SOME RECENT RESULTS ON HYDROLYTIC EQUILIBRIA

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INTRODUCTION

Berzelius (1812)[1] defined a neutral salt as one that contains equivalent amounts of acid and base. He pointed out that neutral salts of sulphuric acid with bases with a weak affinity, like alumina and Fe_2O_3, still have an acid reaction to taste and to plant dyestuffs. Werner (1895)[2] stated that a metal salt hydrate like $Cl_2Cu(OH_2)_2$ may also be an acid, and split off H^+, and that this idea can explain the fact that the aqueous solutions of so many metal salts are strongly acidic. Bjerrum (1910) used formulae such as $Cr(H_2O)_5OH^{2+}$ for the products.

EARLY QUANTITATIVE WORK

Quantitative studies of metal ion hydrolysis became possible in the late 1890s after Arrhenius's theory of ionic dissociation had become accepted, and Ostwald had shown that Guldberg–Waage's equilibrium law could be applied to ionic equilibria. The products of hydrolysis were thought of as OH complexes, and it is natural that they were first assumed to be mononuclear, either the equilibrium constants were determined by solubility methods (*Table 1*) or, say, by measurements of $[H^+]$ by potentiometric or kinetic measurements (*Table 2*).

Table 1. Early work on mononuclear M—OH complexes
equilibrium constants from solubility data

AgOH LEVI 1901; NOYES & KOHR 1902; $Ag(OH)_2^-$ LAUE 1927
$Hg(OH)_2$ SCHICK 1902; $Hg(OH)_3^-$ FUSEYA 1920
$Zn(OH)_4^{2-}$ KLEIN 1912
$Al(OH)_4^-$ RUSS 1904, WOOD 1908, HEYROVSKÝ 1920, KOLTHOFF 1920
$Sn(OH)_2$, $Sn(OH)_3^-$ GOLDSCHMIDT + ECKARDT 1906
$PbOH^+$, $Pb(OH)_2$ PLEISSNER 1907; $Pb(OH)_3^-$ GLASSTONE 1921
$Cu(OH)_4^{2-}$ MÜLLER 1923; $Be(OH)_4^{2-}$, BLEYER + KAUFMANN 1913
$MgOH^+$ GJALDBAEK 1925

Brönsted and Volqvartz (1928) consistently applied Brönsted's acid–base nomenclature to reactions of the type $Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+$, which had earlier been suggested by Werner and Bjerrum. In the following twenty years, almost all work on metal ion hydrolysis was based on the assumption that the only products are mononuclear OH complexes.

There were, however, also a few indications of larger complexes. Bjerrum (1908), studying the hydrolysis of Cr^{3+}, found that he must also assume

polynuclear complexes in order to explain his e.m.f. data, and he gave formation constants for $Cr_2(OH)_2^{4+}$, $Cr_6(OH)_{12}^{6+}$, and $Cr_{12}(OH)_{30}^{6+}$. In this respect, like in so many others, his thinking in solution chemistry was far ahead of his contemporaries, but unfortunately he published these results only in his dissertation, in Danish.

Table 2. Early work on mononuclear M—OH complexes
equilibrium constants from other than solubility data

LEY 1899 (kin), $BeOH^+$, $AlOH^{2+}$
KULLGREN 1904, 1913 (kin) $MgOH^+$, $MnOH^+$, $CoOH^+$, $NiOH^+$, $CuOH^+$, $ZnOH^+$,
(cf. ref. 3) $CdOH^+$, $AlOH^{2+}$, $PbOH^+$
KUNSCHERT 1904 (Zn) $Zn(OH)_4^{2-}$
NIELS BJERRUM 1906–1910 (H, con) $CrOH^{2+}$, $FeOH^{2+}$, $AlOH^{2+}$;
DENHAM 1908 (H) $CrOH^{2+}$, $CoOH^+$ or $Co(OH)_2$, $NiOH^+$, $AlOH^{2+}$
WOOD 1910 (H) $BeOH^+$, $ZnOH^+$, $PbOH^+$
VESTERBERG 1916 $LaOH^{2+}$ (dis)
KOLTHOFF 1917 (sol, col, Hg) $HgOH^+$, $Hg(OH)_2$; 1923 (col) $MgOH^+$, $CaOH^+$
LÖFMAN 1919 (dis, col) $MnOH^+$, $FeOH^+$, $CoOH^+$, $NiOH^+$, $CuOH^+$, $AgOH$,
$ZnOH^+$, $CdOH^+$, $PbOH^+$
BRÖNSTED and VOLQVARTZ 1928: $FeOH^{2+}$, $AlOH^{2+}$
$Fe(H_2O)_6^{3+} \rightleftarrows Fe(H_2O)_5OH^{2+} + H^+$

Table 3. Early work on polynuclear M–OH complexes
equilibrium constants given

NIELS BJERRUM 1908, (H) $Cr_2(OH)_2^{4+}$, $Cr_6(OH)_{12}^{6+}$, $Cr_{12}(OH)_{30}^{6+}$
MILDA PRYTZ 1928–1931 (H) $Sn_2(OH)_2^{2+}$, $Be_2(OH)_2^{2+}$
HOLMQVIST 1936 (Bi, qh) $Bi_2(OH)_4^{2+}$, $Bi_2(OH)_5^+$
HAGISAWA 1939 (gl) $Cu_2(OH)_2^{2+}$
K. J. PEDERSEN 1943, (gl): $Cu_2(OH)_2^{2+}$, Cu_2OH^{3+}
K. J. PEDERSEN 1945, (gl): $PbOH^+$, Pb_2OH^{3+}, $Pb_4(OH)_4^{4+}$
GRANÉR + SILLÉN 1947 (M—Hg, qh), $Bi(BiO)_n^{3+n}$
SOUCHAY + PESCHANSKI 1948 (sp) $Bi_4(OH)_8^{4+}$
MACINNES + LONGSWORTH 1947, GUITER 1947, FAUCHERRE 1948,⎫
AHRLAND 1949, SUTTON 1949 ⎬ $(UO_2)_2(OH)_2^{2+}$
FAUCHERRE 1948 (gl) $Al_2(OH)_2^{4+}$ ⎭
GELOSO and FAUCHERRE 1948 (gl) $Pb_4(OH)_4^{4+}$
HEIDT and SMITH 1948 (photochemical method) $Ce_2(OH)_2^{6+}$

Before 1947, very few equilibrium constants for polynuclear OH complexes were published (*Table 3*) and the only non-Scandinavian in the short list is Hagisawa (1939). From 1947 onwards a number of publications came out on equilibria with polynuclear products. For instance, the hydrolysis of the uranyl ion had been studied to some extent, as a by-product of the atomic energy work, and several authors explained their data in terms of the (2,2) complex, $(UO_2)_2(OH)_2^{2+}$. There was also some evidence for soluble polynuclear OH complexes which did not result in equilibrium constants (*Table 4*); one might have added evidence from preparative work, of several authors.

It may be said about much of this earlier work that it surely indicated polynuclear products but that in general neither was the concentration range broad enough nor the accuracy good enough in order to really exclude other possible mechanisms than that given.

A group of chemists at KTH in Stockholm came into the hydrolysis field

around 1950. Some of them had an earlier training in x-ray structure analysis, which then served us as an ideal for the correspondence between data and model. In the structure analysis of a certain crystal phase, one collects a large amount of accurate data—positions and intensities of diffraction spots or lines—and from them deduces a structure model, that is the dimensions of the unit cell, and the atomic positions. The test of the final model is the good agreement between the positions and intensities calculated from that model, and the observed values.

*Table 4.* Early work on polynuclear M—OH complexes
no equilibrium constants

BRINTZINGER 1934, dialysis
JANDER and JAHR 1936, diffusion
HAYEK 1935, solubility $Hg(OHg)_n^{2+}$
PRYTZ and NAGEL 1936 (con,sp,diffusion): $Bi_2(OH)_4^{2+}$, $Bi_4(OH)_{10}^{2+}$
J. BJERRUM 1941 (gl) Be_2OH^{3+}
SCHAAL and FAUCHERRE 1947 (gl): $Be_4(OH)_4^{4+}$, $Th_4(OH)_8^{8+}$, $Cr_2(OH)_2^{4+}$
SOUCHAY 1948 (fp) $Be_4(OH)_4^{4+}$, $Th_4(OH)_8^{8+}$, $Cr_2(OH)_2^{4+}$

In a similar way, we thought it would be possible to develop methods for accurate equilibrium analysis: to collect accurate equilibrium data over a wide range, from which one might deduce the model (in solution chemistry = the set of species, and their equilibrium constants), and compare calculated and experimental data. The most promising experimental method seemed to be e.m.f. measurements, by which one may get accurate data, varying the concentrations of all the reactants over a wide range. We had reasonable hope to minimize the trouble from the variation of activity coefficients, by using an ionic medium like 3 M $(Na)ClO_4$.

EQUATIONS

Suppose we have a metal ion B^{n+}, which hydrolyses to form one or more products, which we shall denote in general by $(p,q) = B_q(OH)_p^{(nq-p)+}$. (The formula is understood to include also an unknown amount of solvent: H_2O, perhaps medium ions). For each species (p,q), its formation constant β_{pq} is defined as the equilibrium constant for the reaction (Eq. 1). If we

$$p\ H_2O + Bq^{n+} \rightleftharpoons B_q(OH)_p^{(qn-p)+} + p\ H^+ \qquad (1)$$
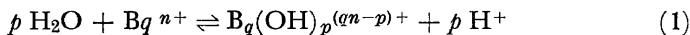
write $b = [B^{n+}]$ and $h = [H^+]$, the concentration of the (p,q) complex is given by Eq. (2). The total concentration of the metal, B, free or in com-

$$c_{pq} = \beta_{pq}h^{-p}b^q \qquad (2)$$

plexes, can be represented as in Eq. (3).

$$B = b + \Sigma qc_{pq} = b + \Sigma q\beta_{pq}h^{-p}b^q \qquad (3)$$

The amount (in mole/litre) of OH^- bound to B or, which is the same, the amount of H^+, set free by reactions of type (1) is

$$BZ = \Sigma pc_{pq} = \Sigma p\beta_{pq}h^{-p}b^q \qquad (4)$$

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If we can measure only h by e.m.f., using a glass, quinhydrone or hydrogen electrode, we will have for each measured equilibrium solution a triplet of values $(B, \log h, Z)$; Z is easily obtained from h and the analytical composition of the solution. If we want to test a model—which in this case means a set of triplets (p,q,β_{pq})—we may solve b from equation (3), where all other quantities are known, insert that b into equation (4) and so obtain Z_{calc}. A good fit might be defined as the one that minimizes the error square sum

$$U = \Sigma \, (Z_{calc} - Z_{exp})^2 \tag{5}$$

If we can also measure the free metal ion concentration $b = [B^{n+}]$ by a metal or amalgam electrode, we may for each equilibrium solution have another triplet $(B, \log h, \log b)$, and we may compare the experimental value for b with that calculated from equation (3), assuming a certain model and using the measured B and h. We have found it convenient to use, instead of $\log b$, the quantity

$$\eta = \log \, (B/b) \tag{6}$$

and in this case the error square sum to minimize would be

$$U = \Sigma \, (\eta_{calc} - \eta_{exp})^2 \tag{7}$$

SOME RESULTS FROM KTH IN THE 1950s

As an example we may take Kakihana's study of the hydrolysis of the beryllium ion. His data *(Figure 1)* were of the form $Z(\log h)_B$, obtained with quinhydrone and hydrogen electrodes and the medium 3 M $(Na)ClO_4$. They could be well explained assuming the (3,3), (1,2) and (2,1) complexes,
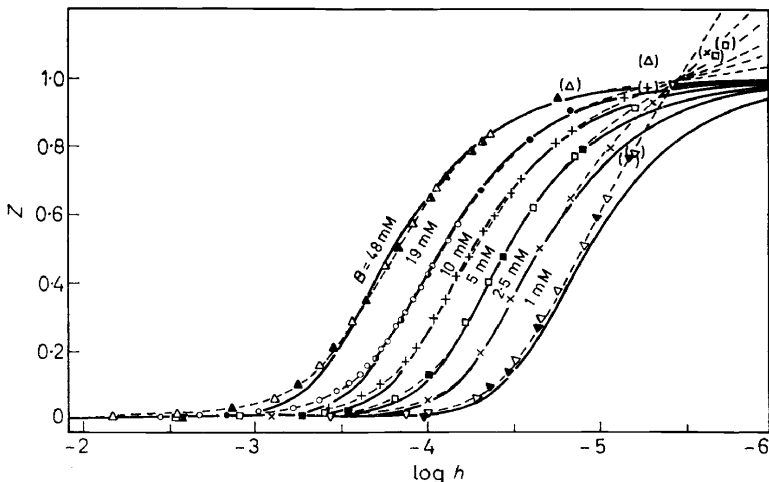
Figure 1. Hydrolysis of Be^{2+} (Kakihana 1956, 3 M $(Na)ClO_4$, 25 °C). $Z =$ average number of OH bound per Be, versus $\log h$, for various total Be concentrations B. Symbols: experimental points, full drawn curves—calculated assuming only the (3,3) species; broken curves: calculated assuming (3,3), (1,2) and (2,1) species. [*Acta Chem. Scand.* **10**, 990, (1956)]

$Be_3(OH)_3^{3+}$ etc. whereas earlier workers had either claimed only the (2,2) or only the (4,4) complex. Kakihana's conclusions have later on been confirmed by several other workers, and last year Ohtaki (1967) found the same main complexes in dioxane–water medium, and also some amount of the (2,2) species.

Hedström (1953) published a study of the hydrolysis of Fe^{3+}. He could measure both h with a glass electrode, and $[Fe^{3+}] = b$ with a redox electrode, and from his data he could deduce that the main product is $Fe_2(OH)_2^{4+}$, whereas only the mononuclear $FeOH^{2+}$ and $Fe(OH)_2^+$ had been described earlier.

Hietanen (1952) studied the hydrolysis of Hg^{2+} and found that the products are mainly mononuclear, and that the acid $Hg(H_2O)_2^{2+}$ differs from most other acids in that its second dissociation constant is larger than the first. This result has later been confirmed by Anderegg, Schwarzenbach *et al.* (1958).

Francis and Hazel Rossotti (1956) studied the hydrolysis of VO_2^+ which proceeds immediately to orange-coloured negative ions, earlier thought to be hexavanadates, thus species containing 6 V. Rossotti and Rossitti could show that their data were well explained only by decavanadates, $H_xV_{10}O_{28}^{(6-x)-}$ with $x = 0$, 1 and perhaps 2. These conclusions have been confirmed by other workers, and Evans (1966) has found the ion $V_{10}O_{28}^{6-}$ in a crystal structure.

Olin (1960) studied the hydrolysis of lead(II). He could measure both Z and η data, and both sets of data agreed very well with the mechanism he derived, involving the species (1,1), (4,4), (4,3), and (8,6). His results agree well with subsequent work, both with e.m.f. and other methods, such as the light scattering studies of Hentz and Tyree (1964).

In these cases and several others, the mechanisms derived at KTH have so far stood the test of time. In some other cases we assumed an infinite series of complexes, but we had to revise this type of mechanism within a few years. It often happens that the $Z(\log h)_B$ or $\eta(\log h)_B$ curves are parallel in some range, and it may be shown that if they are exactly parallel, then all the predominating complexes in the solution can be written under the "core and links" formula $B (A_t B)_n$; t is a constant that can be derived from the spacing of the curves, whereas n may have any value. This rule, by the way, may still be useful in the preliminary analysis of a new system.

For several systems we could get a reasonable agreement, within our accuracy by that time, assuming an infinite series of hydroxo complexes, with the same stepwise equilibrium constant throughout the series. The beauty of this model was that it could be described quantitatively by only two or three parameters and that the complexes could be thought of as fragments of infinite chains or sheets known to appear in the crystal structure of basic salts or hydroxides. It has just one flaw: it did not agree well enough with the facts. In the first case where we suggested such a mechanism, Bi^{3+} (Granér and Sillén 1947) we later found that the data had been slightly distorted by the misbehaviour of the quinhydrone electrode in acidic solutions because of the basicity of quinone (a source of error earlier suspected by nobody). After correction, both the earlier data and Olin's more accurate data could be explained assuming mainly a single complex $Bi_6(OH)_{12}^{6+}$

(Granér, Olin and Sillén 1956, Olin 1957). This agrees well with results from ultracentrifugation (Holmberg, Kraus and Johnson 1956) and x-ray diffraction (Levy, Danford and Agron 1959).

For the other metal ions, too, combinations of a limited number of complexes proved to give a better agreement than an infinite series.

EXPERIMENTAL ACCURACY

If one wants to increase the resolution power of equilibrium analysis— just like for structure analysis—it is necessary both to improve the accuracy of the experimental methods, and to improve the computation methods. In e.m.f. work, the experimental accuracy does not depend so much on the electrical part of the apparatus: even the much slandered-upon glass electrode can, if well treated, be made to read reproducibly to within ± 0.02 mV. The worst errors come from the fact that our solutions do not contain what we think they do, because of unavoidable errors in analysis, and impurities. Biedermann in Stockholm has worked hard to increase our experimental accuracy. Especially the introduction of coulometric methods in a closed system has meant a real advance in accuracy and purity, and nowadays it seems possible to keep the concentration of impurities known and low, of the order of a few μM $(10^{-6} M)$.

We may note that equilibrium analysis will give the more information on a system, the broader concentration range in the reactants (B^{n+} and H^+ for a hydrolytic reaction) that one may cover. A maximum limit for the value of B is set by the deviations of activity factors from unity when a considerable part of the cations of the medium are replaced by B^{n+}. (Even
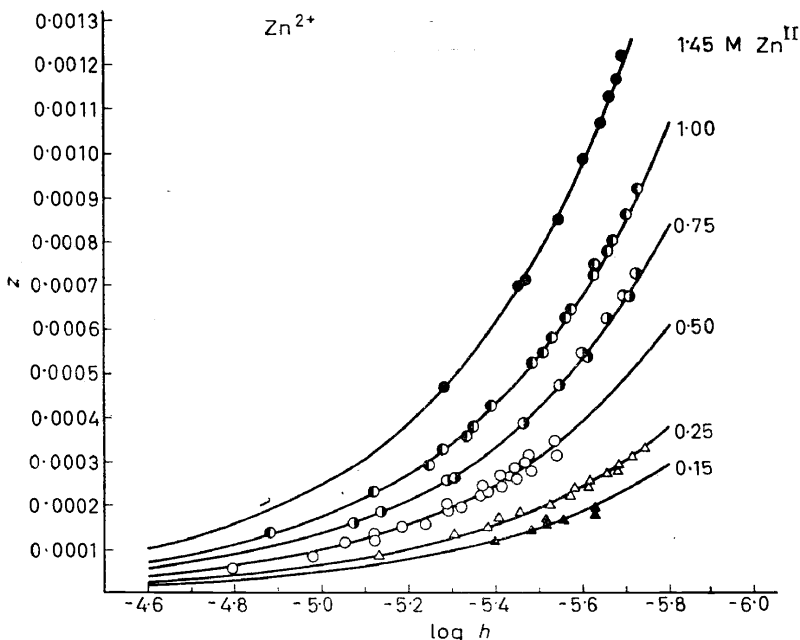

Figure 2. Hydrolysis of Zn^{2+} (Mizumachi and Biedermann, to be published). Symbols: experimental, curves: calculated

at higher B values, some useful information can be obtained using the "self-medium" principle).

The lower limit for B is indicated by the fact that at low metal ion concentrations, the experimental Z becomes a small difference between relatively large numbers, and very sensitive to impurities. Here, increased accuracy can help. *Figure 2* shows some data on the hydrolysis of Zn^{2+} in perchlorate medium, obtained by Mizumachi working with Georg Biedermann. Note that only very low Z values can be reached without precipitation: $Z \approx 0 \cdot 0010$ means that one OH^- is bound per 1000 Zn^{2+} ions.

When one is studying small effects like that, one must be aware of what impurities can do. I have the impression that some of the work on hydrolytic reactions that has been and is being published does not really reflect the hydrolysis of the metal ion in question, but rather the protolysis of impurities, like carbonate and silicate in the solutions.

COMPUTING METHODS

There is a strong interaction between experimental methods and computing methods. As one is getting accurate data over a broad experimental range, one needs better computing methods to get as much information as the data really contain; better computing methods, on the other hand, are a strong incentive to get more and better data.

Around 1960 we had an arsenal of graphical methods that proved quite efficient for cases with only two or three species. However, by that time systems began to come up where we had to consider, say, 4, 5 or 6 species simultaneously, and adjusting so many independent parameters by graphical methods was quite troublesome, to say the least.

By that time we began to use electronic computers for our equilibrium analysis, and within a few years we had developed a general minimizing programme, 'Letagrop', that has proved very useful in this field and others. (Ingri and Sillén 1962, 1964; Sillén 1962, 1964)[4, 5].

Letagrop first of all does what several other "non-linear least-squares" programmes are supposed to do: given a certain set of species (p,q), and data, if finds the set of values for the equilibrium constants (β_{pq}) that gives a minimum value to the error square sum, U, either for the Z data (5) or the η data (7). Other programmes in general work on what is often referred to as Gauss' method; they consider only the first-degree terms in a Taylor series for Z as a function of the β_{pq}, and then apply the standard least-squares treatment for a linear problem. Letagrop uses a somewhat different approach. It considers the surface $U\,(\vec{k})$ that gives U as a function of a set of parameters k_i (here the β_{pq}). It selects a number of sets of k_i values, by systematic variation, calculates U for each of them, and then calculates where the minimum should be for the second-degree surface through the points $(U, k_1, k_2 \ldots .)$ so calculated.

It may be reassuring to check that the final results are the same with various types of programmes. *Table 5* shows the "best" values for a certain set of equilibrium constants, calculated from the data of Baes *et al.* (1965) on thorium hydrolysis; for each temperature, the first set (OR) was calculated by themselves using Rush's least-squares programmes from ORNL,

and the second by us using Letagrop, assuming the absence of analytical errors (LG, $\delta Z = 0$). The "best" values agree as well as one could wish, and so does $\sigma(Z)$, the standard deviation in Z. Comparing the standard deviations for the various equilibrium constants, we should remember that at Oak Ridge they give $\beta \pm \sigma$, whereas at KTH we usually give $\beta \pm 3\sigma$.

Table 5. Comparison of results of non-linear least squares programmes, for given data and set of (p,q)

(Data: Baes *et al.* 1965, Th^{4+} hydrolysis; 1 M $(Na)ClO_4$, $0°$ and $95°C$)

	(1,1)	(2,1)	(2,2)	(8,4)	(15,6)	$\sigma(Z)$	Programme
$0°$	$4\cdot32\pm \cdot02$	$8\cdot48\pm \cdot03$	$5\cdot60\pm \cdot02$	$22\cdot79\pm \cdot02$	$43\cdot84\pm \cdot02$	$0\cdot012$	OR
	$4\cdot33\pm \cdot07$	$8\cdot48\pm \cdot10$	$5\cdot60\pm \cdot06$	$22\cdot79\pm \cdot05$	$43\cdot84\pm \cdot06$	$0\cdot012$	LG, $\delta Z = 0$
	$4\cdot31\pm \cdot06$	$8\cdot46\pm \cdot09$	$5\cdot59\pm \cdot06$	$22\cdot80\pm \cdot05$	$43\cdot81\pm \cdot05$	$0\cdot010$	LG, $\delta Z \neq 0$
$95°$	$2\cdot29\pm \cdot02$	$4\cdot50\pm \cdot01$	$2\cdot55\pm \cdot03$	$10\cdot49\pm \cdot03$	$20\cdot63\pm \cdot02$	$0\cdot015$	OR
	$2\cdot28\pm \cdot06$	$4\cdot50\pm \cdot02$	$2\cdot56\pm \cdot12$	$10\cdot49\pm \cdot09$	$20\cdot63\pm \cdot07$	$0\cdot015$	LG, $\delta Z = 0$
	$2\cdot25\pm \cdot03$	$4\cdot51\pm \cdot02$	$2\cdot59\pm \cdot08$	$10\cdot44\pm \cdot05$	$20\cdot61\pm \cdot05$	$0\cdot009$	LG, $\delta Z \neq 0$

OR = ORNL program (Rush), $- \log (\beta_{pq} \pm \sigma (\beta_{pq}))$ given
LG = Letagrop, $- \log (\beta_{pq} \pm 3\sigma (\beta_{pq}))$ at U_{min}
$\delta Z = 0$: analytical data assumed correct
$\delta Z \neq 0$: small analytical error δZ adjusted together with the β_{pq} to minimize U.

Even for such a simple case our programme Letagrop may have some advantages: it has a robot-like strategy which seems to allow it to find the minimum even starting from very bad initial guesses for the parameters, whereas the Gauss programmes seem to be more particular, if they are not to diverge.
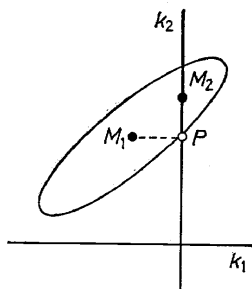

Figure 3. Schematic map. k_1 and k_2 = parameters, M_1 = point with minimum value for U, curve joins points of same U. M_2 = "reduced minimum", with k_1 set = O, P = projection of M_1. [*Acta Chem. Scand* **18**, 109 (1964)]

The third line (LG, $\delta Z \neq 0$) shows another possibility in Letagrop: we make the realistic assumption that there has been, for each "titration", a small analytical error in the excess of acid in the original solution. The corresponding error δZ is treated as another independent parameter, and is adjusted together with the equilibrium constants to get the best fit. A certain improvement results (*Table 5*).

The Letagrop approach also makes it easier to deal with equilibrium constants that tend to turn negative. The diagram (*Figure 3*) indicates a case with two parameters, k_1 and k_2; the error square sum, U, is the third coordinate, perpendicular to the plane of the paper. Suppose that the calculated minimum is at a point M_1 where k_1 is negative; if k_1 is an equilibrium constant, a negative value has no physical meaning. In such a case—usually

with a much larger number of parameters, and sometimes several negative values—Letagrop finds the combination of parameters that give the lowest value for U while all the parameters are either zero or positive. In *Figure 3*, this would be the point M_2, and not the projection P.

Using the same principle, we may tell the computer to reject a certain species (p,q), which means, set its $\beta_{pq} = 0$, if at the calculated minimum the ratio between its equilibrium constant and the standard deviation $\beta_{pq}/\sigma(\beta_{pq})$, comes out lower than a pre-set minimum value, F_σ. If there are at first several rejects, the programme tries, systematically, to save some of them, and at the end selects the combination of species and β values that makes U as low as possible while all "surviving" $\beta_{pq} \geqslant F_\sigma \, \sigma \, (\beta_{pq})$.

For those who like this type of language, we might say that $F_\sigma = 0$ corresponds to the confidence level 50 per cent, $F_\sigma = 1 \cdot 0$ to 84 per cent, $F_\sigma = 1 \cdot 5$ to 93 per cent, $2 \cdot 0$ to 97 per cent, and $3 \cdot 0$ to 99·9 per cent.

This device may be used to let the various species compete with each other. Let us start with a combination of species, symbolized by the vertical axis in *Figure 4*, that gives a minimum for U at M_1. Now we add a new species, whose β is the k' on the horizontal axis, and let the computer find the new minimum M'. The ellipse drawn in *Figure 4* represents the "reject limit",
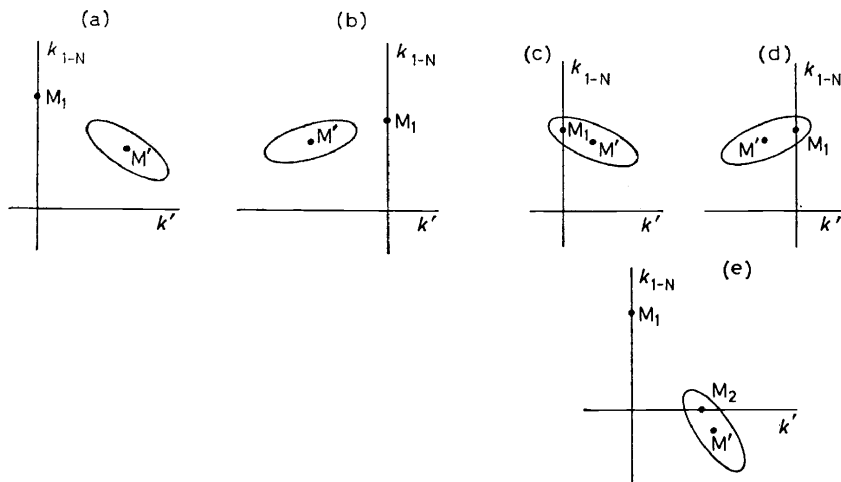
Figure 4. Possible effects of adding new parameter k' to earlier set k_{1-n}. [*Acta Chem. Scand.* **18**, 1096 (1964)]

$U = U_{\mathrm{min}} + [F_\sigma \cdot \sigma(Z)]^2$. Now, three things may happen. (i) The new species is accepted: at the new minimum, M', the β for the new species and all the old ones are acceptable by the F_σ criterion (*Figure 4a*). (ii) The new species is rejected because of the F_σ criterion. *Figure 4b* and *4d* are certain rejects, in *Figure 4c* the new species might have been "saved" by choosing a lower value for F_σ. So, the old minimum, M_1, is retained. (iii) The new species is accepted but some old species is rejected (*Figure 4e*). The resulting "best" accepted minimum is symbolized by M_2.

Applications of computing methods

Indium

The hydrolysis of the indium(III) ion was studied by Biedermann (1956), using indium amalgam, glass and quinhydrone electrodes. The amalgam (η) data were more accurate than the others. Biedermann obtained a good agreement assuming a mechanism where, in addition to the mononuclear (1,1), (2,1), an infinite series of complexes was formed: (2,2), (4,3), (6,4), ... (2n, n + 1).

The same data are now being recalculated by means of Letagrop. *Table 6* indicates one stage of the calculation. Each line represents a set of species that gives a minimum, the corresponding value for U and σ (η), and the

Table 6. Indium hydrolysis
$$q\text{In}^{3+} + p\text{H}_2\text{O} \rightleftarrows \text{In}_q (\text{OH})_p^{(3q-p)+} + p\text{H}^+$$

Species at minimum	$U_{min} \times 10^3$	$\sigma(\eta)$	Rejected ($\beta < 1.5\,\sigma(\beta)$)
(1,1), (2,1), (2,2), (4,3)	3·9063	0·00666	
+ (6,4)	2·9762	0·00589	(5,4), (7,4), (8,4)
+ (8,5) − (6,4)			
(1,1), (2,1), (2,2), (4,3), (8,5)	2·8271	0·00573	(9,5, (10,5), (11,5)
+ (10,6) − (8,5)			
(1,1), (2,1), (2,2), (4,3), (10,6)	2·7455	0·00565	(8,6), (9,6), (11,6), (12,6), (13,6)
+ (12,7) − (10,6) etc.			
(1,1), (2,1), (2,2), (4,3), (12,7)	2·6984	0·00560	(10,7), (11,7), (13,7)
(1,1), (2,1), (2,2), (4,3), (14,8)	2·6735	0·00557	(12,8), (13,8), (15,8)
(1,1), (2,1), (2,2), (4,3), (16,9)	2·6629	0·00556	(15,9), (17,9), (18,9)
(1,1), (2,1), (2,2), (4,3), (18,10)	2·6616	0·00556	(17, 10), (19,10)
(1,1), (2,1), (2,2), (4,3), (26,14)	2·6998	0·00560	(25,14), (27,14), (28,14)
(1,1), (2,1), (2,2), (4,3), (24,13)	2·6866	0·00559	(23,13), (25,13)
(1,1), (2,1), (2,2), (4,3), (22,12)	2·6751	0·00558	(21,12), (23,12)
(1,1), (2,1), (2,2), (4,3), (20,11)	2·6664	0·00556	(19,11), (21,11)

species rejected by the criterium $F_\sigma = 1.5$ (93 per cent "confidence"): By the way, a $\sigma(\eta)$ of 0·005 corresponds to about 0·1 mV in the amalgam e.m.f.

The combination (1,1), (2,1), (2,2), and (4,3) survives throughout this part of calculation, although for each new addition anyone of the old complexes runs the risk of being rejected. Adding (6,4) leads to a considerable improvement, and this combination rejects other tetranuclear species like (5,4), (7,4), and (8,4). However, (6,4) is only a temporary winner. When (8,5) is added, it is accepted but (6,4) is rejected. The process is repeated, with (10,6), (12,7), (14,8), and (16,9) as temporary winners, each giving a slightly "better" value for U.

Starting from complexes with 14 In, again, we find temporary winners (26,14), (24,13), (22,12), and (20,11). In both cases, the lowest minimum is found with (18,10) although the differences are not very great.

We may visualize what Letagrop has done by the diagram (*Figure 5*). The open circles are rejected complexes, the black ones are those remaining so far, and the crossed circles are temporary winners which have once been

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accepted but later thrown out. It may be noticed in passing that the temporary winners all belong to the "core and links" series $(2n, n + 1)$.

From these results, we might be tempted to conclude that the group that always remains, $(1,1)$, $(2,1)$, $(2,2)$, and $(4,3)$ really correspond to species in the solution, and that in addition there is some higher species, perhaps
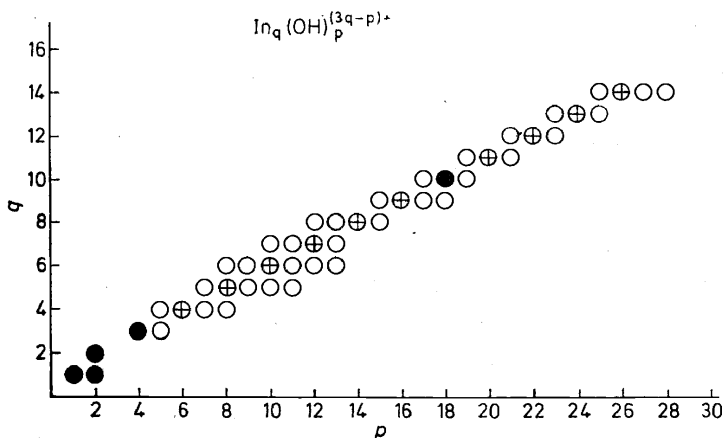

Figure 5. Survey of species competition in *Table 6.* ●, remaining species; ○, rejected species; ⊕, temporary winner.

several, out of the $(2n, n + 1)$ series. Please note, however, that there are a number of conceivable complexes like $(3,2)$ and $(2,3)$ that have not yet been tested at this stage. They may well change some details in the picture, if they are admitted to the competition.

What could one do, in addition to recalculating old data, to learn more about the species in hydrolysed indium solutions? Persson and Johansson are collecting x-ray diffraction data on hydrolysed indium solutions, but unfortunately such data cannot tell us exactly how large the complexes are. From ultracentrifuge data we do not expect much information in addition to what e.m.f. has given, since the solutions are polydisperse, and ultracentrifuge methods are at their best in monodisperse solutions. Raman data (or other spectral data) do not seem promising until one can either explain the Raman spectra from first principles or find a series of crystals where all the suspected complexes exist isolated.

STRUCTURE OF DINUCLEAR UO_2^{2+} AND Th^{4+} COMPLEXES

Of course, one would like to know what such polynuclear complexes look like as are indicated by the equilibrium work. In our group, Lundgren (now at Göteborg University), and Johansson and his coworkers, have tried to study crystal structures that could give some clue to the structure of the complexes in solution. When one precipitates a solid phase from a hydrolyzed metal solution, those complexes that existed in the solution more often than not seem to find the time to join, forming sheets, chains, etc. Nevertheless, in many cases it has been possible to find isolated hydroxo complexes in crystal structures.

Figure 6 is a dinuclear uranyl complex, discovered by Åberg and Johansson. It contains a double OH bridge between the two UO_2^{2+} groups, and each *U* is also coordinated to one Cl^- and two H_2O.

$(UO_2)_2(OH)_2Cl_2(H_2O)_4$

Figure 6. Structure of dinuclear complex in crystal structure of $UO_2OHCl(H_2O)_2$ (s) [Johansson and Åberg]

$Th_2(OH)_2(NO_3)_6(H_2O)_6$

Figure 7. Dinuclear complex in crystal structure of $ThOH(NO_3)_3(H_2O)_4$ [Johansson]

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Figure 7 shows another complex, of thorium, again with a double OH bridge (Johansson). Each thorium is coordinated to three nitrate groups, and to three H_2O molecules.

In both these structures, the anions are coordinated directly to the metal, to form uncharged complexes. Admittedly they occur in crystals, and there may be less anion coordination in the solutions. At any rate, it may be worthwhile studying the hydrolysis of every metal ion in more than one ionic medium. It is rather surprising that in those cases where the hydrolysis of a certain metal ion has been studied in several media, with different medium anions, the formulae of the metal complexes have often come out to be much the same.

Thorium

A few years ago, Hietanen completed a study of the hydrolysis of Th^{4+} in 3 M (Na)Cl medium, over quite a broad concentration range; the lowest concentrations were studied with a coulometric method. Our analysis of the data (Hietanen and Sillén 1964) indicated strongly that the solutions contain complexes with Th_6. It required no great imagination to guess that the complex might be a regular octahedron, like the complexes found by Lundgren (1953, 1956) in the crystal structure of $U_6O_4(OH)_4^{12+} (SO_4^{2-})_6$ and the corresponding Ce compound.

At the same time, Johansson was studying x-ray diffraction on Th(IV) solutions with varying $Z (= n_{OH})$ values. *Figure 8a* shows the reduced radial distribution curves he obtained from a series of nitrate solutions; the chloride and perchlorate solutions gave very similar results. The concentrations were very high, of the order of 3 M, to get a reasonable intensity of the x-ray diffraction effects. At $Z \approx 0$, we have chiefly Th–O peaks. At Z up to 1, a sharp peak appears at ≈ 4.0 Å, which agrees very well with the Th–Th distance in the dinuclear complex (*Figure 7*).
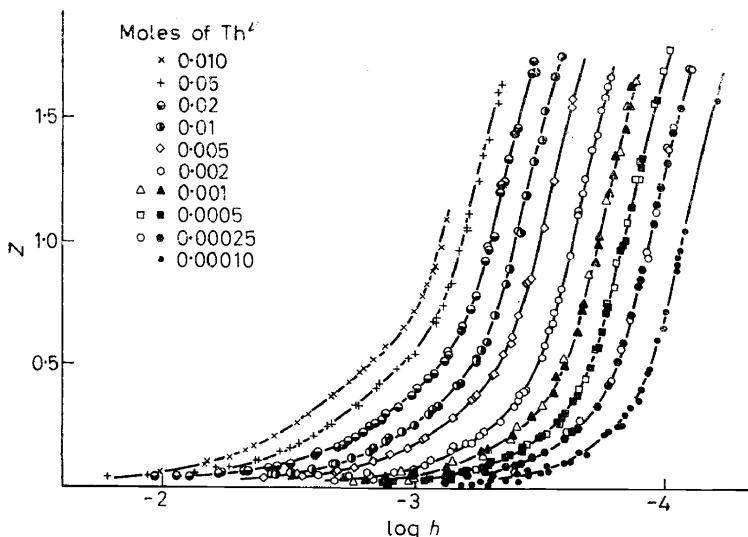

Moles of Th⁴
×	0·010
+	0·05
⊖	0·02
⊕	0·01
◇	0·005
○	0·002
△ ▲	0·001
□ ■	0·0005
○ ●	0·00025
•	0·00010

Figure 8. Hydrolysis of Th^{4+}, 3 M (Na)Cl medium [Hietanen 1967]

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Now, as Z increases up to 1·5, one would have expected hexanuclear complexes to take over. If they had been regular octahedra, with the same Th–Th distances as in the dinuclear complex, one would have expected a new Th–Th peak at $4·0 \sqrt{2} = 5·6$ Å, but no peak is seen there. There are, however, peaks around 6·5 and 7·6 Å, and an accurate analysis indicated that they are likely to be Th–Th distances.
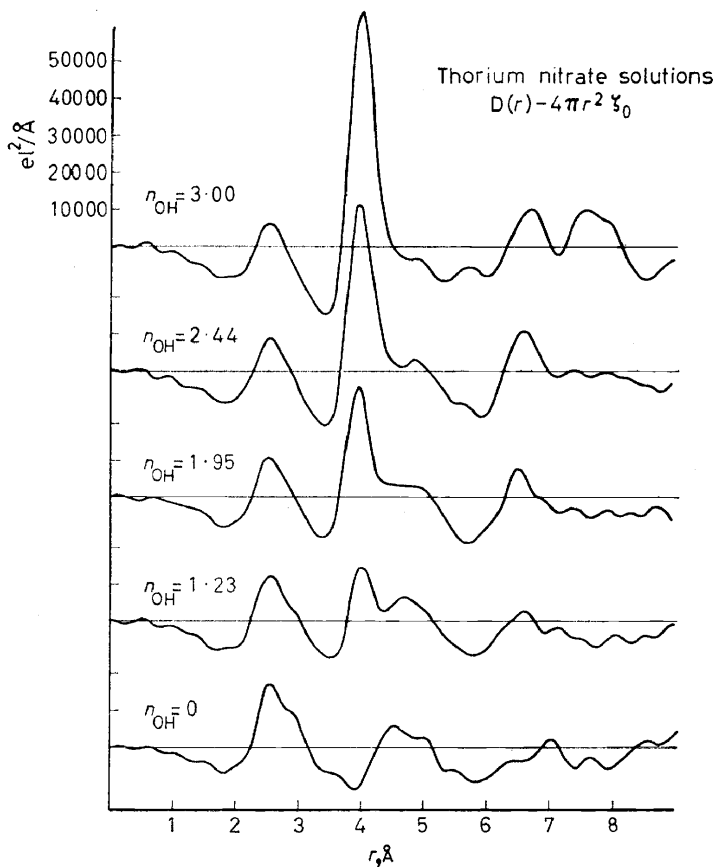

Figure 8a. Reduced radial distribution function for hydrolysed thorium nitrate solutions of various Z (n_{OH}) [Johansson 1967]

We thought it would be instructive to doubt, for the sake of argument, whether there are any Th_6 complexes at all. Perhaps we had been putting too much weight on small deviations in the e.m.f. data. So, we tried to see how the same e.m.f. data could be explained if one made one of the following four assumptions: (I) No species with more than 4 Th; (II) No species with more than 5 Th; (III) No species with more than 6 Th; and (IV) No restriction on the number of Th in the species.

Figure 10 shows which complexes were tried and which remained, in these attempts, and *Figure 9* shows the deviations in Z, with the "best" mechanism, for each total concentration B, two sets of points are

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given. In one set (usually open symbols) our analyses were assumed to be correct, in the other (usually black) we have added an adjustable parameter δZ for each titration, corresponding to an analytical error in determining excess acid in the thorium solution.

With both (I) and (II) there are large systematic deviations, much larger than the expected $\sigma(Z)$, which is around 0·010. Assuming hexanuclear
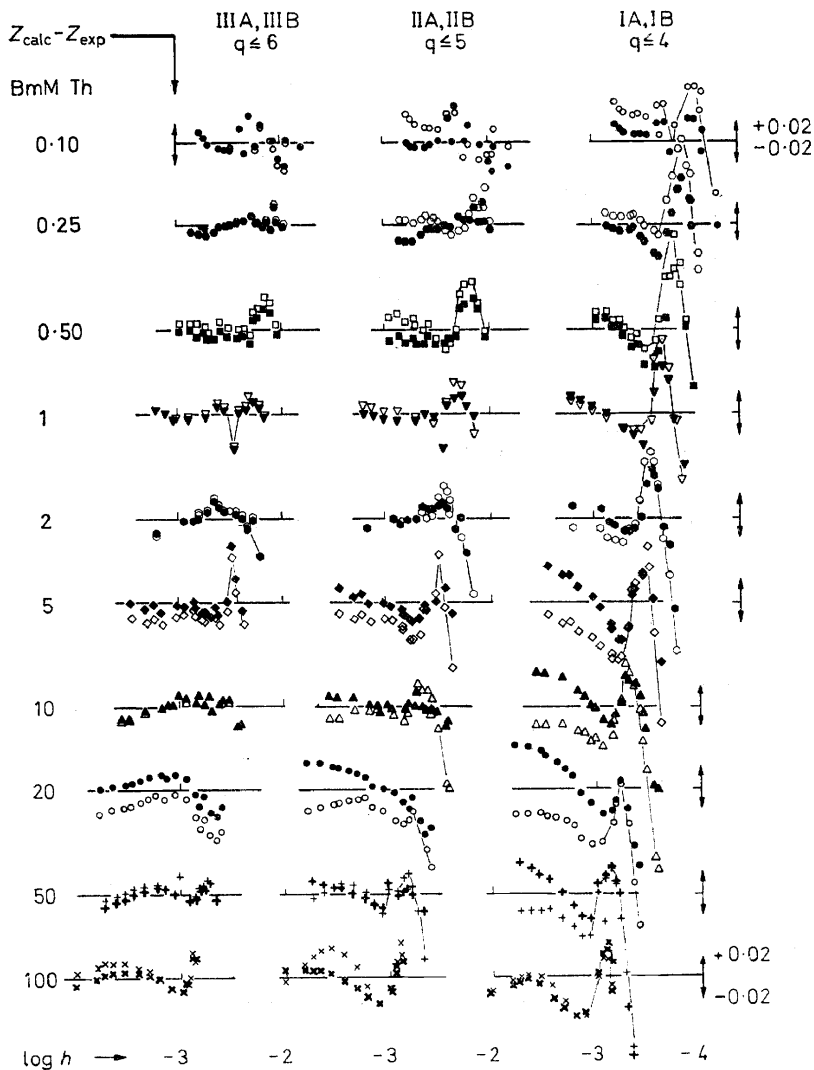

Figure 9. Deviations, $(Z_{calc} - Z_{exp})$, for "best" mechanisms for Th hydrolysis, assuming at most 4(I), 5(II), or 6(III) Th atoms per complex

complexes (III), the fit becomes much better. Table 7 shows the analytical errors δZ one has to assume to get the best fit. One would expect them either to be roughly alike or to spread irregularly; with (I) and (II), there is a
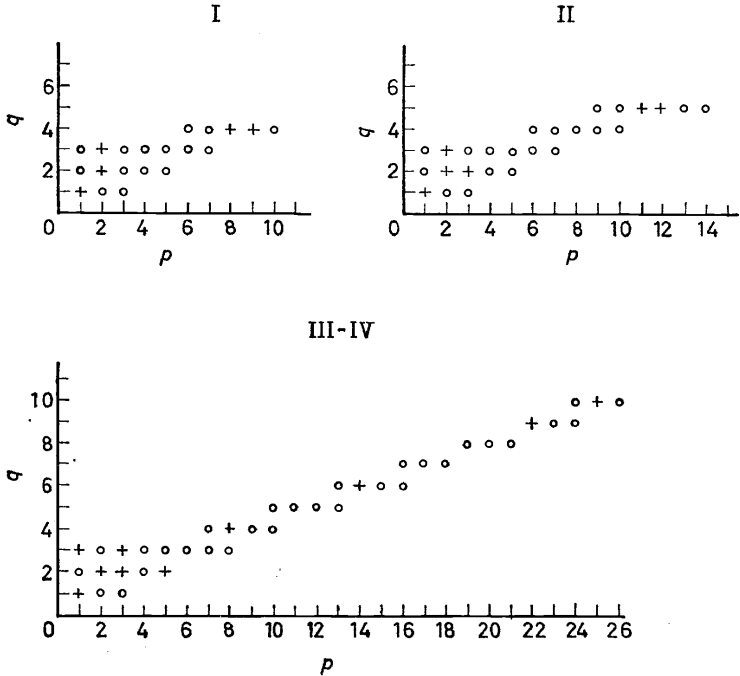
Figure 10. Species tried in species competition, treating data in *Figure 8*

Table 7. Analytical errors $100 \cdot \delta Z$, calculated for various titrations by Letagrop adjustment to best fit

Total concn. of Th^{4+} in M	I B	II B	III B	IV B
0·10	4·46 ± 0·92	3·18 ± 0·62	−0·55 ± 0·25	−0·90 ± 0·30
0·05	6·15 ± 0·91	3·86 ± 0·56	−0·15 ± 0·20	−0·67 ± 0·17
0·02	6·91 ± 0·88	5·27 ± 0·51	2·53 ± 0·34	2·16 ± 0·36
0·01	5·35 ± 0·87	2·76 ± 0·51	0·47 ± 0·20	0·05 ± 0·20
0·005	4·93 ± 0·91	2·73 ± 0·52	1·46 ± 0·39	1·35 ± 0·31
0·002	2·35 ± 0·99	−0·03 ± 0·58	0·14 ± 0·34	0·20 ± 0·31
0·001	4·86 ± 0·99	−1·34 ± 0·58	−0·06 ± 0·33	0·05 ± 0·27
0·00050	−1·05 ± 0·95	−2·91 ± 0·59	−0·61 ± 0·25	−0·50 ± 0·23
0·00025	−1·79 ± 0·95	−3·32 ± 0·61	−0·14 ± 0·18	−0·02 ± 0·14
0·00010	−2·68 ± 0·98	−4·11 ± 0·65	−0·35 ± 0·32	−0·73 ± 0·33

systematic trend, showing that the experimental curves are closer, and steeper than the calculated ones.

We may conclude that the solution is likely to contain complexes with 6 Th, but that they are not regular octahedra. It would be nice if Johansson or someone else could catch a Th_6 complex in a crystal and look at its atomic arrangement.

Aluminium

The aluminium ion has often been discussed as "typical" in connection with metal ion hydrolysis. Really, it reacts slowly, so it is not easy to apply equilibrium analysis, at 25°C. Attempts by Biedermann (1963) and Aveston (1965) have indicated large complexes, of the order of 13 Al. Johansson (1960, 1962, 1963, 1966) has found a number of isolated Al—OH complexes in crystal structures. The complex $Al_2(OH)_2(H_2O)_8^{4+}$ (*Figure 11*) looks as one might have expected: two octahedra share an edge
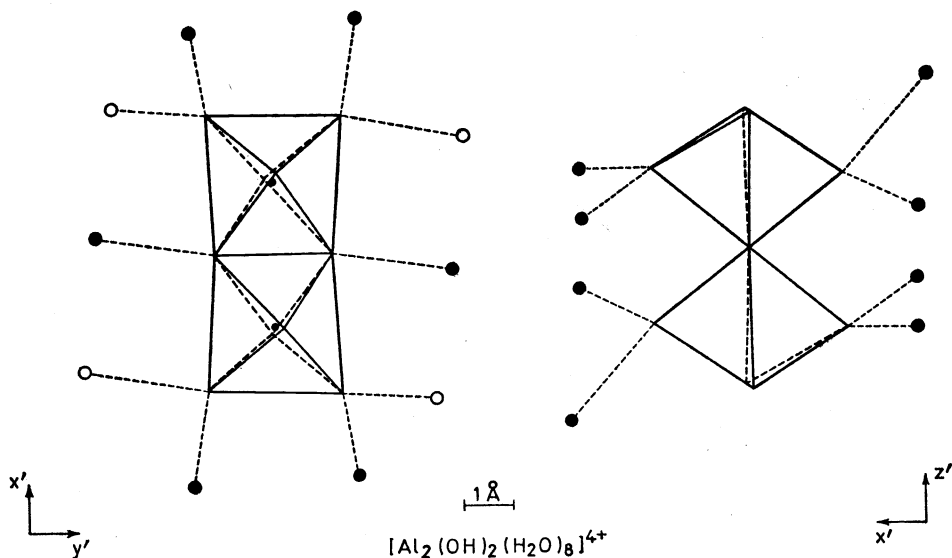
Figure 11. Structure of complex $Al_2(OH)_2(H_2O)_8^{4+}$. *Acta Chem. Scand.* **16**, 403 (1962); *Sv Ken Tid* **75**, 41 (1963)

with two OH⁻, but it was nice to be sure (this may have been the first structure determination of a complex of this type). On the alkaline side one may expect complexes $Al(OH)_4^-$ with a tetrahedral coordination, or perhaps octahedral $Al(H_2O)_2(OH)_4^-$. A crystal structure determination of "potassium aluminate" showed a quite unexpected binuclear complex, $(HO)_3AlOAl(OH)_3^{2-}$ (*Figure 12*) but we may guess that the solutions contain mainly mononuclear complexes.

In the crystal structures of several phases, appearing at intermediate acidities, Johansson (1960) found a discrete complex with 13 Al, which may be written $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (*Figure 13*). The central Al is 4-coordinated, and the other 12 are 6-coordinated. The general layout of the structure resembles very much that of heteropoly complexes like $SiMo_{12}O_{40}^{3-}$. Johansson has also made n.m.r. studies of Al solutions with various Z (*Figure 14*). The resonance peaks may be ascribed to ^{27}Al in AlO_4 and AlO_6 groups. In acidic solution, all Al is 6-coordinated; in alkaline solutions, it is all 4-coordinated, and in solutions corresponding to the Al_{13}

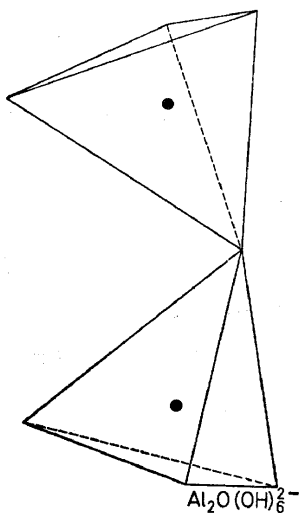complex, there are both kinds. Time reactions occur, but we shall not discuss them here.

$Al_2O(OH)_6^{2-}$

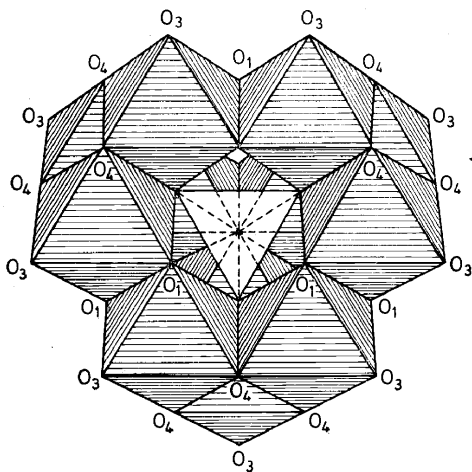*Figure 12.* Structure of dinuclear anion in "potassium aluminate" [Johansson 1966]

Figure 13. Structure of complex $Al_{13} O_4(OH)_{24}(H_2O)_{12}^{7+}$. *Acta Chem Scand.* **19**, 771 (1960)

Molybdates

The formation of polyanions, such as polymolybdates, may be studied by the same experimental and mathematical methods as metal ion hydrolysis. Many papers have been written about the state of molybdate in solution, and species with 2, 3, 4, 6 Mo etc. have been suggested. In the following, we shall, for brevity, let the (p, q) species mean the species $(H^+)_p(MoO_4^{2-})_q$, and Z will be the average number of H^+ bound per MoO_4^{2-}.

NMR ^{27}Al

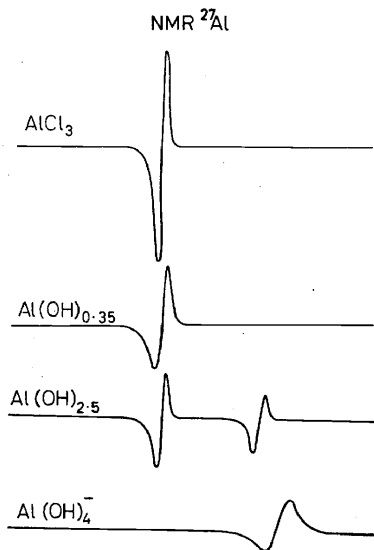*Figure 14.* N.M.R. curves for Al(III) solutions of various Z. Absorption to left ascribed to AlO_6 groups, that to right to AlO_4 groups.

From crystal structure data of Lindqvist (1950), two isolated complexes are known, namely $(8, 7) = Mo_7O_{24}^{6-}$ (paramolybdate), and $(12, 8) = Mo_8O_{20}^{4-}$ (octamolybdate). The simple molybdate, MoO_4^{2-}, is also known from crystals.

Three sets of e.m.f. data are available which are good enough for an accurate treatment; however, the conclusions of the authors, in spite of the similarity of methods, differ considerably (*Table 8*).

Table 8. Emf data on molybdates (Z from 0 to 1·5, 25°C)

SASAKI 1958–60, gl + qh, 3 M (Na)ClO$_4$
   [Mo]$_{tot}$ = B = 0·312 to 160 mM
Conclusion: (1,1), (2,1), (8,7), (9,7), (10,7), (11,7)
SCHWING 1961, qh, 3 M (Na)Cl
   [Mo]$_{tot}$ = B = 0·312 to 50 mM
Conclusion: (8,7), (8,6), probably also (9,6)
AVESTON, ANACKER and JOHNSON 1964, gl, 1 M (Na)Cl
   [Mo]$_{tot}$ = B = 1·25 to 80 mM
Conclusion: (8,7) and (12,8), from Raman data + other species with 7 or 8 Mo.
Best fits: (1,1), (2,1), (8,7), (9,7), (10,7), (11,7)
       (1,1), (2,1), (8,7), (9,7), (10,7), (12,8)
       (1,1), (2,1), (9,8), (10,8), (11,8), (12,8)

Figure 15 shows the experimental results of Sasaki, in the usual form $Z(\log h)_B$. The experiments were made around 1958, and preliminary results have been published (Sasaki, Lindqvist and Sillén 1959; Sasaki and Sillén 1964). The mono- and heptanuclear complexes were indicated by what we call the Mesak method, and they also seemed to give the best agreement, although quite a few others were tried. Sasaki has also data for

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$Z > 1.5$, which indicate a large anion, of the order of 20 Mo, and a cationic complex. The other two sets of data only go to $Z \approx 1.5$.

Aveston, Anacker and Johnson (1964) also applied ultracentrifuge and Raman measurements. The ultracentrifuge data could only tell that in the interesting range, the average species probably contain more than 6 and less than 9 Mo atoms. Raman spectra of crystals known to contain the (8,7) and
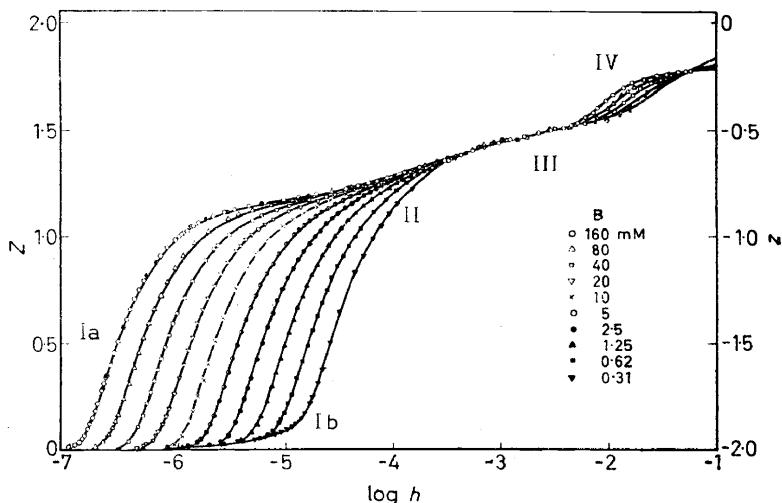

Figure 15. Reactions $H^+ + MoO_4^{2-}$: Z = average number of H^+ bound per $Mo\,O_4^{2-}$ z = average charge per Mo [Sasaki 1958, 1967]

the (12,8) complex were compared with the Raman spectra of quite concentrated solutions of lithium molybdate of the corresponding Z. For (8,7), there was a very good agreement between Raman spectra of solution and crystal. For (12,8) Aveston *et al.* expressed themselves much more cautiously but they still thought that (12,8) predominated in the solution. In addition they thought there are other species with 7 or 8 Mo, and they accepted the (1,1) and (2,1) species claimed by Sasaki. They listed a number of combinations, and the three with the best fits are given in *Table 8*. The very best fit they obtained with the first one, which is identical with Sasaki's, but they did not put much weight on that.

We have now allowed ourselves a little innocent game (*Table 9*), letting the various species with 6, 7 and 8 Mo fight it out over each of these three sets of data. The rule of the game has been, always to accept the set of species and equilibrium constants that gave the lowest value for U and still had all $\beta > 1.5$ times the corresponding $\sigma(\beta)$.

With Sasaki's data, we started with the set with mono- and heptanuclear complexes, which was found to reject all the species with 6 Mo. After that, (9,8) and (10,8) were accepted and gave some improvement. However, (11,8), (12,8), (6,5) and a number of others were rejected.

Schwing's data (*Table 9b*) gave quite a large $\sigma(Z)$ with the two complexes

Table 9. Molybdates. Species competition. Letagrop. $F\sigma = 1.5$

(a) Sasaki's Data ($Z \leqslant 1.5$)

Species accepted	$U_{min} \times 10^3$	$\sigma(Z)$	Rejected
(1,1), (2,1), (8,7) (9,7) (10,7) (11,7)	2.8195	0.0061	(7,6), (8,6), (9,6)
+ (9,8)	2.6580	0.0059	
+ (10,8)	2.2341	0.0054	(11,8), (12,8) etc.

(b) Schwing's Data

Species accepted	$U_{min} \pm 10^2$	$\sigma(Z)$	Rejected
(8,7), (8,6)	17.61	0.0363	
+ (9,6)	3.887	0.0172	
+ (1,1)	3.265	0.0157	
+ (2,1)	1.623	0.0111	
+ (9,7)	1.252	0.0098	
+ (10,7) − (8,6)			
(1,1), (2,1), (9,6), (8,7), (9,7), (10,7)	1.244	0.0090	
+ (11,7) − (9,6)			
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7)	0.923	0.0085	(9,8), (10,8), (11,8)

(c) Aveston's Data

Species accepted	$U_{min} \times 10^3$	$\sigma(Z)$	Rejected
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7)	2.3345	0.0067	(7,6)
+ (8,6)	2.1820	0.0065	(9,6)
+ (9,8) − (8,6)			
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (9,8)	1.4942	0.0054	(10,8), (11,8), (12,8), (6,5) (5,4) (6,4)
(1,1), (2,1), (9,8), (10,8), (11,8), (12,8)	3.504	0.0082	(8,7)
+ (9,7)	2.030	0.0064	
+ (10,7) − (10,8) − (11,8)			
(1,1), (2,1), (9,7), (10,7), (9,8), (12,8)	1.6836	0.0057	(11,7)
+ (8,7)	1.5578	0.0055	
+ (11,7) − (12,8)			
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (9,8)	1.4942	0.0054	(7,6), (8,6), (9,6) (8,8), (10,8), (11,8) (4,4), (5,4), (6,4)

he suggested, (8,7) and (8,6). Adding (9,6), as suggested by Schwing, improved the fit. Then, (1,1), (2,1) and (9,7) from Sasaki's list were accepted with considerable improvement in U. When (10,7) was added (8,6) was rejected, and (11,7) was accepted, rejecting (9,6).

Finally, with Aveston's data (*Table 9c*) we started with Sasaki's combination of mono- and heptanuclear species. It rejected (7,6), accepted (8,6), then again rejected (9,6). When (9,8) was added, (8,6) was rejected, and we were left with the combination of the earlier complexes with 1 Mo and 7 Mo, plus (9,8). No other complex with 8 Mo was accepted.

One might say that this was not fair. The species with 7 Mo may stick together and throw out newcomers, and perhaps one should have started instead with an all-eight-Mo team. We tried (*Table 9c*), and this team obviously could throw out (8,7) but accepted (9,7). When (10,7) was offered, it was accepted but threw out (10,8) and (11,8). The remaining combination did not accept (11,7). Now comes another important point.

A complex that has once been rejected may have a better chance together with another combination, so one should try again until no changes are obtained by playing the whole game with the winning group against each one of the rejected ones. In the next turn of the game (8,7) was accepted, and when (11,7) was offered, it was accepted but it threw out (12,8), and so we had the same winning combination as we got, starting from the set of mono- and heptanuclear species.

The position after this little innocent game is given in *Table 10*. It is anyone's privilege to say that this is only a play with numbers, and that the combinations of species that come up have no real significance. If one thinks

Table 10. Molybdates, set with best fit, Letagrop, $F_\sigma = 1.5$

SASAKI, 3 M (Na)ClO$_4$
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (9,8), (10,8)
SCHWING, 3 M (Na)Cl
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7)
AVESTON *et al.*, 1 M (Na)Cl
(1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (9,8)

---

the game has some singificance, one might wish to try more species, and to extend the calculation on Sasaki's data to the highest Z values. The additional species (large anions, cations) may influence also the upper points in the range $Z < 1.5$. The possibility of small analytical errors should also be considered.

I might add, at any rate, that this game is great fun. As the size and speed of computers is increasing, it is becoming practicable to test all conceivable species by this type of competition.

Mononuclear species

Sekine has used the distribution method, with radioactive tracers, to study the hydrolysis of vanadium(v) (Dyrssen and Sekine 1961) and of
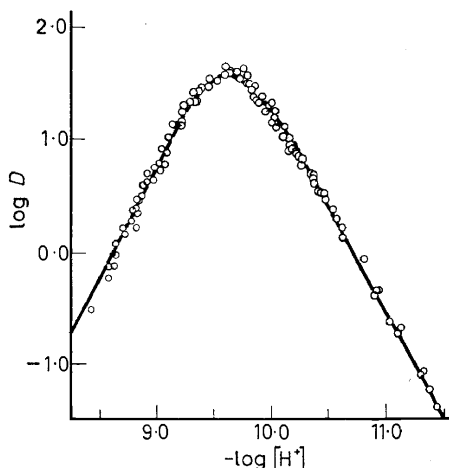
Figure 16. Distribution of Zn(II) between 3 M NaClO$_4$ and benzene containing 5 per cent Amberlite LA 1. Solid curve: calculated [*Acta Chem. Scand.* **11**, 1532 (1965)]

zinc(II) (Sekine 1965). From the variation of the distribution ratio D with log h (*Figure 16*) he deduced the formation constants of the mononuclear complexes, from which *Figure 17* was calculated.

Of course this type of work has some difficulties: one has to find some suitable organic system, or rather several for a check, and one must be very much aware of the risk of impurities. On the other hand, by this method one
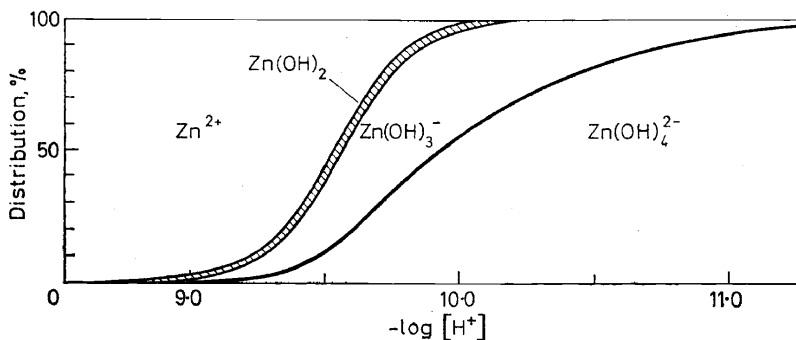

Figure 17. Distribution of Zn(II) over various mononuclear species as a function of log h
[*Acta Chem. Scand.* **19**, 1535 (1965)]

can study a range of very low concentrations, which cannot be reached by the e.m.f. method, and in which mononuclear complexes will often predominate.

In Nature, for instance in sea water, and in various fresh waters, the concentrations of most metals are quite low, of the order of 10^{-8} M or less. Either the metals exist as hydroxo complexes, carbonato or chloro complexes or in some other form, this is the form in which the various organisms will have to eat iron, manganese, vanadium, copper, etc. and it seems quite interesting to know what they are. Many metals may really be present in Nature in the form of uncharged mononuclear hydroxo species, like $Fe(OH)_3$, $Al(OH)_3$, etc. (+ water).

This field would surely be worth more study.

Automation

Perhaps the greatest obstacle to getting a large number of accurate studies of hydrolytic equilibria is the large amount of work involved. Now that the main part of the calculations can be made automatically, by computer, the idea has struck us that much of the hand work connected with precision e.m.f. titrations could be taken over by automatic devices, so that the chemists could get more time free for the job they are best trained for: making pure solutions, planning the experiments, and interpreting in chemical terms whatever comes out from the computer. Biedermann and Wallin have set up an automatic e.m.f. titration apparatus working day and night in our laboratory, reading glass electrode e.m.fs reliably to within ± 0.02 mV, and we hope that there will be soon many of these devices.

ACKNOWLEDGEMENTS

References

For most of the papers referred to, a full bibliographic reference can easily be found in *Table 2* (OH⁻), 3(vanadate) or 6(molybdate) of the second edition of *Stability Constants, Chem. Soc. Special Publ No.* 17 (1964), or the supplementary tables (for 1963–1967) which will hopefully soon be published. The others are listed here:

[1] J. J. Berzelius. *Gilberts Ann. Phys.* **40**, 290 (1812).
[2] A. Werner. *Z. anorg. Chem.* **9**, 408 (1895).
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