QUANTITATIVE STUDIES OF HYDROLYTIC EQUILIBRIA

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Introduction

IF an iron(III) salt, say, the nitrate or perchlorate, is dissolved in water, the solution has an acidic reaction. Thus, reaction with the water, a "hydrolysis", has taken place:*

$$xFe^{3+} + yH_2O \rightleftharpoons Fe_x(OH)_y^{(3x-y)+} + yH^+ \qquad (1)$$

Iron(III) is by no means unique in this respect: almost all cations undergo this reaction perceptibly in aqueous solution, *e.g.*, Be^{2+}, Al^{3+}, UO_2^{2+}, Cu^{2+}. Many explanations have been offered, but not always supported by sufficient experimental evidence.

Some of the older textbooks, for instance, state that uncharged hydroxide is formed:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

This requires either microcrystals or a true solution of the hydroxide, and both these explanations can be ruled out by applying the law of mass action even to rather crude measurements.

It was suggested by Werner[1] and by Pfeiffer[2] that protons are split off from the water molecules bound to the cation ("aquo-acidity"), *e.g.*:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+} + H_3O^+$$

or, more briefly:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad (2)$$

The equilibrium constant of this reaction would be the acidity constant, K_a, of the Fe^{3+} ion. Niels Bjerrum,[3,3a] who was the pioneer in this field as in many others, determined K_a for Cr^{3+} as early as 1906. Brönsted and Volqvartz,[4] in 1928, from kinetic measurements of $[H^+]$ and solubility

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* Editor's note: As written in equation (1), this reaction appears to be fission (lysis) *of* water, rather than fission *by* water, the latter being the sense in which the term "hydrolysis" is generally used in other fields. The reaction, however, assumes the form of hydrolysis *by* water if it is written in the old (inadequate) non-ionic form such as:

$$FeCl_3 + H_2O \rightarrow FeCl_2{\cdot}OH + HCl$$

The word "hydrolysis" is used in this Review for any such reactions in which water takes part, as is customary in other publications in this field.

[1] A. Werner, *Ber.*, 1907, **40**, 272; "Neuere Anschaungen auf dem Gebiete der anorganischen Chemie", Vieweg and Son, Braunschweig, 2nd edn., 1909, p. 238.

[2] P. Pfeiffer, *Ber.*, 1907, **40**, 4036.

[3] N. Bjerrum, *Kgl. danske Videnskab. Selskab. Skrifter, Nat.-mat. Afd.*, 1906, **4**, 1; *Z. phys. Chem.*, 1907, **59**, 336; 1910, **73**, 724.

[3a] N. Bjerrum, Thesis, 1908, Copenhagen, pp. 110—117.

[4] J. N. Brönsted and K. Volqvartz, *Z. phys. Chem.*, 1928, **134**, 97

data, calculated K_a for Al^{3+}, Fe^{3+}, and six other cations. As a result, and perhaps also under the influence of the success of the Brönsted–Lowry acid–base concept in other fields, it was thereafter often assumed that reactions such as (2) are the general explanation of cation hydrolysis.

If this were so, it would provide an extremely simple picture of the behaviour of elemental ions in aqueous solution. Consider, for instance, the series of ions with $2s^2p^6$ structure: Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, P^{5+}, S^{6+}, Cl^{7+}. The electrostatic field close to the ions increases strongly from Na^+ to Cl^{7+}, since the radius decreases and the charge increases; thus it would be increasingly hard for protons to remain near the central ion. The field of Na^+ barely suffices to direct the surrounding water dipoles, whereas Mg^{2+} and Al^{3+} hold 6 water molecules strongly enough to bring them into the lattice when a salt crystallises. The increased repulsion of protons is illustrated by the species that may reasonably be assumed to exist in acidic and alkaline solution:

at pH = 0 : $Mg(H_2O)_6{}^{2+}$, $Al(H_2O)_6{}^{3+}$, $Si(OH)_4$, $PO(OH)_3$, $SO_3{\cdot}OH^-$, $ClO_4{}^-$
at pH = 14: $Mg(H_2O)_5OH^+$, $Al(H_2O)_2(OH)_4{}^-$, $SiO_2(OH)_2{}^{2-}$, $PO_4{}^{3-}$, $SO_4{}^{2-}$, $ClO_4{}^-$

Obviously, the simple electrostatic picture goes a long way towards explaining the facts. However, it is certainly an oversimplification.

Already in 1908, Niels Bjerrum[3a] had found that the hydrolysis of Cr^{3+} also gives polynuclear complexes, *i.e.*, complexes with several metal atoms: $Cr_2(OH)_2{}^{4+}$, etc. This work was, however, for a long time not the centre of attention. Jander,[5] by diffusion measurements, later gave qualitative evidence for polynuclear complexes of many cations. Nevertheless, and in spite of the fact that polynuclear complexes have long been recognised among the hydrolysis products from anions such as molybdate and silicate, the idea of aquo-acidity with mononuclear products predominated for many years

Previous work on hydrolytic equilibria of cations and anions is listed in the recent Tables of Stability Constants for inorganic ligands,[6] Tables 1—4 (ligand OH^-); anionic hydrolyses will be found in Tables 5, 6, 7, 8, and 50. The present Review deals mainly with work carried out in Stockholm in the last 10 years.

Symbols and Equations.—The basis of all the work to be described is the law of mass action. Consider two reagents A and B (omitting the charges), which can form one or several complexes, A_pB_q, each with a formation constant β_{pq}. Let a be the concentration of free A, and b the concentration of free B. If the activity factors are kept constant, for instance, by using a concentrated ionic medium, we may choose the standard states so

[5] For a review, see G. Jander and K. F. Jahr, *Kolloid-Beih.*, 1936, **43**, 295.

[6] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part II: Inorganic Ligands", Chem. Soc. Special Publ. No. 7, 1958, published under the auspices of I.U.P.A.C.

that they are equal to unity and then use concentrations in place of activities. The law of mass action then gives:

$$[A_pB_q] = \beta_{pq}[A]^p[B]^q = \beta_{pq}a^pb^q \quad . \quad . \quad . \quad . \quad (3)$$

If B is the total concentration of B, and Z the average number of A atoms bound per B atom, we have:

$$B = [B] + \Sigma q[A_pB_q] = b + \Sigma q\beta_{pq}a^pb^q \quad . \quad . \quad . \quad . \quad . \quad (4)$$
$$BZ = \Sigma p[A_pB_q] = \Sigma p\beta_{pq}a^pb^q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We shall moreover define a convenient variable, η,

$$\eta = \log(B/b) = \log(1 + \Sigma q\beta_{pq}a^pb^{q-1}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . (6)$$

For the special case of hydrolysis, let A be OH^- and B the metal ion; here, however, we shall still often leave out the charges of complexes. The general formula of a complex may conventionally be written as $B_q(OH)_p$; it must be stressed at once that equilibrium measurements cannot distinguish between species which differ only in the number of solvent molecules or ions of the ionic medium. For instance, it is not possible to distinguish, from equilibrium measurements in a perchlorate medium alone, between $Fe_2(OH)_2^{4+}$, Fe_2O^{4+}, $Fe_2(OH)_2ClO_4^{3+}$, or a mixture of these and similar species such as $Fe_2(OH)_2(H_2O)_x(ClO_4^-)_y^{4-y}$.

To conform with the published Tables[6] we shall denote by $*\beta_{pq}$ the equilibrium constant for the reaction written with $(H_2O - H^+)$ as a reagent, rather than OH^-:†

$$pH_2O + qB \rightleftharpoons B_q(OH)_p + pH^+$$
$$[B_q(OH)_p] = *\beta_{pq}[H^+]^{-p}[B]^q = *\beta_{pq}h^{-p}b^q \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where h is the concentration of H^+

Equations (4), (5), and (6) then are changed to the forms:

$$B = [B] + \Sigma q[B_q(OH)_p] = b + \Sigma q*\beta_{pq}h^{-p}b^q \quad . \quad . \quad . \quad (4a)$$
$$BZ = \Sigma p[B_q(OH)_p] = \Sigma p*\beta_{pq}h^{-p}b^q \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$
$$\eta = \log(B/b) = \log(1 + \Sigma q*\beta_{pq}h^pb^{q-1}) \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

The problem is to find the sets of numerals p, q that correspond to complexes present in appreciable amounts, and the equilibrium constants $*\beta_{pq}$ for their formation.

† In this Review, as in ref. 6, β_{pq} is the equilibrium constant for the formation of A_pB_q from the reagents A (the ligand) and B (usually a metal ion, cf. eqn. 3). For mononuclear complexes, A_pB, $q = 1$, and the second subscript is usually left out, β_2 being written instead of β_{21}, etc. The equilibrium constant for step-wise formation of a mononuclear complex, $A_{p-1}B + A \rightleftharpoons A_pB$ is denoted by K_p. An asterisk on a β or a K denotes that the reactions are written with HA–H^+ as ligand, instead of A (for instance in the F^-–Fe^{3+} system $*\beta_2$ is the equilibrium constant for $Fe^{3+} + 2HF \rightleftharpoons FeF_2^+ + 2H^+$). For OH^- complexes, HA is, of course, water, $*\beta_{pq}$ is the equilibrium constant defined by eqn. (7), and $*K_1$, $*K_2$, etc., are the acidity constants, as in equations (8) and (9).

Experimental methods

To provide numerical values for p, q, and $^*\beta$ in equations (4*a*—6*a*), we have to measure B, Z, b, and h over as wide a range as possible. B (= the total concentration of B) is always known from the amount of component B added to the solution. h (= $[H^+]$) may often be measured with a hydrogen or quinhydrone electrode, and almost always with a glass electrode. Z (= the average number of OH groups bound per atom of B) is obtained from h and the simple argument that the number of protons in the solution should be the same as that originally added. In many cases, b and thus η [= log (B/b)] may be obtained by using cells with a metal (Ag^+, Hg_2^{2+}), amalgam (Cd^{2+}, Pb^{2+}, Bi^{3+}, In^{3+}), or redox (Hg^{2+}, Tl^{3+}, Fe^{3+}) electrode.

The experiments are conveniently carried out as "titrations": to, say, 100 ml. of a solution S are made successive additions of a solution T (for practical reasons, sometimes of two different solutions T_1 and T_2). The compositions of the solutions are so chosen that B, the concentration of B in the mixture, remains constant whereas Z is varied by the addition of acid or base. Moreover, the ionic medium is kept as constant as possible, usually by the aid of sodium perchlorate. After each addition, the equilibrium values for h and, if possible, b are measured by suitable electrodes. After a small correction for the liquid junction potential E_j, which is proportional to h, the e.m.f.s give the concentration directly, and may be calibrated with solutions of known h and b. It seems, for instance, that with 3M-(sodium) perchlorate as medium, one may replace as much as 0·6 mole per l. of Na^+ by H^+ before deviations in the activity factors of metal cations correspond to more than ±0·2 mv in the e.m.f.s.[7]

All the data used for the calculations refer to clear solutions (no colloid or precipitate may be present), where it has been proved that the same values are obtained from whichever direction the equilibrium between the dissolved species is approached, *e.g.*, from higher or from lower Z.

To increase Z, a base is added, often OH^-. Sometimes, however, *e.g.*, for Fe^{3+}, a local excess of OH^- gives rise to a local precipitate which dissolves very slowly. It has then been proved practicable to add HCO_3^- instead: it is proved that complex-formation by carbonate is negligible by bubbling carbon dioxide and nitrogen alternately through the solution and observing the effect on the e.m.f.s.[8]

By such titrations at constant total concentration of B and in a constant ionic medium, but with varying Z values (first used by I. Leden[9] in a study of a number of cadmium complexes) it is possible to obtain in a limited time a much larger number of experimental results than could be obtained in the same time by the older "point-wise" method. Moreover, from the course of a titration curve it is possible to correct for small errors in the

[7] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, 1953, **5**, 425.

[8] B. O. A. Hedström, *Arkiv Kemi*, 1953, **6**, 1.

analysis: for instance, to determine accurately the excess of acid concentration in a metal-salt solution.[10] This incidentally gives the titration method an advantage over the time-honoured method of measuring the pH of a solution of a "pure salt" (see the case of Fe^{2+} below[11]).

Treatment of results

For each system studied, it is essential to obtain a series of measurements as accurate as possible and over as wide a range of concentrations (B, h) as possible. The results are conveniently displayed, as in many cases in this Review, as graphs of Z against $\log h$ (or as graphs of η against $\log h$) for specified values of total concentration of reagent B. These families of curves will be represented in the text below by $Z(\log h)_B$ and $\eta(\log h)_B$.

If a certain set of $*\beta_{pq}$ is to be acceptable as the final solution of the problem, the curves $Z(\log h)_B$ calculated by use of these constants must, within the experimental error, agree with the experimental results over the whole range studied. It is important that the whole range rather than a limited part of it shall be covered.

Even when the numerical equations derived give acceptable agreement with the experimental results over the whole range, the question still remains whether the explanation in terms of chemical reactions is unique or not. Therefore it has been necessary to devise mathematical and graphical methods for treating the results that are free from preconceived opinions as to what the complexes should be, and to apply as many such independent methods as possible. For details of the mathematical and graphical methods the original papers[12] should be consulted.

Sometimes, the set of curves gives important information at a first glance. For instance, if the data in $Z(\log h)$ coincide for different values of B, and thus are independent of B, then only one value of q is represented. In that case all the complexes present in appreciable amounts are homonuclear; then, as a rule, $q = 1$, and the complexes are mononuclear. [If $\eta(\log h)$ is independent of B, the complexes must be mononuclear.] This is exceptional with OH^- but common with other ligands; for OH^- the Z and η curves generally change with B, so that polynuclear complexes must also be present.

If the curves are parallel with a constant spacing, $(\Delta \log B)/(\Delta \log h)_z = t$, then Z and η are functions of the single variable $x = \log B - t \log h$, and it can be shown that all complexes present in appreciable amounts can be written in the form $B\{(OH)_tB\}_n$, the "core + links" formula.[12a] However, it requires a more accurate analysis of the curves to find whether

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[10] C. Berecki-Biedermann, *Arkiv Kemi*, 1956, **9**, 175.

[11] B. O. A. Hedström, *Arkiv Kemi*, 1953, **5**, 457.

[12] L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, (*a*) 299, (*b*) 318; S. Hietanen and L. G. Sillén, *ibid.*, p. 1607; B. O. A. Hedström, *ibid.*, 1955, **9**, 613; G. Biedermann and L. G. Sillén, *ibid.*, 1956, **10**, 1011; F. J. C. Rossotti and H. S. Rossotti, *ibid.*, 1955, **9**, 1166; L. G. Sillén, *ibid.*, 1956, **10**, 186; F. J. C. Rossotti, H. S. Rossotti, and L. G. Sillén, *ibid.*, p. 203; L. G. Sillén, *ibid.*, p. 803.

only one or two values of n are represented, or whether there are several such, perhaps a series of complexes.[12b]

In the following pages, our results for several systems will be discussed. The chemical picture will be stressed, and for some systems the degree of agreement between experiment and theory will be indicated. Since the same species and equilibrium constants have been deduced by several independent mathematical approaches—often also several independent experimental methods—it seems that the main reactions are generally well established; it is, however, possible that species existing in minor amounts escaped detection.

Cationic systems

Mononuclear Species.—Mercury(II) is one of the few ions which, on hydrolysis, fulfil the criterion for mononuclearity: Z and η are functions of $\log h$ only, and independent of B. The two independent sets of data, $Z(\log h)$ obtained by use of a glass electrode, and $\eta(\log h)$ obtained by use of a redox electrode, may be explained by an acid dissociation in two steps; the same values are obtained for the acidity constants:[13]

$$H_2OHgOH_2{}^{2+} \rightleftharpoons HOHgOH_2{}^{+} + H^+;\ {}^*K_1 = {}^*\beta_1\ (= {}^*\beta_{11}) \quad . \quad (8)$$

$$HOHgOH_2{}^{+} \rightleftharpoons HOHgOH + H^+;\ {}^*K_2 = {}^*\beta_2/{}^*\beta_1\ (= {}^*\beta_{21}/{}^*\beta_{11}) \quad (9)$$

The symbols given for the equilibrium constants are those used in the Tables of Stability Constants[6] (cf. footnote† on p. 148).

For other polyprotic acids, such as H_3PO_4 and H_2SO_4, the ratio between successive acidity constants is often around 10^{-5}. For $PO(OH)_3$, for instance, the logarithms of the constants are −2·1, −7·2, and −12·3. This is easily understood: it must become harder to pull protons from molecules of increasing negative charge: $PO(OH)_3$, $PO_2(OH)_2{}^-$, PO_3OH^{2-}.

By analogy, one might perhaps expect that for mercury(II) a proton would be more easily split from an ion of charge +2 than from one of charge +1. The first acidity constant, ${}^*K_1$ (at 25°; in 0·5M-$NaClO_4$) is $10^{-3\cdot7}$, so the second might be expected to be of the order 10^{-8}. In fact it is $10^{-2\cdot6}$, and this is a case where the second dissociation constant of an acid is greater than the first. This means that the following disproportionation is favoured:

$$2HgOH^+ \rightleftharpoons Hg(OH)_2 + Hg^{2+};\quad K = {}^*K_2/{}^*K_1 = 10^{1\cdot1} \quad . \quad (10)$$

Fig. 1 shows the distribution of Hg^{II} and, for comparison, P^V, over various complexes for variations of $\log h$. It is seen that the fraction of mercury(II) present as the intermediate complex $HgOH^+$ is at most about 14%. If we assume that there are N equivalent possible sites for OH groups on a Hg^{II} atom and that the probability that one of these is occupied by an OH is independent of whether the other sites are occupied

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[13] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 747.

or not, then one may derive the "statistical" value for the equilibrium constant K in equation (10). We have:

$$K_{\text{stat.}} = ({}^*K_2/{}^*K_1)_{\text{stat.}} = (N - 1)/2N \qquad (11)$$

If we assume $N = 2$, we find that $\log K_{\text{stat.}} = \log 1/4 = -0{\cdot}6$; for higher values of N, $\log K_{\text{stat.}}$ would have values between $-0{\cdot}6$ and $-0{\cdot}3$.

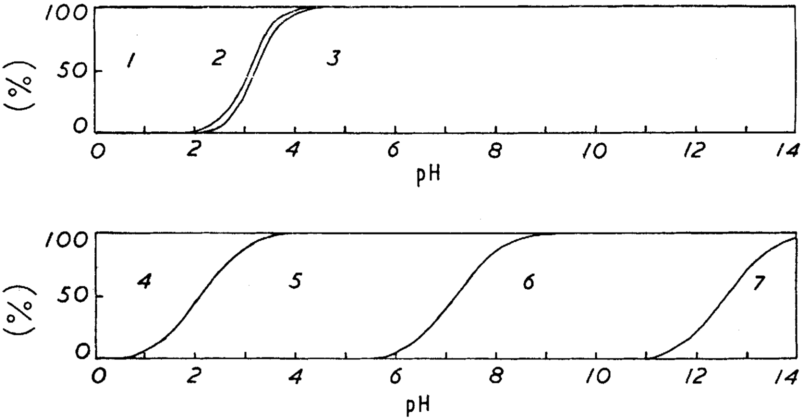

FIG. 1. *Distribution of* P^{V} *and* Hg^{II} *over different species in solutions of various* pH. *For each* pH, *one can draw a vertical line; the section of this line falling within the field of each species is proportional to the amount of that species present at equilibrium*, e.g., *at* pH = 3·0 *we have* 12% *of* H_3PO_4 *and* 88% *of* $H_2PO_4^{2-}$; *at the same* pH *we have* 59% *of* Hg^{2+}, 12% *of* $Hg(OH)^+$, *and* 29% *of* $Hg(OH)_2$.

1, Hg^{2+}; 2, $Hg(OH)^+$; 3, $Hg(OH)_2$; 4, H_3PO_4; 5, $H_2PO_4^-$; 6, HPO_4^{2-}; 7, PO_4^{3-}.

[Reproduced, with permission, from *J. Inorg. Nuclear Chem.*, 1958, **8**, 193.]

In fact, although the electrostatic effects would have tended to decrease $\log K$, it is greater than the statistical value. (Our conclusion was, incidentally, later confirmed by work in Schwarzenbach's school at Zürich.[14])

It appears at first sight possible to relate the high value for K with the *sp*-bonds in Hg(II) complexes, to consider that the two symmetrical species are favoured by mesomerism, but this view cannot be maintained in face of the accumulated data. The Table (p. 167) is a survey of equilibrium constants for mono- and di-nuclear hydroxo-complexes studied at Stockholm. Some of the products are only secondary while in the available concentration range polynuclear complexes predominate. In other cases, however, the data have been accurate enough to afford ${}^*K_1$ and ${}^*K_2$ independently, and so to give K in equation (10). It is true that Tl^{3+} and In^{3+}, with electronic structures similar to Hg^{2+}, also have $\log K$ greater than the statistical value; but so have Fe^{3+} and Sc^{3+}, with very different

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[14] G. Anderegg, G. Schwarzenbach, M. Padmoyo, and Ö. F. Borg, *Helv. Chim. Acta*, 1958, **41**, 988.

electronic structures. It seems, therefore, that this behaviour is typical of OH_2 acidity, as distinguished from the OH acidity of, say, $PO(OH)_3$ and $SO_2(OH)_2$. Perhaps, the second complex is not $M(OH)_2$, but rather MO: FeO^+, HgO, InO^+, etc. (cf VO^{2+}).

One specific case, that of the iron(II) ion, has general interest. An early investigator[15] very carefully applied what was then the standard method for cation hydrolysis. He prepared a very pure specimen of iron(II) perchlorate, recrystallising it many times in the absence of air, and measured the pH of solutions of this salt in air-free water. He then calculated $*K_1$ (the equilibrium constant for $Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$) as $10^{-5 \cdot 9}$. [Other workers,[15a] using pure solutions of iron (II) chloride, found a value of $10^{-7 \cdot 9}$.] The same reaction was studied by Bengt Hedström,[11] by what has become our standard method. He prepared a solution containing iron(II) and perchlorate ions, and a small amount of H^+ in excess. From the changes in log h on addition of increasing amounts of base he calculated accurately the amount of H^+ in the solution; the part of the titration curve where Fe^{2+} and $FeOH^+$ were both present gave $*K_1$, namely, $10^{-9 \cdot 5}$: iron(II) is thus a much weaker acid than was previously thought. It is not hard to explain the discrepancy: it is difficult to avoid presence of small amounts of H^+ and Fe^{3+}, which may be adsorbed on the crystals of $Fe(ClO_4)_2$; although the resulting solutions do not change their pH after a number of recrystallisations, the acidity is then much too high. Unfortunately, most older work, and some more recent, on cation hydrolysis is founded on measurements of pH in "pure salt" solutions.

Dinuclear and polynuclear complexes

Iron(III).—The hydrolysis of the iron(III) ion has been studied by many workers,[6] who, however, have until recently usually tried to explain their results in terms of reaction (2) only, with an equilibrium constant $*K_1$. Now, by various methods it is possible to obtain approximately constant values for $*K_1$ over limited ranges of h and total iron concentration. However, accurate measurements over a wide concentration range show that the calculated $*K_1$ varies by more than can be accounted for by activity factors or by a second mononuclear complex, $Fe(OH)_2^+$. From deviations in both spectrophotometric[16] and magnetic measurements[17] it was concluded that there must exist some other species, presumably a polynuclear complex $Fe_x(OH)_y^{(3x-y)+}$.

Bengt Hedström[8] in Stockholm studied the hydrolysis of iron(III) using glass and redox electrodes and deduced very straightforwardly from both sets of results that the main product in his experimental conditions [3M (Na)ClO_4; 25°] had the formula $Fe_2(OH)_2^{4+}$ and that two mononuclear

[15] F. Lindstrand, Diss., Lund, 1939.

[15a] K. H. Gayer and L. Woontner, *J. Amer. Chem. Soc.*, 1956, **78**, 3944.

[16] T. H. Siddall, tert., and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1951, **73**, 4270.

[17] P. W. Selwood, personal communication (1952).

complexes occurred as by-products, becoming important at low concentrations:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+; \qquad \log {}^*K_1 = -3{\cdot}05$$
$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^{+} + H^+; \qquad \log {}^*K_2 = -3{\cdot}26$$
$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+; \qquad \log {}^*\beta_{22} = -2{\cdot}91$$

Once the formulae of the complexes, and the approximate equilibrium constants, were known, it was possible to explain the magnetic[18] and spectrophotometric results,[19] though it seems that these methods alone did not permit determination of x and y in $Fe_x(OH)_y$ with certainty.

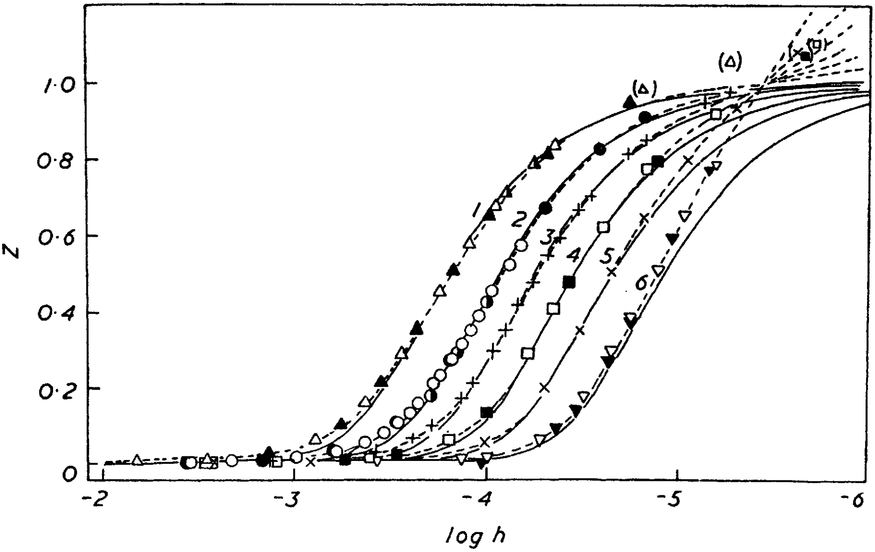

FIG. 2. *Average number, Z, of* OH *bound per* Be, *as a function of* log *h. All experimental points are given. Completely filled or open symbols represent points from different titrations, half-filled symbols represent points from back-titrations (decreasing Z). A hydrogen electrode was used for* ● *and* ■, *quinhydrone for other symbols. Full curves are calculated by assuming* $Be_3(OH)_3^{3+}$ *as the only complex, with* $\log {}^*\beta_{33} = -8{\cdot}66$. *Broken curves are calculated with the constants given in the text, by assuming* Be_2OH^{3+}, $Be(OH)_2$, *and* $Be_3(OH)_3^{3+}$ *to be present. Total* Be *concentration; B;* 1, 48 mM; 2, 19 mM; 3, 10 mM; 4, 5 mM; 5, 2·5 mM; 6, 1 mM.

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The Table lists also a number of other ions, where a complex $B_2(OH)_2$ or B_2O is formed, either as main product or together with mono- or poly-nuclear species. The column "$\dagger K_{22}$" gives the "dimerisation constant" of BOH to $B_2(OH)_2$. This often has a fairly high value, in spite of

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[18] L. N. Mulay and P. W. Selwood, *J. Amer. Chem. Soc.*, 1954, **76**, 6207; 1955, **77**, 2693.
[19] R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1955, **77**, 1352.

the fact that the reaction is an association of two positive ions. The fact that strong forces are involved is demonstrated by Mulay and Selwood's discovery[18] that the dinuclear $Fe_2(OH)_2^{4+}$ is diamagnetic, whereas the mononuclear $FeOH^{2+}$ is strongly paramagnetic, like Fe^{3+}.

Beryllium.—It has been known since Berzelius's time that solutions of beryllium salts remain clear on the addition of up to 1 OH^- per Be^{2+}. Previous work on this reaction can be divided into two groups: that[20] in which the main product is held to be $Be_2(OH)_2^{2+}$ (or its equivalent Be_2O^{2+}), and that[21] in which it is claimed as $Be_4(OH)_4^{4+}$ (or $Be_4O_2^{4+}$). The hydrolysis of beryllium (in 3M-$NaClO_4$ at 25°) was studied by modern methods by Kakihana and Sillén,[22] whose results [in the form of $Z(\log h)_B$ curves] are reproduced in Fig. 2. This Figure shows that Z increases (*i.e.*, more OH is bound per Be) with decreasing $\log h$ (B constant), and with increasing B ($\log h$ constant). The first result must be so; the second indicates that there are polynuclear products. The detailed measurements are incompatible with the assumption of either $Be_2(OH)_2^{2+}$ or $Be_4(OH)_4^{4+}$ as the main product, whereas mathematical analysis of them strongly indicates $Be_3(OH)_3^{3+}$. Assuming this as the single product gives fair agreement over a fairly wide range (full curves in Fig. 2), but deviations at the two ends of the curves lead to the formulae and formation constants of two further complexes present in minor amounts (but still not those assumed by previous workers). The broken curves in Fig. 2 have been calculated by assuming the following equilibria:[22]

$$3Be^{2+} + 3H_2O \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+; \quad \log {}^*\beta_{33} = -8{\cdot}66$$
$$2Be^{2+} + H_2O \rightleftharpoons Be_2OH^{3+} + H^+; \quad \log {}^*\beta_{12} = -3{\cdot}24$$
$$Be^{2+} + 2H_2O \rightleftharpoons Be(OH)_2 + 2H^+; \quad \log {}^*\beta_{2} = -10{\cdot}9$$

Fig. 3 is a distribution diagram like Fig. 1. For each species in the solution, a field is given. If a vertical line is drawn at a specific value of $\log h$, the section of this line falling within each field denotes the fraction of total beryllium present as the corresponding complex at the $\log h$ in question. Since polynuclear complexes are formed, the distribution depends also on the total concentration, B: diagrams are given for $B = 1$, 10, and 100 millimolar.

The predominance of $Be_3(OH)_3^{3+}$ suggests that it contains a ring of 3Be and 3OH, with $6H_2O$ to fill out the co-ordination tetrahedra of beryllium. The other two complexes have narrower fields of existence; it seems likely that other complexes might also appear, presumably with still narrower ranges, if more sensitive experimental methods were available.

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[20] M. Prytz, *Z. anorg. Chem.*, 1929, **180**, 355; 1931, **197**, 103; R. A. Gilbert and A. B. Garrett, *J. Amer. Chem. Soc.*, 1956, **78**, 5501.

[21] R. Schaal and J. Faucherre, *Bull. Soc. chim. France*, 1947, 927; J. Faucherre, *ibid.*, 1953, 1117; 1954, 253; P. Souchay, *ibid.*, 1948, 143; M. Teyssèdre and P. Souchay, *ibid.*, 1951, 945.

[22] Ref. *a* of the Table, p. 167.

Tin(II).—In early work on the hydrolysis of Sn^{2+} it was assumed that either[23a] the mononuclear $SnOH^+$ or[23b] the dinuclear $Sn_2(OH)_2^{2+}$ (or Sn_2O^{2+}) was formed. This system was studied by Tobias[24] who measured h with glass electrodes, and b (= [Sn^{2+}]) with tin amalgam electrodes. The two sets of data, Z (log $h)_B$ and η (log $h)_B$ (Figs. 4 and 5) independently gave the same set of species and equilibrium constants, namely:

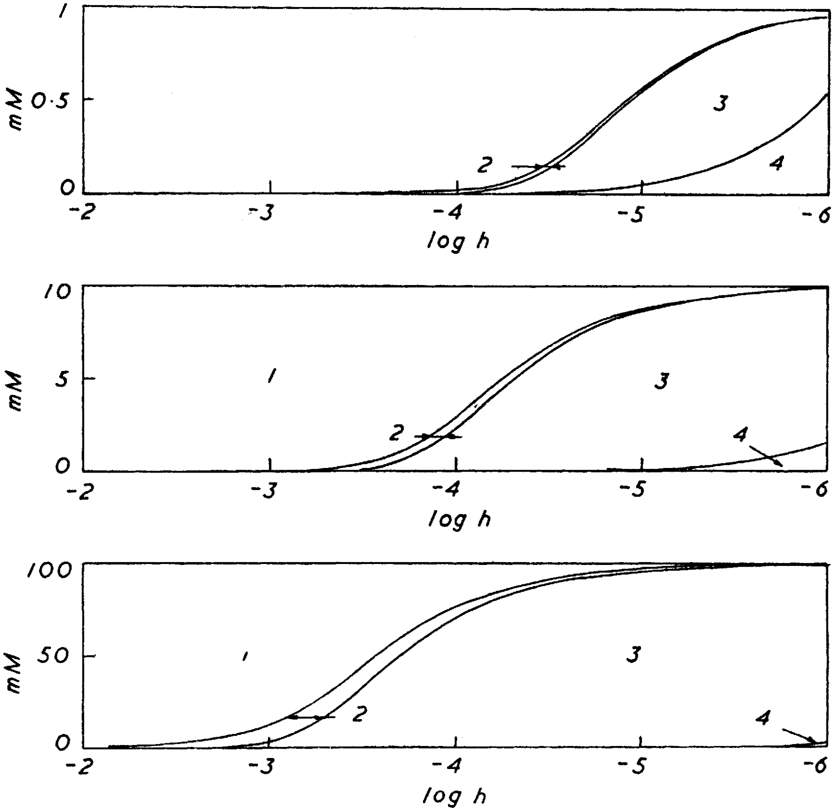

FIG. 3. *Distribution of beryllium over complexes for total beryllium concentration B = 1, 10, and 100 millimolar as a function of* log h.

1, Be^{2+}; 2, Be_2OH^{3+}; 3, $Be_3(OH)_3^{3+}$; 4, $Be(OH)_2$.

[Reproduced, with permission, from *Acta Chem. Scand.*, 1956, **10,** 1002.]

		Older values
$3Sn^{2+} + 4H_2O \rightleftharpoons Sn_3(OH)_4^{2+} + 4H^+$;	log $^*\beta_{43} = -6{\cdot}77$	—
$2Sn^{2+} + 2H_2O \rightleftharpoons Sn_2(OH)_2^{2+} + 2H^+$;	log $^*\beta_{22} = -4{\cdot}45$	~-3
$Sn^{2+} + H_2O \rightleftharpoons SnOH^+ + H^+$;	log $^*K_1 = -3{\cdot}9$	$\sim-1{\cdot}7$

[23a] M. Gorman and P. A. Leighton, *J. Amer. Chem. Soc.*, 1939, **61,** 3342; 1942, **64,** 719; A. B. Garrett and R. E. Heiks, *ibid.*, 1941, **63,** 562; C. E. Vanderzee and D. E. Rhodes, *ibid.*, 1952, **74,** 3552, 4806; (*b*) M. Prytz, *Z. anorg. Chem.*, 1928, **174,** 355.

[24] Ref. *f* of the Table, p. 167.

The solid curves in Figs. 4 and 5 were calculated by assuming only $Sn_3(OH)_4^{2+}$, which suffices to account for a large part of the data fairly well. The broken curves were calculated by assuming also the two secondary products.

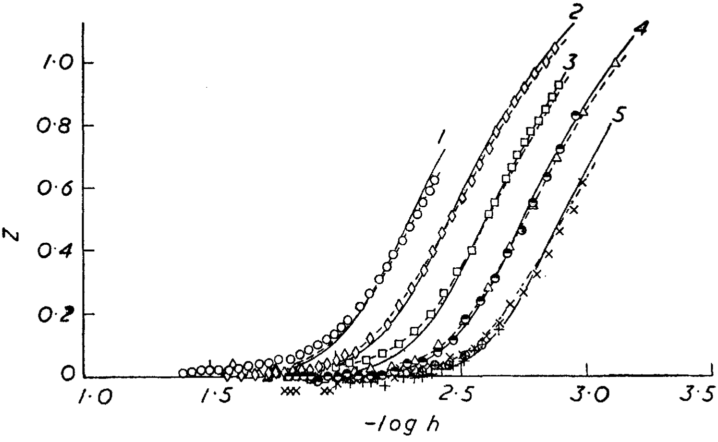

FIG. 4. *Hydrolysis of tin*(II)*; glass electrode used for measurements. Average number, Z, of* OH *bound per* Sn *as a function of* log *h* (*molar scale*)*; B as a parameter. Full curves are calculated by assuming* $Sn_3(OH)_4^{2+}$ *as the only complex with* log $^*\beta_{43} = -6{\cdot}69$. *Broken curves are calculated by also assuming the presence of* $Sn_2(OH)_2^{2+}$ *and* $SnOH^+$, *and using equilibrium constants given in the text.*

Sn^{2+} *concn.:* 1, 40·00 mM; 2, 20·00 mM; 3, 10·00 mM; 4, 5·00 mM; 5, 2·50 mM.

[Reproduced, with permission, from *Acta Chem. Scand.*, 1958, **12,** 205.]

The two minor products happened to be the same as those proposed earlier as main products. Knowing the species and the approximate equilibrium constants, Tobias recalculated the old data. In most of the old work, the tin(II) solutions must have been much too acidic because of a rather high content of tin(IV), which is harder to avoid than might be expected. The purest tin(II) solutions seem to have been those of Milda Prytz,[23b] who concluded correctly that a polynuclear complex was formed; but because she used too narrow a concentration range she missed the correct formula.

The fact that Tobias obtained the same reactions and the same equilibrium constants by two independent experimental methods[24] justifies some confidence in his results.

Bismuth(III).—The hydrolysis of bismuth(III) was studied by Olin[25] who measured $b(=[Bi^{3+}])$ and thus η, using bismuth amalgam electrodes.

[25] Ref. *j* of the Table, p. 167.

His results (Fig. 6) indicate that the main product is a hexanuclear complex of charge 6+ : $Bi_6(OH)_{12}^{6+}$ (or, *e.g.*, $Bi_6O_6^{6+}$). The deviations at the lowest values of η give evidence for another species, $BiOH^{2+}$. The curves in Fig. 6 were calculated by assuming the equilibrium constants [25°; 3M-(Na)ClO$_4$]:

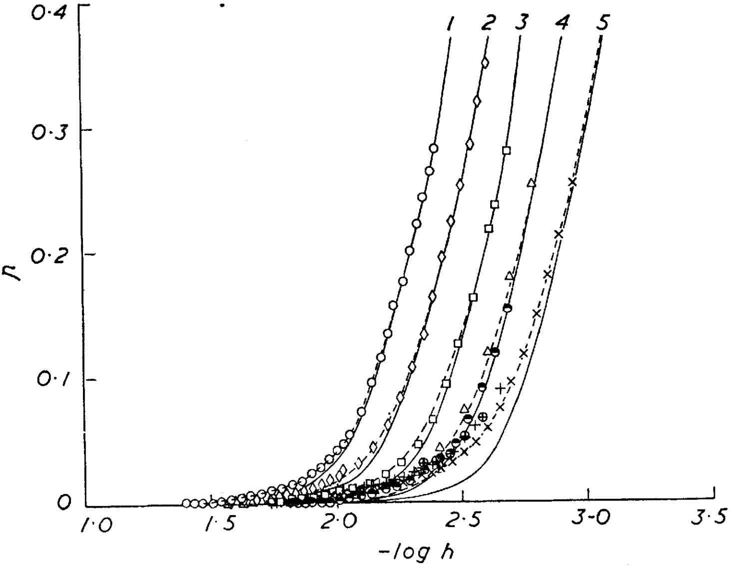

FIG. 5. *Hydrolysis of tin*(II)*; amalgam electrode used for measurements.* $\eta = \log B/b$ *as a function of* log *h*, *B as a parameter. Curves are calculated for the same sets of constants and same* Sn^{2+} *concns. as in Fig.* 4.

[Reproduced, with permission, from *Acta Chem. Scand.*, 1958, **12,** 205.]

$$6Bi^{3+} + 12H_2O \rightleftharpoons Bi_6(OH)_{12}^{6+} + 12H^+;\ \log {}^*\beta_{12,6} = 0{\cdot}33$$
$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+;\qquad \log {}^*K_1 = -1{\cdot}58$$

The agreement is as good as could be desired in a range of B 0·1—50 millimolar, *i.e.*, a ratio of 1:500. Since the solutions are rather acidic, Z is a difference between large numbers and is not very accurate; the agreement, however, is good within experimental error. For $Z > 2{\cdot}0$, slightly larger complexes are formed, probably[26] with 9Bi atoms and charges 5+, 6+, and 7+.

About twelve years ago, Granér and the Reviewer,[27] studying the hydrolysis of Bi^{3+}, concluded that a series of species $Bi\{(OH)_2Bi\}_n^{3+n}$ was formed. This also seemed to give fair agreement with the experimental results, though not as good as that in Fig. 6. Two factors contributed to the shortcoming. In this early work, the concentration B was varied only fivefold (from 10 to 50 millimolar). Secondly, there was a systematic, unexpected experimental error: the quinhydrone electrode which was used

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[26] Unpublished work at Stockholm.
[27] F. Granér and L. G. Sillén, *Acta Chem. Scand.*, 1947, **1,** 631.

for certain standardisations deviates from the ideal formula at higher acidities because *p*-benzoquinone is a base and attracts a proton.[28] The resulting error (maximum, 1·2 mv) shifted the experimental points so that the distance between the η curves corresponded to the general formula $Bi\{(OH)_{2·0}Bi\}_n^{3+n}$ rather than $Bi\{(OH)_{2·4}Bi\}_n^{3+0·6n}$.

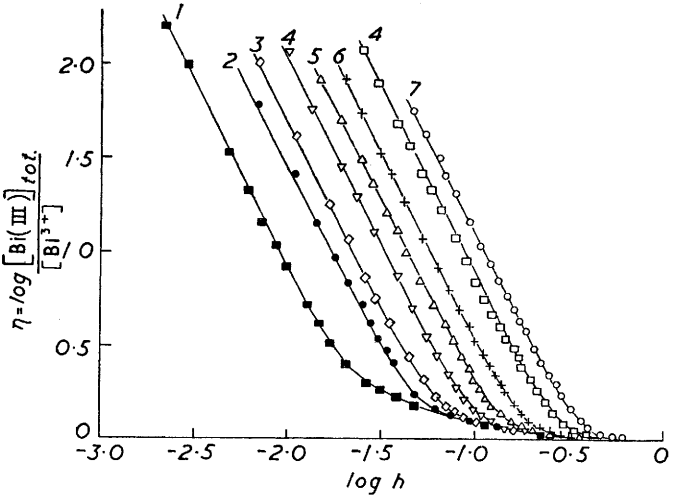

FIG. 6. *Hydrolysis of bismuth*(III). $\eta = \log B/b$ *as a function of* log *h*. *The curves are calculated by assuming the presence of the complexes* $Bi_6(OH)_{12}^{6+}$ *and* $BiOH^{2+}$ *with equilibrium constants given in the text. For clarity not all of the experimental points are shown for low values of* η.

1, 0·1 mM; 2, 0·5 mM; 3, 1 mM; 4, 25 mM; 5, 5 mM; 6, 10 mM; 7, 50 mM.

[Reproduced, with permission, from *Acta Chem. Scand.*, 1957, **11**, 1452.]

This experience stresses the importance of using a broad concentration range. When Olin later studied Bi^{3+} over a wider range of *B*, a deviation was found which was traced back to the basicity of quinone. It should be mentioned, however, that the mechanism which was first proposed for bismuth and was erroneous in that case sufficed to explain the results very well for a number of other ions, especially indium, thorium, uranyl, and scandium.

Series of complexes

For the cations discussed above, one or at most two polynuclear species have been found; if two, one of them has had a much wider "range of existence" in distribution diagrams such as Fig. 3 $\{Be_3(OH)_3^{2+}$, $Sn_3(OH)_4^{2+}\}$. For a number of other systems, the predominating complexes seem to have the general formula $B\{(OH)_tB\}_n$, with *t* constant, and there is no preferred value of *n*. Good agreement with experiment is obtained

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[28] G. Biedermann, *Acta Chem. Scand.*, 1956, **10**, 1340.

by assuming that complexes with all values for $n = 1, 2, 3 \ldots$ are formed, and that the equilibrium constants for their formation vary with n in some regular manner, usually linearly.

For In^{3+}, Biedermann[29] deduced the following equilibrium constants (as well as those for the mononuclear complexes, see Table) from two independent sets of measurements, $Z(\log h)_B$ and $\eta(\log h)_B$ (glass or quinhydrone, and In–Hg electrodes):

$$In^{3+} + 2H_2O + In^{3+} \rightleftharpoons In(OH)_2In^{4+} + 2H^+; \log {}^*\beta_{22} = -5{\cdot}21$$

$$In\{(OH)_2In\}_n{}^{n+3} + 2H_2O + In^{3+} \rightleftharpoons In\{(OH)_2In\}_{n+1}^{n+4} + 2H^+; \quad \log K = -4{\cdot}69 \text{ for } n>0$$

or, in general:

$$(n + 1)In^{3+} + 2nH_2O \rightleftharpoons In\{(OH)_2In\}_n{}^{n+3} + 2nH^+; \quad \log {}^*\beta_{2n,n+1} = -0{\cdot}52 - 4{\cdot}69n$$

The following reactions have been deduced exclusively from $Z(\log h)_B$ curves:

$$(n + 1)UO_2{}^{2+} + 2nH_2O \rightleftharpoons UO_2\{(OH)_2UO_2\}_n{}^{2+} + 2nH^+; \quad \log{}^*\beta_{2n,n+1} = 0{\cdot}30—6{\cdot}35n \quad \text{ref. 30}$$

$$(n + 1)Sc^{3+} + 2nH_2O \rightleftharpoons Sc\{(OH)_2Sc\}_n{}^{n+3} + 2nH^+; \quad \log {}^*\beta_{2n,n+1} = 0{\cdot}70—6{\cdot}87n \quad \text{ref. 31}$$

$$(n + 1)Th^{4+} + 3nH_2O \rightleftharpoons Th\{(OH)_3Th\}_n{}^{4+n} + 3nH^+; \quad \log {}^*\beta_{3n,n+1} = —7{\cdot}50n \quad \text{ref. 32}$$

It should be mentioned that there is evidence for other complexes as well, namely, $(UO_2)_2OH^{3+}$, $Th_2(OH)_2{}^{6+}$, Th_2OH^{7+} $ScOH^{2+}$, $Sc(OH)_2{}^+$(Table, refs. *g* and *k*), and that the equations for the equilibrium constants $\beta_{tnn,+1}$ must be understood as approximations only. This simple approximation, in spite of its having only two arbitrary constants, gives fairly good agreement with experiment; it might perhaps have been improved by introducing more than two adjustable constants.

Structure of the complexes

When one complex predominates, it seems reasonable to assume a closed structure (cyclic, tetrahedral, or octahedral, etc.) and attempts are being made to determine their crystal structures. For aluminium, earlier equilibrium studies by Cyrill Brosset[33] indicated rather larger complexes, contrary to previous opinion. Alkali can be added to a solution of aluminium chloride up to a ratio of $2{\cdot}5OH^-$ per Al^{3+} without causing permanent

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[29] Ref. *h* of the Table, p. 167. The mononuclear complexes were also studied, by a distribution method, by F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1956, **10,** 779.

[30] Ref. *c* of Table, p. 167.

[31] Ref. *g* of Table, p. 167.

[32] S. Hietanen, *Acta Chem. Scand.*, 1954, **8,** 1626.

[33] C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.*, 1954, **8,** 1917.

precipitation. Such solutions have important cosmetical uses. The aluminium complex they contain has been conventionally written as $Al_2(OH)_5^+$; it is formed rather slowly but, once it is formed, one may precipitate well-crystallised salts with, *e.g.*, SO_4^{2-}, SeO_4^{2-}, and $C_2O_4^{2-}$. In the hope of finding the structure of the complex "$Al_2(OH)_5^+$", some of these salts were studied by *X*-ray methods. They were found[26] to contain also alkali metal; a typical formula is $NaAl_{13}(OH)_{32}(SO_4)_4(H_2O)_x$. The crystal structure of a corresponding selenate has been studied thoroughly by Georg Johansson.[26] Aluminium was found to form separate groups with 13 Al and charge +7; the formula, conventionally $Al_{13}(OH)_{32}^{7+}$, is really $Al_{13}O_{40}H_{48}^{7+}$, and the structure is reminiscent[34] of that of dodecaheterotungstates such as $PW_{12}O_{40}^{3-}$. The equilibria in Al^{3+} solutions are now under study by Biedermann and it seems probable that these large Al_{13} ions will form a part of the final picture.

In crystal structures, units $U_6O_4(OH)_4^{12+}$ and $Ce_6O_4(OH)_4^{12+}$ have been found[35] as separate building-stones: they contained an octahedron of U (or Ce) and a cube of O atoms. Recent *X*-ray studies[36] of solutions seem to indicate that the "$Bi_6(OH)_{12}^{6+}$" complex may have a similar structure, $Bi_6O_4(OH)_4^{6+}$. However, no direct evidence has yet been found for existence of the Ce and U complexes in solution.

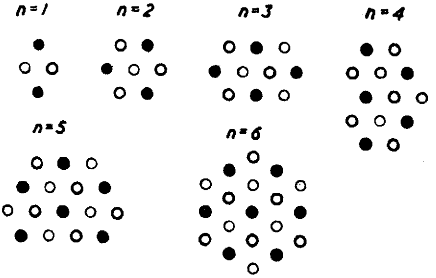

FIG. 7. *Possible structures of complexes* $UO_2[(OH)_2UO_2]_n^{2+}$ *with* $n = 1$ *to* 6, *shown as increasing fragments of a sheet from* α- $UO_2(OH)_2$. ● *uranyl groups with* U *in the plane of the paper and the two uranyl* O (*not shown here*) *above and below, perpendicular to the paper;* O *oxygen atoms above* (*thick*) *and below* (*thin*) *the plane of the paper.*

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In those cases where a series of complexes is formed, it seems reasonable to assume open structures, chains or sheets, so that addition of each new "link" has approximately the same equilibrium constant. It is tempting to make comparisons with crystal structures of compounds which are known to be precipitated from such solutions. For instance, Fig. 7 shows the geometry of the sheets in the crystal structure[26] of α-$UO_2(OH)_2$.

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[34] J. F. Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.

[35] G. Lundgren, *Arkiv Kemi*, 1953, **5**, 349; 1956, **10**, 183.

[36] H. Levy and K. A. Kraus, 1958, personal communication.

The black dots are the U atoms of $UO_2{}^{2+}$ groups; the two oxygen atoms are one above and one below the plane of the paper. The open circles are OH groups, in two layers, one above and one below the level of the U atoms. If well-rounded fragments are cut from such a sheet, their formulae will be $(UO_2)_{n+1}(OH)_{2n}$, as seen for $n = 1$—6 in Fig. 7. From the e.m.f. data the same formula was deduced for the complexes in solution, and it is attractive to regard them as fragments of the $UO_2(OH)_2$ crystal structure, pre-formed in the solution.

Similarly, the series of indium and thorium complexes may be related to the chains that have been found in the crystal structures of "basic" thorium[37] and indium salts.[38] Their composition would then be $\mathrm{In(OIn)}_n{}^{n+3}$ and $\mathrm{Th}({}^{\mathrm{OH}}_{\mathrm{O}}\mathrm{Th})_n{}^{n+4}$; by equilibrium measurements in aqueous medium one cannot distinguish between species with $2OH^-$ and $1O^{2-}$. The assumption that Th^{4+} on hydrolysis forms chain-like complexes is supported by recent work on colloidal thorium hydroxide,[39] especially electron-microscopy which shows the particles to be threadlike.

Anionic hydrolysis

General.—*Borates.* It has long been known that polynuclear species are formed in certain anionic hydrolytic systems: examples are borates, germanates, tellurates, chromates, molybdates, tungstates, and vanadates. There is no fundamental difference between anionic and cationic systems. The same graphical and mathematical approaches can be used for both, and the experimental methods are similar except that in anionic systems as a rule it is necessary to work at higher pH and there are some extra experimental difficulties (*e.g.*, exclusion of carbonate). In some systems with polyions, both cations and anions are formed in the ordinary pH range, for example, with aluminium, vanadium(v), and molybdenum(vi).

One of the first systems studied by our methods was the borates.[40] Besides the mononuclear species $B(OH)_3$ and $B(OH)_4{}^-$, polyborate ions are known to exist, especially at high total concentrations; they have previously been described in general as $B_4O_7{}^{2-}$. From the $Z(\log h)_B$ curves it was, however, deduced that in the more acidic range the predominant polynuclear species is a triborate of charge -1, presumably $B_3O_3(OH)_4{}^-$, a 6-membered ring compound. For higher Z, the accuracy of the equilibrium measurements in ref. 40 did not permit distinction with certainty between $B_3O_3(OH)_5{}^{2-}$ and $B_4O_5(OH)_4{}^{2-}$; it is possible that both exist in solution, and both have been claimed to exist in crystal lattices.[41] Recent work by a "self-medium" method[26] indicates that the tetraborate ion of

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[37] G. Lundgren and L. G. Sillen, *Arkiv Kemi*, 1949, **1**, 277; G. Lundgren, *ibid.*, 1950, **2**, 535.

[38] H. E. Forsberg, *Acta Chem. Scand.*, 1956, **10**, 1287; 1957, **11**, 676.

[39] A. Dobry, S. Guinand, and A. Mathieu-Sicaud, *J. Chim. phys.*, 1953, **50**, 501.

[40] N. Ingri, G. Lagerström, M. Frydman, and L. G. Sillén, *Acta Chem. Scand.*, 1957, **11**, 1034.

[41] C. L. Christ and J. R. Clark, *Acta Cryst.*, 1956, **9**, 830; N. Morimoto, *Mineralog. J.*, 1956, **2**, 1.

charge —2, and the triborate ion of charge —1, are the two predominating polyions.

Molybdates. Fig. 8 gives $Z(\log h)_B$ curves for hydrolysis of MoO_4^{2-}, measured by Sasaki[42] [25°; 3M-$NaClO_4$]. In this case it was practicable to let Z be the average number of H^+ bound per MoO_4^{2-} [$A = H^+$, $B = MoO_4^{2-}$ in equations (3—6)]. A related quantity is $z = Z - 2$, the average charge per Mo atom.

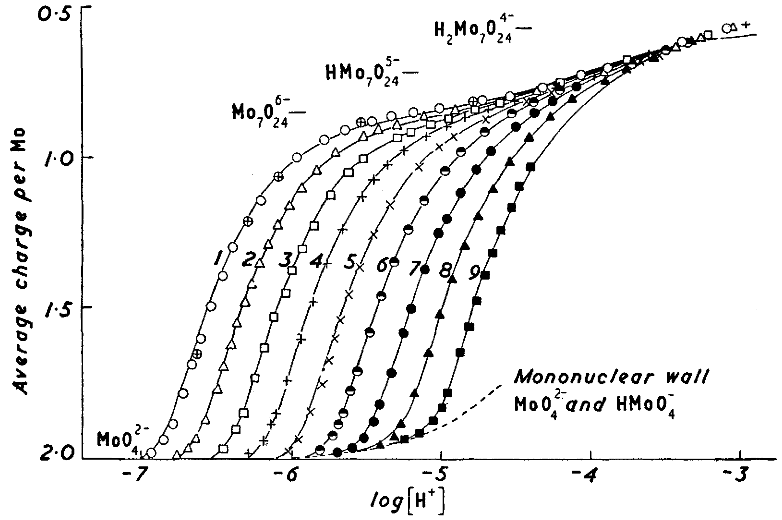

FIG. 8. *Hydrolysis of molybdate ions. Average charge per* Mo *atom* (*z*) *plotted against* log *h. Points are for different total concentrations, B, of* Mo. *Circles with crosses in them* (*curve* 2) *refer to back-titrations. The curves are calculated by assuming the species and equilibrium constants given in the text.*

$[Mo]_{total}$: 1, 160 mM; 2, 80 mM; 3, 40 mM; 4, 20 mM; 5, 10 mM; 6, 5 mM; 7, 2·5 mM; 8, 1·2 mM; 9, 0·6 mM.

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At low log h, $Z=0$ ($z = -2$) at all values of B, since MoO_4^{2-} is the predominant species. The shape and spacing of the curves show conclusively that the first polynuclear complex formed is one with 7Mo and a charge of 6—. It is reasonable to identify this species with $Mo_7O_{24}^{6-}$, the paramolybdate ion which exists[42a] as a separate unit in the crystal structure of $(NH_4)_6Mo_7O_{24}(H_2O)_4$.

Most of the results in Fig. 8 require only the two species MoO_4^{2-} and $Mo_7O_{24}^{6-}$. Deviations at low concentrations of molybdenum indicate the presence of $HMoO_4^-$, and at higher Z that of $HMo_7O_{24}^{5-}$. The curves in

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[42] Y. Sasaki, I. Lindqvist, and L. G. Sillén, *J. Inorg. Nuclear Chem.*, 1959, **9**, 93.

[42a] I. Lindqvist, *Arkiv Kemi*, 1950, **2**, 325; *Nova Acta Regiae Soc. Sci. Upsaliensis*, 1950, Cl. IV, **15**, 1.

Fig. 8 were calculated by assuming the following equilibrium constants (there is as yet no standard symbolism for such constants):

$$MoO_4^{2-} + H^+ \rightleftharpoons HMoO_4^-; \qquad \log K = 4{\cdot}08$$
$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O; \qquad \log K = 57{\cdot}7$$
$$Mo_7O_{24}^{6-} + H^+ \rightleftharpoons HMo_7O_{24}^{5-}; \qquad \log K = 4{\cdot}33$$
$$HMo_7O_{24}^{5-} + H^+ \rightleftharpoons H_2Mo_7O_{24}^{4-}; \qquad \log K = \sim 3{\cdot}7$$

Agreement is quite good. The species $HMo_7O_{24}^{5-}$ is well supported; some doubt may be expressed about $H_2Mo_7O_{24}^{4-}$, in spite of the very good agreement, since at the end of the range there must anyhow be some unknown species.[42a]

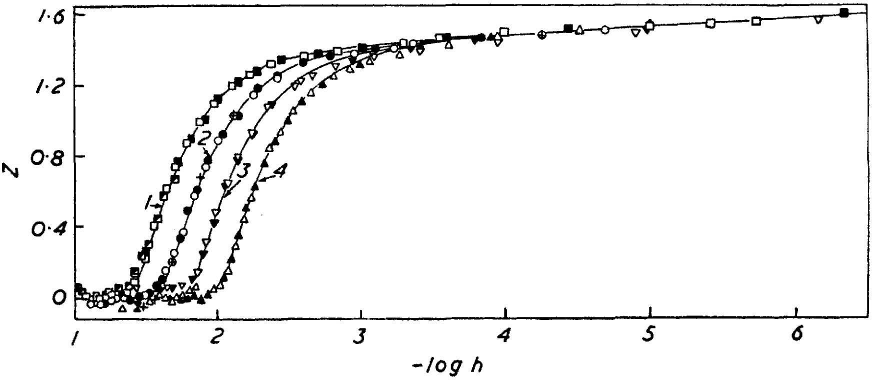

FIG. 9. *Hydrolysis of vanadium*(V). *Average number of hydroxyl groups, Z, bound to each* VO_2^+ *ion as a function of* log *h for different total concentrations, B, and vanadium. The curves are calculated by assuming the presence of the species and equilibrium constants given in the text.*

$[V]_{total}$: 1, 0·0200 M; 2, 0·0100 M (+, *reverse titration*); 3, 0·0050 M; 4, 0·0025 M.

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Vanadium(V). Fig. 9 gives curves for vanadium(V) hydrolysis;[43] Z is the average number of OH^- bound per VO_2^+ ion. In highly acidic solutions, VO_2^+ seems to be the only species ($Z = 0$); increasing the acidity from 0·05 to 3M-H^+ does not change the vanadium absorption spectrum.

With decreasing h, Z increases up to ~1·4, and the solution becomes orange-coloured. An uncharged species, corresponding to $Z = 1$ (VO_2OH, or HVO_3, or V_2O_5, etc.), might have been expected but there has been no evidence of its presence. The data indicate that the main reaction is the formation of a single polynuclear species, namely, an anion with 10 vanadium atoms. Assuming a complex with 11 vanadium atoms gives

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[43] F. J. C. Rossotti and H. Rossotti, *J. Inorg. Nuclear Chem.*, 1956, **2,** 201; *Acta Chem. Scand.*, 1956, **10,** 957.

acceptable agreement for $Z = 0$—$\sim$1·1, but deviations at higher Z values. With V_9 or V_{12} complexes, neither the spacing between the curves nor their shape gives acceptable agreement with experiment. Moreover, *X*-ray studies[44] of orange vanadates crystallised from similar solutions indicate a multiple of 10 V per unit cell. The full curves of Fig. 9 were calculated by assuming the following equilibrium constants [1M-(Na)ClO$_4$; 25°]:

$$10VO_2^+ + 8H_2O \rightleftharpoons H_2V_{10}O_{28}^{4-} + 14H^+; \quad \log {}^*\beta_{14,10} = -6{\cdot}75$$
$$H_2V_{10}O_{28}^{4-} \rightleftharpoons HV_{10}O_{28}^{5-} + H^+; \quad \log K = -3{\cdot}6$$
$$HV_{10}O_{28}^{5-} \rightleftharpoons V_{10}O_{28}^{6-} + H^+; \quad \log K = -5{\cdot}8$$

The agreement is satisfactory. The formulae are written in the conventional way, with as little water as possible. Structural studies may show them to contain more water.

From a study[26] of the alkali side of vanadate equilibria the following equilibrium constants have been deduced [0·5M-NaCl; 25°]:

$$VO_4^{3-} + H^+ \rightleftharpoons HVO_4^{2-}; \quad \log K = 12{\cdot}6^a$$
$$2HVO_4^{2-} + H^+ \rightleftharpoons HV_2O_7^{3-} + H_2O; \quad \log K = 10{\cdot}6^b$$
$$HVO_4^{2-} + H^+ \rightleftharpoons H_2VO_7^-; \quad \log K = 7{\cdot}7^b$$
$$3HVO_4^{2-} + 3H^+ \rightleftharpoons V_3O_9^{3-} + 3H_2O; \quad \log K = 30{\cdot}7^b$$

[a] By spectrophotometry. [b] By e.m.f. measurements.

Fig. 10 gives a schematic survey of all the vanadate equilibria: the average charge z per V is plotted as a function of log h for different total concentrations of vanadium. We may neglect the difference in ionic medium between different parts of the diagram. In each of the ranges $z = +1$ to $-0{\cdot}6$ and -1 to -3, there are rapid, reversible equilibria. As long as the solution is kept within one of these regions, equilibrium is obtained practically instantaneously on change of composition. If, however, a solution or a part of it has once been brought into the region z between $-0{\cdot}6$ and $-1{\cdot}0$, it requires a long time to attain equilibrium. This "instability range" may be one reason for difficulties that some previous authors have experienced with vanadate equilibria. Similar instability ranges have been observed also for silicate equilibria.[26]

It is pertinent to ask why VO_4^{3-}, HVO_4^{2-}, $HV_2O_7^{3-}$, and $V_3O_9^{3-}$ predominate, of all the conceivable species. It may be these formulae seem arbitrary because they are written on the pattern of ortho-, pyro-, and meta-phosphates. It is true that some vanadates are isomorphous with phosphates, indicating a tetrahedral VO_4^{3-} ion. However, the more common co-ordination number of vanadium(v) seems to be 5, two oxygen atoms being bound in a linear group OVO, and three more lying in the equatorial

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[44] I. Lindqvist, personal communication; H. T. Evans, jun., M. E. Mrose, and R. Marvin, *Amer. Min.*, 1955, **40**, 314.

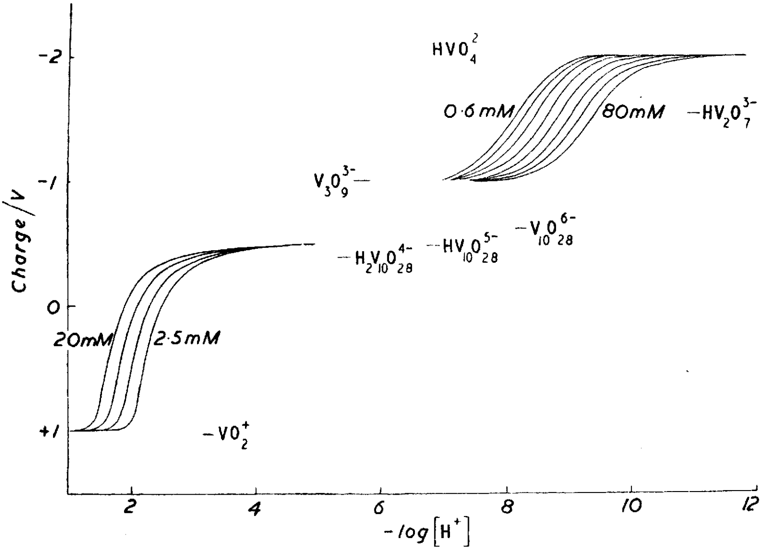

FIG. 10. *Schematic survey of the hydrolysis of vanadium*(V). *Average charge per* V *atom, z, plotted against* log *h. The lower left part corresponds to Fig.* 9, *the upper right part to unpublished measurements by Ingri and Brito.*[26] *Between them is an "instability range" with slow equilibria.*

plane. One may then imagine the following structures for the three species that predominate between $z = -1$ and -2 (B = VO_2^+, A = OH^-):

A A B A	$VO_2(OH)_3^{2-}$	$= HVO_4^{2-}$
A AB A A B A	$(VO_2)_2(OH)_5^{3-}$	$= HV_2O_7^{3-}$
A A B A B A A B A	$(VO_2)_3(OH)_6^{3-}$	$= V_3O_9^{3-}$

The equilibrium data, as usual, give only the average charge of a species, and the number of vanadium atoms, but not the amount of water. So there is no way of distinguishing between, say, HVO_4^{2-} and $VO_2(OH)_3^{2-}$, by equilibrium data alone. There is, however, no proof for these formulae.

Conclusion

In the systems discussed above, it seems that the e.m.f. methods, when applied over a wide concentration range and with a constant ionic medium, have been able to give, independently of other data, sufficient information to allow reliable conclusions about the species present and the equilibrium constants. Even if the e.m.f. method is perhaps the most versatile single method, there is every reason to supplement it, wherever possible, by other equilibrium methods such as solubility and distribution studies, and by spectral "finger-print" methods. With the last one may check the results obtained with e.m.f. data, and also extend the measurements in the ranges where the accuracy of the e.m.f. data is unsufficient.

Logarithms of equilibrium constants for cations with mono- and di-nuclear hydrolysis products.

Ion	$^*K_1$	$^*K_2$	$^*\beta_{22}$	$^*K_2/^*K_1$	$\dagger K_{22}$	Other p, q	Ref.
Be^{2+}	($^*\beta_2$	−10·9)	—	—	—	3,3;1,2	*a*
VO^{2+}	−6·0	—	−6·9	—	5·1	—	*b*
UO_2^{2+}	—	—	−6·05	—	—	$2n,n+1$	*c*
Fe^{2+}	−9·5	—	—	—	—	—	11
Cu^{2+}	(−8)	—	−10·6	—	(~5)	—	10
Cd^{2+}	−9·0	—	—	—	—	—	*d*
Hg_2^{2+}	−5·0	—	—	—	—	—	*e*
Hg^{2+}	−3·70	−2·60	—	1·1	—	—	13
Sn^{2+}	−3·9	—	−4·45	—	3·35	4,3	*f*
Sc^{3+}	−5·1	−5·1	−6·2	0	4·0	$2n,n+1$	*g*
Fe^{3+}	−3·05	−3·26	−2·91	−0·21	3·2	—	8
In^{3+}	−4·4	−3·9	−5·2	0·5	3·6	$2n,n+1$	*h*
Tl^{3+}	−1·14	−1·49	—	−0·35	—	—	*i*
Bi^{3+}	−1·58	—	—	—	—	12,6	*j*
Th^{4+}	—	—	−4·7	—	—	$3n,n+1$	*k*
U^{4+}	−2·0	—	—	—	—	$3n,n+1$	*l*

The medium is usually 3M-(Na)ClO_4, and the temperature 25°; 1M-(Na)ClO_4 for UO_2^{2+}, Fe^{2+}, and Sc^{3+}; 0·5M-(Na)ClO_4 for Hg_2^{2+} and Hg^{2+}. For UO_2^{2+}, the temperature was 20°.

† $K_{22} = {}^*\beta_{22}{}^*K_1^{-2}$: $2BOH \rightleftharpoons B_2(OH)_2$.

(*a*) H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, 1956, **10**, 985. (*b*) F. J. C. Rossotti and H. S. Rossotti, *ibid.*, 1955, **9**, 1177. (*c*) S. Ahrland, S. Hietanen, and L. G. Sillén, *ibid.*, 1954, **8**, 1907. (*d*) Y. Marcus, *ibid.*, 1957, **11**, 690. (*e*) W. Forsling, S. Hietanen, and L. G. Sillén, *ibid.*, 1952, **6**, 901. (*f*) R. S. Tobias, *ibid.*, 1958, **12**, 198. (*g*) G. Biedermann, M. Kilpatrick, L. Pokras, and L. G. Sillén, *ibid.*, 1956, **10**, 1327. (*h*) G. Biedermann, *Arkiv Kemi*, 1956, **9**, 277; *Rec. Trav. chim.*, 1956, **75**, 716. (*i*) *Idem*, *Arkiv Kemi*, 1953, **5**, 441; *Rec. Trav. chim.*, 1956, **75**, 716. (*j*) Å. Olin, *Acta Chem. Scand.*, 1957, **11**, 1445; F. Granér, Å. Olin, and L. G. Sillén, *ibid.*, 1956, **10**, 476. (*k*) S. Hietanen and L. G. Sillén, unpublished work. (*l*) S. Hietanen, *Acta Chem. Scand.*, 1956, **10**, 1531; *Rec. Trav. chim.*, 1956, **75**, 711.

The structure of the polynuclear complexes, formed on hydrolysis, is of considerable interest. Much remains to be done by diffraction work, both on crystals and solutions.

The equilibrium work gives only the ΔG of the reaction, whereas it would be desirable to know the ΔH and ΔS components. It seems that the accuracy that may be obtained from the variation of equilibrium constants with temperature is rather low, so an attack with calorimetric methods seems more promising.

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