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THE THERMODYNAMICS OF CATION HYDROLYSIS*

C. F. BAES, JR. and R. E. MESMER
Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

ABSTRACT. Data for the hydrolysis of aqueous cations are reviewed, enthalpy and entropy values for the various kinds of reactions are compiled, and correlations are drawn with the object of predicting behavior at elevated temperatures. Such information is essential for understanding the chemistry and the transport of metallic elements in hydrothermal environments. The enthalpy of the first hydrolysis step, $M^{z+} + H_2O \rightleftharpoons MOH^{(z-)1+} + H^+$, is always positive and usually near the enthalpy of dissociation of water (13.3 kcal/mole); hence, hydrolysis in solution increases with temperature. The enthalpy for the precipitation reaction, that is, $M^{z+} + zH_2O \leftrightharpoons M(OH)_z(c) + zH^+$, is usually positive as well, but as the temperature rises hydrolysis in solution should proceed further before precipitation occurs. Polynuclear species are less important in solution as the temperature increases because of decreasing stability and because the maximum concentration of the hydrolyzing ion in solution is lowered by the decreasing solubility of the oxide or hydroxide. The limited data available for the formation of successive mononuclear hydroxide complexes by the reaction $M(OH)_y{}^{(z-y)+} + H_2O \rightleftharpoons M(OH)_{y+1}{}^{(z-y-1)+} + H^+$ suggest the accompanying entropy change will decrease with the charge on the reacting species and that the enthalpy of such successive hydrolysis steps will decrease for most cations. Consequently the pH range of dominance of each species, especially the neutral one, should increase with temperature. The equilibrium between the oxide or hydroxide solid phase and the neutral species $M(OH)_z(aq)$, which usually determines the minimum solubility of the solid, is expected to have a small temperature dependence. In more alkaline solutions, where anionic complexes are formed, the solubility should show a positive temperature coefficient at a given pH. Projections based on these correlations of hydrolysis behavior at elevated temperature depend on a knowledge of the stepwise hydrolysis constants for mononuclear species, and more such information is badly needed.

INTRODUCTION

When a metallic element enters an aqueous solution, its chemical behavior is of course determined by the nature of the ionic or molecular species that it forms. In the absence of strongly complexing ligands and depending on the acidity of the solution, the simple cation of the element often reacts with water itself (hydrolyzes) to form complexes with the hydroxide ion. These complexes may be cations, neutral molecules, or anions. They may be mononuclear or polynuclear; that is, they may contain one metal atom or several. These hydrolysis reactions play a dominant role in the aqueous chemistry of most metallic elements. Moreover, their importance grows as the temperature is increased. Knowledge of this class of reactions therefore is essential in dealing with a wide variety of aqueous systems encountered in the environment, in geochemistry, and in numerous technological applications.

The hydrolysis of metal ions in aqueous solution has been studied extensively at or near room temperature for the last 30 yrs (see reviews by Sillen and Martell, 1971; Baes and Mesmer, 1976; Smith and Martell, 1976). The potentiometric determination of pH has been the principal method of measurement, but its sensitivity has generally limited measure-

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ments to metal concentrations above 0.001 molal (m). Polynuclear hydrolysis species often form in such solutions and consequently have been the principal subject of study. In the more dilute solutions produced by the hydrolytic precipitation that usually occurs with increasing pH or temperature, the dominant species are mononuclear ones and are often less well characterized. Increasingly, measurement of the solubility of the hydroxide or oxide phase has been the method of choice in the study of such solutions. Measurements are often tedious and time-consuming, however, and progress has been slow. As a consequence the stability of important hydrolytic species of many cations in aqueous solutions, especially at elevated temperatures, remains unknown.

In the absence of such information, the only alternative is to project behavior in dilute solutions or at elevated temperatures from the data available for the element of interest and to make use of whatever generalizations and correlations about the thermodynamics of the hydrolysis of cations that may be expected to apply. It is the primary purpose of this review to consider the extent to which estimates of behavior at elevated temperatures can be drawn from what is presently known of the thermodynamics of the various hydrolysis processes that can ocur.

First of all, the important kinds of hydrolysis reactions will be reviewed briefly. Then from the available data some correlations will be made of the equilibrium constants, the enthalpies, and the entropies of these reactions. Finally an attempt will be made to project typical behavior for the hydrolysis of metal ions as the temperature is increased.

KINDS OF HYDROLYSIS REACTIONS

The initial step in the hydrolysis of a cation is usually the formation of the species $MOH^{(z-1)+}$, and is generally represented by the reaction

$$M^{z+} + H_2O \rightleftharpoons MOH^{(z-1)+} + H^+. \tag{1}$$

A more realistic representation of this process is the reaction

$$M(OH_2)_n{}^{z+} \rightleftharpoons M(OH)(OH_2)_{n-1}{}^{(z-1)+} + H^+, \tag{2}$$

in which a proton is lost by a solvating water molecule. It is perhaps not surprising, therefore, to find that the enthalpy of this reaction, ΔH_{11}, is usually close to the enthalpy of dissociation of water (13.3 kcal/mole at 25°C).

If the metal ion concentration is low enough to avoid precipitation as the pH is increased, additional hydroxide ligands are formed (that is, protons are lost by additional water ligands) in a stepwise fashion up to a total that often reaches four or more.

$$M^{z+} \rightarrow MOH^{(z-1)+} \rightarrow M(OH)_2{}^{(z-2)+} \ldots\ldots M(OH)_y{}^{(z-y)+}.$$

The equilibrium quotients for the formation of such mononuclear species from the unhydrolyzed cation will be designated as Q_{11}, $Q_{12} \ldots Q_{1y}$,

$$\begin{aligned} Q_{11} &= [MOH^{(z-1)+}][H^+]/[M^{z+}] \\ Q_{1y} &= [M(OH)_y{}^{(z-y)+}][H^+]^y/[M^{z+}] \end{aligned} \tag{3}$$

(wherein the bracketed quantities denote the molality of each species). More often we will refer to the limiting value of Q at zero ionic strength, which will be denoted by K.

At concentrations $>10^{-3}$ m, polynuclear species often become dominant soon after the appearance of the initial mononuclear species. Their formation may be represented by the general reaction

$$xM^{z+} + yH_2O \rightleftharpoons M_x(OH)_y^{(xz-y)+} + yH^+. \tag{4}$$

The equilibrium quotient for such a reaction will be designated Q_{xy},

$$Q_{xy} = [M_x(OH)_y^{(xz-y)+}][H^+]^y/[M^{z+}]^x. \tag{5}$$

A variety of such species have been identified, ranging from dimers to sizeable polymers. For metals of valence IV or less, they are usually cations.

The extent of hydrolysis of a cation in solution at ordinary concentrations is usually limited by the appearance of a hydroxide or oxide precipitate. It will be convenient to consider the equilibrium of such a phase with the unhydrolyzed cation.

$$M(OH)_z(c) + zH^+ \rightleftharpoons M^{z+} + zH_2O. \tag{6}$$

The equilibrium quotient will be designated Q_{s10},

$$Q_{s10} = [M^{z+}]/[H^+]^z. \tag{7}$$

The majority of such precipitates are gelatinous, amorphous, active solids of high surface energy, and this has greatly limited the usefulness of solubility measurements involving them.

The relationship that typically exists among the various hydrolysis reactions is illustrated in figures 1 and 2. In figure 1 the concentrations of species at equilibrium with an oxide or hydroxide phase are plotted on

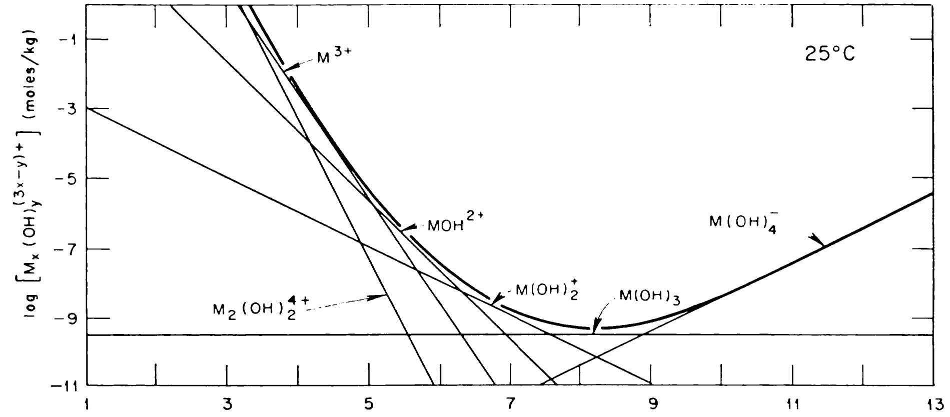

Fig. 1. Distribution of hydrolysis products in solution at equilibrium with a hydroxide solid phase for a hypothetical trivalent cation. The heavy curve is the total concentration of M(III) in solution.

a logarithmic scale versus the pH. These concentrations are controlled by reactions of the type

$$xM(OH)_z(c) + (xz-y)H^+ \rightleftharpoons M_x(OH)_y^{(xz-y)+} + (xz-y)H_2O, \qquad (8)$$

and, except for the effects of variation in water activity or ionic activity coefficients the resulting curves on such a plot are linear. The slope of each line is equal to $-(xz-y)$, which is the negative of the charge on the corresponding species if no charged ligands other than OH^- or O^{2-} are bound. The heavy curve shown in figure 1 represents the total concentration of the metal (of valence z) in a saturated solution. Over most of the pH range this total concentration is so low that only mononuclear species are formed in appreciable amounts, and, as can be seen, it is the stability of these species that largely determine the shape of this "solubility" curve.

The solubility of the oxide or hydroxide phase initially decreases rapidly with increasing pH but levels off as hydrolysis in solution proceeds. It reaches a minimum, often with the neutral species $M(OH)_z$ dominant in solution, and finally increases again as anionic species appear. Because the polynuclear species formed by metals of valence IV or less usually have a relatively high positive value for the quantity $(xz-y)$, they generally contribute to the solubility curve in the region of lowest pH and highest solubility.

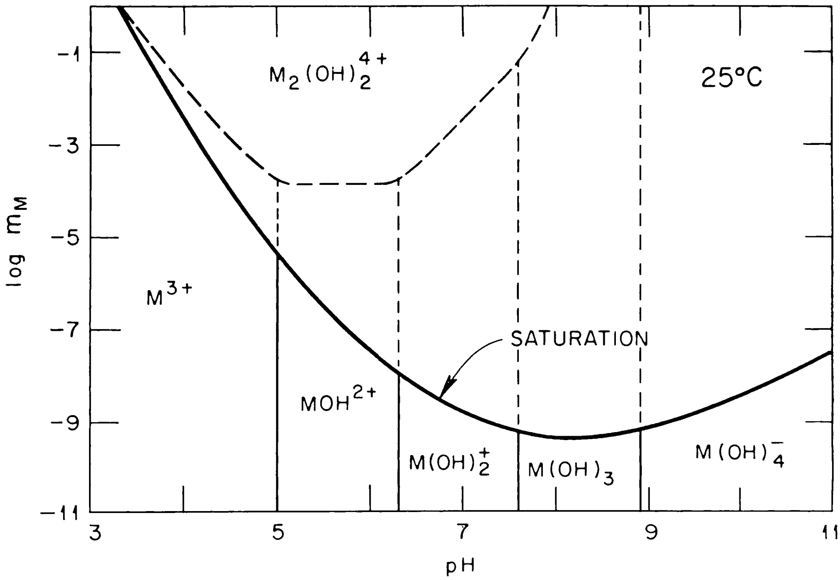

Fig. 2. Regions of dominance of the hydrolysis products in solution for a hypothetical trivalent cation. The boundaries are defined by the equilibria listed in table 1. The curve (from fig. 1) represents the solubility limit of the hydroxide solid phase. This figure and figs. 1, 7, and 8 were constructed assuming only values for K_{11} and the typical spacing of 1.3 log units per each mononuclear hydrolysis step. The other boundaries were inferred from correlations described in the text.

The regions of stability of the various species in solution can be seen more clearly in figure 2. In this diagram the boundaries denote conditions of pH and total metal concentration under which the species in adjacent regions will be present in equal concentrations. Movement away from a boundary will, of course, cause one species to become dominant and the other relatively less abundant. The heavy curve in the figure again indicates the solubility of the oxide or hydroxide phase. At low metal concentrations successive mononuclear species become dominant with increasing pH. The polynuclear species, here represented by the typical dimer $M_2(OH)_2^{4+}$, are generally confined to a relatively small region at the lower end of the pH range and at high metal concentration. Moreover, as can be seen, this region is usually supersaturated with respect to the oxide or hydroxide phase. In the more basic supersaturated solutions the mononuclear species of metals of valence IV or less usually become dominant, because they reach higher y/x (that is, OH/M) ratios than do the polynuclear species.

The hydrolysis behavior depicted in figures 1 and 2, with appropriate shifts in the pH scale, approximates the behavior of many M(II), M(III), and M(IV) metals. The regularity of stability suggested for the mononuclear species has not been confirmed in many cases, but such regularity is often exhibited by complexes of metal ions with fluoride ion, a ligand with the same size and charge as the hydroxide ion. Several post-transition metal cations, however, form neutral hydroxide complexes of relatively high stability. Metals of valence higher than IV are extensively hydrolyzed above $\mathrm{pH} = 0$, and many form anions and polyanions at higher pH.

THE THERMODYNAMICS OF HYDROLYSIS REACTIONS

In the following sections we will consider what is known of the equilibrium constants, enthalpy changes, and entropy changes of the reactions (summarized in table 1) that determine the boundaries and intersections in figures 1 and 2 and hence their temperature dependence. The system of subscripts used with Q, K, ΔG, ΔH, and ΔS to define the reaction involved may be summarized as follows: Two integers (*xy*) indicate the general reaction (4), in which x is the number of cations M^{z+} and y is the number of OH^- ligands in the species formed. If an s is present in the subscript (*sxy*), then the solubility reaction (8) is referred to.

The $M^{z+}/MOH^{(z-1)+}$ boundary.—Generally, it is to be expected from consideration of the electrostatic energy changes involved in the first hydrolysis step (reaction 1) that the logarithm of the equilibrium constant K_{11} (that is, the value of Q_{11} as the ionic strength approaches zero) should increase linearly with the ratio of the cation charge z to the M-O distance d (Baes and Mesmer, 1976, p. 398). This indeed proves to be a useful correlation provided the various cations in the periodic table are grouped according to type (table 2). In the table the equilibrium constant for reaction (1), K_{11}, has been represented by the expression.

$$\log K_{11} = A + 11.0\,(z/d). \tag{9}$$

TABLE 1
Summary of hydrolysis reactions

Boundary (fig. 1 or 2)	Reaction	Equilibrium constant
$M^{z+}/MOH^{(z-1)+}$	$M^{z+} + H_2O \rightleftharpoons MOH^{(z-1)+} + H^+$	K_{11}
$M(OH)_y^{(z-y)+}/M(OH)_{y+1}^{(z-y-1)+}$	$M(OH)_y^{(z-y)+} + H_2O \rightleftharpoons M(OH)_{y+1}^{(z-y-1)+} + H^+$	$K_{1,y+1}/K_{1y}$
$M(OH)_z(c)/M^{z+}$	$M(OH)_z(c) + zH^+ \rightleftharpoons M^{z+} + zH_2O$	K_{s10}
$M(OH)_z(c)/M(OH)_y^{(z-y)+}$	$M(OH)_z(c) + (z-y)H^+ \rightleftharpoons M(OH)_y^{(z-y)+} + (z-y)H_2O$	$K_{s10}K_{1y}$
$M^{z+}/M_x(OH)_y^{(xz-y)+}$	$xM^{z+} + yH_2O \rightleftharpoons M_x(OH)_y^{(xz-y)+} + yH^+$	K_{xy}

TABLE 2

The first hydrolysis step, 25°C

$\log K_{11} = A + 11.0\,(z/d)$

Cation	M-O Distance* d (Å)	Log K_{11}**	A	Avg A
Mg^{2+}	2.120	−11.44	−21.8	
Ca^{2+}	2.40	−12.85	−22.0	
Sr^{2+}	2.56	−13.29	−21.9	
Ba^{2+}	2.76	−13.47	−21.4	
Al^{3+}	1.930	−4.97	−22.1	
Y^{3+}	2.292	−7.7	−22.1	
La^{3+}	2.461	−8.5	−21.9	
Sm^{3+}	2.364	−7.9	−21.9	
Lu^{3+}	2.248	−7.6	−22.3	−21.9
Li^{+}	2.14	−13.64	−18.8	
Na^{+}	2.42	−14.18	−18.7	
K^{+}	2.78	−14.46	−18.4	
Be^{2+}	1.65	−5.40	−18.7	
Mn^{2+}	2.220	−10.59	−20.5	
Fe^{2+}	2.170	−9.5	−19.6	
Co^{2+}	2.145	−9.65	−19.9	
Ni^{2+}	2.100	−9.86	−20.3	
Cu^{2+}	2.13	−7.93***	−18.3	
Zn^{2+}	2.145	−8.96	−19.2	
Cd^{2+}	2.35	−10.08	−19.4	
Sc^{3+}	2.130	−4.3	−19.8	
Ti^{3+}	2.07	−2.2	−18.1	
V^{3+}	2.040	−2.26	−18.4	
Cr^{3+}	2.015	−4.0	−20.4	
Fe^{3+}	2.045	−2.19	−18.3	
Co^{3+}	1.923	−1.25****	−18.4	
Rh^{3+}	2.065	−3.4	−19.4	
Ga^{3+}	2.020	−2.6	−18.9	
In^{3+}	2.190	−4.00	−19.1	
Th^{4+}	2.48	−3.20	−20.9	
Pa^{4+}	2.43	0.84	−17.3	
U^{4+}	2.42	−0.65	−18.8	
Np^{4+}	2.40	−1.49	−19.8	
Pu^{4+}	2.38	−0.5	−19.0	−19.1
Ag^{+}	2.55	−12.0	−16.3	
Tl^{+}	2.90	−13.21	−17.0	
Pb^{2+}	2.71	−7.71	−15.8	
Tl^{3+}	2.42	−0.62	−14.3	
Bi^{3+}	2.53	−1.09	−14.1	−15.5
Hg^{2+}	2.42	−3.40	−12.5	
Sn^{2+}	2.64	−3.40	−11.7	
Pd^{2+}	2.02	−2.1	−13.0	−12.4

* Shannon and Prewitt (1969); ** Baes and Mesmer (1976); *** Paulson and Kester (1980); **** Sutcliffe and Weber (1956).

The numerical constant (11.0) has been adjusted such that cations of similar type will, insofar as possible, produce similar values for the constant A. It is seen that after allowance is thus made for size and charge, the "hard" pre-transition metal cations are generally the most resistant to hydrolysis. Thus the alkaline earth ions, and Al^{3+}, Y^{3+}, and the trivalent lanthanides give the most negative values of A in the above expression, about −22. A second group of "hard" cations, slightly less resistant to hydrolysis, includes principally the alkali-metal ions, the transition-metal ions, and the tetravalent actinide ions. Here the value of A is less negative by about two and a half log units. A third much smaller group, containing most of the soft transition cations, shows K_{11} values about four log units less negative for ions of the same size and charge — A

TABLE 3

The enthalpy of the first hydrolysis step

Cation	Medium	Method*	Temperature Range (°C)	ΔH_{11} (kcal/mole)	Source**
Li^+	→0	pot.	15–35	13.4 ± 2	1 from 2
Na^+	→0	pot.	0–50	13.4 ± 3	1 from 3
Ca^{2+}	→0	pot.	0–40	15.6 ± 0.7	1 from 4
Mn^{2+}	→0	pot.	15–42	14.4 ± 1	5
Fe^{2+}	dil.	sol.	25–300	13.2 ± 1.5	6
Fe^{2+}	dil.	sol.	150–330	12.7 ± 0.7	7
Co^{2+}	1 M KCl	pot.	25–200	14.6 ± 0.5	from 8
Co^{2+}	→0	pot.	25–200	14.6 ± 0.5	from 8
Ni^{2+}	dil.	sol., pot.	15–300	11.9 ± 2	from 9, 10
Zn^{2+}	→0	pot.	15–42	13.4 ± 1	11
Cd^{2+}	3 M $LiClO_4$	cal.		13.1 ± 2	12
Cd^{2+}	3 M $NaClO_4$	pot.	60–100	12.5 ± 2	13
Hg^{2+}	3 M $LiClO_4$	cal.		7.23 ± 0.18	12
Al^{3+}	dil.	pot.	10–40	11.9 ± 0.7	1 from 14
Sc^{3+}	1 M $NaClO_4$	pot.	10–40	14.4 ± 1.4	from 15
Cr^{3+}	→0	pot.	0–100	9.7 ± 1	from 16
Fe^{3+}	dil.	pot.?	18–32	10.2 ± 1	from 17
Co^{3+}	1 M $NaClO_4$	spt.	12–28	10.2 ± 2	18
Bi^{3+}	3 M $NaClO_4$	cal.		4.1 ± 1.4	19
Th^{4+}	1 M $NaClO_4$	pot.	0–95	11.2 ± 2	from 20, 21
U^{4+}	0.5 M $NaClO_4$	spt.	10–43	11.2 ± 0.5	from 22
U^{4+}	→0	spt.	25–150	10.0 ± 0.4	23
Pu^{4+}	2 M $LiClO_4$	pot?	15–34	7.2 ± 1.2	from 24

* The abbreviations pot., sol., cal., and spt. denote, respectively, potentiometric, solubility, calorimetric, and spectrophotometric methods.

** Sources: (1) Baes and Mesmer (1976); (2) Harned and Copson (1933): (3) Harned and Mannweiler (1935); (4) Bates and others (1959); (5) Perrin (1962a); (6) Sweeton and Baes (1970); (7) Ziemniak and Jones (1978); (8) Glassen and Tewari (1978); (9) Tremaine and LeBlanc (1979); (10) Perrin (1964); (11) Perrin (1962b); (12) Arnek and Kakolowicz (1967); (13) Burkov, Garmash, and Lilich (1977); (14) Volokhov and others (1971); (15) Kilpatrick and Pokras (1953); (16) Bjerrum (1907); (17) Milbern (1957); (18) Sutcliffe and Weber (1956); (19) Olin (1975); (20) Baes, Meyer, and Roberts (1965); (21) Kraus and Holmberg (1954); (22) Kraus and Nelson (1955); (23) Nikolaeva (1978); (24) Rabideau (1957).

being about −15.5. The remaining ions, Hg^{2+}, Sn^{2+}, and Pd^{2+}, are the most readily hydrolyzed cations with A values three log units higher still and over nine log units more positive than "hard" cations of the same size and charge in the first group.

Values for the enthalpy of the first hydrolysis step, ΔH_{11}, are summarized in table 3. Since all but three (for Cd^{2+}, Hg^{2+}, and Bi^{3+}) are derived from the observed temperature dependance of the equilibrium quotient Q_{11} (or, by extrapolation to zero ionic strength, of the equilibrium constant K_{11}), they have fairly large uncertainties, usually in the range 0.7 to 2 kcal/mole. These ΔH_{11} values have been combined with the corresponding values of K_{11} to obtain the entropy change ΔS_{11} at zero ionic strength.

$$\Delta S_{11} = \Delta H_{11}/T + R \ln K_{11}. \tag{10}$$

In so doing it was assumed in a number of cases that the effect on ΔH_{11} of changing the ionic strength from the values at which the equilibrium quotient was measured (up to 3 m) to zero is less than the uncertainty in ΔH_{11}. In at least two cases (Fe^{3+} and Zn^{2+}), where ΔH_{11} or the temperature coefficient of Q_{11} has been determined as a function of ionic strength, this seems to be true.

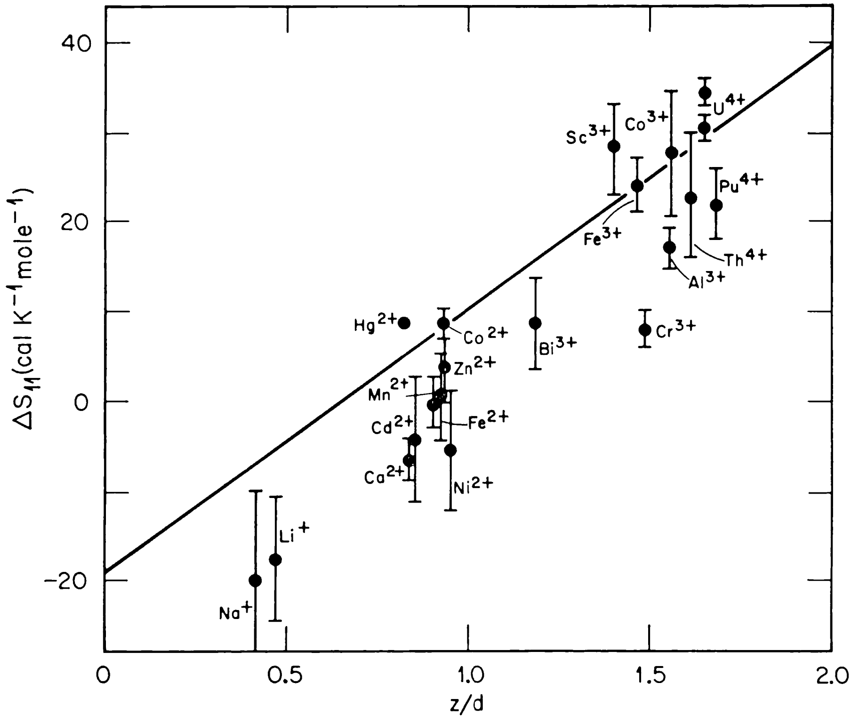

Fig. 3. Correlation of the entropy of the first hydrolysis step (reaction 1) with the ratio of the cation charge (z) to the metal-oxygen distance (d). The line is the least-squares fit to the data weighted according to the uncertainties.

TABLE 4

Calculated entropies and enthalpies of the first hydrolysis step, 25°C

Cation	ΔS_{11} (obs)	ΔS_{11} (calc)	ΔH_{11} (obs)	ΔH_{11} (calc)
	(cal K^{-1} mole^{-1})		(kcal/mole)	
Li^+	−17.5 ± 7	−15.2	13.4 ± 2	14.1
Na^+	−19.9 ± 10	−17.2	13.4 ± 3	14.2
K^+		−18.7		14.1
Ag^+		−13.8		12.3
Tl^+		−16.8		13.0
Be^{2+}		−13.6		11.4
Mg^{2+}		−2.2		14.9
Ca^{2+}	−6.5 ± 2.4	−6.8	15.6 ± 0.7	15.5
Sr^{2+}		−8.6		15.6
Ba^{2+}		−10.0		15.4
Mn^{2+}	−0.2 ± 3	−1.5	14.4 ± 1	14.0
Fe^{2+}	0.8 ± 5	0.8	13.2 ± 1.5	13.2
	−0.9 ± 2.4		12.7 ± 0.7	
Co^{2+}	4.8 ± 1.7	0.7	14.6 ± 0.5	13.4
Ni^{2+}	−5.4 ± 7	0.7	11.9 ± 2	13.7
Pd^{2+}		15.2		7.4
Cu^{2+}		3.9		12.0
Zn^{2+}	3.9 ± 3	2.0	13.4 ± 1	12.8
Cd^{2+}	−2.2 ± 7	−1.6	13.1 ± 2	13.3
	−4.2 ± 7		12.5 ± 2	
Hg^{2+}	8.7 ± 0.7	9.8	7.2 ± 0.2	7.6
Sn^{2+}		8.5		7.2
Pb^{2+}		0.4		10.7
Al^{3+}	17.2 ± 2.4	20.9	11.9 ± 0.7	13.0
Sc^{3+}	28.6 ± 5	19.3	14.4 ± 1.4	11.6
Y^{3+}		11.4		13.9
La^{3+}		8.2		14.1
Sm^{3+}		10.3		13.8
Lu^{3+}		12.0		14.0
Ti^{3+}		23.8		10.1
V^{3+}		24.1		10.3
Cr^{3+}	14.2 ± 2.2	21.4	9.7 ± 1	11.8
Fe^{3+}	24.2 ± 3	24.2	10.2 ± 1	10.2
Co^{3+}	27.8 ± 7	27.6	10.0 ± 2	9.9
Rh^{3+}		21.8		11.1
Au^{3+}		30.3		7.0
Ga^{3+}		23.8		10.6
In^{3+}		19.1		11.2
Tl^{3+}		22.6		7.6
Bi^{3+}	8.8 ± 5	20.7	4.1 ± 1.4	7.7
Zr^{4+}		34.4		9.8
Hf^{4+}		33.6		10.3
Th^{4+}	22.9 ± 7	25.2	11.2 ± 2	11.9
Pa^{4+}		33.0		8.7
U^{4+}	34.6 ± 1.4	30.5	11.2 ± 0.5	10.0
	30.6 ± 1.4		10.0 ± 0.4	
Np^{4+}		29.2		10.7
Pu^{4+}	21.9 ± 4	31.3	7.2 ± 1.2	10.0

The resulting values of ΔS_{11} vary approximately linearly with z/d (fig. 3), though Hg^{2+}, the softest cation with the strongest tendency to hydrolyze, shows a positive deviation several times the small uncertainty ($\pm$ 0.7 cal K^{-1} mole^{-1}) involved. This suggests that a dependence on K_{11} should be included in the representation of ΔS_{11}. The following expression was found to give a satisfactory fit to the observed values,

$$\Delta S_{11} = 1.772 \log K_{11} + 19.12\,(z/d), \tag{11}$$

producing a standard error to fit 1.47 times the uncertainty in ΔS_{11}. The corresponding standard error of fit for the line in figure 3 is 2.68. Assuming this relationship, ΔH_{11} can be calculated from K_{11} and z/d for most of the simple cations (table 4).

$$\Delta H_{11} = -0.836 \log K_{11} + 5.70\,(z/d). \tag{12}$$

All 45 values of ΔH_{11} thus obtained are positive, 27 are within 2.3 kcal/mole of the enthalpy of dissociation of water (13.3 kcal/mole), and only 9 of the enthalpy values are less than 10 kcal/mole. The lowest values are found for the "soft" ions Pd^{2+} (7.4), Hg^{2+} (7.6), Sn^{2+}(7.2), Au^{3+} (7.0), Ti^{3+} (7.6), and Bi^{3+} (7.7).

The $M(OH)_z(c)/M^{z+}$ boundary.—The enthalpy of reaction of the oxide or hydroxide phases to produce the simple cations in solution (ΔH_{s10}, reaction 6) have been calculated (table 5) by combining values of the equilibrium constant, K_{s10}, with the corresponding entropy changes, ΔS_{s10}, derived mainly from the National Bureau of Standards compilation (Wagman and others, 1968). In a number of cases where values of the equilibrium constant and the entropy were not for the same solid phase, the required entropy value was estimated by assuming the entropy change for the reaction

$$MO_{(z-u)/2}(OH)_u \rightarrow MO_{(z-v)/2}(OH)_v + (u-v)/2\ H_2O \tag{13}$$

to be 3.64 (u—v) cal K^{-1} mole^{-1}. This value was derived by inspection from the NBS tables.

The resulting 28 enthalpy values are all negative, signifying that the boundary in figures 1 and 2 between the solid phase and the simple cation will fall as the temperature is increased. For cations of the same charge, ΔH_{s10} tends to be less negative for the softer ions.

The $M(OH)_z(c)/M^{z+}/MOH^{(z-1)+}$ intersection.—As we have already noted (Baes and Mesmer, 1976), there is a correlation between the equilibrium constant for the solubility of an oxide or hydroxide, K_{s10}, and the constant for the first hydrolysis step, K_{11}, such that

$$K_{11}{}^{z}K_{s10} \cong 10^{-5.6}. \tag{14}$$

This corresponds to approximate constancy of the equilibrium constant for the reaction

$$M(OH)_z(c) + (z-1)M^{z+} \rightleftharpoons zMOH^{(z-1)+}, \tag{15}$$

TABLE 5
Calculated enthalpies of reaction of oxides and hydroxides, 25°C

Cation	Solid phase	Log K_{s10}	z log K_{11} + log K_{s10}	ΔS_{s10} (cal K^{-1} $mole^{-1}$)	ΔH_{s10}	z ΔH_{11} + ΔH_{s10}	Sources[a]
					(kacl/mole)		
Ag^{+}	½Ag_2O	6.29 ± 0.05	−5.7 ± 0.3	11.2 ± 0.2	−5.23 ± 0.1	7.0 ± 1.0	1, 1
Be^{2+}	$Be(OH)_2$	6.69 ± 0.02	−4.1 ± 0.2	−10.0 ± 1	−12.10 ± 0.3	10.7 ± 1.8	1, 1
Mg^{2+}	$Mg(OH)_2$	16.84 ± 0.03	−6.0 ± 0.2	−14.4 ± 1	−27.26 ± 0.3	2.6 ± 1.8	2, 1
Ca^{2+}	$Ca(OH)_2$	22.8 ± 0.02	−2.9 ± 0.2	0.09 ± 0.14	−31.08 ± 0.05	−0.1 ± 1.8	3, 1
Mn^{2+}	$Mn(OH)_2$	<15.2	<-5.98	−7.9 ± 2.2	>-23.1	>4.9	1, 1
Fe^{2+}	$Fe(OH)_2$	<12.85	<-6.2	−20.5 ± 2	>-23.6	>2.8	1, 1
Co^{2+}	$Co(OH)_2$	12.3 ± 0.1	−7.00 ± 0.14	−12.6 ± 3	−20.5 ± 0.9	6.2 ± 2.0	1, 1
Ni^{2+}	$Ni(OH)_2$	10.8 ± 0.1	−8.92 ± 0.12	−18.4 ± 2.2	−20.2 ± 0.7	7.1 ± 1.9	1, 1
Pd^{2+}	$Pd(OH)_3$	−0.8 ± 0.1	−5.0 ± 0.2				
Cu^{2+}	CuO	7.62 ± 0.05	−8.24 ± 0.1	−17.28 ± 0.3	−15.55 ± 0.10	8.5 ± 1.8	1, 1
Zn^{2+}	ZnO	11.14 ± 0.03	−6.78 ± 0.1	−20.5 ± 0.5	−21.32 ± 0.16	4.3 ± 1.8	1, 1
Cd^{2+}	$Cd(OH)_2$	13.65 ± 0.04	−6.5 ± 0.2	−6.5 ± 0.5	−20.56 ± 0.16	6.0 ± 1.8	3, 3[b]
Hg^{2+}	HgO	2.56 ± 0.05	−4.24 ± 0.15	−8.76 ± 0.21	−6.10 ± 0.09	9.0 ± 1.8	3, 3
Sn^{2+}	SnO	1.76 ± 0.1	−5.0 ± 0.8	6.8 ± 1	−0.36 ± 0.3	14.0 ± 2.1	3, 3
Pb^{2+}	PbO	12.72 ± 0.05	−2.7 ± 0.2	4.49 ± 0.2	−16.01 ± 0.09	5.3 ± 1.8	3, 3
Al^{3+}	$Al(OH)_3$	8.5 ± 0.1	−6.4 ± 0.1	−39.8 ± 4	−23.5 ± 1	15.6 ± 2.9	4, 4
Sc^{3+}	ScO(OH)	9.4 ± 0.1	−3.5 ± 0.3	−42.2 ± 3	−25.4 ± 0.9	9.5 ± 2.9	1, 1[c]
Y^{3+}	$Y(OH)_3$	17.5 ± 0.3	−5.6 ± 0.7	−35.9 ± 2	−34.6 ± 0.7	7.1 ± 2.9	1, 1[b]
La^{3+}	$La(OH)_3$	20.3 ± 0.3	−5.2 ± 0.7	−31.1 ± 1	−36.98 ± 0.5	5.2 ± 2.9	1, 1[b]
Sm^{3+}	$Sm(OH)_3$	16.5 ± 0.3	−7.2 ± 0.7	−32.7 ± 2	−32.25 ± 0.7	9.3 ± 2.9	1, 1[b]
Lu^{3+}	$Lu(OH)_3$	14.5 ± 0.3	−8.3 ± 0.7	−40.2 ± 2	−31.75 ± 0.7	10.1 ± 2.9	1, 1[b]
Cr^{3+}	$Cr(OH)_3$	<12.0	<0.0				

Fe^{3+}	FeO(OH)	0.5 ± 0.8	−6.1 ± 0.8	−58.15 ± 0.6	−18.0 ± 1.1	12.6 ± 2.9	1, 1[c]
Rh^{3+}	$Rh(OH)_3$	<9.0	<−1.2				
Au^{3+}	$Au(OH)_3$	−5.51 ± 0.07	−0.98 ± 0.6				
Ga^{3+}	GaO(OH)	2.9 ± 0.3	−4.9 ± 0.9	−60.2 ± 3	−21.9 ± 1	10.0 ± 3	1, 1[c]
In^{3+}	$In(OH)_3$	5.07 ± 0.1	−6.9 ± 0.3	−12.5 ± 3	−10.6 ± 0.9	22.8 ± 2.9	1, 1[b]
Tl^{3+}	$\frac{1}{2}Ti_2O_3$	−3.9 ± 0.1	−5.8 ± 0.3				
Bi^{3+}	$\frac{1}{2}Bi_2O_3$	3.46 ± 0.1	0.19 ± 0.14	−35.4 ± 3	−15.3 ± 0.9	7.7 ± 2.8	5, 1
Zr^{4+}	ZrO_2	−1.9 ± 1	−0.7 ± 1				
Hf^{4+}	HfO_2	−1.2 ± 1	−2.2 ± 1.6				
Th^{4+}	ThO_2	6.3 ± 1	−6.5 ± 1.3	−83.2 ± 4	−33.4 ± 1.8	14.1 ± 4	6, 6
Pa^{4+}	PaO_2	0.6 ± 3	4.0 ± 3				
U^{4+}	UO_2	−1.8 ± 1	−4.4 ± 1	−84.0 ± 5	−22.6 ± 2	17.3 ± 4	7, 8
Np^{4+}	NpO_2	−4.0 ± 2	−10.0 ± 2	−78.8 ± 5	−18.0 ± 3	25.0 ± 5	7, 8
Pu^{4+}	PuO_2	−6.5 ± 3	−8.5 ± 3	−79.3 ± 5	−14.8 ± 4	25.2 ± 6	7, 8

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[a] Sources: Log K_{11} values are from table 2 and Log K_{s10} values are from Baes and Mesmer (1976). ΔS_{11} values are the calculated values from table 4, the first number listed indicates the source of the M^{z+} ion entropy used, the second number listed indicates the source of the solid-phase entropy used: (1) Wagman and others (1968..); (2) Parker, Wagman, and Garvin (1976); (3) Cox (1977); (4) Hemingway and Robie (1977); (5) Vasil'ev and Glavina (1969); (6) Wagman, Schumm, and Parker (1977); (7) Fuger and Oetting (1976); (8) Wagman (1978).

[b] The entropy of the oxide was used with eq 13 in calculating ΔS_{s10} and ΔH_{s10} (see text).

[c] The entropy of the hydroxide was used with eq 13 in calculating ΔS_{s10} and ΔH_{s10} (see text).

and a corresponding constancy of the position of the $M(OH)_z(c)/M^{z+}/MOH^{(z-1)+}$ intersection along the vertical axis in figure 2, independent of the cation involved. Of the 36 values for the equilibrium constant of this reaction listed in table 5, 22 fall within 1.6 log units of $10^{-5.6}$ at 25°C, only 7 give values with deviations of more than 3 log units. While the deviations in most cases exceed the uncertainties in the values of the product $K_{11}{}^zK_{s10}$, in view of the wide range of the K_{11} and K_{s10} values involved, this appears to be a significant correlation.

Since a similar correlation might well be expected for the corresponding enthalpy of the solution of the solid phase and the enthalpy of the first hydrolysis step, values of $\Delta H_{s10}/z$ have been plotted versus the observed values of ΔH_{11} in figure 4. Clearly there is a decrease in $\Delta H_{s10}/z$ as ΔH_{11} increases. The straight line shown in the figure corresponds to the expression

$$\Delta H_{s10} = z\,(9.30 - 1.588\,\Delta H_{11}), \qquad (16)$$

obtained by a least-squares fit of the ΔH_{s10} values in table 5 using smoothed values of ΔH_{11} from eq (12). The correlation in this case approaches the uncertainties of the quantities involved. The resulting expression for the enthalpy of reaction (15) is

$$\Delta H(15) = z\,\Delta H_{11} + \Delta H_{s10} = z\,(9.30 - 0.588\,\Delta H_{11}), \qquad (17)$$

Values for the enthalpy of reaction (15), calculated from values of ΔH_{s10} in table 5 and smoothed values of ΔH_{11} (from eq 12), are included in table 5. With the single exception of Ca^{2+} ion, enthalpies of reaction (15) are positive and, as eq (17) suggests, tend to increase with the charge of the cation.

As will be seen, these correlations involving the stability of the initial hydrolysis product in solution, $MOH^{(z-1)+}$, and the solubility of the hydroxide or oxide phase are fairly useful. The small value of the equilibrium constant for reaction (15) reflects the strong tendency for precipitation to occur shortly after hydrolysis begins. The positive heat means this tendency is weakened by increasing the temperature. Hence, the intersection of the $M^{z+}/MOH^{(z-1)+}$ boundary with the solubility curve in figure 2 will tend to rise with temperature, the more so the higher the charge on the cation.

The $M^{z+}/MOH^{(z-1)+}/M_x(OH)_y{}^{(xz-y)+}$ *intersection.*—We have previously noted (Baes and Mesmer, 1976) that the tendency of the species $MOH^{(z-1)+}$ to polymerize according to the reaction

$$MOH^{(z-1)+} \rightleftharpoons (1/y)M_x(OH)_y{}^{(xz-y)+} + (1 - x/y)M^{z+} \qquad (18)$$

was about the same for all cations. At the high ionic strengths involved in most measurements (1-3 m), the equilibrium quotient for this reaction is usually given to within 0.3 log units by the expression

$$\log(Q_{xy}{}^{1/y}/Q_{11}) = 2.8 - (x - 1)/y\,\log(55.5) \qquad (19)$$

at 25°C. The last term on the right converts from the mole fraction con-

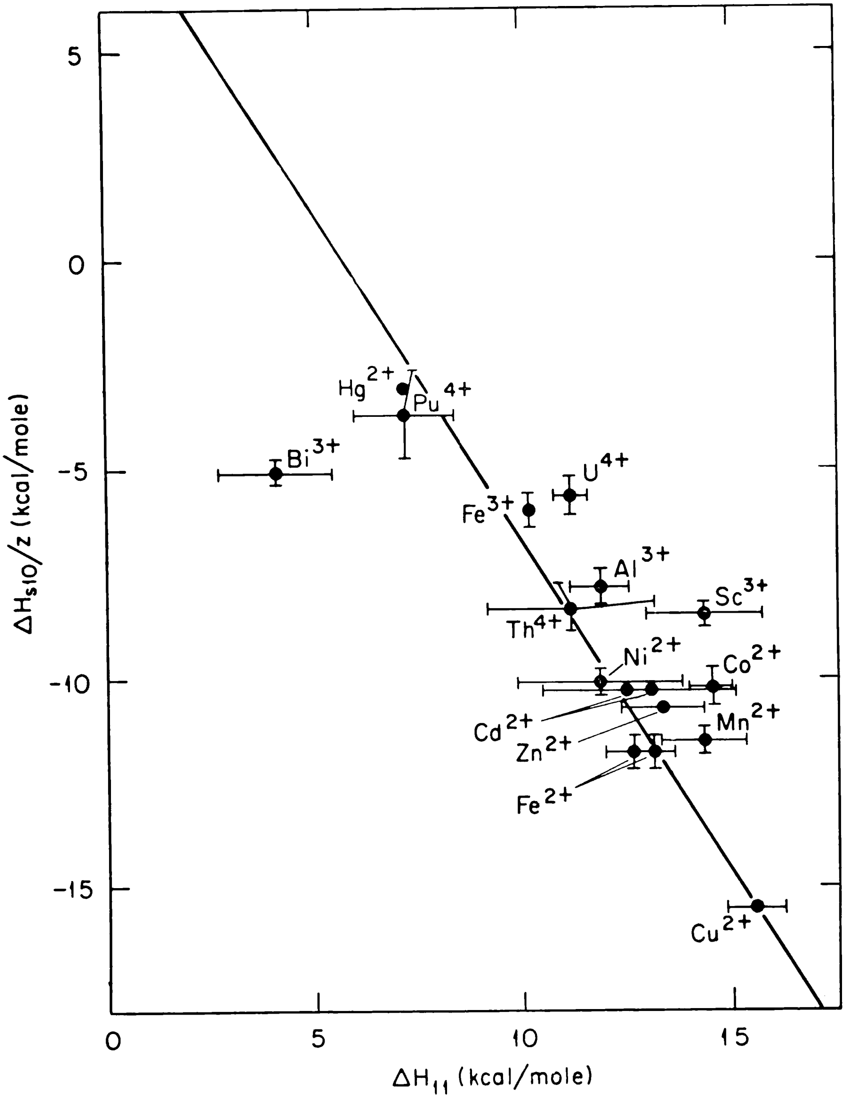

Fig. 4. Correlation of the enthalpy of solution of an oxide or hydroxide phase in acid (reaction 6) with the enthalpy of the first hydrolysis step (reaction 1). The line represents the least-squares fit to the ΔH_{s10} values in table 5 and the calculated values of ΔH_{11} from table 4. The points are the observed values of ΔH_{11} from table 3.

centration scale, on which the equilibrium quotient for reaction (18) is a better constant, to the molal concentration scale. We also noted that the entropy change of the formation reaction for a polynuclear species (reaction 4) could be correlated with z/d, again on the mole fraction scale. On the molality scale the expression for this entropy change, ΔS_{xy}, was

$$\Delta S_{xy}/y = -17.5 + 16.2(z/d) + (1 + y - x)/y\ R\ \ln(55.5). \qquad (20)$$

This expression and that for ΔS_{11} (eq 11) may be combined with the above approximation for the equilibrium quotient (eq 19) to estimate the enthalpy of reaction (18).

$$\Delta H(18) = \Delta H_{xy}/y - \Delta H_{11} \approx -6.6 - 0.53 \log K_{11} - 0.9\,(z/d). \qquad (21)$$

The resulting enthalpy change for reaction (18) is negative and falls in the range −6 to −13 kcal/mole. Hence the effect of increasing temperature is to reverse the polymerization reaction (18) and to cause the intersection of the $M^{z+}/MOH^{(z-1)+}$ and the $M^{z+}/M_x(OH)_y^{(xz-y)+}$ boundaries in figure 2 to rise.

The $M(OH)_y^{(z-y)+}/M(OH)_{y+1}^{(z-y-1)+}$ *boundary.*—In order to project the effect of increasing temperature on the course of hydrolysis, it remains for us to consider the mononuclear species formed beyond the first one, $MOH^{(z-1)+}$. Unfortunately there is relatively little information available concerning those species that lie between the first hydrolysis product and the anionic mononuclear species that often terminate the series. Such information almost invariably comes from measurements of the solubility of the oxide or hydroxide formed by the cation, and, as we have noted, there has been a limited supply of accurate data. Increasingly, hydroxide and oxide solubility measurements are being made at elevated temperatures (compare references cited in tables 6 and 7), where there is less difficulty from the traditional problems of long equilibration times and active, amorphous phases.

Of particular interest to us is the enthalpy associated with each successive mononuclear hydrolysis step.

$$\begin{gathered} M(OH)_y^{(z-y)+} + H_2O \rightleftharpoons M(OH)_{y+1}^{(z-y-1)+} + H^+, \\ \Delta H(22) = \Delta H_{1,y+1} - \Delta H_{1y}. \end{gathered} \qquad (22)$$

The limited amount of information presently available (summarized in table 6) suggests that for the divalent cations the heat of the second hydrolysis step is usually close to that of the first step, though perhaps a bit less positive. For these cations the enthalpy of hydrolysis of the neutral species $M(OH)_z(aq)$ is usually lower still. The entropy changes accompanying the hydrolysis of the various mononuclear species in table 6 show a fairly uniform decrease as the charge on the reacting species decreases (fig. 5). By including the anions of C(IV), P(V), As(V), S(VI), Cr(VI), and Se(VI), we see that the decrease in the entropy continues beyond the neutral species. Until more data are available this correlation may be the best way to estimate the temperature dependence of the stepwise hydrolysis of metal cations for which equilibrium constants are available.

The trend in figure 5 suggests the approximation

$$\Delta S(22) = -17.8 + 12.2\,(z - y). \qquad (23)$$

This permits us to estimate the enthalpy of reaction (22) as a function of the stepwise hydrolysis constant K(22) ($= K_{1,y+1}/K_{1y}$) and the charge on the reacting species (z-y),

$$\Delta H(22) = -1.36 \log K(22) - 5.3 + 3.64\,(z\text{-}y). \qquad (24)$$

The results are summarized in figure 6, wherein the horizontal axis, $-\log$ K(22), corresponds to the pH at which $M(OH)_y^{(z-y)+}$ and $M(OH)_{y+1}^{(z-y-1)+}$ are present in equal amounts. Since the uncertainty in the estimated entropy is about ±10 cal K^{-1} $mole^{-1}$, the uncertainty in the resulting enthalpy is about ± 3 kcal/mole.

It can be seen from figure 6 that if the successive stepwise hydrolysis constants of a cation were to decrease by about 2.7 log units per step, then the enthalpy associated with each step would be about the same. As a consequence, except for heat capacity effects, the pH range over which each species is dominant would remain unchanged as the temperature in-

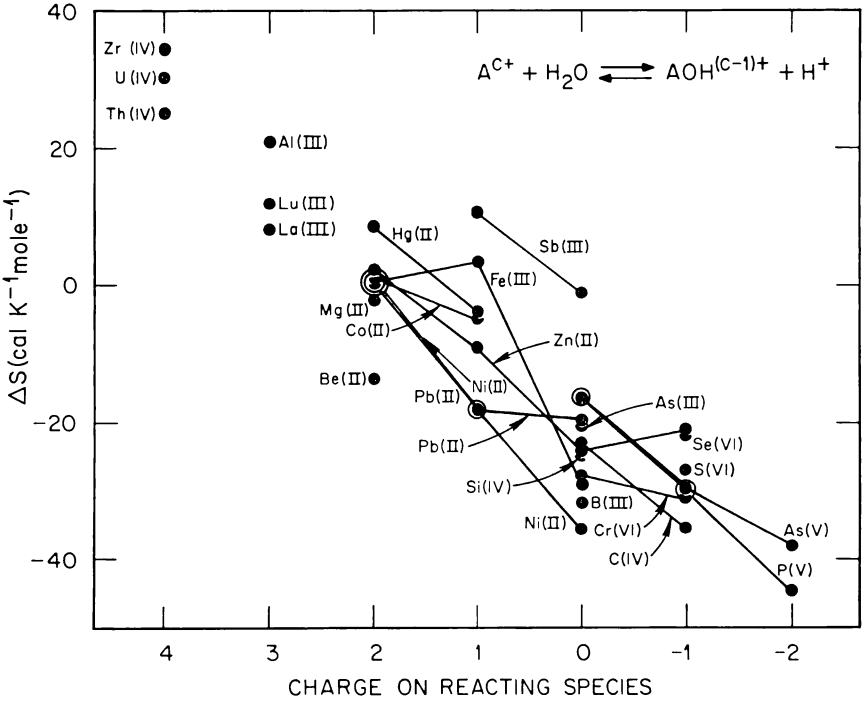

Fig. 5. Correlation of the entropy of stepwise hydrolysis with the charge on the reacting species. All species involve water, hydroxide ion, or oxide ion as ligands. The points connected by lines denote stepwise hydrolysis for the metal valence indicated.

TABLE 6
The thermodynamics of stepwise hydrolysis of mononuclear species, 25°C
$M(OH)_y^{(z-y)+} + H_2O \rightleftharpoons M(OH)_{y+1}^{(z-y-1)+} + H^+$

Hydrolyzing Species	Log K	ΔH (kcal/mole)	ΔS (cal K^{-1} $mole^{-1}$)	Source* Log K	ΔH	ΔS
Fe^{2+}	−9.5 ± 0.1	13.2	0.8	1		2
$FeOH^+$	−11.1 ± 1	16.2 ± 1	3.5 ± 6	1	3	
$Fe(OH)_2$ (aq)	−8.4 ± 1.5	2.8 ± 1.7	−29 ± 9	3	3	
Co^{2+}	−9.65 ± 0.05	13.4	0.7	1		2
$CoOH^+$	−9.15 ± 0.1	11.2 ± 1.7	−4.3 ± 6	1	4	
Ni^{2+}	−9.86 ± 0.03	13.7	0.7	1		2
$NiOH^+$	−10.4 ± 0.7	8.7 ± 2	−18.4 ± 7	5	5	
$Ni(OH)_2$ (aq)	−9.53 ± 0.8	2.4 ± 3	−35.6 ± 11	5	5	
Zn^{2+}	−8.96 ± 0.05	12.8	2.0	1		2
$ZnOH^+$	−7.8 ± 0.3	8.0 ± 2	−9 ± 7	6	6	
$Zn(OH)_2$ (aq)	−11.5 ± 0.2	8.5 ± 2	−24 ± 7	6	6	
$Zn(OH)_3^-$	−12.9 ± 0.1	11.4 ± 3	−21 ± 10	6	6	
Hg^{2+}	−3.40 ± 0.07	7.23 ± 0.18	8.7 ± 1	1	7	
$HgOH^+$	−2.77 ± 0.08	2.61 ± 0.24	−3.9 ± 1	1	7	
Pb^{2+}	−7.71 ± 0.1	10.7	0.4	1	2	
$PbOH^+$	−9.41 ± 0.2	7.4 ± 2	−18 ± 7	1	8	
$Pb(OH)_2$ (aq)	−10.94 ± 0.1	9.1 ± 1	−19.5 ± 3	1	8	
$Sb(OH)_2^+$	−1.41 ± 0.05	5.1 ± 0.6	10.7 ± 2	1	9	
$Sb(OH)_3$ (aq)	−11.82 ± 0.1	15.9 ± 0.5	−0.8 ± 2	1	9	
$PO(OH)_3$ (aq)	−2.148	−1.90	−16.2	10	11	
$PO_2(OH)_2^-$	−7.198	0.99	−29.6	12	11	
$PO_3(OH)^{2-}$	−12.38	3.53	−44.8	13	11	
$AsO(OH)_3$ (aq)	−2.24	−1.69	−15.9	1	11	
$AsO_2(OH)_2^-$	−6.94	0.77	−29.2	1	11	
$AsO_3(OH)^{2-}$	−11.50	4.35	−38.0	1	11	
$SO_3(OH)^-$	−1.99	−5.24	−26.7	11	11	
$SeO_3(OH)^-$	−1.663	−4.2	−21.7	1	11	
$B(OH)_3$ (aq)	−9.236 ± 0.003	3.22 ± 0.1	−31.46 ± 0.4	1	14	
$Si(OH)_4$ (aq)	−9.825 ± 0.033	6.12 ± 0.3	−24.43 ± 1	15	15	

* Sources: (1) Baes and Mesmer (1976); (2) from eq 11.; (3) Zieminak and Jones (1978); (4) from ΔH_{s12} (table 7) and ΔH_{s10} (table 5); (5) from values given by Tramaine and LeBlanc (1980); and K_{11} and ΔH_{11}; (6) from results of Reichle and others (1975); (7) Arnek and Kakolowicz (1967); (8) from results of Tugarinov and others (1975); (9) from results of Popova and others (1975); (10) Vanderzee and Quist (1961); (11) Wagman and others (1968..); (12) Bates and Acree (1943); (13) Bates (1951); (14) Mesmer and others (1972); (15) Busey and Mesmer (1977).

TABLE 7

The thermodynamics of reactions of oxides and hydroxides to form neutral aqueous species, 25°C

$$M(OH)_z(c) \rightleftharpoons M(OH)_z(aq)$$

$$MO_{z/2}(c) + z/2\ H_2O \rightleftharpoons M(OH)_z(aq)$$

Cation	Solid Phase	Log K_{s1z}	ΔH (kcal/mole)	ΔS (cal K^{-1} $mole^{-1}$)	Source[a]		
					Log K	ΔH	ΔS
Ag^+	½Ag_2O	−5.71 ± 0.3	7.07 ± 2	−2.4 ± 7	1		2
Fe^{2+}	$Fe(OH)_2$	<−7.8	>5.8	~−16	1	3	
Co^{2+}	$Co(OH)_2$	−6.5 ± 0.14	4.1 ± 1	−16.0 ± 3.4	1	4	
Ni^{2+}	NiO	−8.1 ± 0.5	−1.26 ± 1	−41.3 ± 4	5	5	
Zn^{2+}	ZnO	−5.62 ± 0.2	−0.52 ± 0.5	−27.5 ± 2	6	6	
Hg^{2+}	HgO	−3.61 ± 0.07	3.74 ± 0.18	−4.0 ± 0.7	1	7	
Pb^{2+}	PbO (red)	−4.4 ± 0.1	5.4 ± 1	−2.0 ± 3.4	1	6	
B(III)	$B(OH)_3$		5.26	17.6		7	7
As^{3+}	¼ As_4O_6	−0.68 ± 0.01	3.58 ± (0.1)	8.9 ± (0.3)	1	7	
Sb^{3+}	½ Sb_2O_3	−4.24 ± 0.1	7.7 ± 0.5	6.4 ± 1.7	1	9	
Bi^{3+}	½ Bi_2O_3	−5.40 ± 0.15					
Si(IV)	SiO_2 (α-quartz)	−4.0 ± 0.1	7.0 ± 0.5	5.2 ± 1.7	10	10	

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[a] Sources: (1) Baes and Mesmer (1976); (2) from Δ S_{11} given by eq 11 and Δ S_{s10} from Wagman and others (1968-); (3) from Δ H_{s10} (table 5) and Δ H_{12} (Ziemniak and Jones, 1978); (4) from temperature dependence of K_{s12} values from Eguchi and Yazawa (1975) and Mesmer and Baes (1976); (5) Tremaine and LeBlanc (1980); (6) K_{12} and Δ H_{12} values from table 6 were combined with K_{s10} and Δ H_{s10} values from table 5; (7) Wagman and others (1968-); (8) from temperature dependence of K_{s12} from Tugarinov and others (1975); (9) Popova and others (1975); (10) Walther and Helgeson (1977).

creases. For a few cations, ranges of stability of one mononuclear hydrolysis product (usually the neutral one) wider than 2.7 pH units do occur, and in such cases this range should narrow with increasing temperature. For most cations, however, ranges of stability are narrower, typically 1.3 pH units per hydrolysis step. Stepwise enthalpies in such cases should decrease as hydrolysis proceeds, and the range of stability for each intermediate species should widen with increasing temperature (fig. 7).

The $M(OH)_z(c)/M(OH)_z(aq)$ boundary.—The location of the boundary determined by the equilibrium between the hydroxide or oxide solid phase and the neutral hydroxide complex in solution

$$\begin{aligned} M(OH)_z(c) &\rightleftharpoons M(OH)_z(aq) \\ MO_{z/2}(c) + z/2\, H_2O &\rightleftharpoons M(OH)_z(aq) \end{aligned} \qquad (25)$$

is of special interest since it determines the minimum in the solubility curve for many solids. While estimates of the corresponding equilibrium constant K_{s1z} are generally of poor accuracy, for all but the soft cations they appear to decrease as the cation charge increases. Indeed it may be seen from the following argument that such should be the case: If a cation produces a series of mononuclear hydrolysis products for which the

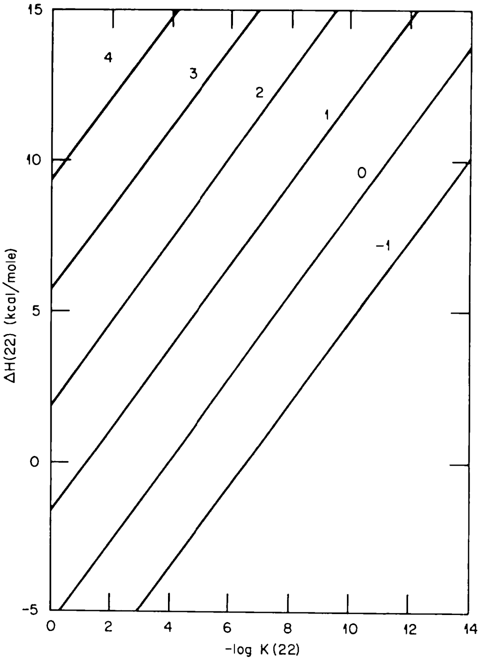

Fig. 6. Estimated enthalpy of stepwise hydrolysis (reaction 22) as a function of the equilibrium constant and the charge on the reacting species. The abscissa corresponds to the pH at which the reactant and the product species would be present at equal concentrations.

successive stepwise constants, K(22), decrease by a constant factor B (typically about 1.3 log units) then it would follow that for the reaction

$$M^{z+} + z\,H_2O \rightleftharpoons M(OH)_z(aq) + z\,H^+, \tag{26}$$

the equilibrium constant would be given by

$$\log K_{1z} = z \log K_{11} - 0.5\,z(z-1)\,B. \tag{27}$$

The equilibrium constant K_{s1z} (for reaction 25) is related to K_{1z} by

$$\log K_{s1z} = \log K_{s10} + \log K_{1z}. \tag{28}$$

Combining eqs (27) and (28) and introducing the approximation given by eq (14), we obtain

$$\log K_{s1z} \approx -5.6 - 0.5\,z(z-1)\,B. \tag{29}$$

For $B = 1.3$ log units this expression gives $\log K_{s1z} \approx -5.6$, -6.9, -9.5, and -13.4 respectively for $z = 1$, 2, 3, and 4. Since the variability of B is considerable, these are quite approximate estimates, as may be judged by comparison with the K_{s1z} values listed in table 7. Those for Ag^+, Fe^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} are within one or two log units of the predicted values. The soft cations Hg^{2+}, Pb^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, and Si(IV) give much higher values because of the extra stability of the neutral complexes they form in solution.

Table 7 summarizes the limited information about the enthalpy and entropy changes associated with reaction (25). The enthalpy values, ΔH_{s1z}, are in the range -1.3 to 7.7 kcal/mole, suggesting that the temperature

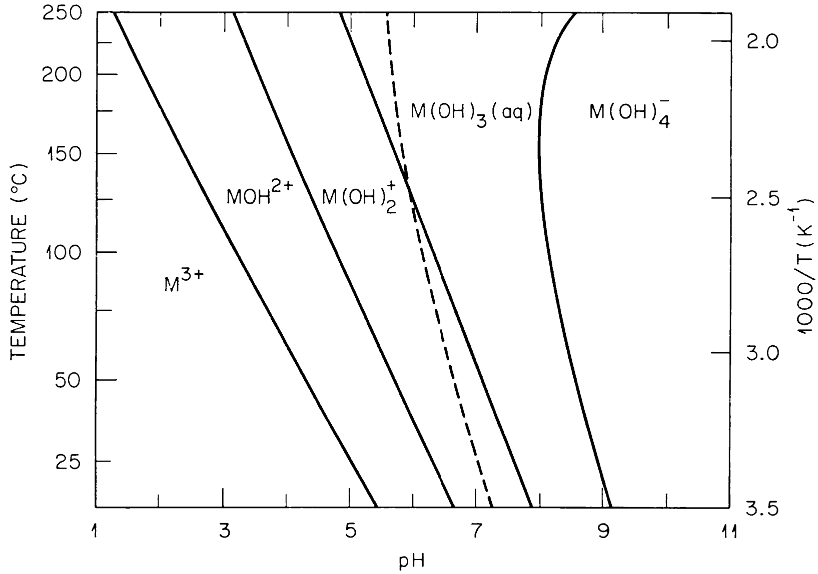

Fig. 7. Regions of dominance of the mononuclear species of the trivalent cation from figures 1 and 2 as a function of temperature. The temperature scale is linear in 1/T K^{-1}, hence the curvature of the boundaries indicates the effect of estimated ΔC_p values (from table 8). The dashed curve indicates neutral pH.

dependence of such solubility is likely to be relatively small and, especially for a hydroxide solid, positive.

The $M(OH)_z(c)/M(OH)_{z+1}^-$ boundary.—The temperature dependence of the equilibrium

$$M(OH)_z(c) + H_2O \rightleftharpoons M(OH)_{z+1}^- + H^+ \qquad (30)$$

may be estimated as follows: The enthalpy for this reaction is the sum of ΔH_{s1z} and the enthalpy for the reaction

$$M(OH)_z(aq) + H_2O \leftrightarrows M(OH)_{z+1}^- + H^+. \qquad (31)$$

The approximate value of the latter enthalpy is given by eq (24) as

$$\Delta H(31) \approx - 1.36 \log K(31) - 5.3, \qquad (32)$$

and hence

$$\Delta H(30) = \Delta H_{s1z} - 1.36 \log K(31) - 5.3 \qquad (33)$$

Since ΔH_{s1z} is usually positive and of the order of the last term on the right in eq (32), then

$$\Delta H(30) \approx -1.36 \log K(31).$$

Log K for reaction (31) is generally less than −7, hence ΔH for reaction (30) should be positive and usually greater than 10 kcal/mole.

Of perhaps greater interest is the equilibrium representing the tendency of the hydroxide (or oxide) phase to dissolve in basic solutions,

$$M(OH)_z(c) + OH^- \rightleftharpoons M(OH)_{z+1}^-. \qquad (34)$$

Since the enthalpy of this reaction will be that just estimated for reaction (30) less the enthalpy of dissociation of water (13.3 kcal/mole), it is likely to be small.

Estimating ΔC_p for hydrolysis reactions.—It is of course desirable to estimate ΔC_p for hydrolysis reactions in order to predict changes in the associated ΔH and ΔS values with temperature. In the virtual absence of information about the partial molal heat capacities of hydroxide complexes, the best that can be done is to make estimates from the partial molal heat capacities of other ionic species and from the values of ΔC_p for other protolytic reactions.

The partial molal heat capacities for monatomic ions assigned by Criss and Cobble (1964) exhibit such a smooth variation with the ionic radius that it is possible to predict the heat capacity of a simple cation of specified size and charge with an accuracy comparable to the measured values. We will approximate the heat capacity of a mononuclear hydroxide complex $M(OH)_y^{(z-y)+}$ as that of a monatomic cation of the same charge as the complex and the same size as the hydrolyzing cation M^{z+}. This seems reasonable since the hydroxide complex and the cation that produced it probably differ only by the protons that have been lost in hydrolysis (reaction 2). The resulting values of ΔC_p for various hydrolysis reactions involving mononuclear species of cations of several sizes are summarized in table 8.

TABLE 8

Estimated ΔC_p values for hydrolysis reactions[a]

Reaction	Pauling Radius of M^{z+} (Å)	Ave. ΔC_p (cal K^{-1} mole^{-1}) 25 (°C)	25–60	25–100	25–150	25–200
$M^{4+} + H_2O \rightleftharpoons MOH^{3+} + H^+$	0.5	−10	−8	−5	−4	−1
	0.8	−9	−8	−6	−5	−4
	1.1	−8	−9	−7	−6	−6
$M(OH)^{3+}_{z-3} + H_2O \rightleftharpoons M(OH)^{2+}_{z-2} + H^+$	0.5	−11	−11	−10	−10	−10
	0.8	−10	−11	−8	−8	−8
	1.1	−8	−9	−6	−5	−5
$M(OH)^{2+}_{z-2} + H_2O \rightleftharpoons M(OH)^{+}_{z-1} + H^+$	0.5	−15	−14	−10	−10	−10
	0.8	−11	−11	−7	−7	−6
	1.1	−7	−9	−6	−4	−4
$M(OH)^{+}_{z-1} + H_2O \rightleftharpoons M(OH)_z\,(aq) + H^+$		0	0	0	0	0
$M(OH)_z\,(aq) + H_2O \rightleftharpoons M(OH)^{-}_{z+1} + H^+$		−55	−47	−44	−45	−51
$H_2O \rightleftharpoons H^+ + OH^-$		−55	−47	−44	−45	−51

[a] The ΔC_p values for the first three reactions were obtained by assuming that the partial molal heat capacity of each hydroxide complex is equal to that for a monatomic cation of the same radius as M^{z+} but with a charge equal to that of the complex. The estimates of the average heat capacities of monatomic cations as a function of radius and temperature were made using the values of Criss and Cobble (1964). ΔC_p values for water dissociation are from Sweeton, Mesmer, and Baes (1974).

From a number of recent studies of protolytic reactions over the temperature range 0° to 300°C (Mesmer, and others, 1972; Mesmer and Baes, 1974; Hitch and Mesmer, 1976; Busey and Mesmer, 1977), it appears that ΔC_p is close to zero for reactions that produce no change in the number or in the magnitude of the ion charges. Accordingly ΔC_p has been asumed zero (table 8) for the reaction

$$M(OH)_{z-1}^{+} + H_2O \rightleftharpoons M(OH)_z(aq) + H^{+}. \tag{35}$$

A similar assumption is made for the reaction

$$M(OH)_z(aq) + OH^{-} \rightleftharpoons M(OH)_{z+1}^{-}, \tag{36}$$

which in combination with the dissociation reaction for water gives the final hydrolysis reaction listed in table 8.

The quantities listed in table 8 are average heat capacity values over the specified temperature interval. Enthalpies and entropies of reaction may be estimated with sufficient accuracy from the approximate relationships

$$\Delta S_T = \Delta S_{298} + \Delta C_p \ln(T/298.15) \tag{37}$$

$$\Delta H_T = \Delta H_{298} + \Delta C_p (T-298.15). \tag{38}$$

The accuracy of these estimated heat capacities depends of course primarily on the reliability of the assumptions employed, namely, (1) that the partial molal heat capacity of a mononuclear hydroxide complex is the same as that of a simple cation with the size of the unhydrolyzed cation and the charge of the complex, and (2) that ΔC_p is zero for a reaction in which there is no change in the number or magnitude of the ion charges. These assumptions are expected to produce ΔC_p values reliable to 10 cal mole^{-1} K^{-1} up to 200°C and hence should lead to errors of extrapolation in ΔH and ΔS no larger than the uncertainties in the observed values in most cases.

SUMMARY AND CONCLUSIONS

In summary we may make the following observations about the hydrolysis of cations and its dependence on temperature.

1. The tendency for a cation to hydrolyze increases with its charge and decreases with its size. There is also a strong effect of the position of the element in the periodic table, post-transition metals showing the greatest tendency to hydrolyze and the pre-transition metals the least. For cations of a similar type, the equilibrium constant K_{11} for the first hydrolysis step (reaction 1) varies approximately linearly with the ratio of the cation charge z to the metal-oxygen distance d (table 2).

2. The enthalpy of the first hydrolysis step (ΔH_{11}, table 4) is positive and often close to the enthalpy of dissociation for water (13.3 kcal/mole). Hence the tendency of cations to hydrolyze increases with temperature. The post-transition metal ions with the strongest tendency to hydrolyze exhibit the least positive values (as low as 7 kcal/mole). Expressions are suggested that give ΔH_{11} (eq 12) and ΔS_{11} (eq 11) as a function of K_{11} and z/d.

3. The enthalpy (ΔH_{s10}) of the reaction of an oxide or hydroxide phase with H^+ to produce the unhydrolyzed cation in solution (for example, reaction 6) is negative (table 5), and hence such solids show a decreasing solubility in acid as the temperature is increased. There appears to be a fairly good correlation between ΔH_{s10} and ΔH_{11} (eq 16 and fig. 4).

4. The tendency for the oxide or hydroxide phase to react with the cation to produce the first hydrolysis product (reaction 15) is comparable for all cations, the equilibrium constant being approx $10^{-5.6}$ at 25°C. Accordingly the intersection $M(OH)_z(c)/M^{z+}/MOH^{(z-1)+}$ in figure 2 typically should occur at a total metal concentration of about $10^{-5.3}$m. Since the enthalpy of reaction (15) is generally positive (table 5), this intersection should rise with temperature.

5. The entropy of reaction of the cation to form a polynuclear hydrolysis product (ΔS_{xy} of reaction 4) correlates well with the ratio z/d (eq 20). The tendency of $MOH^{(z-1)+}$ to polymerize to such a species according to reaction (18) is about the same for all cations (eq 19). The enthalpy change for this reaction is in the range −2.6 to −7.5 kcal/mole, and hence the intersection $M^{z+}/MOH^{(z-1)+}/M_x(OH)_y^{(xz-y)+}$ in figure 2 will rise with temperature, reflecting a decreasing stability of polynuclear species.

6. The limited data available for mononuclear hydrolysis products beyond the first one suggest the approximation that the entropy of stepwise hydrolysis (of reaction 22) decreases linearly with the charge on the reacting species (eq 23 and fig. 5). From this it can be predicted that for typical cations the enthalpy of each successive hydrolysis step should decrease, and that the pH-range of dominance of each successive mononuclear species (fig. 2) should increase with temperature. For unusually stable neutral species, the wide pH range of dominance should decrease with increasing temperature.

7. The solubility of the oxide or hydroxide phase to produce the neutral species, $M(OH)_z$, in aqueous solution usually determines the minimum in the solubility curve (fig. 1) and generally decreases as the charge on the cation increases. Cations such as Pb^{2+}, As^{3+}, Sb^{3+}, and Bi^{3+} which exhibit extra stability for the neutral species show higher minimum solubilities for the oxide or hydroxide phase than would otherwise be expected. The limited data available suggest that the temperature dependence of the solubility reaction that produces the neutral species is relatively small and usually positive (table 7).

8. Similarly, the tendency for the oxide or hydroxide to react with basic solutions to produce the anion $M(OH)_{z+1}^-$ (reaction 34) is expected to have a small temperature dependence.

9. The heat capacity changes (table 8) are expected to be small for stepwise hydrolysis reactions involving mononuclear species, except for those producing anions.

On the basis of these correlations it is possible to construct a diagram such as that in figure 7, which indicates as a function of temperature the regions of dominance of the various species produced in solution by hydrolysis of the hypothetical trivalent cation in figures 1 and 2. The concentration of the metal is assumed to be low enough that polynuclear species can be neglected. As the temperature increases the onset of hydrolysis occurs at a rapidly decreasing pH because of the large positive value of ΔH_{11}, dropping about two log units by the time 100°C is reached. At the same time the region of dominance of each hydrolysis product—especially the neutral one—widens. The temperature scale on this diagram is plotted as the reciprocal of the absolute temperature and hence the boundaries of each region may be viewed as Arrhenius plots of the stepwise equilibrium constants. The first three boundaries—M^{3+}/MOH^{2+}, $MOH^{2+}/M(OH)_2^+$, and $M(OH)_2^+/M(OH)_3(aq)$—are linear or nearly so, because ΔC_p values for the reactions involved are small. The next boundary, $M(OH)_3(aq)/M(OH)_4^-$, curves toward higher pH in the manner indicated because ΔC_p for the reaction involved is appreciable, comparable to that for the dissociation of water.

The curves shown in figure 8 indicate the temperature dependence to be expected for the solubility of the hydroxide of our hypothetical cation (neglecting ΔC_p for reaction 6). On the acid side the solubility falls rapidly with increasing temperature. At the minimum the temperature dependence is small. On the alkaline side the moderate positive temperature coefficient of solubility is reduced and finally reversed by the heat capacity effect as the temperature rises. The contribution from the polynuclear species shown in figures 1 and 2 decreases as the temperature is increased.

Projections to elevated temperatures of the sort indicated in figures 7 and 8 require primarily a knowledge of the formation constants of the successive mononuclear hydroxide complexes in solution at one temperature at least. The rest may be inferred, with useful accuracy we hope, from the correlations offered in this review. More accurate information

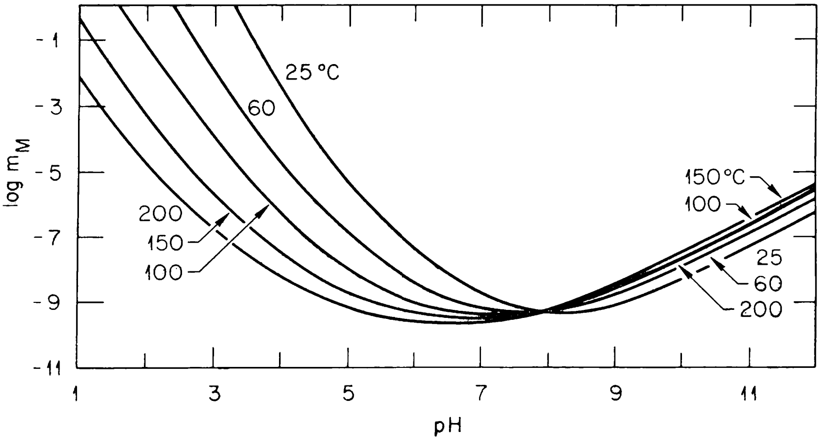

Fig. 8. Solubility of the hydroxide solid phase from figure 1 as a function of temperature.

about the mononuclear species is badly needed. It will most probably come from measurements of the solubility of crystalline oxide and hydroxide phases as a function of pH and temperature. Such measurements will not only yield needed information about specific cations, they will also further test and improve correlations needed to deal with the numerous species of other metallic elements formed in dilute aqueous solutions at elevated temperatures.

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