University of Idaho

GEOL578

Advanced Geochemistry of Natural Waters

LESSON 5
Aqueous Complexes
(Coordination Chemistry)

MODULE 2
Hydrolysis

Start Audio Lecture!

HYDROLYSIS

The waters surrounding a cation may function as acids. The acidity is expected to increase with decreasing ionic radius and increasing ionic charge. For example:

$$Zn(H_2O)_6^{2+} \leftrightarrow Zn(H_2O)_5(OH)^+ + H^+$$

Hydrolysis products may range from cationic to anionic. For example:

$$Zn^{2+} \rightarrow ZnOH^+ \rightarrow Zn(OH)_2^0\ (ZnO^0)$$
$$\rightarrow Zn(OH)_3^-\ (HZnO_2^-) \rightarrow Zn(OH)_4^{2-}\ (ZnO_2^{2-})$$

May also get polynuclear species.

Kinetics of formation of mononuclear hydrolysis products is rather fast, polynuclear formation may be slow.

GENERAL RULES OF HYDROLYSIS

- The tendency for a metal ion to hydrolyze will increase with dilution and increasing pH (decreasing $[H^+]$)
- The fraction of polynuclear products will decrease on dilution
- Compare

$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+$ $\log {}^*K_1 = -8.0$

$Mg^{2+} + H_2O \leftrightarrow MgOH^+ + H^+$ $\log {}^*K_1 = -11.4$

$$^*K_1 = \frac{[MOH^+][H^+]}{[M^{2+}]}$$

$$\alpha_{MOH^+} = \frac{[MOH^+]}{[MOH^+]+[M^{2+}]} = \frac{[MOH^+]}{[MOH^+]+\frac{[MOH^+][H^+]}{^*K_1}}$$

$$\alpha_{MOH^+} = \frac{1}{1+\frac{[H^+]}{^*K_1}}$$

At infinite dilution, pH ≈ 7 so

$\alpha_{CuOH^+} = (1 + 10^{-7}/10^{-8})^{-1} = 1/11 = 0.091$

$\alpha_{MgOH^+} = (1 + 10^{-7}/10^{-11.4})^{-1} = 1/25119 = 4\times10^{-5}$

Only salts with $p^*K_1 < (1/2)pK_w$ or $p^*\beta_n < (n/2)pK_w$ will undergo significant hydrolysis upon dilution. Progressive hydrolysis is the reason some salts precipitate upon dilution. This is why it is necessary to add acid when diluting standards.

POLYNUCLEAR SPECIES DECREASE IN IMPORTANCE WITH DILUTION

Consider the dimerization of $CuOH^+$:

$2CuOH^+ \leftrightarrow Cu_2(OH)_2^{2+}$ log $^*K_{22}$ = 1.5

Assuming we have a system where:

$Cu_T = [Cu^{2+}] + [Cu(OH)^+] + 2[Cu_2(OH)_2^{2+}]$

we can write:

$$\frac{[Cu_2(OH)_2^{2+}]}{[CuOH^+]^2} = \frac{[Cu_2(OH)_2^{2+}]}{(Cu_T - [Cu^{2+}] - 2[Cu_2(OH)_2^{2+}])^2} = {}^*K_{22}$$

So $[Cu_2(OH)_2^{2+}]$ is clearly dependent on total Cu concentration!

HYDROLYSIS OF IRON(III)

Example 1: Compute the equilibrium composition of a homogeneous solution to which 10^{-4} (10^{-2}) M of iron(III) has been added and the pH adjusted in the range 1 to 4.5 with acid or base.

The following equilibrium constants are available at I = 3 M ($NaClO_4$) and 25°C:

$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$ log $^*K_1$ = -3.05

$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$ log $^*\beta_2$ = -6.31

$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$ log $^*\beta_{22}$ = -2.91

$Fe_T = [Fe^{3+}] + [FeOH^{2+}] + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}]$

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$$Fe_T = [Fe^{3+}]\left(1+\frac{{}^*K_1}{[H^+]}+\frac{{}^*\beta_2}{[H^+]^2}+\frac{2[Fe^{3+}]{}^*\beta_{22}}{[H^+]^2}\right)$$

Now we define: α_0 = $[Fe^{3+}]/Fe_T$; α_1= $[FeOH^{2+}]/Fe_T$; α_2= $[Fe(OH)_2^+]/Fe_T$; and α_{22}= $2[Fe_2(OH)_2^{4+}]/Fe_T$.

$$\alpha_0 = \left(1+\frac{{}^*K_1}{[H^+]}+\frac{{}^*\beta_2}{[H^+]^2}+\frac{2Fe_T\alpha_0{}^*\beta_{22}}{[H^+]^2}\right)^{-1}$$

$$\frac{\alpha_0^2 2Fe_T{}^*\beta_{22}}{[H^+]^2}+\alpha_0\left(1+\frac{{}^*K_1}{[H^+]}+\frac{{}^*\beta_2}{[H^+]^2}\right)-1=0$$

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This last equation can be solved for α_0 at given values of Fe_T and pH. The remaining α values are obtained from the following equations:

$$\alpha_{22} = \frac{\alpha_0^2 2Fe_T{}^*\beta_{22}}{[H^+]^2}$$

$$\alpha_1 = \frac{\alpha_0{}^*K_1}{[H^+]} \qquad \alpha_2 = \frac{\alpha_0{}^*\beta_{22}}{[H^+]^2}$$

These equations can then be employed to calculate the speciation diagrams on the next slide.

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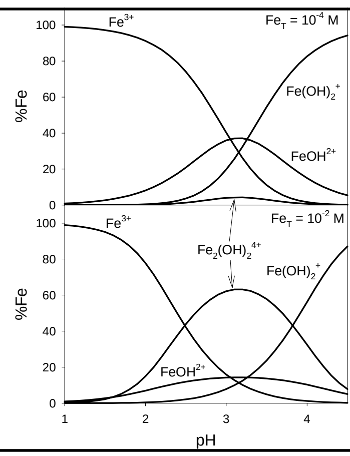

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Example 2: Compute the composition of a Fe(III) solution in equilibrium with amorphous ferric hydroxide given the additional equilibrium constants:

$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$ $\log {}^*K_{s0} = 3.96$

$Fe(OH)_3(s) + H_2O \leftrightarrow Fe(OH)_4^- + H^+$ $\log {}^*K_{s4} = -18.7$

Fe^{3+}

$$\log [Fe^{3+}] = \log {}^*K_{s0} - 3pH$$

$Fe(OH)_4^-$

$$\log [Fe(OH)_4^-] = \log {}^*K_{s4} + pH$$

$FeOH^+$

$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	$\log {}^*K_{s0} = 3.96$
$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$	$\log {}^*K_1 = -3.05$
$Fe(OH)_3(s) + 2H^+ \leftrightarrow FeOH^{2+} + 2H_2O$	$\log {}^*K_{s1} = 0.91$

$$\log [FeOH^{2+}] = \log {}^*K_{s1} - 2pH$$

$Fe(OH)_2^+$

$Fe(OH)_3(s) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	$\log {}^*K_{s0} = 3.96$
$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+$	$\log {}^*\beta_2 = -6.31$
$Fe(OH)_3(s) + H^+ \leftrightarrow Fe(OH)_2^+ + H_2O$	$\log {}^*K_{s2} = -2.35$

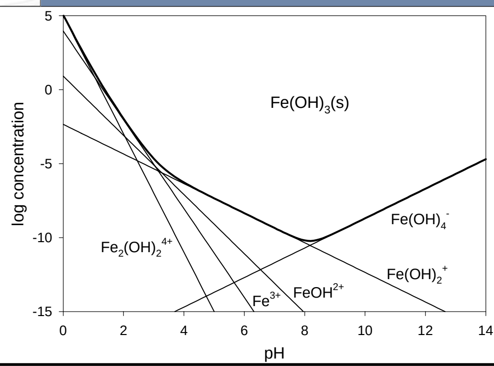
$$\log [Fe(OH)_2^+] = \log {}^*K_{s2} - pH$$

$Fe_2(OH)_2^{4+}$

$2Fe(OH)_3(s) + 6H^+ \leftrightarrow 2Fe^{3+} + 6H_2O$	$2\log {}^*K_{s0} = 7.92$
$2Fe^{3+} + 2H_2O \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	$\log {}^*\beta_{22} = -2.91$
$2Fe(OH)_3(s) + 4H^+ \leftrightarrow Fe_2(OH)_2^{4+} + 4H_2O$	$\log {}^*K_{s22} = 5.01$

$$\log [Fe_2(OH)_2^{4+}] = \log {}^*K_{s22} - 4pH$$

These equations can be used to obtain the concentration of each of the Fe(III) species as a function of pH. They can all be summed to give the total solubility.



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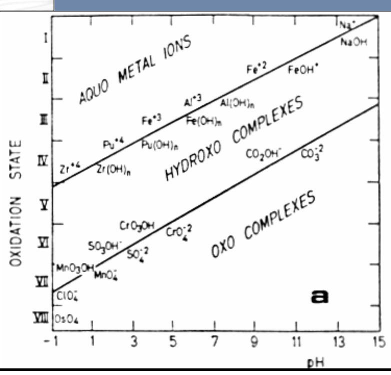

Figure 6-4a from Stumm and Morgan: Predominant pH range for the occurrence of various species for various oxidation states

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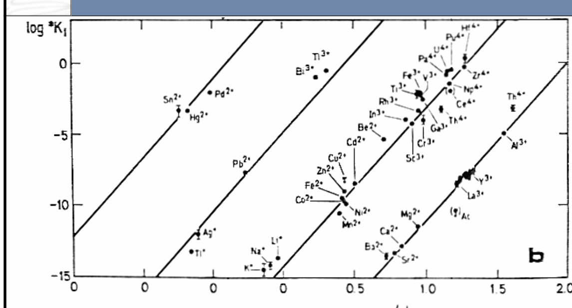

Figure 6-4b from Stumm & Morgan: The linear dependence of the first hydrolysis constant on the ratio of the charge to the M-O distance (z/d) for four groups of cations at 25°C.

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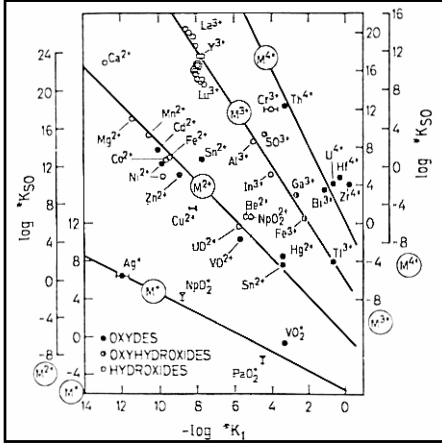

Figure 6-6 from Stumm & Morgan: Correlation between solubility product of solid oxide/hydroxide and the first hydrolysis constant.

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