

The Solubility of Calcium Sulfate

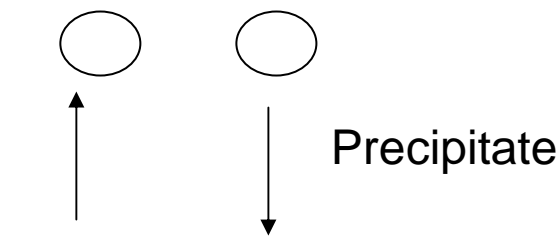
Complexometric titration

Solubility

- When dissolution rate > precipitation rate, solid dissolves.

- When dissolution rate = precipitation rate, solution become saturated (under the condition of sufficient amount of solid), the equilibrium is reached.

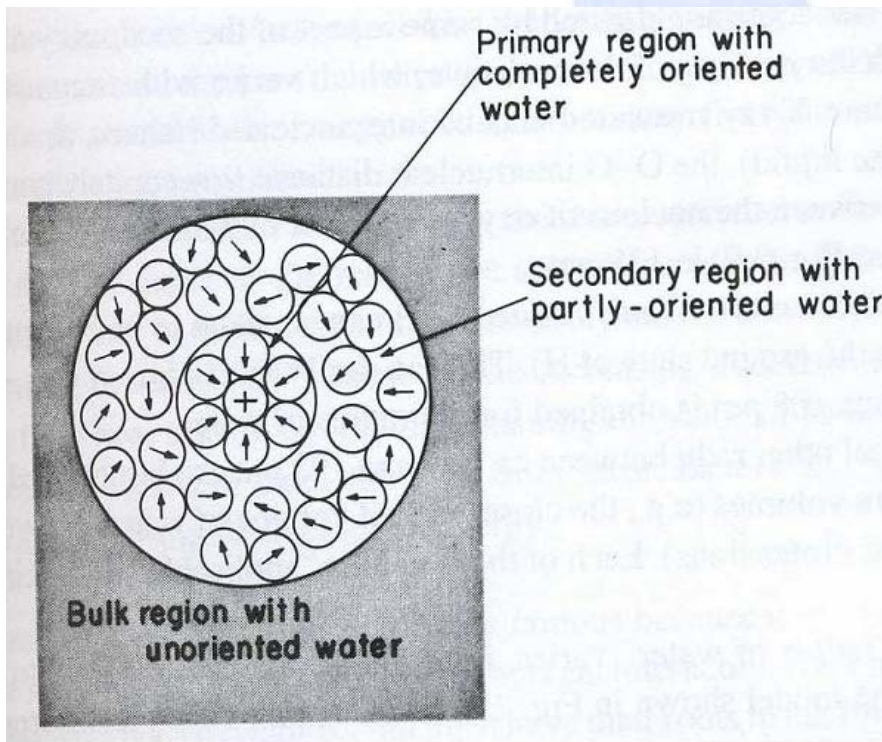
Dissolve



- The concentration of the solid = 1, so for $A (s) \rightleftharpoons B + C$; $K = [B][C] = K_{sp}$, when the solution becomes saturated, K_{sp} is reached.

Activity

- The picture of ion in solution: Hydration shell



- The dissolved ion will interact with solvent e.g. water dipole. The ion-dipole force will immobilize the solvent dipole around it to a hydrated ion, the ion is surrounded by the shell, the whole cluster move together as an single kinetic entity. The region can be sharply defined
- Primary region: solvent dipoles are well completely oriented
Secondary region: solvent dipoles are partially oriented. The region cannot be sharply defined.

Ionic Strength

- Ionic Strength: the measure of the total concentration of **ions (charges)** in the solution:

$$\mu = \frac{1}{2}(C_1Z_1^2 + C_2Z_2^2 + \dots) = \frac{1}{2}\sum C_iZ_i^2$$

- The greater the ionic strength of a solution, the higher the charge in the ionic atmosphere (hydrated shell), each hydrated ion contains less net charge and there is less attraction between any particular cation and anion.

Activity

- Since the ions in the solution are hydrated complexes rather than the simple bare ions, “effective concentration” is no longer the same as the regular concentration. The “effective concentration” which taking into the consideration of ionic strength is called activity:

$$\alpha = [A] \gamma_A$$

γ_A : activity coefficient

Activity coefficient

- Extended Debye Hückel Equation

$$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)} \quad (\text{at } 25^\circ \text{C})$$

α : effective hydrated radius
(picometers 10^{-12}m)

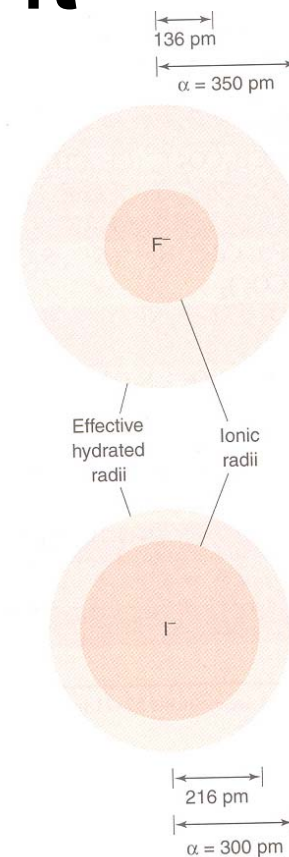
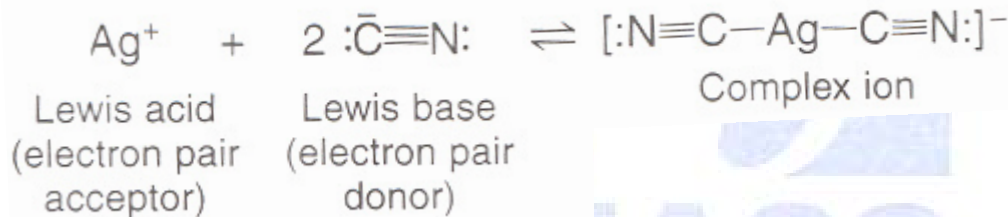


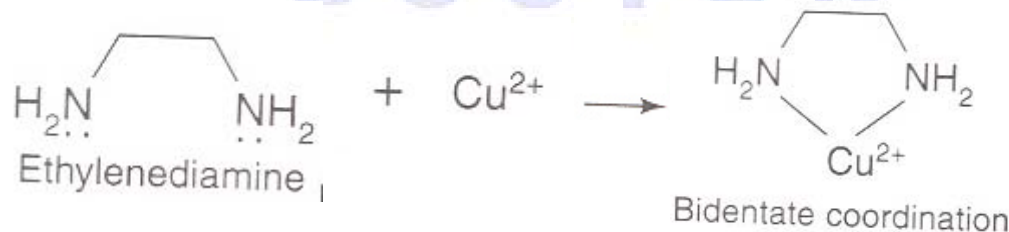
Figure 8-4 Ionic and hydrated radii of fluoride and iodide. The *smaller* F⁻ ion binds water molecules more tightly than does I⁻, so F⁻ has the *larger* hydrated radius.

Terminologies

- Complexometric titration: A titration based on complex formation.
- Lewis acid: accepting electron pairs from electron donating ligands.
- Lewis base: donating electrons to Lewis acid.
- Monodentate ligand: the ligand binds to a metal ion through only one atom e.g. Cyanide (CN^-).

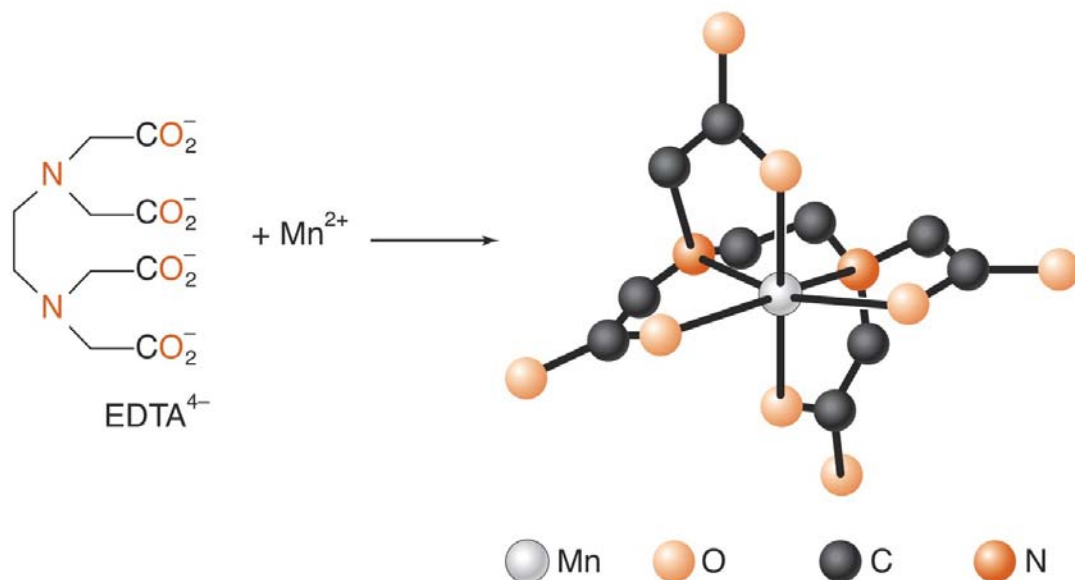


- Multidentate Ligand: a ligand attaches to a metal ion through more than one ligand atoms: **chelating ligand**.



The most important chelator - EDTA

- EDTA can form strong complex with almost all metal ions, binding through four oxygen and two nitrogen atoms. The complex is 1:1 six coordinate geometry. (almost all chelate complexes are 1:1, due to the space limitation)



EDTA Titration techniques

- Direct titration
 - Control pH, in buffer solution
 - Auxiliary complexing agent to prevent hydrolysis
- Back titration
 - HOW: adding known excess amount of EDTA, the excess EDTA will be titrated by the second ion solution with known concentration (standard solution)
 - WHY:
 - The ion will precipitate without EDTA
 - The reaction is slow under normal titration condition
 - No good indicator
 - Conditions: the bond between the second ion and EDTA has to be weaker than that of analyte ion with EDTA.

EDTA Titration techniques

- Displacement titration
 - How: adding known amount of EDTA complex solution, the analyte metal ion can replace the metal ion bonded with EDTA.
 $\text{Ca}^{2+} + \text{MgY}^{2-} \rightarrow \text{CaY}^{n-4} + \text{Mg}^{2+}$, Mg is then titrated with EDTA.
 - Why: no good indicator.
- Indirect titration: determine anions
- Masking: to prevent the interfering between ions. **Cyanide (CN⁻) is the typically used to mask (caution!!).** Demasking