particles from the surfaces of the small crystals into the solution, (c) diffusion of the particles out of the solution onto the surfaces of larger crystals, (d) adsorption of the ions or molecules on the surfaces of the larger crystals, (e) transition to the surface, (f) transport on the surface to a suitable site."

"As in the case of growth, the diffusion (b and c) or the surface reaction (a, e, and f) could be the rate-determining step."

II.A.5. Recrystallization

"Recrystallization processes differ from ripening in that they extend over a longer period and become noticeable only after growth. The number of crystals and their size generally show little change. The supersaturation is usually zero or very small. The crystals and the solution are in a dynamic equilibria, which leads to a continuous exchange of matter. This does not cause any externally recognizable changes, but can be followed radiochemically over a period of many months."

"A crystal formed and grown at a high supersaturation usually has many internal defects and disorders. It is therefore relatively far removed from the equilibrium state, even when it is comparatively large. If it remains in contact with the solution for a long time, it has the opportunity to change into a less disturbed crystal by recrystallization. Thus it is well known that in the quantitative separation of substances by precipitation, better results are obtained by allowing the precipitate to stand for some time in contact with the mother liquor."

"The experimental observation of recrystallization has not progressed very far, and no theory yielding information about the effects of various parameters

(concentration of the ions of the substance itself and of foreign ions, temperature) has

not yet been developed."

II.B. Surface Area of Precipitates

"Figure II.16 shows the specific surface area of freshly precipitated barium

sulfate as a function of time (II.22). The precipitation from concentrated solutions

shows a pronounced maximum that is not observed in precipitation from very dilute
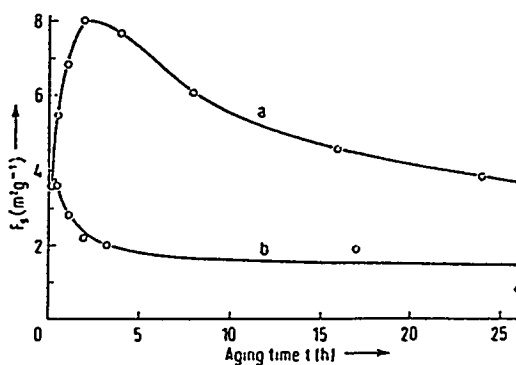
solutions.

Figure II.16.   **Change in the specific surface area of the solid phase BaSO$_4$ as a result of recrystallization after precipitation by mixing of equal volumes of 10^{-1}M (a), and 10^{-3}M (b) solutions of Ba(NO$_3$)$_2$ and Na$_2$SO$_4$ at 20°C (reference II.22).**

It can be seen from the diagram that recrystallization can cause marked changes in

the solid phase, which extend over a period of about 1 day at room temperature, and

take place at a correspondingly higher rate at higher temperatures (Figure II.17)."

The specific surface area of the solid phase (II.22) passes through a maximum

during recrystallization only in precipitations from relatively concentrated solutions

(Figure II.16). To explain this maximum, which is observed at various temperatures

(Figure II.17), it must be assumed that the crystals formed under these conditions are
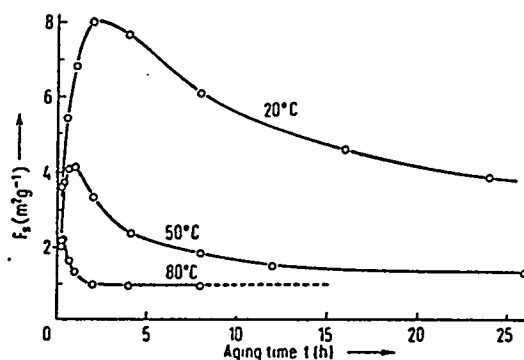
Figure II.17. Change in the specific surface area of freshly precipitated $BaSO_4$ (by mixing of equal volumes of 0.1M solutions of $Ba(NO_3)_2$ and Na_2SO_4) as a function of temperature (reference II.11).

so strongly disordered that they break down during recrystallization to give smaller crystals, which then recombine and grow into larger crystals again. This process may be due to crystal imperfections that are gradually healing."

II.C.   Precipitation Involving Reactions

The precipitation of hydroxides differs from the precipitation of ionic crystals in many respects: (a) hydroxide precipitates are generally amorphous, or have sufficiently small crystals as to appear amorphous to X-rays, (b) chemical reactions (e.g., reactions between OH groups with loss of water) preclude the use of the treatments proposed by Kossel (II.16) and Stranski (II.17) which cannot be applied to hydroxides, i.e., the nucleation and growth cannot be described merely by the deposition of ionic or molecular units, and (c) the course of the precipitation of hydroxides depends on pH as well as concentration, temperature, and time.

The precipitation of hydroxides is therefore a very much more complicated process than the precipitation of ionic crystal. Though simple models exist, e.g., for the course of the chemical reaction and the formation of basic salts as intermediates,

there are as yet no more advanced schemes for the quantitative treatment of the precipitation of hydroxides.

Fabrikanos and Lieser (II.23) obtained information about the effects of time and pH from radio paper chromatography. Figure II.18 shows the pH dependence of the quantity of high molecular weight condensation products present at the start of the chromatogram for the precipitation of cerium (III) hydroxide. The vertical arrows show the effect of time. The experimental values obtained immediately after the adjustment of the pH (fast precipitation) are given as well as the limiting values found after several hours at a constant pH value. This diagram clearly shows the characteristic features of a hydroxide precipitation, i.e., the start of the precipitation of the hydroxide and the aging of the hydroxide at constant pH value.
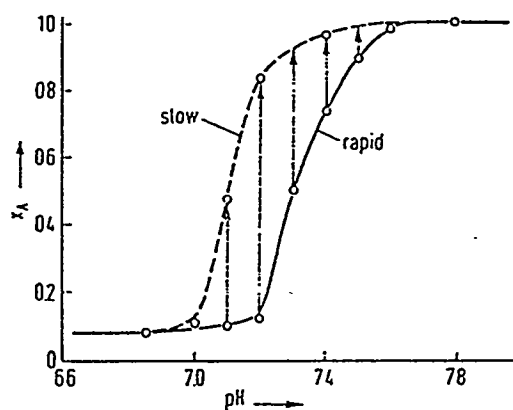

Figure II.18. **Fraction of high molecular weight condensation products remaining at the start of the paper chromatogram for the precipitation of cerium(III) hydroxide as a function of the pH value and of time (reference II.23).**

The corresponding diagram for the precipitation of iron (III) hydroxide is shown in Figure II.19.
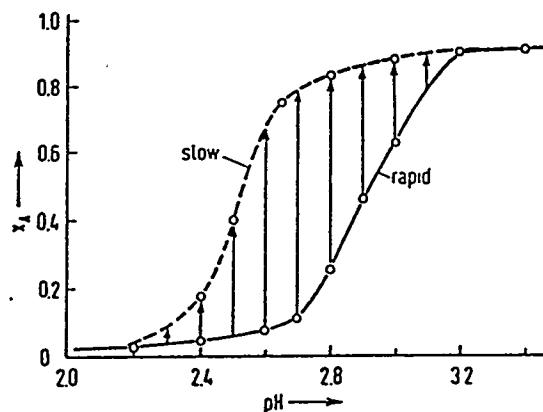
II.28

Figure II.19. Fraction of high molecular weight condensation products remaining at the start of the paper chromatogram for the precipitation of iron(III) hydroxide as a function of the pH value and of time (reference II.23).

This method yields quantitative information on the course of the hydroxide precipitation. Intermediates can also be detected on the paper chromatograms in the region between the start and the solvent front (Figure II.20); however, these intermediates cannot be identified.
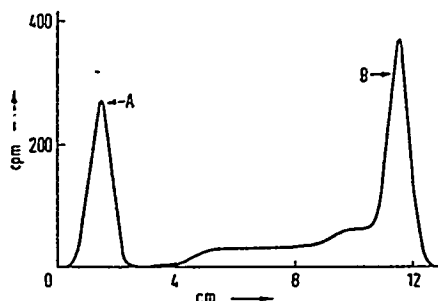
Figure II.20. Activity distribution on a paper chromatogram. A: Start, B: Solvent front (reference II.11).

Lieser (II.29) discusses the dependence of the precipitation of hydroxides on pH and time on the basis of the scheme shown in Figure II.21. Important processes involved in the precipitation are hydrolysis reactions, which lead to hydroxo complexes and hydroxides, and condensation reactions in which products having higher

II.29

molecular weights are formed. The hydrolysis reactions are relatively fast, whereas the condensation reactions are slow. It is therefore not surprising that the path followed varies according to whether the pH change is fast or slow. The products may also be different. Thus the probability of occlusion of foreign substances (particularly of hydroxides being formed at higher pH values) is considerably greater when the pH change is fast. Diagrams of the types shown in Figures II.20 and II.21 therefore yield important information for the practical precipitation of hydroxides.

II.D.   Metal Cation Hydrolysis

Metal cations in aqueous solutions are hydrolyzed to some extent since metal ions form strong bonds to oxygen or hydroxyl ions and even bond to the oxygen
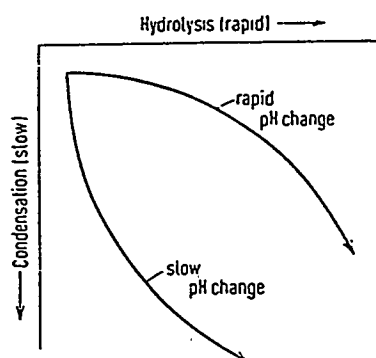

Figure II.21.   The course of hydroxide precipitation (from reference II.29).

present in water. The OH⁻ ligand is always present in aqueous solutions and its concentration can vary over an unusually wide range (> 1 to $< 10^{14}$) due to the small self-dissociation contact of water:

$$Q_{H_2O} = [H^+][OH^-] \approx 10^{-14} \qquad\qquad [\text{II.46}]$$

[In the following the nomenclature is that used by Baes and Mesmer (II.24). In this notation, Q is used to represent the formation quotient and K is the formation constant that includes ionic activity coefficients. Thus, the formation quotient can be written:

$$Q_{xy} = \frac{[M_x(OH)_y^{\ (xz-y)+}][H^+]^y}{[M^{z+}]^x}$$
[II.47]

where z is the charge on an ion, x represents the number of cations in a hydrolysis product, y denotes the apparent number of OH⁻ ions in a hydrolysis product, M^{z+} is the concentration of of the metal cation. The corresponding formation constant is then

$$K_{xy} = Q_{xy}[(g_{xy}\ g_{H+}^{\ \ y})/(g_{M^{z+}}^{\ \ x}\ a_{H_2O}^{\ \ y})]$$
[II.48]

where $g_{M^{z+}}$ is the ionic coefficient of M^{z+}, etc. and a_{H_2O} is the activity of water.]

In general, the formation reaction for a soluble hydrolysis product might be written

$$xM(OH_2)_w^{\ z+} + yOH^- + aA^- \rightleftharpoons M_xO_u(OH)_{y-2u}(OH_2)_{wA_a}^{\ \ (yz-y-a)+} + (xw^o + u - w)H_2O$$
[II.49]
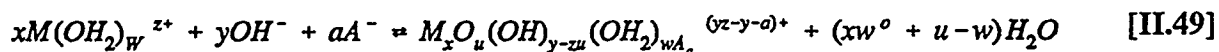
where the oxygen ligands are O^{2-}, OH⁻, H_2O and another anion A⁻. A limitation in distinguishing by experiment between O^{2-} and two OH⁻ ligands and the ability to detect water ligands causes the reaction to usually be written to include only hydroxide as ligand:

$$xM^{z+} + yOH^- \rightleftharpoons M_x(OH)_y^{\ (xz-y)+}$$
[II.50]
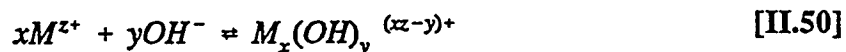
A determination of the identity and stability of dissolved hydrolysis products has proven to be difficult, primarily because:

1. The hydroxide complexes formed are often polynuclear; that is, they contain more than one metal ion. This permits a wide variety of products to be present at any one time. Furthermore, three dimensional structures may be formed.

2. The range of pH over which the formation of soluble hydrolysis products can be studied is nearly always limited by the precipitation of the hydroxide or the hydrous oxide of the metal cation. While the range of conditions studied usually can be extended to quite supersaturated solutions, the limitations imposed by hydrolytic precipitation are often severe, rendering the problem of characterizing the hydrolysis products formed in solution even more difficult than would otherwise be the case.

The following historical background is taken directly from Baes and Mesmer (II.24). The quantitative examination of such equilibria had an auspicious beginning with the thesis work of N. Bjerrum (II.25), which was a study of the hydrolysis of Cr^{3+}. He recognized that polynuclear species were formed in addition to mononuclear ones. Over the next 40 years his students contributed other careful studies, making use primarily of potentiometric methods. At about the same time as Bjerrum's initial study, however, Werner (II.26) and Pfeiffer (II.27) proposed the concept of "aquo-acidity", in which cation hydrolysis was viewed as the stepwise removal of protons from hydrate water molecules, for example,

$$M(H_2O)_6{}^{3+} \rightarrow M(H_2O)_5OH^{2+} \rightarrow M(H_2O)_4(OH)_2{}^{+}.... \qquad [II.51]$$
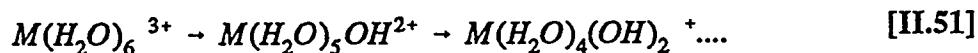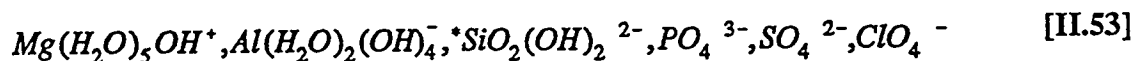
This pleasingly simple picture is probably a good representation of the process by which most mononuclear hydrolysis products are rapidly and reversibly formed.

II.32

Sillén (II.28) has illustrated the usefulness of this concept by considering the

aqueous species formed by the $2s^2 2p^6$ ions of the third row of the period table,

namely, Na^+ to Cl^{7+}. In acid solution, the following species may reasonably be

assumed:

$$Mg(H_2O)_6{}^{2+}, Al(H_2O)_6{}^{3+}, Si(OH)_4, PO(OH)_3, SO_3(OH)^-, ClO_4{}^- \qquad [\text{II.52}]$$
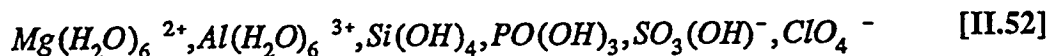
while in basic solutions we might find

$$Mg(H_2O)_5OH^+, Al(H_2O)_2(OH)_4^-, {}^*SiO_2(OH)_2{}^{2-}, PO_4{}^{3-}, SO_4{}^{2-}, ClO_4{}^- \qquad [\text{II.53}]$$

This clearly shows the widely varying tendency of aqueous ions to release protons, a

tendency which is related to the charge density about the central cation, while at the

same time preserving their coordination number.

The concept of "aquo-acidity" was widely accepted. Unfortunately it was often

assumed to be the only process involved in cation hydrolysis. Until about 1950,

except in a few instances, the formation of polynuclear hydrolysis products was

ignored. While their reality was clearly established by the work of Bjerrum, Sillén, and

a few others, the methods had not been developed for identifying them in systems

where several hydroxide complexes were present in labile equilibrium. Hence their

occurrence was not often considered.

As a result, measurements in this period were usually insufficient in both scope

and accuracy for a correct characterization of the hydrolysis products. For example, a

frequent practice was simply to measure the acidity of a series of dilutions of a

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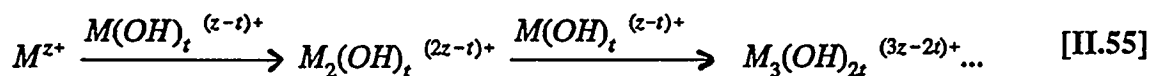*However, it now appears that this species is $Al(OH)_4{}^-$ (II.28).

stoichiometric solution of a metal salt and then to calculate the formation quotient of the species $MOH^{(z-1)+}$:

$$Q_{11} = \frac{[MOH^{(z-1)+}][H^+]}{[M^{z+}]} \qquad [\text{II.54}]$$

with the assumption that it was the only hydrolysis product formed. Such an assumption was often a poor approximation.

With improvement of the experimental methods, in particular the increasingly convenient and accurate measurement of pH by means of the glass electrode, it became apparent to some investigators by 1950 that more often than not, hydroxide complexes of cations were polynuclear. There was a renewed interest in the subject, particularly on the part of Sillén and his school at Stockholm. It was recognized that measurements - usually of pH as a function of solution composition - should include the metal concentration as a variable. Sillén (II.28) was a leader in developing graphical methods for the interpretation of such data in terms of simultaneously occurring equilibria involving polynuclear species.

Sillén was led to propose a general mechanism of hydrolysis in which $M(OH)_t^{(z-t)+}$ groups are added stepwise to the cation:

$$M^{z+} \xrightarrow{M(OH)_t^{(z-t)+}} M_2(OH)_t^{(2z-t)+} \xrightarrow{M(OH)_t^{(z-t)+}} M_3(OH)_{2t}^{(3z-2t)+}\ldots \qquad [\text{II.55}]$$

This hypothesis of continuing polymerization (the "core-plus-links" hypothesis) was not only an appealing simple concept, it also permitted a relatively simple treatment of the data to evaluate the few equilibrium constants involved. Unfortunately, however, as

II.34

methods of measurement continued to improve in accuracy, it became clear by the late 1950's and early 60's that this stepwise polymerization process rarely, if ever, occurred. Without such a simplifying hypothesis to deal with the numerous possible hydrolysis species which might form in solution, more accurate and extensive measurements were needed as well as computer-based methods of data interpretation.

From such measurements and data analysis an interesting pattern of behavior is emerging. While cations generally appear to hydrolyze to give mononuclear species at sufficiently low concentration, they often produce a small number, usually one to three, of polymer species which predominate at ordinary concentrations. All but a few such species are to be found among the following dimers, trimers, and tetramers:

$$M_2OH^{(2z-1)+}, M_2(OH)_2^{(2z-2)+}, M_3(OH)_3^{(3z-3)+}, M_3(OH)_4^{(3z-4)+}, M_3(OH)_5^{(3z-5)+}, M_4(OH)_4^{(4z-4)+} \qquad \text{[II.56]}$$
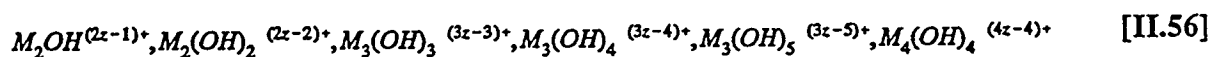
Occasionally, higher polymers occur such as

$$Bi_6(OH)_{12}^{6+}, Th_6(OH)_{15}^{9+}, Al_{13}(OH)_{32}^{7+} \qquad \text{[II.57]}$$

Even with the relatively small number of species, compared with the much larger number possible, the problem of identifying the ones which are in fact produced by the hydrolysis of a given cation remains a difficult task. Even among those who specialize in such studies, there is often disagreement about such hydrolysis products. Others view the proposed species with a skepticism which is quite understandable, considering the history of the subject. The more charitable of the

latter suggest that such interpretations are not unique ones, that alternative interpretations could be made equally consistent with the data. The less generous consider the whole process to be no more than an elaborate exercise in "curve fitting" of data which are insufficient to make species identification possible.

II.E. Formation and Characteristics of Oxide Sols

II.E.1. Hydrous Oxide or Hydroxide Colloids (II.29)

A schematic mechanism in which hydrous oxide or hydroxide colloids are formed from an aqueous solution of metal cations is illustrated in Figure II.22. This step-wise process involves the hydrolysis of a solvated aquo-ion followed by condensation to give a polynuclear ion. Such a sequence of hydrolytic and condensation reactions leads, under conditions of oversaturation of the metal hydroxide, to the formation of colloidal hydroxy-polymers which can eventually form hydroxide or hydrous oxide precipitates. This tendency for cation hydrolysis, involving the coordination of -OH ligands (which act as electron pair donors) increases with the acidity, or charge density of the metal ion. Consequently ions of small ionic radius

<u>Hydrolysis</u>

$$M^{4+} + H_2O \rightleftharpoons M(OH)^{3+} + H^+ \rightleftharpoons M(OH)_2^{2+} + 2H^+$$

<u>Condensation</u>

$$2 M(OH)_3^+ \longrightarrow \begin{bmatrix} HO \\ HO \end{bmatrix} M - O - M \begin{matrix} OH \\ OH \end{matrix} \end{bmatrix}^{2+} + H_2O$$

$$COLLOIDS \longleftarrow \begin{bmatrix} M & O & M & O & M \\ O & O & \end{bmatrix}^{n+} + nH_2O$$

Figure II.22. **Hydrolysis and polymerization of polyvalent metal ions in aqueous solution (reference II.29).**

II.36

and high charge are extensively hydrolysed in solution, as is illustrated by silicic acid,

$Si(OH)_4$, which can exist as a monomer in aqueous solutions of high pH. The

tendency for hydrolysis can furthermore be generalized for a wide range of cations as

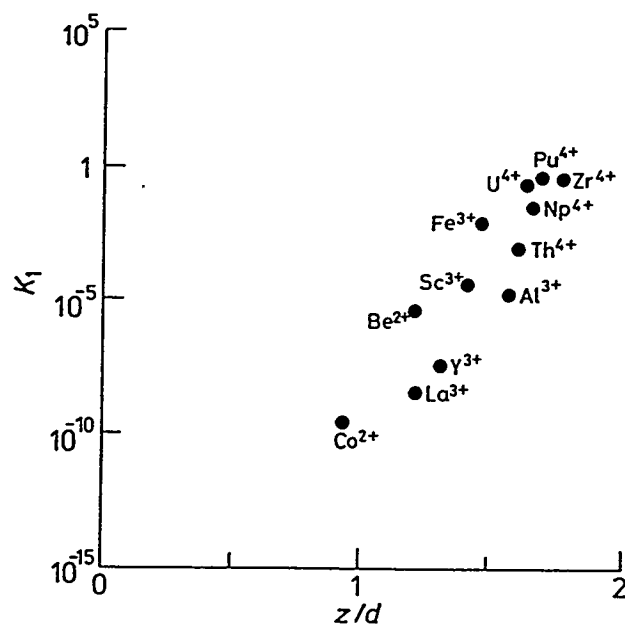is demonstrated by the dependence of the first hydrolysis constant K_1, on the ratio of

the charge to the M-O distance (z/d) shown in Figure II.23. The tendency for cation

hydrolysis is also paralleled by the ease of polynuclear ion formation. Thus, most

trivalent and quadrivalent ions form polynuclear species, whereas the process only

occurs with the smallest of the divalent ions, Be^{2+}. Such polynuclear species are

formed by oversaturating a salt solution with respect to the solid hydroxide or hydrous
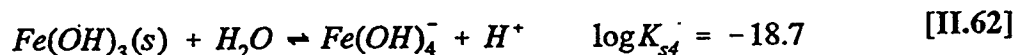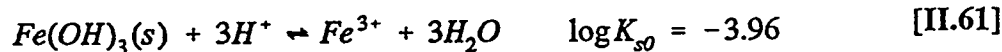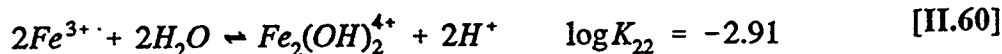
oxide, by adding a base for example.

Figure II.23. **Dependence of the first hydrolysis constant, K_1, on the ratio of the charge, z, to M-O distance, d, for different cations (reference II.29).**

"This process can be illustrated by the behavior of aqueous solutions of Fe^{3+}

for which the following equilibrium constants have been reported (II.30).

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad \log K_1 = -3.05 \qquad \text{[II.58]}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+ \qquad \log K_2 = -6.31 \qquad \text{[II.59]}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad \log K_{22} = -2.91 \qquad \text{[II.60]}$$

$$Fe(OH)_3(s) + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O \qquad \log K_{s0} = -3.96 \qquad \text{[II.61]}$$

$$Fe(OH)_3(s) + H_2O \rightleftharpoons Fe(OH)_4^- + H^+ \qquad \log K_{s4} = -18.7 \qquad \text{[II.62]}$$

Using the representative equilibrium constants it is possible to construct

distribution diagrams for the different species, as depicted in Figure II.24. In the

hatched areas shown the solutions become oversaturated with respect to $Fe(OH)_3(s)$
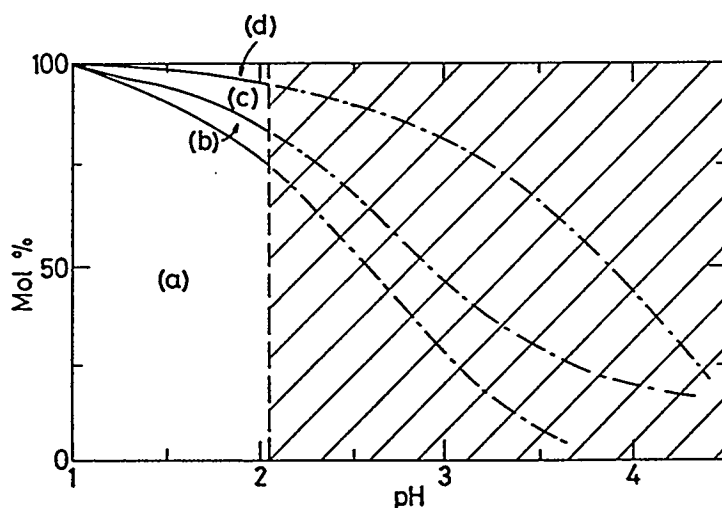

Figure II.24. Distribution diagram for Fe^{III} species in aqueous solution at a total Fe^{III} concentration of 10^{-2} mol dm^{-3} as a function of pH. (a), (b), (c), and (d) correspond to proportions of Fe^{3+}, $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$, and $Fe(OH_2^+$ respectively. Broken line corresponds to saturation limit with respect to $Fe(OH)_3(s)$. --- depicts proportion of metastable species in hatched zone where polynuclear hydrolysis species will form as intermediates before the eventual precipitation of the hydroxide occurs (from reference II.29)

II.38

($K_s = 10^{-38}$) and in consequence polynuclear hydrolysis species will form as intermediates in the formation of $Fe(OH)_3(s)$ which occurs in this range of relatively low pH. If neutralized completely, solutions of Fe^{3+} ions will rapidly precipitate $Fe(OH)_3$ which may age. Furthermore, in alkaline solution (pH > 10) the formation of ferrate ions, $Fe(OH)_4^-$, becomes increasingly important. Although there is extensive evidence for the existence of small polynuclear ions containing a few metal atoms the structure and stoichiometry of larger thermodynamically stable species still remain obscure."

II.E.2.   Sol Formation (II.29)

"A vast number of specialized procedures are described in the patent literature for the preparation of oxide sols. In general, colloid formation is achieved either by controlled nucleation and growth processes in solution or by the peptization of powders or precipitates of metal oxides and hydroxides. The mechanism of the first process is frequently based on the controlled growth from a seed nucleus, first described by Zsigmondy (II.31) and later refined and developed by La Mer and coworkers (II.32-II.34) for the preparation of monodispersed colloids. These principles have been applied to numerous systems, particularly by Matijevic as discussed in a subsequent section. This is illustrated simply in Figure II.25 by the behavior which occurs when a reaction proceeds and produces a partially soluble product, such as an oxide or hydroxide for example, having a solute concentration, C_p. In this process C_p will rise, passing the saturation concentration, C_s, until the

II.39

critical supersaturation or nucleation concentration, C_n, is reached. At this point nuclei

will form, and proceed to grow at a rate determined by the diffusion of neighboring

solute species, which are consumed. This growth process will continue until the

solute concentration falls to C_s. To obtain a monodispersed system, nucleation should

occur in a short time interval or burst; growth must then proceed by the slow

production of solute species which have adequate time to diffuse to the seed nuclei,

thus avoiding a reoccurrence of supersaturation and further nucleation."

"The stability and fate of particles so formed depends on their surface

properties and the nature of the aqueous medium. Two distinct situations can arise
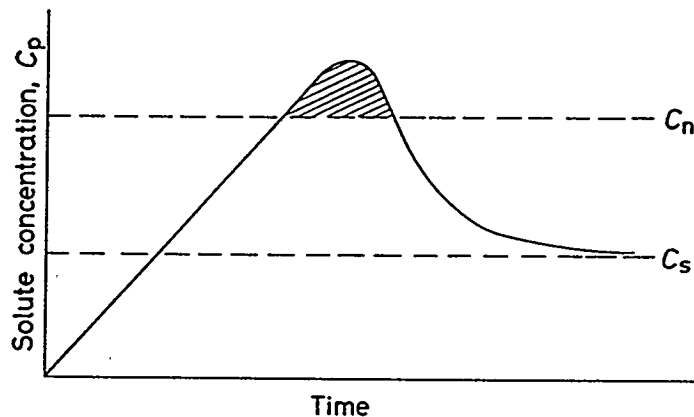

Figure II.25. **Diagram illustrating the formation of colloidal dispersion by controlled nucleation and growth. Initially the solute concentration C_p rises passing the saturation limit, C_s, and continues until the critical nucleation concentration is reached, C_n, at which precipitation occurs in the hatched zone. Further controlled growth of these nuclei results in a decrease in C_p as depicted (from reference II.29).**

depending on the interparticle interactions. In the first, where there is strong

interparticle repulsion, discrete particles remain as a stable colloidal dispersion. This

situation occurs where the particles have a high surface charge and the concentration

II.40

of electrolyte in the solution is low. For monovalent counterions this is typically $< 10^{-3}$

mol dm^{-3}, although for silica stability may still be maintained up to $\sim 10^{-1}$ mol dm $^{-3}$.

Where these conditions are not fulfilled the particles will tend to aggregate and may

eventually form a precipitate. These extreme situations are illustrated by the behavior

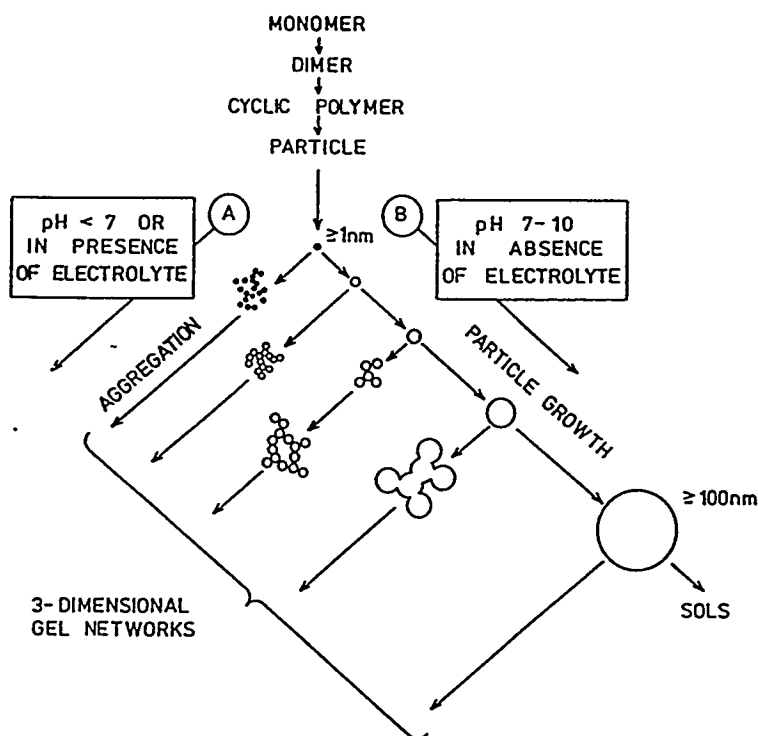of silica dispersions as depicted schematically by Iler (II.35) in Figure II.26."

Figure II.26.   **Schematic illustration of the polymerization of monosilic acid to form seed particles. In basic solution, (B), these can grow to give sols of different particle size (viz. Ostwald ripening), whereas at lower pH or in the presence of electrolyte, (A), aggregation occurs, which can lead to the formation of three-dimensional gel networks (from reference II.29).**

"Another more general route to concentrated sols is by the peptization of

hydrous oxide precipitates which have been prepared under controlled conditions

(II.36). Referring to Figure II.24 it can be seen that the rapid neutralization of a

concentrated metal salt solution will cause the solute supersaturation limit to be far

II.41

exceeded, resulting in the sudden production of a vast number of nuclei which have only a limited possibility for further growth. Such a process will yield a precipitate containing very small amorphous or poorly crystalline particles, typically ~10 nm in size. If washed, to remove excess counterions, such precipitates can be peptized by controlled addition of either a dilute acid or alkali to give a stable concentrated sol containing particles which have a relatively narrow size distribution (II.29)."

II.E.3. The Oxide/Water Interface (II.29)

"The surface charge and nature of oxide/water interfaces have a dominant effect on the stability and properties of oxide sols. A hydroxylated oxide surface in contact with water can develop either a positive or negative surface charge, as shown schematically in Figure II.27. This demonstrates that oxide surfaces have amphoteric properties and that the charge-determining ions are either H^+ or OH^-. The surface charge will consequently be dependent on pH and will vary depending on the type of oxide surface studied."

"The pH of zero point of charge (z.p.c.), which can be determined by potentiometric titration methods, reflects the acid/base character of the surface; a low z.p.c. corresponds with a more acidic nature, as is the case for silica. Values of z.p.c. for a number of oxides are given in Table 1."
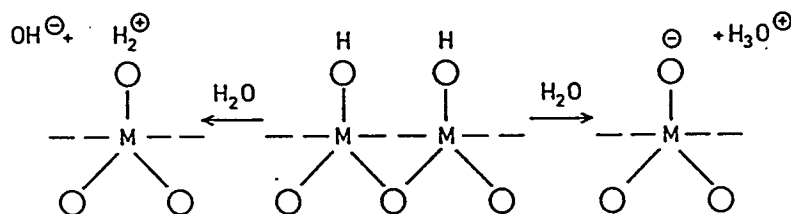

Figure II.27.   **Schematic illustration of surface charge generation on an oxide surface (from reference II.29).**

II.42

Table II.1
Typical pH Values for Oxides at the Zero Point of Charge (II.37)

Oxide	z.p.c.	Oxide	z.p.c.
WO_3	~0.5	ZrO_2	~5
SiO_2	~2	$\gamma\text{-}Al_2O_3$	7.5
SnO_2	~4.3	$\alpha\text{-}Fe_2O_3$	8.5
TiO_2	~6	CeO_2	6.8
		Co_3O_4	11.4

Ramsay (II.36) provides an illustrative diagram for the conversion of a sol to a gel which may have a low or high porosity (Figures II.28 and II.29).
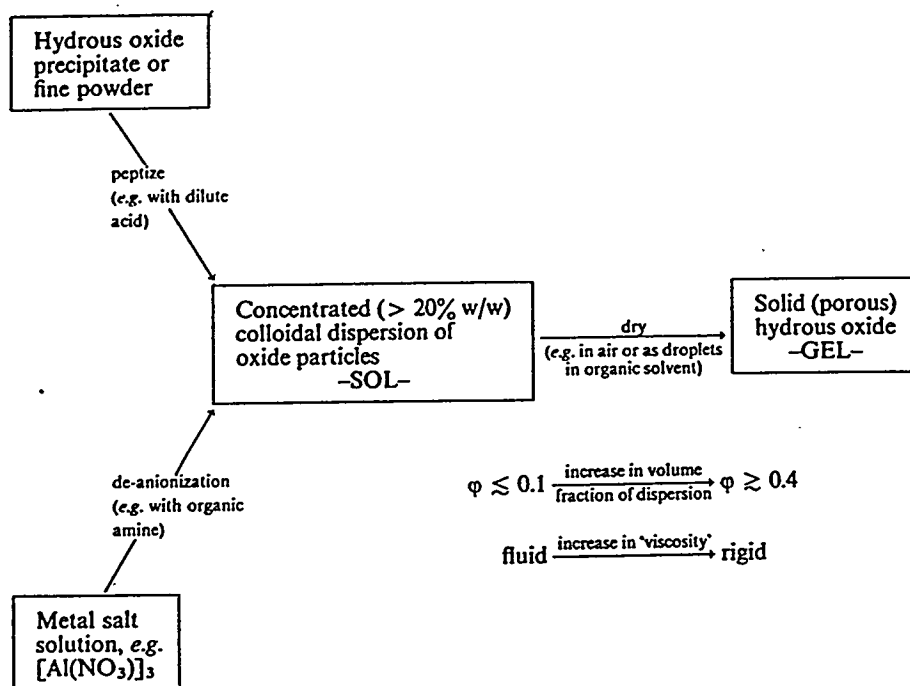

Figure II.28. Features of the Sol-Gel process (from reference II.29).

In this view, the sol should be treated to cause aggregation prior to the formation of the gel if a high porosity is desirable.
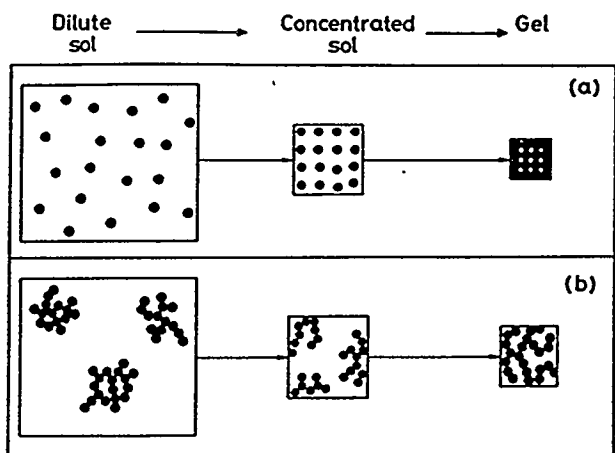
II.43

Figure II.29. Diagram depicting the formation of gels of low and high porosity
from (a) unaggregated and (b) aggregated sols respectively (from
reference II.29).

II.F.   Uniform Colloidal Hydrous Metal Oxides

The term hydrous metal oxide is used to cover a broad range of materials that

include oxides, hydroxides, hydrated oxides, oxyhydroxides, etc. These materials are

of great importance since they are encountered in nature in many minerals and are

used in numerous industrial materials as catalysts, catalyst supports, pigments, fillers,

intermediates, etc. These materials have been studied over the years but the

mechanism leading to these materials remains elusive. The primary reason for this is

the large number of species in solution at any condition, and the charge of species

with the composition of the solution. The properties of the hydrous metal oxide

obtained by homogeneous precipitation depend strongly on the conditions of the

environment in which it is generated; these include temperature, concentration, anionic

species, pH and rate of charge of pH. With all of these complications, it is not

surprising that "monodisperse" sols of these materials were infrequently encountered.

Matijević (II.37) considers a circular β-FeOOH first reported by Heller and associates

II.44

(II.38, II.39), to be the only truly uniform hydrous metal oxide obtained by

homogeneous precipitation until recent work dating from the 1970's.

II.F.1. General Considerations

LaMer's qualitative explanation of the mechanism of formation of

monodispersed sulfur sols by the decomposition of sodium thiosulfate in acidic

solution is illustrated in Figure II.30 (II.32-II.40). The concentration of the molecularly

dispersed sulfur that is slowly released from $Na_2S_2O_3$ increases until critical
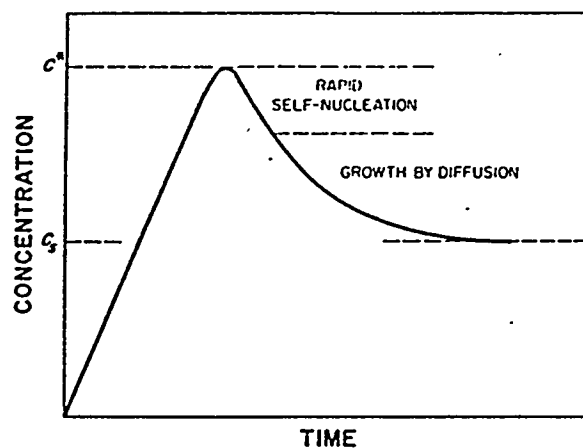

Figure II.30. Schematic presentation of the concentration change with time of a particle forming solute species generated in-situ before and after self-nucleation. C_s = solubility, C^* = critical supersaturation of the particle forming solute species (similar to figure II.25; from reference II.41).

supersaturation is reached; at that time nucleation of the solid sulfur takes place. The

nuclei then grow by diffusion. The preparation of uniform particles requires the

controlled generation of solutes which eventually precipitate; thus, burst of nuclei

II.45

occurs. The species added to the nuclei must then continue to be formed at a rate which allows their removal by diffusion onto the existing particles so that no secondary nucleation takes place. Thus, the original nuclei grow uniformly, yielding monodispersed systems. The actual mechanism of the formation of LaMer sulfur sols may be somewhat more involved (II.42), but the underlying principle is valid.

In order to apply the same ideas to generation of colloidal metal (hydrous) oxides, it is necessary to control the hydroxylation of metal ions (M^{z+}). The following follows closely the outline given by Matijević (II.41). The commonly written equation

$$M^{z+}(aq) + zOH^-(aq) = M(OH)_z(s) \qquad [\text{II.63}]$$
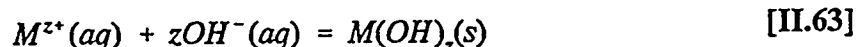
represents only the mass balance of a precipitation process. The appearance of the solid phase is preceded by the formation of dissolved metal complexes which include as ligands hydroxide ions and, possibly, other anions present in the solution. Some metals may also utilize oxide ion as a ligand as, for example, the zirconyl species, ZrO^{2+}. Assuming only hydroxylation, the mechanism of precipitation involves a scheme like

$$n[M(H_2O)_p]^{z+} \xrightarrow{\ OH^-\ } [M_n(H_2O)_{np-m}(OH)_m]^{(nz-m)+} \xrightarrow{\ OH^-\ } nM(OH)_z \qquad [\text{II.64}]$$
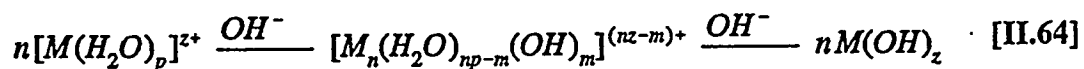
Both $\underline{n}$ and $\underline{m}$ can vary over a wide range, furthermore, a range of $\underline{n}$ and $\underline{m}$ may occur for a given set of conditions. Obviously, the complexes act as precursors to nucleation and they affect the particle growth. The composition and rate of generation of these solutes will determine the chemical and physical natures of the resulting precipitate. Furthermore, not all complexes in solution need to participate in the

II.46

formation of the solid phase. Since the compositions of solutions of a metal salt are often extremely sensitive to various parameters, it is obvious that a control of the precipitation of metal (hydrous) oxides would be a difficult task. Indeed, it may be almost impossible to assure reproducible precipitation by adding a base directly to an electrolyte solution.

II.F.2. Forced Hydrolysis

Hydroxylation of metal ions can be greatly accelerated by raising solution temperature. Such forced hydrolysis can facilitate the formation of the complex precursors to nucleation of hydrous metal oxides. The process involves deprotonation of hydrated metal ions according to

$$n[M(H_2O)_p]^{z+} \rightarrow [M_n(H_2O)_{np-m}(OH)_m]^{(nz-m)+} + mH^+ \qquad [\text{II.65}]$$
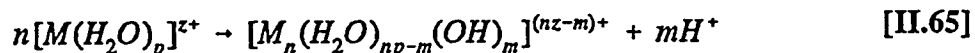
By adjusting the initial pH of the solution and the temperature of aging, it should be possible to generate the complexes responsible for particle nucleation and growth under conditions schematically given in Figure II.30. In principle, then, monodispersed hydrous metal oxides should result from the appropriate forced hydroxylation of solutions of metal salts.

Thus, the method requires an acidic solution containing a metal salt at a given concentration to be heated in order to produce hydroxide ligands in-situ by deprotonation of bound water. The hydroxylation process can sometimes be accelerated by the homogeneous generation of hydroxide ion, such as by decomposition of urea. It is possible to reserve the procedure by starting with a solution of a stable metal complex, e.g., a metal chelate, at high pH. If the complex is

<div align="center">II.47</div>

then slowly decomposed by heating, the liberated metal ions will react with hydroxide ions to yield precursors of the solid phase. The latter procedure offers certain advantages over forced hydrolysis in that it allows a broader set of experimental conditions, e.g., addition of reducing or oxidizing agents into the system, changing ionic composition, and easier control of decomposition rate by choosing different ligands complexed with the same metal ion.

All that is necessary to generate uniform particles of different hydrous metal oxides by forced hydrolysis is to keep acidified solutions of metal salts undisturbed at elevated temperatures for a definite period of time. The difficulty is that the conditions of salt concentration, pH, nature of the anion, temperature, etc., are in most cases very restrictive. With so many variables it takes a great deal of effort to establish the requirements illustrated by Figure II.30. However, once the proper conditions are set, the reproducibility in generating 'monodispersed' sols is rather good. While this technique provides uniform particles, the long reaction time (hours, days or weeks) is a decided disadvantage.

II.G. Chemistry of Iron

Baes and Mesmer (II.24) have concisely summarized the hydrolysis of Fe(II) and Fe(III). The following material in IIG, 1-IIG.3 section, with minor changes, is taken directly from their reference II.24.

The +2 and +3 oxidation states of iron are stable over broad regions of potential and pH. Ferric ion is easily reduced by hydrogen, while ferrous ion is only slowly oxidized by air. The powerfully oxidizing +6 state is stable in basic solutions

II.48

but decomposes with evolution of oxygen and formation of Fe(III) in neutral or acidic solutions.

Ferric ion forms octahedral complexes such as the purple hexaaquo ion. Hydrolysis of ferric ion begins at about pH 1 with the formation of $Fe(H_2O)_5OH^{2+}$, which is yellow due to charge-transfer absorption bands in the ultraviolet with a tail extending into the visible. The high-spin ferrous hexaaquo ion $Fe(H_2O)_6^{2+}$ has a transition occurring at around 1000 nm. A tail of this absorption band extends into the visible at the red end, giving rise to the pale blue-green color of its solutions. The splitting of this absorption peak may result from the Jahn-Teller effect (II.43).

Iron in the +2 and +3 oxidation states forms numerous complexes with a variety of ligands. Fluoride complexes more strongly than the larger halides, as it common for the "hard" cations. Precipitation of an insoluble ferrous hydroxide occurs before appreciable hydrolysis products are formed in solution, whereas hydroxyl numbers of about 0.5 have been attained for ferric ion. The most insoluble hydroxide of Fe^{3+} is α-FeO(OH), but in the presence of ferrous ion the stable phase may be magnetite, Fe_3O_4.

II.G.1. Fe^{2+} Hydrolysis in Solution

The Fe^{2+} ion hydrolyzes only slightly, n < 0.01, before precipitation of $Fe(OH)_2$ or Fe_3O_4 commences even in quite dilute solutions of iron. This fact, along with the ease with which Fe^{2+} is oxidized to Fe^{3+}, contributes to the great difficulty experienced by the many investigators in arriving at a consensus on the stability of the $FeOH^+$ species. Baes and Mesmer anticipate that the value for log K_{11} for Fe^{2+} would fall in