# Studies on the Hydrolysis of Metal Ions

VIII. Methods for Deducing the Mechanism of Polynuclear Hydrolysis Reactions

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It is a well-known fact that a large number of metal ions Me^{z+} may react with water in such a way that hydrogen ions are set free, while the solution remains clear and no visible precipitate is formed. Common examples are Fe^{3+}, Al^{3+}, and Hg^{2+}. Leaving out the water of hydration, we may write the general formula for a reaction of this kind in the form:

$$q\ Me^{z+} + p\ H_2O \rightleftharpoons Me_q(OH)_p^{(qz-p)+} + p\ H^+ \tag{1}$$
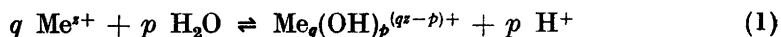
Many earlier attempts have been made to formulate such hydrolysis reactions. Among the products that have been proposed we may mention:

1) the uncharged hydroxide, in molecular or colloidal solution, without intermediate steps, *e.g.* $Al^{3+} + 3\ H_2O \rightleftharpoons Al(OH)_3 + 3\ H^+$

2) one or more mononuclear complexes, formed by splitting off protons from aquo complexes [10], *e.g.* $Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5OH^{2+} + H^+ \rightleftharpoons Al(H_2O)_4(OH)_2^+ + 2\ H^+$.

3) one or a few polynuclear complexes, *e.g.* $Bi_2(OH)_4^{2+}$ and $Bi_2(OH)_5^+$ [11], or Pb_2OH^{3+} and $Pb_4(OH)_4^{4+}$ [12].

In Part I of the present series [1—7] an attempt was made to explain the data for Bi^{3+} with still another mechanism: the formation of a series of polynuclear complexes, in this case $Bi(OBi)_n^{n+3}$, $n = 1, 2, 3 \ldots$

It may be said that many previous data on metal ion hydrolysis do not permit one to distinguish between various types of mechanism. Generally the total concentration (M) of the metal ion, and the hydrogen ion concentration h of the solution, have been varied either within only narrow limits, or not at all. The old practice of measuring the pH of solutions of "pure salts" is especially very likely to give erroneous results because of impurities: for an example, see part VI[6.p.467]. Moreover, the ionic strength has generally not been kept constant, so that variations in the activity factors cause large uncertainties.

Our research group has tried to study each metal ion over a not too narrow concentration range. We have been working with solutions in a constant ionic medium (usually 1.0 or 3.0 C $NaClO_4$) and have measured the hydrogen ion concentration and, if possible, the free metal ion concentration by electrometric methods [1-7]. Similar investigations are also available from other laboratories [13-15].

Even in our limited experience the ions have shown such a variety of individual behavior that we think it very improbable that one single type of product could account for the hydrolysis of all different metal ions.

For two of the ions studied by our group, namely Hg^{2+} and Tl^{3+}, the main products of the reaction proved to be *mononuclear:* $HgOH^+$ and $Hg(OH)_2$, part II; $TlOH^{2+}$ and $Tl(OH)_2^+$, part V. For a number of other ions, the main products are obviously *polynuclear*, and various polynuclear mechanisms have also been proposed, both by our group (Bi^{3+} part I; Fe^{3+} part VII) and by others (UO_2^{2+}, Ahrland [13]; Al^{3+}, Brosset,[14]; Sc^{3+}, Kilpatrick and Pokras [15]). Now, once one knows that polynuclear complexes are formed, the number of possible products becomes very great. So, even if one polynuclear mechanism seems to explain the data, one may reasonably doubt whether the same data could not equally well be explained by several other mechanisms, perhaps radically different from the one chosen.

Recently, one of us has developed some general equations for the formation of polynuclear complexes between two reactants A and B. It was also shown how the data may be treated in order to find out the nature of the reaction products [8,9]. In the following, these papers will be denoted by ABI and ABII. We shall not repeat here the whole argument in ABI and ABII, but shall instead give a "key" for transforming the equations for the general case to the special case of the hydrolysis of a metal ion. We shall then give some of the main conclusions of ABI and ABII for the special case of hydrolysis equilibria, and finally illustrate their use by application to a few ions.

List of symbols*

A	total concentration of A* (ABI, 2)
a	concentration of free A (ABI, 1)
B	total concentration of B (ABI, 2)
b	concentration of free B (ABI, 1)
c_n	concentration of n:th complex (30)
f	$= \Sigma k_n u^n$ (32)
g	parameter in (37) and (38)
H	total analytical excess concentration of hydrogen ions assuming Me^{z+} not to be hydrolyzed; H may be negative (5)
h	free concentration of H^+ ions (2)
k_n	equilibrium constant for the formation of the n:th complex (30)
k_0	constant, defined by (36) for each of the hypotheses IIIa, IIIb and IIIc
k	equilibrium constant, defined by (36) for IIIa—c, and by the text above (36) for hypotheses II and I

* *N. B.* Chemical symbols in Roman, *concentrations* in *italic* type!

k_{pq} equilibrium constant for formation of $Me_q(OH)_p$ from Me^{z+} and OH^- (12)
k_s solubility product in hypothesis I
k_w ionic product of water
M total concentration of Me in the solution (4)
m concentration of free Me^{z+} (2)
N unique value for n, in hypothesis II
n number of links in complex (15) or (19)
p number of A, or OH, units in complex
q number of B, or Me, units in complex
R partial derivative in (14)
r number of OH in "core", writing the complex as $(OH)_r((OH)_tMe)_n$ (19)
S complexity sum (9)
s number of Me in "core", writing the complex as $Me_s((OH)_tMe)_n$
t number of OH units per Me in "link" (15) or (19)
u $= mh^{-t}$ (31)
v $= ku$ (ABII, 6); $v_0 =$ value of v for $\xi = 0$ (39)
x $= \log M - t \log h$ (17)
X $= x + \log 2 - x_{\frac{1}{2}}$ (ABII, 10)
$x_{\frac{1}{2}}$ value of x for $y = \frac{1}{2}$ (ABII, 10)
y $= Z/t$ (18)
Z Average number of OH^- bound, or H^+ split off, per Me (6)
z charge of Me^{z+} ion
η $= \log M/m$ (10); $\eta_0 =$ value of η for $\xi = 0$ (39)
$\varkappa_{pq}$ equilibrium constant for the formation of $Me_q(OH)_p$ from Me^{z+} and H_2O (3)
ξ $= x +$ constant, chosen either to make the asymptote of $\eta(\xi)$ pass through the origin (ABII 51, 53) or to make all curves pass through $\eta = \xi = \log 2$ (ABII 69, III c).

Hydrolysis equilibria; general equations

Let us assume that the metal ion Me^{z+} reacts with water to form one or several products. If, say, the ionic medium is aqueous $NaClO_4$, the most general formula for the soluble complexes would be

$$Me_q(H_2O)_\alpha(H^+)_{-p}(Na^+)_\beta(ClO_4^-)_\gamma^{(qz-p+\beta-\gamma)+}$$
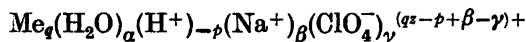
However, equilibrium data in an ionic medium do not allow us to distinguish between species containing varying amounts of the solvent H_2O, or of the medium ions (say, Na^+ and ClO_4^-). Thus we suffer no loss in generalization if we write the general formula of the complexes as

$$Me_q(OH)_p^{(qz-p)+}$$
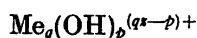
remembering that they may contain, in addition, an unknown amount of H_2O, Na^+ and ClO_4^-. One O^{2-} in an oxo complex would count as $2\ OH^-(= O^{2-} + H_2O)$ in the formula.

Let $\varkappa_{pq}$ denote the equilibrium constant of the reaction

$$q \;\; Me^{z+} + p \;\; H_2O \;\rightleftharpoons\; Me_q(OH)_p^{(qz-p)+} + p \;\; H^+ \tag{1}$$
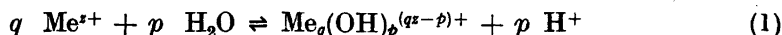
In the following we shall often leave out the charges of the complexes.

We shall introduce the symbols m and h for the concentrations of the "free" Me^{z+} and H^+ (free = bound to water of hydration and inert medium ions only)

$$[Me^{z+}] = m; \qquad [H^+] = h \tag{2}$$

From (1) we have the concentration of each complex

$$[Me_q(OH)_p] = \varkappa_{pq}m^qh^{-p} \tag{3}$$

The total concentration M of metal ion, free or complexed, is

$$M = [Me^{z+}] + \Sigma q \; [Me_q(OH)_p] = m + \Sigma q\varkappa_{pq}m^qh^{-p} \tag{4}$$

and the analytical excess H of hydrogen ions (proton excess in the water minus the proton deficiency in the complexes) is:

$$H = [H^+] - [OH^-] - \Sigma p[Me_q(OH)_p] = h - k_wh^{-1} - \Sigma p\varkappa_{pq}m^qh^{-p} \tag{5}$$

Here k_w is the ionic product of water, and the summations are taken over all sets of (p,q), except $(0,1)$ and $(1,0)$ which correspond to Me^{z+} and OH^-.

A useful quantity, which can in general be obtained directly from the experimental data, is the average number of OH^- groups bound per Me atom, or the average number of H^+ split off per Me

$$Z = \frac{\Sigma p[Me_q(OH)_p]}{M} = \frac{h - H - k_wh^{-1}}{M} \tag{6}$$

Equations (4) and (6) may also be written in the form

$$M - m = m \left(\frac{\partial S}{\partial m}\right)_h \tag{7}$$

$$ZM = h^{-1}\left(\frac{\partial S}{\partial h^{-1}}\right)_m = -h\left(\frac{\partial S}{\partial h}\right)_m \tag{8}$$

where S, the complexity sum, is

$$S = \Sigma[M_q(OH)_p] = \Sigma \varkappa_{pq} m^q h^{-p} \tag{9}$$

Experimental data

Of the four quantities M, H, m, and h, the first two should always be known from the analytical data for each equilibrium solution studied. Generally, h is also known with some accuracy, whereas m can be measured only in certain favorable cases.

M is the total concentration of the metal in question, eq. (4), whether present as free ion Me^{z+} or bound in complexes. As a rule it is advantageous

to plan the experiments in such a way that M is constant in each group of measurements. Thus M has only a limited number of values: M_1, M_2, M_3 etc., whereas H is varied freely.

H is the analytical excess of hydrogen ions, which may be calculated neglecting the hydrolysis reactions and assuming the solution to be made up of only H_2O, H^+, and Me^{z+}, in addition to the inert medium ions. In solutions with a deficiency of protons, H is negative, see e.g. (5).

m is the concentration of "free" metal ions Me^{z+} and can in some cases be measured by means of a metal, amalgam, or redox electrode.

h, the concentration of "free" hydrogen ions can be measured by means of a glass, hydrogen, or quinhydrone electrode. If Me^{z+} forms complexes with quinone or quinol, the quinhydrone electrode should be avoided. If Me^{z+} enters into redox reactions with hydrogen or quinhydrone, one may have to resort to the glass electrode in spite of its lower accuracy.

Z, the average number of H^+ split off from (OH⁻ bound per) Me atom is easily calculated from (6) if k_w has been determined by separate experiments — often the small correction $k_w h^{-1}$ can be neglected. Z is a much more convenient quantity than H for the following calculations.

If data (M,H,h) are available, it is convenient to transform them to a diagram giving $Z(\log h)_M$, i.e. to plot Z as a function of $\log h$ and join all points with the same value of M by a separate curve.

If data concerning m are also available, one may calculate the quantity

$$\eta = \log \frac{M}{m} \qquad (10)$$

and draw a diagram $\eta(\log h)_M$.

Our experimental data can thus be represented in one or two diagrams: the family of curves $Z(\log h)_M$, and in favorable cases also $\eta(\log h)_M$. We may then try to use the methods given in ABI and ABII to find the composition of the complexes and, if possible, the details of the reaction mechanism.

Transformation of A—B equations

Let us first compare the formulas derived for the special case of Me^{z+} hydrolysis with the equations derived in ABI for the general case of polynuclear complex formation between A and B. Our equations (1,2,3) may be considered as special cases of (ABI, 3 and 1) transforming the reactants and the free concentrations as follows:

$$B \rightarrow Me^{z+} \; ; A \rightarrow - H^+ \qquad (11\ a)$$

$$b \rightarrow m \; ; a \rightarrow h^{-1} \qquad (11\ b)$$
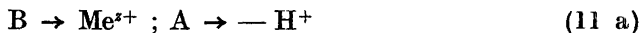
The total concentration M in (4) corresponds to B in (ABI, 2)

$$B \rightarrow M \qquad (11\ c)$$

The amount of A bound in complexes in (ABI, 5 and 7) corresponds to the amount of H^+ split off, in (6) and (8)

$$A—a = BZ \rightarrow MZ = h — H — k_w h^{-1} \qquad (11\ d)$$

Except for a, b, A and B, all quantities Z, η etc. will be denoted by the same symbols as used in ABI and ABII.

The fact that the reactant $-H^+$ is involved in an equilibrium with the solvent H_2O is expressed by the term $k_w h^{-1}$ in (11 d) — similar correction terms would be necessary for any other reactant A which reacts with the solvent.

Some readers may find it over-sophisticated to consider the "proton deficiency" as a reactant and may prefer to use the reactant OH^-. Denoting the equilibrium constant for the formation of the complex $Me_q(OH)_p$ by k_{pq}, one would then replace (3) by

$$[Me_q(OH)_p] = k_{pq} m^q [OH^-]^p = k_{pq} k_w^p m^q h^{-p} \tag{12}$$

The new set of constants k_{pq} are related to the $\varkappa_{pq}$ by the equation (cf. 3):

$$\varkappa_{pq} = k_{pq} k_w^p \tag{13}$$

but the treatment of the data will be analogous to that given here, and in ABI and ABII. Since, however, the measurements generally give $[H^+]$ directly we have preferred the formulation using H^+.

We shall now use (11 a—d) to transform the main conclusions of ABI and ABII to a form applicable to measurements of metal ion hydrolysis. For proofs and further discussion see the general papers ABI and ABII.

DEDUCTION OF THE GENERAL FORMULA OF THE COMPLEXES

Coinciding curves

It may result that the quantities Z and η depend only on h and are independent of M. One then gets a single curve $Z(\log h)$ and a single curve $\eta(\log h)$, irrespective of the value of M. This implies that only *mononuclear* complexes, of the general formula $Me(OH)_n$, are formed in appreciable amounts.

In the case where only Z (log h) data are available and m is negligible compared with M in the whole range studied, there is an additional theoretical possibility that all complexes are "homonuclear", i. e. of the general formula $Me_Q(OH)_n$, with Q constant, and n variable (ABI, p. 311—312).

To find the equilibrium constants, when only mono- (or homo-)nuclear complexes are formed, one may apply methods previously worked out by N. and J. Bjerrum, Leden, Fronæus and others for studying complex equilibria. For examples, the reader is referred to part II and part V, on the hydrolysis of the ions Hg^{2+} and Tl^{3+}.
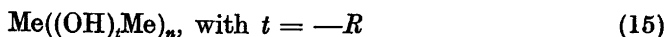
Parallel curves

It has been found in a number of cases that the curves $Z(\log h)_M$ for different M values are parallel within the experimental error, and that the horizontal spacing between two curves, $\Delta \log h$, is proportional to the difference between the two $\log M$ values, $\Delta \log M$. This may be expressed in the mathematical form:

$$\left(\frac{\partial \log M}{\partial \log h} \right)_Z = -R = \text{constant} \tag{14}$$

Hence

$$Z = \text{function of } (\log M + R \log h) \tag{14 a}$$

First let us suppose that m is not negligible compared with M, at least in some part of the range where (14) is valid. (The opposite case will be dealt with in the text accompanying equations (19—21) below.) Then it follows from (14) (see deduction of equations ABI, 19 and 19 a from ABI, 16) that all complexes formed in appreciable amounts can be written in a "core + links" form.

$$\text{Me}((\text{OH})_t\text{Me})_n, \text{ with } t = -R \tag{15}$$

Thus t is the constant obtained from (14), whereas the value(s) of n are as yet undetermined. It follows from (14 a) and (15) that

$$Z = \text{function of } x \text{ only}; \quad x = \log M - t \log h \tag{15 a}$$

If measurements of m are also available, the curves $\eta(\log h)_M$ often prove to be parallel with a displacement represented by the equation:

$$\left(\frac{\partial \log M}{\partial \log h}\right)_\eta = t = \text{constant} \tag{16}$$

Hence

$$\eta = \text{function of } x \text{ only}; \quad x = \log M - t \log h \tag{16 a}$$

As shown in (ABI, 40—44), equation (16), like (14), implies that all complexes formed in appreciable amounts can be written in the "core + links" form $\text{Me}((\text{OH})_t\text{Me})_n$ where t is a constant but n may vary.

To determine with what accuracy equations (15 a) and (16 a) are valid, one may plot Z and η as functions of the variable (ABI, 26)

$$x = \log M - t \log h \tag{17}$$

This is the same as to displace the curves $Z(\log h)_M$ or $\eta(\log h)_M$ along the $\log h$ axis to see whether they coincide. This method can also be used if data are available for varying values of M, and not for a discrete set of M values. From a few points one can easily find an approximate value for t; one may then use tentative values 2, 3, etc. for t, plotting Z or η against $\log M - 2 \log h$, $\log M - 3 \log h$ etc. or, if one prefers, against $\log h - \frac{1}{2} \log M$, $\log h - \frac{1}{3} \log M$ etc. If data from a sufficiently broad M range are available, all values for t except one can easily be ruled out.

Before discussing the details of the mechanism (see below) it is convenient to divide Z by t (ABI, 25).

$$y = \frac{Z}{t} \tag{18}$$

and to consider the curve $y(x)$.

There is one special case we should treat separately, namely that where only Z data are available and m is negligible within the whole range studied. Let us suppose that the curves are parallel so that (14) and (14 a) are still valid. In this case the general formula of the complexes is (ABI, p. 308)

$$(\text{Me(OH)}_t)_n(\text{OH})_r, \text{ with } r = R; \tag{19}$$
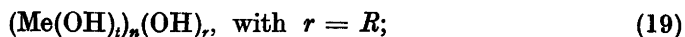
Thus r is the constant obtained from the spacing, and t is another constant which may be deduced from the limiting values for $Z : t + r/n_{max}$ and $t + r/n_{min}$ (ABI, 14)

In this case it is convenient to consider the smallest possible complex $Me(OH)_{r+t}$ as the core and $Me(OH)_t$ as the link. The functions to be plotted take the form (ABI, 33 and 34):

$$x = \log\ M + r\ \log\ h \tag{20}$$

$$y = \frac{r + t - Z}{r} \tag{21}$$

This treatment will be exemplified in forthcoming papers on Al^{3+} in the alkaline range and on silicate equilibria.

Equation (14) is closely related to one given by Byé (Ref. [16], eq. 22) and applied by him to the reactions of molybdate ions, by Carpéni and Souchay [17] to other anion systems, and by Schaal and Faucherre [18] to the hydrolysis of Th^{4+}, UO_2^{2+} and other ions. There are, however, two differences: 1) Byé discussed the case where only two species need be considered (two complexes, or Me^{s+} and one complex) and did not formulate the implications of (14) in their most general form. 2) Byé used the function $(-H/M)$, or rather $-H/2M$, instead of Z. In cases where h and $[OH^-]$ can be neglected, this makes no difference — in other cases his equations are not exact.

Other cases

Even if the curves are not parallel, one may tentatively assume that the reaction products can be written in some other "core + links" form, in general $(Me(OH)_t)_n(OH)_r$ [or $Me_s(Me(OH)_t)_n$, where $r = -ts$; AB I, 8]. From equations to be given presently, one can then find the most probable values for r and t; subsequent calculation will show whether or not the "core + links" formulation is a useful approximation.

Data (h, M, Z). Provided m is not negligible in the whole range, the *limiting values for Z* should be (AB I, 15):

$$\left.\begin{array}{ll} Z \to 0 & \text{for increasing } \log h\ (m \approx M) \\ Z \to t + r/n_{max} & \text{for decreasing } \log h\ (m \ll M). \end{array}\right\} \tag{22}$$

From the spacing of the curves $Z(\log h)_M$, (ABI, 35 and 36)

$$\left(\frac{\partial\ \log\ M}{\partial\ \log\ h}\right)_Z \quad \begin{array}{l} \nearrow\ \dfrac{r + n_{min}t}{n_{min}-1}\ \text{for}\ m \approx M \\[2ex] \searrow\ -r\ \text{for}\ m \ll M \end{array} \tag{23}$$

The curves $Z(\log h)_M$ will thus tend to coincide (the horizontal spacing tends to zero) for $m \approx M$, provided $n_{min} = 1$, and $r + t \neq 0$.

To test a possible value for r one may calculate $h^r MZ$ and plot it as a function of $(\log h)_M$. From the spacing of these curves we should find (ABI, 37)

$$\left(\frac{\partial \log M}{\partial \log h}\right)_{h^r MZ} \nearrow \quad \begin{array}{l} t \text{ for } m \approx M \\[1em] \searrow \quad -r \text{ for } m \lll M \end{array} \tag{24}$$

If one suspects that the general formula of the complexes is $(Me(OH)_t)_n$, i.e. that $r = 0$, one may plot MZ as a function of $[\log (M - \frac{MZ}{t}) - t \log h]$. Then all points should fall on the same curve irrespective of the value of M (ABI, p. 313).

If m data are not available, and m is always $\lll M$, as is the case with many polyanion equilibria, it is convenient to replace Me^{z+} in the equations of this paper (or in general B in any treatment founded on ABI and ABII) by the smallest possible complex. An example is uranium(VI): as U^{6+} does not seem to exist in solution it is convenient to use the smallest complex, UO_2^{2+}, instead of U^{6+}.

Data (m, h, M, Z). The limiting slopes of the curves $\eta(\log h)_M$ will be (ABI, 39):

$$\left(\frac{\partial \eta}{\partial \log h}\right)_M = -\left(\frac{\partial \log m}{\partial \log h}\right)_M \quad \begin{array}{l} \nearrow \quad 0 \text{ for } m \approx M \\[1em] \searrow \quad -(t + \frac{r}{n_{max}}) \text{ for } m \lll M \end{array} \tag{25}$$

The spacing of these curves gives the limiting values (ABI, 46)

$$\left(\frac{\partial \log M}{\partial \log h}\right)_\eta \quad \begin{array}{l} \nearrow \quad \dfrac{r + n_{min}t}{n_{min}-1} \text{ for } m \approx M \\[1em] \searrow \quad \dfrac{r + n_{max}t}{n_{max}-1} \text{ for } m \lll M \end{array} \tag{26}$$

Thus the horizontal spacing between the curves $\eta(\log h)_M$ will tend to disappear for $m \approx M$, provided $n_{min} = 1$ and $r + t \neq 0$.

If one wants to test a special value for s, one may plot $m^{-s}(M-m)$ as a function of $(\log h)_M$ or $(\log h)_m$, and see whether the spacing gives acceptable values for t and $r = -ts$, (ABI, 47 and 48):

$$\left(\frac{\partial \log M}{\partial \log h}\right)_{m^{-s}(M-m)} \quad \begin{array}{l} \nearrow \quad t \text{ for } m \approx M \\[1em] \searrow \quad ts = -r \text{ for } m \lll M \end{array} \tag{27}$$

$$\left(\frac{\partial \log m}{\partial \log h}\right)_{m^{-s}(M-m)} = t \text{ in the whole range} \tag{28}$$

The methods now mentioned here may give plausible values for r and t, provided a core + links formula is at all applicable. More rigid tests can then be devised depending on the accuracy of the data. For instance, one may plot $h^r(M—m)$ as a function of $\log m — t \log h$, which should give a single curve. This curve could then be analysed to find the details of the mechanism (ABI, p. 316).

Depending on the accuracy of the data other functions may prove useful for finding the general formula of the complexes, and the details of the mechanism, $e.g.$ $MZ/(M—m)$ or perhaps $(M—m)/H$ (ABI, p. 316).

Applications to data for certain ions

The treatment described above has been applied to the experimental data on the hydrolysis of a number of metal ions. In two cases, as mentioned above, mononuclear complexes were indicated. In all the others, the $Z(\log h)_M$ curves were found to be parallel — application of (14) and (15) gave integral values of t, either 2 or 3. In those cases where $\eta(\log h)_M$ curves were available, they were also parallel and indicated the same t value as did the $Z(\log h)_M$ curves. The results are summarized in Table 1.

Table 1.

Metal ion	Ref.	Data	$— R$	General formula of complexes
Bi^{3+}	1	Z, η	2	$Bi((OH)_3Bi)_n^{3+n}$ or $Bi(OBi)_n^{3+n}$
Fe^{3+}	7	Z, η	2	$Fe((OH)_2Fe)_n^{3+n}$
UO_2^{2+}	13	Z	2	$UO_2((OH)_2UO_2)_n^{2+}$ or $UO_2(OUO_2)_n^{2+}$
Al^{3+} acid	14	Z	3	$Al((OH)_3Al)_n^{3+}$
Al^{3+} alkaline	14	Z	-1	$OH((OH)_3Al)_n^-$, from eq (19)
Th^{4+}	19	Z	3	$Th((OH)_3Th)_n^{4+n}$ or $Th(OOHTh)_n^{4+n}$

In Figs. 1 and 2, Hedström's data for Fe^{3+} (Part VII) are represented as plots of Z(or rather $y = \frac{1}{2}Z$) and η as functions of $x = \log M — 2 \log h$. The points for $M = 5$—50 mC are seen to be independent of M within the limits of error, whereas those for 1 and 2 mC differ a little. For the lowest concentrations, 0.1 and 0.2 mC, the η values differ considerably from those for higher M (no Z values are given for low M because of the large uncertainty). Hedström's reasonable explanation is that at these low M values the formation of mononuclear complexes becomes appreciable.

We may for the moment neglect the lowest M values and consider the range $M = 1$—50 mC, $i.e.$ a range of 1.7 $\log M$ units. It is seen that good agreement is only obtained for $t = 2$; if Z or η were plotted as functions of, say, $\log M — \log h$ or $\log M — 3 \log h$, the points for different values of M would be systematically spread out along the x axis.

The same is true for the Bi^{3+} curves, Figs. 3 and 4. The range of concentrations is not quite as wide (0.7 $\log M$ units); — however, it is clear that reasonable agreement would not be obtained with any value of t except 2.

The remaining ions will be discussed in following papers in this series.

SELECTING A "CORE + LINKS" MECHANISM

Method

Let us suppose that (15 a) and (16 a) are valid within a certain range, *i.e.* that Z and η have proved to be functions of $x = \log M - t \log h$. This indicates that we need primarily consider only complexes of the general formula $Me((OH)_t Me)_n$ (excepting the special case of eq. 19—21). However, we do not know whether only one complex, or a few, or a great number of complexes is formed. To attack this problem we must consider the shape of the experimental curve $y(x)$ and, if available, of $\eta(x)$.

With "core + links" complexes (15), the only reactions we need consider are of the following type:

$$Me^{z+} + tn \; H_2O + n \; Me^{z+} \rightleftharpoons Me((OH)_t Me)_n + tn \; H^+ \qquad (29)$$
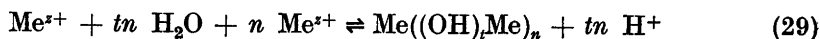
Denoting the equilibrium constant of (29) by k_n, we have (AB I, 21):

$$c_n = [Me((OH)_t Me)_n] = k_n m(h^{-t} m)^n = k_n \, m \, u^n \qquad (30)$$

with the abbreviation (ABI, 10)

$$u = m \, h^{-t} \qquad (31)$$

If moreover, we put (ABI, 22)

$$f(u) = \sum k_n u^n \qquad (32)$$

we may prove (ABI, 26, 25, 44)

$$x = \log u + \log(1 + f + uf') \qquad (33)$$

$$y = uf'(1 + f + uf')^{-1} \qquad (34)$$

$$\eta = \log(1 + f + uf') \qquad (35)$$

Thus x, y and η are all functions only of the variable u.

Curves calculated for a few mechanisms have been drawn in ABII, giving y and η as functions of x, or rather of X and ξ, which are $= x + a$ constant, containing one of the equilibrium constants, which we shall call k.

The mechanisms considered involve either one equilibrium constant (k) or two $(k$ and $k_0)$ and are, for the special case of the hydrolysis of metal ions:

I. No soluble hydroxo complex is formed; solid $Me(OH)_t$ precipitates *, solubility product $k_s = mh^{-t} = k^{-1}$

II. Only one soluble complex, $Me((OH)_t Me)_N$ is formed, with the equilibrium constant $k_N = k^N$.

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* As before, "$Me(OH)_t$" may also contain water and the medium ions (say Na+, and ClO₄⁻) and may thus have the general formula $Me(H_2O)_\alpha(OH)_t Na_\beta(ClO_4)_{z+\beta-t}$.
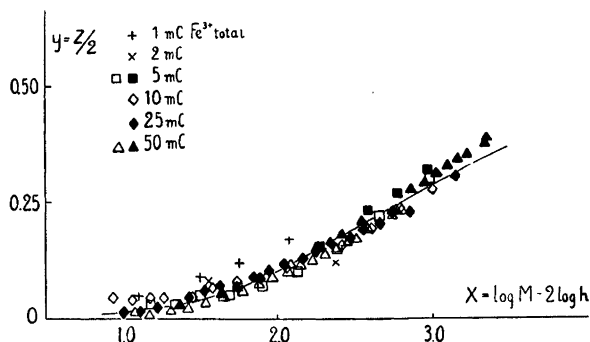
Fig. 1. Hydrolysis of Fe³⁺. Points: y (x), from Hedström's data ⁷. Curve: calculated for mechanism II, N = 1, log k = —2.80.

III. By repeated reaction, an unlimited series of complexes is formed where n may have any positive integral value.

Three equations expressing the variation of k_n with n (ABII, 28) were considered

$$
\begin{aligned}
\text{IIIa}: k_n &= k_0 k^n \\
\text{IIIb}: k_n &= k_0 n k^n \\
\text{IIIc}: k_n &= \frac{k_0 k^n}{|n|}
\end{aligned}
\quad\Biggr\} \quad (36)
$$

Hypotheses III a—c are similar to but not identical with three cases of polymerization discussed by Connick and Reas [20].

Hypothesis I gives only one possible shape for $y(X)$(limiting curve in ABII, Figs. 1—3), and one for $\eta(\xi)$ (limiting curve in ABII, Figs. 4 and 5). Hypothesis II gives families of curves $y(X)_N$ and $\eta(\xi)_N$, with N as parameter (ABII, Figs. 1 and 4). With hypotheses IIIa, IIIb and IIIc one finds families of curves $y(X)_{k_0}$ and $\eta(\xi)_{k_0}$ (ABII, Figs. 2 a—c and 5 a—c) with k_0 as parameter.

For comparison with the experimental data, the calculated curves should be drawn on not too small a scale.

Let us now suppose that the experimental data in the form $y(x)$ and perhaps also $\eta(x)$ are plotted on the same scale as the calculated curves. By moving them along the x axis an attempt can be made to make the data fit in with some of the curves. Hypotheses I and II, which involve the formation of only one hydrolysis product, and allow only a discrete set of shapes of the curves, are then rather easy to recognize or to rule out.

With IIIa, IIIb, and IIIc, such a clear decision is hard to make. In any real case, the assumption that the equilibrium constants may be represented by one of the simple equations (36) is certainly a very rough approximation. Thus small deviations from the ideal calculated curves are to be expected.

At any rate, after some study of the data and the curves, one may state which of these mechanisms can be definitely excluded, and whether one may get an acceptable agreement with any of them, by choosing an appropriate value for N or k_0. If so, one may find the equilibrium constant k from the position of the experimental curves.
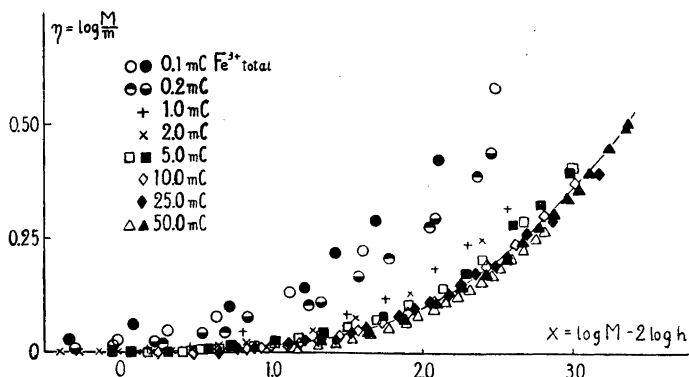
Fig. 2. Hydrolysis of Fe^{3+}. Points: $\eta(x)$, from Hedström's data [7]. Curve: calculated for mechanism II, $N = 1$, $\log k = -2.80$.

Application to the iron (III) ion

Let us again consider Figs. 1 and 2, which give the experimental data $y(x)$ and $\eta(x)$ for Fe^{3+}, calculated with $t = 2$, i.e. assuming the general formula $Fe((OH)_2Fe)_n^{3+n}$. We shall compare them with the calculated curves, disregarding the points for $M = 0.1$, 0.2 and 1 mC where the mononuclear complexes begin to exist in appreciable concentrations.

Hypothesis I would involve the precipitation of, say, very fine-grained $Fe(OH)_2ClO_4$. This mechanism would require a much steeper rise of both curves than is actually found, and can thus be immediately excluded. In the choice between the remaining mechanisms, it is a drawback that data are available only for a limited range in y ($0 < y < 0.4$, corresponding to $0 < Z < 0.8$) and also in $\eta(0 < \eta < 0.5)$. However, it was hard to extend the range because of the precipitation of FeOOH.

When the experimental data are superimposed on the family of curves for hypothesis II (only one polynuclear complex formed), a remarkably good agreement is obtained with $N = 1$, both for $y(x)$ and for $\eta(x)$ — no other N value gives an acceptable agreement.

With IIIa—c a good agreement with the experimental points $y(x)$ and $\eta(x)$ was obtained for all sufficiently high k_0 values: with IIIa for $k_0 \geq 5$, with IIIb for $k_0 \geq 10$, and with IIIc for $k_0 \geq 2$. On comparing the calculated curves it will be found that with increasing k_0, the lower parts of all the curves $y(x)$ and $\eta(x)$ for these three mechanisms tend to the same shape, namely that of the curve for II with $N = 1$. The explanation is that if k_0 is high, the first complex $Me(OH)_tMe$ will predominate over higher complexes in the first stages of hydrolysis, as may be realized intuitively and also proved, starting from equations (30) and (36).

In Figs. 1 and 2, the curves are calculated for hypothesis II with $N = 1$ — they would almost coincide with the curves for IIIa with $k_0 = 10$, 5 or 1. With the higher values for k_0, the polynuclear complexes after the first are only a small correction in the part of the curves that was available from the
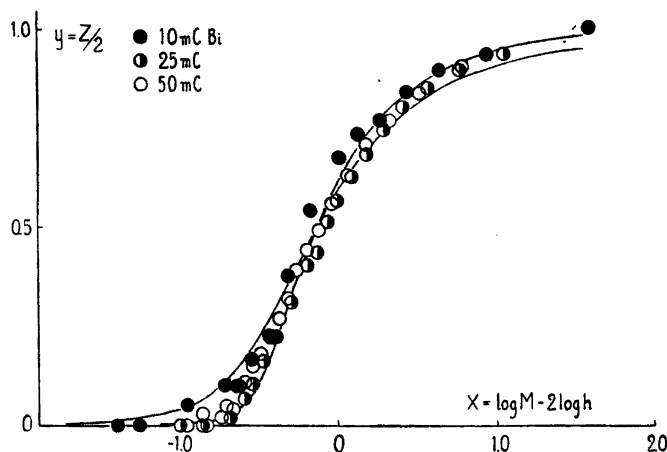
Fig. 3. Hydrolysis of Bi^{3+}, Points: $y(x)$, from Granér and Sillén [1]. Curves: hypothesis IIIa with log $k = 0.48$, $k_0 = 0.01$ and 0.1.

experiments. Since the data do not give any clear proof of the existence of higher polynuclear complexes, we shall assume that the only polynuclear complex formed is $Fe((OH)_2Fe)_N$ with $N = 1$, i.e. $Fe_2(OH)_2^{4+}$. This is the same mechanism as that found by Hedström [7] by another approach.

To find the equilibrium constant k, we may try to fit the curves calculated for $N = 1$ to the experimental data as well as we can — as we shall see, the points with $y = 1/4$ and $\eta = \log 2$ are especially useful.

Equations (ABII, 22, 23, 58) give, for $N = 1$:

$$y = \frac{g}{1 + 2g} \; ; \; x + \log k = \log g + \log(1 + 2g); \; \eta = \log(1 + 2g) \quad (37)$$

The significance of g (here $= ku$) need not concern us here.
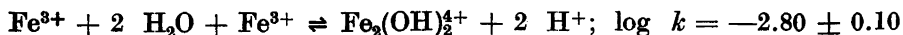Setting $y = 1/4$ we find:

$$y = 1/4; \; g = \tfrac{1}{2}; \; \eta = \log 2; \; x = - \log k \quad (38)$$

From the best fitting curves, disregarding the very low M values we may read off:

$y(x); \; y = 1/4$ for $x = 2.85 \pm 0.15$, thus log $k = -2.85 \pm 0.15$

$\eta(x); \; \eta = \log 2$ for $x = 2.80 \pm 0.10$, thus log $k = - 2.80 \pm 0.10$

With our approach we have thus deduced the following main reaction:

$$Fe^{3+} + 2 \; H_2O + Fe^{3+} \rightleftharpoons Fe_2(OH)_2^{4+} + 2 \; H^+; \; \log \; k = -2.80 \pm 0.10$$

This is substantially the same result as deduced by Hedström [7], whose value was log $k = -2.91 \pm 0.04$. In addition, Hedström could give equilibrium constants for the formation of mononuclear $FeOH^{2+}$ and $Fe(OH)_2^+$ at the very low Fe
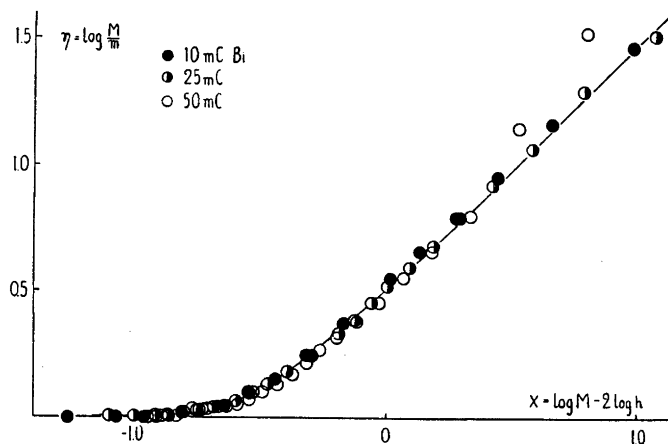
Fig. 4. Hydrolysis of Bi^{3+}. Points: $\eta(x)$ from Granér and Sillén [1]. Curve: hypothesis IIIa with log $k = 0.48$, $k_0 = 0.025$.

concentrations where the points fall off the $y(x)$ and $\eta(x)$ curves. The small difference between our values for log k and his may be due to the fact that we have made no corrections for mononuclear complexes.

Application to the bismuth(III) ion

Figs. 3 and 4 give the experimental data of Granér and Sillén (Part I) for Bi^{3+}, recalculated to $y(x)$ and $\eta(x)$ using the value $t = 2$ previously deduced. By comparison with the curves in ABII we found that *hypothesis I*, which would have implied the formation of solid $BiOClO_4$ (+ perhaps an unknown amount of H_2O and $NaClO_4$) is ruled out. Nor could a reasonable agreement be obtained with any of the curves calculated for *hypothesis II* and various values of N. Thus we found, as did Granér and Sillén, that the data cannot be explained by the formation of only one complex.

With *hypothesis IIIa*, the experimental points $y(x)$ were found to fall in between the curves for $k_0 = 0.01$ and 0.1. Values for k_0 in the range 0.03 ± 0.02 were obtained both by using values of the slope at $y = \frac{1}{2}$ and equation (ABII, 35), and by using values of the distance $(x—x_{\frac{1}{2}})$ for various y, together with equation (ABII, 37).

To find k, one may use (ABII, 33), $x_{\frac{1}{2}} = \log 2 — \log k$. In practice, when the family of calculated curves $y(X)$ is moved across the experimental points, one reads the x value corresponding to the point $X = 0$, $x = — \log k$ in the position where a good fit is obtained (see (ABII, 34)). We thus found log $k = 0.43 \pm 0.08$.

When the family of calculated curves $\eta(\xi)$ for IIIa was moved along the experimental points $\eta(x)$, a good fit was obtained with k_0 values ≈ 0.025. One may find log k from the $\eta(x)$ plot by reading the value of x corresponding to $\xi = 0$ at the best fit (equation ABII, 63: when $\xi = 0$, $x = — \log k$).

We thus found $\log k = 0.48 \pm 0.02$; this value is chiefly determined by the points with high values of η, which are close to the asymptote and insensitive to changes in k_0.

To find k_0, one may then read the value η_0 for $\xi = 0$, and calculate v_0 and k_0:

$$\xi = 0; \eta = \eta_0 \; ; \; v_0 = 10^{-\eta_0}$$

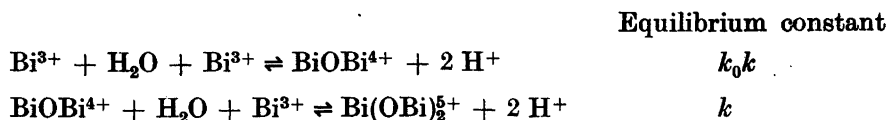$$k_0 = (1-v_0)^3 v_0^{-2}(2-v_0)^{-1} \tag{39}$$

The equations (39) can be derived from (ABII, 64 and 63). In this way we found $k_0 = 0.025 \pm 0.010$.

With *hypothesis IIIb*, the low $y(x)$ values agree fairly well with the calculated curves for $k_0 = 0.01$, whereas the higher y values deviate somewhat ; from the $y(x)$ curve one finds $\log k = 0.43 \pm 0.08$. The $\eta(x)$ curve for IIIb and $k_0 = 0.01$ also agrees rather well with the experimental data except at the highest values. From this curve one finds $\log k = 0.43 \pm 0.03$.
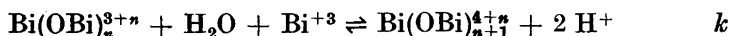
Finally, with *hypothesis IIIc*, the lower half of the $y(x)$ or $\eta(x)$ data give a tolerable agreement with $k_0 \approx 10^{-4}$, but for higher y or η the calculated curves definitely do not fit the experimental data.

To sum up, we find that with our present approach we have established the general formula of the complexes formed to be $\mathrm{Bi(OBi)}_n^{3+n}$, and seem to have ruled out explanations assuming only one polynuclear complex. Of the "repeated" mechanisms tested, the best agreement was obtained by assuming the addition of new links after the first to be either equally easy for all n (hypothesis IIIa), or somewhat easier for higher n (hypothesis IIIb), whereas the agreement was not as good, when it was assumed that the formation of higher complexes is disfavored (hypothesis IIIc).

Assuming meachanism IIIa, the data would be explained by the following reactions:

	Equilibrium constant
$\mathrm{Bi}^{3+} + \mathrm{H_2O} + \mathrm{Bi}^{3+} \rightleftharpoons \mathrm{BiOBi}^{4+} + 2\,\mathrm{H}^+$	$k_0 k$
$\mathrm{BiOBi}^{4+} + \mathrm{H_2O} + \mathrm{Bi}^{3+} \rightleftharpoons \mathrm{Bi(OBi)}_2^{5+} + 2\,\mathrm{H}^+$	k

in general:

$\mathrm{Bi(OBi)}_n^{3+n} + \mathrm{H_2O} + \mathrm{Bi}^{+3} \rightleftharpoons \mathrm{Bi(OBi)}_{n+1}^{4+n} + 2\,\mathrm{H}^+$	k

with $\log k = 0.48 \pm 0.02$, $k_0 = 0.025 \pm 0.010$

It may be noted that Granér and Sillén, who considered only the mechanism IIIa, found $\log k = 0.47 \pm 0.03$ and $k_0 = 0.022 \pm 0.006$. It is especially gratifying that with our present representation the $\eta(x)$ data for high η are also in good agreement with hypothesis IIIa; in the graphical representation chosen in part I, these values came close to the m/M axis, and the agreement was therefore not so easy to check.

We shall not discuss the bismuth equilibria in detail since we hope to have data available for a wider range of concentrations, both with emf and ultra-centrifuge methods, in the near future.

DISCUSSION

The $y(x)$ and $\eta(x)$ curves contain in a compact form the information one can get out of the emf data. The examples given here and in the following few papers may indicate what conclusions one may draw from them and what their limitations are.

First of all, the fact that the $Z(\log h)_M$ curves are parallel, so that Z (and η) are functions of $x = \log M - t \log h$, indicates strongly that the formula of all complexes can be written in the form $Me((OH)_nMe)_n$ but it implies nothing about how many and which n values are actually represented.

If the $y(x)$ and $\eta(x)$ curves rule out the simple hypotheses I and II, with only one product, then there are certainly several kinds of polynuclear complexes present. In such cases we have resorted to the hypotheses IIIa—c, where all n values are represented and about equivalent — this however arises from sheer ignorance. We simply do not know any argument that could guide us in choosing three or four values for n and stating that these are the only possible ones occurring among all conceivable n values. On the other hand we have no doubt that if one chooses at random some combination such as $n = 1, 3, 7,$ and $13,$ or $1, 2, 4, 8,$ and $16,$ one might adjust the equilibrium constants to get an agreement which is about as good as that obtained with "unlimited" mechanisms.

Since the crystal structures of bismuth oxide compounds contain $(BiO)_n$ sheets, it is tempting to consider the soluble bismuth complexes, with formulas close to $Bi(OBi)_n^{3+n}$, as fragments of such sheets.[1] The crystal structure gives no indication of certain values for n being preferred to all others; this may be one argument for treating all n as roughly equivalent.

An additional support may be found in the work of Kraft and Ryumshin [21] who have prepared a series of bismuth oxide salts of α-phenylbutyric acid (HA), to which they ascribe the general formula "$A_2Bi(OBiA)_nOBiA_2$", or $Bi(OBi)_nA_{3+n}$, with n varying continuously from 0 to ∞. Molecular weights and analytical compositions seem to agree well with this formula for three specimens with n ranging from 3 to 12. From the low viscosity of the solutions of these compounds in organic liquids, Kraft and Ryumshin concluded that the molecules are round rather than thread-like; this agrees well with the picture of a fragment of the $(BiO)_n$ sheet from a crystal structure, surrounded on both sides by α-phenylbutyrate groups.

From emf data one may thus conclude, by applying the methods given in this paper, and in ABI and ABII, that many inorganic ions form a series of hydrolysis products of varying molecular weight, in equilibrium with each other. It would be desirable to check this conclusion by some quite independent method. As already discussed in ABI, solubility data give too limited information when polynuclear complexes are formed. With distribution or ion exchange data one will have to introduce a number of new assumptions and unknown constants. Moreover, just as with the emf data, they give more accurate information on the very smallest complexes rather than on the higher ones. Diffusion data will be hard to interpret, since the complexes are continually breaking up and reforming.

Equilibrium ultracentrifugation is not an altogether ideal method since the complexes have a rather low molecular weight; due regard must also be paid to the variation of ionic strength, equilibrium constants, and activity factors with the distance from the axis of rotation. However the method may give some new useful information, if due consideration is taken of its limitations. Dr. Kurt Kraus, of Oakridge, has already done some work in this field. We are planning to start work on ultracentrifugation in the near future, in collaboration with Professors Ole Lamm and Hugo Theorell.

Whichever mechanism one proposes for a hydrolysis reaction, one must demand that it should be able to explain with reasonable accuracy the rather detailed data obtained by methods founded on the law of mass action.

SUMMARY

Experimental data for the hydrolysis of a metal ion Me^{z+} are conveniently summarized in the form of diagrams of $Z(\log h)_M$ and $\eta(\log h)_M$. (Z = average number of H^+ set free per Me, M = total concentration of Me, $m = [Me^{z+}]$, $h = [H^+]$, $\eta = \log M/m$.)

The formation of polynuclear hydrolysis products may be treated formally as a complex formation between the hydrated Me^{z+} and the reactant "$-H^+$". The general methods given in the papers ABI[8] and ABII[9] for treating complexes between two reactants A and B have been transformed to this special case and applied to a number of systems.

The general formula of the complexes is obtained from the spacing of the Z and η curves, as described in ABI. Of the ions for which data are available in a wide concentration range, only two (Hg^{2+}, Tl^{3+}) give chiefly mononuclear hydrolysis products. A number of others (Fe^{3+}, Al^{3+}, Th^{4+}, UO_2^{2+}, etc.) give a set of parallel Z (or η) curves which implies that the complexes can be written in the general "core + links" form $Me((OH)_t Me)_n$ with t a constant $= 2$ or 3, and n variable.

To find the details of the reaction mechanism, the experimental data for Fe^{3+} and Bi^{3+} have been treated by methods analogous to those in ABII. The data for Fe^{3+} indicate only one polynuclear complex, $Fe_2(OH)_2^{4+}$ while for Bi^{3+}, a series of complexes $Bi(OBi)_n^{3+n}$ with $n = 1, 2, 3, 4 \ldots$ is indicated. The results are thus in agreement with the conclusions in part I and part VII of this series, and the equilibrium constants obtained with the new methods also agree rather well with those obtained earlier.

In the following papers, the hydrolysis of the ions Th^{4+}, UO_2^{2+}, Al^{3+}, In^{3+}, and others will be discussed.

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