)_3^{5+}]}{[Be_3(OH_2^{4+}][BeOH^+]} = \cdots$$

On this basis it was possible to calculate $\bar{n}$, but the values were smaller than the observed, and increased more rapidly with pH. Now if the constant for n-mer formation, where $n > 2$, were smaller than the above assumption caused it to be, the calculated $\bar{n}$ values would be even smaller. On the other hand, if it were larger, it would cause the calculated $\bar{n}$ to increase even more rapidly with pH.

(f) It is concluded from (a), (b), (c), (d) and (e) that the hydrolysis of beryllium involves the formation of a large number of polynuclear species, the series suggested in (e) being representative of one group; another may be the series $Be_n(OH)_n^{n+}$. It is also to be appreciated that the simplifying assumption that the formation constants of each polymer are all equal is probably not too reliable.

It is apparent that complete analysis of the system is rendered speculative by the fact that only the $[H^+]$ parameter is determinable experimentally. Should X-ray studies of beryllium solutions prove feasible, these would probably provide more information on the system.