GEOL 414/514

AQUEOUS COMPLEXES

Chapter 3

LANGMUIR

INTRODUCTION

• A complex is a dissolved species because of the assoc'n of a cation & anion or neutral molecule

• A ligand is an anion or neutral molecule that can combine with a cation to form a complex

• Importance of Complexes:

1. Complexing of a dissolved species that also occurs in a mineral tends to increase the solubility of that mineral over its solubility in the absence of aqueous complexing.

2. Some elements occur in solution more often in complexes than as free ions.

INTRODUCTION, CONTINUED

Complexes, con't:

3. Adsorption of cations or anions may be greatly favored or inhibited when they occur as complexes rather than as free (uncomplexed) ions.

4. The toxicity and bioavailability of metals in natural waters depends on the aqueous speciation or complexation of those metals.

• A simple example of the effect of complexation on solubility is given by the case of calcite in water.

Example: Complexation & Solubility

A) Solubility of calcite in pure water:

K_{sp} **(calcite)** $= 10^{-8.5} = (mCa^{+2})(mCO_3^{-2})$

$mCa^{+2} = 10^{-8.5}/10^{-5.0} = 10^{-3.5} = 3.2 \times 10^{-4}$

$\sum mCa = mCa^{+2}$ **(mass-balance equation)**

B) Solubility of calcite with complexation:

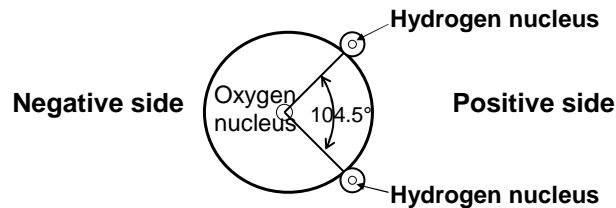$\sum mCa = mCa^{+2} + mCaSO_4 + mCaHCO_3^+$ **(mass-bal)**

$\sum mCa = mCa^{+2} + 10^{-0.3}mCa^{+2} + 10^{-1.9}mCa^{+2}$

$mCa^{+2} = 3.2 \times 10^{-4}$, **so** $\sum mCa = 9.6 \times 10^{-4}$

Outer- & Inner-Sphere Complexes

• **Water molecular structure and polarity:**

Hydrogen nucleus

Negative side Oxygen nucleus 104.5° **Positive side**

Hydrogen nucleus

• **Properties of:**

H-bonding - bonding of H^+ to O^{-2}
Cohesion - like-to-like - H_2O to H_2O
Adhesion - unlike - H_2O to (soil) solids
Surface tension - H_2O to H_2O vs H_2O to air
Capillarity - H_2O rise in capillary tube

INFLUENCE OF POLARITY OF H_2O

O^{2-}

$105°$ $0.96Å$

H^+ H^+

(a)

Solvated cation → Solvated complex ← Solvated anion

(b)

● = Cation

○ = Anion

◑ = H_2O Dipole
— (Focus of positive charge)
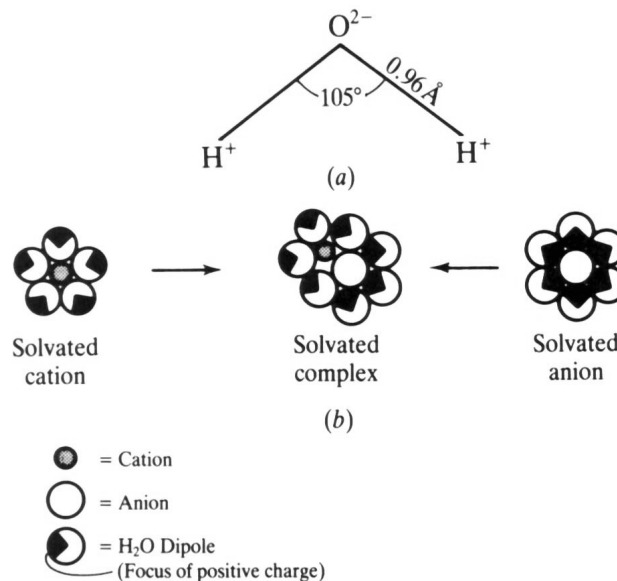
Outer- & Inner-Sphere Complexes-2

• **Outer-sphere complexes, ion pairs, involve the association of a hydrated cation & anion, held by long-range electrostatic forces.**

   There are water molecules between the ions

      - major monovalent & divalent cations
      - major anions, Cl^-, HCO_3^-, SO_4^{-2}, CO_3^{-2}

      $Ca(H_2O)_6^{+2} + SO_4^{-2} \Rightarrow Ca(H_2O)_6SO_4^0$ or $CaSO_4^0$

$$K_{assoc} = \frac{[CaSO_4^0]}{[Ca^{+2}]\,[SO_4^{-2}]}$$

  • **What is difference: $CaSO_4$ vs $CaSO_4^0$**

Outer- & Inner-Sphere Complexes-2

• **Inner-sphere complexes have an ionic/covalent association of two ions where there are no intervening H_2O molecules**

• **Cations generally form increasingly inner sphere complexes as the charge (z) increases and size (r) decreases**

• **The higher the ionic potential (Ip = z/r) of the cation (Table 3.1), the more covalent bonding, the stronger and more inner sphere the complex.**

• **Examples: HCO_3^-, AgS^-, $CdSH^-$**

• **General Observations on Complexation - see text**

METAL CATION-LIGAND RELATIONSHIPS IN COMPLEXES

- Metal cations are appreciably smaller than assoc ligands

- Charge of cation usually exceeds that of ligand

- Generally one cation surrounded by several anions

- Maximum number of ligands surrounding cation equals maximum coordination number (4 & 6 common)

- This is number of ligands in inner-coordination sphere

- Most ligands are not spherical - see text for common geometric forms

- Lewis acid: an electron pair acceptor (cations)
- Lewis base: an electron pair donor (complexing ligands)

COMPLEXATION MASS-BALANCE & EQUILIBRIA EQUATIONS

- Sum of cationic species:
  (mass balance)

$$\sum M = M + ML + \dots + ML_N = L + \sum_{i=0}^{N} ML_i$$

M = metal
L = Ligand
N = max No. Ligand groups

- Mass balance for Ligand is similar

- See text for full derivation and explanation

- Most often we write dissociation expressions and determine dissociation constants

COMPLEXATION MASS-BALANCE & EQUILIBRIA EQUATIONS

• **Example: Calculate the conc'n of all species in a solution containing 1.00 M HCl & 0.010 M Cd(NO$_3$)$_2$**

• **Mass balance equations for total Cl and Cd are:**

$\sum$Cl = (Cl-) + (CdCl$^+$) + 2(CdCl^0) + 3(CdCl$_3^-$) + 4(CdCl$_4^{-2}$) = 1

$\sum$Cd = (Cd^{+2}) + (CdCl$^+$) + (CdCl^0) + (CdCl$_3^-$) + (CdCl$_4^{-2}$) = .01

• **See text for approximate solution**

• **See Fig 3.3 for Cd species conc'n as a function of Cl$^-$ conc**

HYDROLYSIS

• **Hydrolysis is the formation of excess H$^+$ or OH$^-$ when the salt of a weak acid or base is dissolved in H$_2$O**

• **"Hydrolysis" literally means "breakup by means of water" where the H$_2$O was supposed to split a salt into an acid and a base**

• **We now describe the reaction differently, with the first step being the dissociation of the salt into ions and the ion of the weak acid or base reacting with either H$^+$ or OH$^-$ from H$_2$O**

• **Example:**

$$Na_2CO_3 + H_2O \leftrightarrows 2Na^+ \ CO_3^{-2} + H_2O$$

simultaneously: $H_2O \leftrightarrows H^+ + OH^-$

SOLUTE HYDROLYSIS - 1
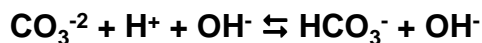
$$CO_3^{-2} + H^+ + OH^- \leftrightarrows HCO_3^- + OH^-$$

$$K = [HCO_3^-][OH^-] / [CO_3^{-2}]$$

- **To calculate the $K_{hydrolysis}$:**

- **Trick: multiply the numerator & denominator by 1**

$$K = \frac{[HCO_3^-][OH^-][H^+]}{[CO_3^{-2}][H^+]} = \frac{[HCO_3^{-2}]}{[CO_3^{-2}][H^+]} [OH-][H^+]$$

Know K
For this

Know K
For this

$$K_{hydrolysis} = K_{H2O} / K_{ionization} = 10^{-14} / 5 * 10^{-11} = 2 * 10^{-4}$$

- **Read how to calculate the pH of 0.01 m Na_2CO_3**
  - **Table VII-3, p. 600: Dissoc K's of hydroxide**

SOLUTE HYDROLYSIS - 2
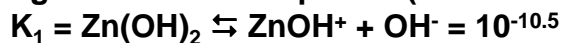
Hydrolysis of $ZnSO_4$

$$ZnSO_4 + H_2O \leftrightarrows Zn^{+2} + SO_4^{-2} + H_2O$$

$$Zn^{+2} + H_2O \leftrightarrows ZnOH^+ + H^+ \text{ - hydrolysis reaction}$$
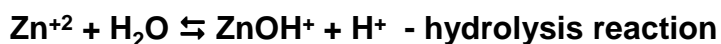
$$K = [ZnOH^+][H^+] / [Zn^{+2}]$$

- **multiply by $[OH^-] / [OH^-]$**

$$K = [ZnOH^+] / [Zn^{+2}][OH^-] * [H^+][OH^-]$$

$$K_H = 1 / 10^{-5.0} * 10^{-14} = 10^{-9}$$

- **Finding K value for Zn species (handout appendix):**
  $$K_1 = Zn(OH)_2 \leftrightarrows ZnOH^+ + OH^- = 10^{-10.5}$$

  $$K_2 = ZnOH^+ \leftrightarrows Zn^{+2} + OH^- = 10^{-5.0}$$

SOLUTE HYDROLYSIS - 3

If the solution is 10^{-2} m $ZnSO_4$, what is the pH?

- Assume no other source of Zn^{+2} or H^+
1. $[ZnOH^+] [H^+] / [Zn^{+2}] = 10^{-2} - [H^+]$

    a) 10^{-2} m is total conc'n; b) $[Zn^{+2}]$ = total minus $[H^+]$
2. For each Zn^{+2} formed, there is one H^+ formed
3. $[ZnOH^+] = [H^+]$

    $K = [ZnOH^+] [H^+] / [Zn^{+2}]$, therefore

    $[Zn^{+2}] = [10^{-2} - [H^+]]$

SOLUTE HYDROLYSIS - 4

write all substances in terms of H^+

$$K = [H^+] / 10^{-2} - [H^+] = 10^{-9}$$

$$[H^+] + 10^{-9}[H^+] - 10^{-11} = 0$$

$$[H^+]^2 = 10^{-11}$$

$$[H^+] = 10^{-5.5}$$

$$pH = 5.5$$

HYDROLYSIS OF CATIONS IN WATER & IONIC POTENTIAL

- **The extent of hydration of a cation is proportional to the effective size of the hydrated ion**

- **The charge density of the cation is also important**

- **A useful concept is the ionic potential, Ip, where Ip = z/r, which is essentially a measure of the charge density**

- **Note in Fig 3.4 which elements fall into the three major groups: cations & aquocations; oxycations, hydroxycations & hydroxyanions; and oxyanions**

- **Species formed by hydrolysis of cations are given in Table 3.3**

- **Metal-hydroxy species are common (Fig 3.5)**

ELECTRONEGATIVITY & STABILITIES OF INNER-SPHERE COMPLEXES

- **Concept of electronegativity (EN) helps to explain stabilities of complexes that have some inner-sphere character**

- **Atoms with high EN's (esp >2) are Lewis bases**

- **Atoms with EN's <2 are gen. metal cations (Lewis acids)**

- **Bonding in inner-sphere complexes depends partly on ΔEN, diff in EN of cation and ligand**

- **When $\Delta EN = 0$, bonding is purely covalent (C-C in diamond)**

- **See Fig 3.6 for relationship between cation EN & K_{assoc}**

SCHWARZENBACH'S CLASSES A, B, & C & PEARSON'S HARD & SOFT ACIDS & BASES

- Pearson classified Lewis acids and bases as either hard or soft, depending upon nature of bonding

- Hard species form chiefly strong ionic bonds

- Soft species form mostly covalent bonds

- Most often: hard acid-hard base or soft acid-soft base combinations; usually not hard-soft combinations

- Schwarzenbach based his classification on the e⁻ configuration of the ions

- These two classifications are compared in Table 3.5

MODEL-PREDICTION OF THE STABILITIES OF COMPLEXES

- Previous information can be used as the basis of predicting stability of complexes

- K_{assoc} proportional to electrostatic function, $z_m z_L/d$, where z_m & z_L are charges of metal & Ligand and $d = r_M + r_L$, sum of crystal radii

- Several useful models for predicting stabilities of complexes that involve partially ionic & partially covalent bonding
  - electronegativity, electronicity, degree of hardness or softness are used

- Langmuir used graphical methods for predicting stabilities of complexes - plot K_{assoc} values for cations & two similar ligands (Fig 3.10)

DISTRIBUTION OF COMPLEX SPECIES AS A FUNCTION OF pH

See examples in text for Th species

We will study other, more common species later in the course

TOXICITY AND THE ROLE OF SOFT-ACID METAL CATIONS

• A toxic substance or toxicant "is harmful to living organisms because of its detrimental effects on tissues, organs or biological processes"

• We will examine inorganic toxicants in water

• The relationship between [avg conc's in world streams] and [permissible conc's in U.S. publis water supplies] is shown in Fig 3.15.

- there is a strong correlation, the reasons for which are not obvious
- perhaps this is due to humans evolving in a similar environment

TOXICITY AND THE ROLE OF SOFT-ACID METAL CATIONS - 2

• Plant macronutrients: C, H, O, N, P, S, K, Ca & Mg
- C, H & O - biomass
- N & P - proteins
- S - proteins & enzymes
- Ca, Mg, Ca - metabolic functions

• Plant micronutrients: B, Cl, Co, Cu, Fe, Mn, Mo, Na, Si, V & Zn
- all - metabolic function or enzyme activation
- most impt for enzymes: Cu, Co, Fe, K, Mg, Mn, Zn

• Toxicity of several metals to some plant groups (phytotoxicity) is shown in Table 3.8
• most toxic: soft-acid cations
• next most toxic: borderline hard-soft acid cations

TOXICITY AND THE ROLE OF SOFT-ACID METAL CATIONS - 3

Possible mechanisms for toxicity:

- relate to tendency to form strong complexes with generally soft functional groups on biomolecules
- Ex of Cd displacement of Ca

- newly bound metal blocks normal enzyme function, i.e., deactivation
- enzymes that are activated by micronutrients are especially susceptible
- may also modify structure - molecular configuration is often crucial to its function