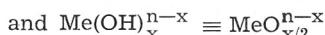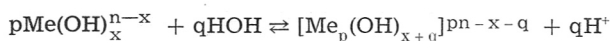# Metal Hydrolysis and Oxide-Hydroxide Precipitation*

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Methods used to study the hydrolysis behavior of metal cations and metallate anions are reviewed. Some results in the cases of bismuth(III), iron(III), aluminum(III), gallium(III), and zirconium(IV) show that the approach to equilibrium can vary from immeasurably fast to immeasurably slow. Thus, caution is urged in the use of published equilibrium constants relating hydrolyzed solute species and oxide/hydroxide heterogeneous phases.

The precipitation of oxide/hydroxide phases from aqueous solution and the dissolution of said phases in aqueous solution are important to the interfacial scientist. In a supplement to the Bjerrum, Schwarzenbach, and Sillen IUPAC publication of equilibrium constants (1958), Feitknecht and Schindler[1] published a critical review of solubility data relating the equilibrium constants of a number of metal oxide/hydroxide phases to a number of variables. In many cases neither the true equilibrium solute species nor the rate at which equilibrium is approached are considered to be well established. A few specific cases, some well-established and some poorly so, will be reviewed in this article.

Metal cation hydrolysis and metallate anion hydrolysis reactions are represented by the equations:

$$pMe^{n+} + qHOH \rightleftarrows [Me_p(OH)_q]^{np-q} + qH^+$$

$$pMe(OH)_x^{n-x} + qHOH \rightleftarrows [Me_p(OH)_{x+q}]^{pn-x-q} + qH^+$$

$$\text{and } Me(OH)_x^{n-x} \equiv MeO_{x/2}^{n-x}$$

The entire range of hydrolysis should be considered, and, furthermore, it must be realized that such systems are good buffers. Thus a cation such as Al^{3+} will hydrolyze to the extent of only 1—2% in acid solutions of pH < 3. On the other hand, relatively large amounts of OH^-, HCO_3^-, or CO_3^{2-}, etc. can be added to solution of Al^{3+} without effecting a concomitant large change in pH. Thus solutions can be prepared such that the ratio of OH^- added to total Al^{3+} is *ca.* 2 without giving a permanent precipitate. For convenience of communication the ratio of combined OH^- to metal ion in a solution will be designated as $\bar{n}$. It is calculated from the known stoichiometry of a solution together with the precise pH of the solution.

During the past 25 years much data has been accummulated and tables of solubility products and hydrolysis constants have been published from

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which the distribution of metal among phases and solute species are to be calculated. The indiscriminant use of such constants is hazardous, since in many of the investigations adequate precautions were not taken to see if equilibrium had been established. The purpose of this article is to review the status of several metal salt hydrolysis systems in order to clarify the extent to which existing information can be used with confidence.

The techniques which have been used to infer equilibrium solute species are:

(a) potentiometric titration, from which values of $\tilde{n}$ may be calculated, and whose chief protagonist has been the late L. G. Sillen[2];

(b) chromatography of several kinds, liquid-liquid extraction[3], ion-exchange[4], self-diffusion[5];

(c) various spectroscopic methods, such as, x-ray diffraction[6], Raman spectra[7], visible and ultraviolet spectra[8], NMR spectra[9], and magnetic susceptibility[10];

(d) cryoscopy[11];

(e) surface chemical methods[12];

(f) ultracentrifugation[13] and light-scattering[14].

Most of the foregoing techniques are also of value in the estimation of kinetics of conversion among two or more solute species. In addition the so-called temperature and pressure jump techniques have been used to measure relatively fast kinetics involving small solute particles. Biological activity has also been shown to be of value in estimating kinetics.

A very few cases are known for which the building blocks of crystals can be identified with solute species in the solution from which the crystals are grown. An example is the heptamolybdate species present in molybdate solutions within a limited range of conditions[15].

An example of a case in which many techniques combine to indicate, unambiguously, a two specie hydrolysis equilibrium, at room temperature, for $0 \leq \tilde{n} \leq 2$, is that of bismuth (III). The equilibrium, in perchlorate media, is represented by the equation:

$$6 \, Bi^{3+} + 12 \, H_2O \rightleftharpoons [Bi_6(OH)_{12}]^{6+} + 12 \, H^+;$$

supported by the ultracentrifuge work of Holmberg, Kraus, and Johnson[13]. the light-scattering work of Tobias and Tyree[14], the x-ray structure determination of Levy, Danford, and Agron[6], and the Raman spectra interpretation of Maroni and Spiro[7]. The pH titration data are also explained best in terms of the same equilibrium. Independent potentiometric titration studies by Olin[16] and by Tobias[17] report constants in solution of different ionic strengths which vary in the expected manner.

Unfortunately, relatively few hydrolytic equilibria are so simple and so well understood within such a wide range of $\tilde{n}$ values. In many cases a large number of solute species appear to be involved, some of which are not stable, but which persist with very long half-lives of decomposition into stable species or phases. Typical of such cases are aluminum (III), gallium (III), iron (III), and zirconium (IV).

For the iron (III) case, $[Fe_2(OH)_2]^{4+}$ is well established as the most important hydrolysis product at room temperature, at ordinary concentrations, and in the very low n range ($\tilde{n} \leq 0.1$). There is even agreement upon the kinetics of its dissociation[18]. However in the range $1 \leq \tilde{n} \leq 2$ much larger hydroxopolymers

exist which exhibit very slow reaction kinetics[19]. Such species are, undoubtedly, the explanation of the documented supersaturation of iron (III) hydroxide[20].

Likewise aluminum hydrolysis appears to result in a very few labile species and other, larger, rather inert species. Under some conditions, even at 125 °C, equilibrium is approached slowly[21]. Often the results of structural analyses of crystals grown from solutions are used to decide among several possible solute species in the solutions from which the crystals are obtained[22,23]. An excellent picture of the general relationships among the equilibrium and non-equilibrium hydrolysis products of aluminum (III) ion has been presented by Smith[24].

The gallium (III) case is similar to the two preceding cases in that rather fast kinetics relate the small monomeric and dimeric hydrolysis products at low $\tilde{n}$ values[25], whereas other, metastable, large species are much slower to decompose to the ultimate equilibrium state[26]. For such a case, where the slow changes result in large changes in the size of the solute species, and where the solutions will not absorb appreciably in visible regions of the spectrum, the light-scattering technique offers a simple, inexpensive means of monitoring the rate of change. For the case of a simple polymerization, the degree of polymerization, N, is related to the measured turbidity, τ, through the relationship,

$$1/N = \frac{H\,c\,M'}{\tau},$$

where M', is the monomer molecular weight and

$$H = \frac{32\,\pi^3\,n^2\,(d\,n/d\,c)^2}{3\,N\,\lambda^4}.$$

Then $\tau = Hc\,(NM')$. Note that c is usually epressed in g. ml^{-1}. Thus for a given weight solute concentration, N is directly proportional to τ, as long as simple Rayleigh scattering is observed. The complications due to ionic solutes do not negate the applicability to estimation of N^{27}. Using the foregoing technique, the effect of several variables upon the rate of formation of polymeric hydrolysis products from simple gallium (III) ion have been reported[28]. The rate of isotopic exchange between simple gallium (III) ion and its EDTA complexes has been described as immeasurably slow in just that region where the large, ill-defined hydrolytic solute species exist[29]. Hayes has shown the hydrolytic behavior of gallium salts to be very important in the preparation of radiogallium pharmaceuticals[30].

For the zirconium and hafnium cases, attempts have been made to estimate the half-times of approach to hydrolytic equilibrium as functions of total metal concentration, temperature, and $\tilde{n}^{31}$. It is my opinion that the nature of the true equilibrium hydrolysis products of zirconium and hafnium salts are unknown as yet, and that equilibrium constants published for such solutions, such as those of Peshkova and Ang[32], should not be used. Extreme caution should be used in the use of hydrolysis constants as published for most systems, since many of the so-called equilibrium constants may be the result of data taken on solutions which will be shown subsequently to be metastable and changing with half-times of months or years.

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IZVOD

Hidroliza metala i taloženje oksida i hidroksida

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Podaci literature o hidrolizi metala i o taloženju produkata hidrolize predmet su kraćeg kritičkog osvrta. U radu se posebno navode literaturne reference za hidrolizu Bi(III), Fe(III), Al(III), Ga(III), Zr(IV) i Hf(IV).

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