

Lecture 14: Surface Chemistry and Adsorption

Solid-solution interactions

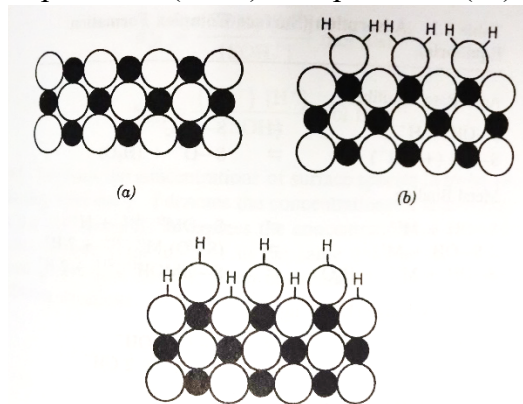
- Chemical reactions in natural waters often occur on the surfaces of solid particles
 - Minerals such as clays, metal (hydr)oxides, carbonates, sulfides – hydrophilic interactions
 - Particulate organic matter (> 0.5 μm diameter) – hydrophilic and hydrophobic interactions
- Some particles that scavenge metal and organic contaminants are useful in remediation systems

Solid particles have surfaces with topographic and chemical variabilities that create high energy sites where reactions can occur

- What type of sites exist?
- What are the properties of these sites?
- How do these sites change as a function of pH?

How do mineral surfaces acquire charge?

- 1) *Isomorphic substitution* in the crystal lattice generates net charge on the mineral (e.g., when Al^{3+} substitutes for Si^{4+} in tetrahedral layer of a silicate)
- 2) *Ionizable functional groups* that occur on surfaces change charge depending on pH, which controls degree of protonation
 - For example, many mineral surfaces can be regarded as a plane of hydroxyl (OH) groups that can protonate (OH_2^+) or deprotonate (O^-) to create a charged surface



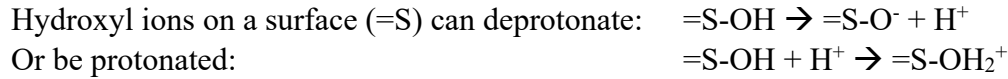
- 3) *Specific adsorption* of ligands onto a mineral surface (*surface complexation reaction*) changes the charge on the surface

Example: phosphate (HPO_4^{2-}) binding to an aluminum hydroxide surface ($\equiv\text{Al-OH}$)
 $\equiv\text{Al-OH} + \text{HPO}_4^{2-} \rightarrow \equiv\text{Al-OPO}_3^{2-} + \text{H}_2\text{O}$

Mineral surface charge as a function of pH

Acid-Base Reactions on Surfaces - Protonation and deprotonation of a mineral surface can give it a (+) or (-) charge

Protonation/Deprotonation of Hydroxyl groups represented as chemical reactions:



These reactions can be described by equilibrium constants!

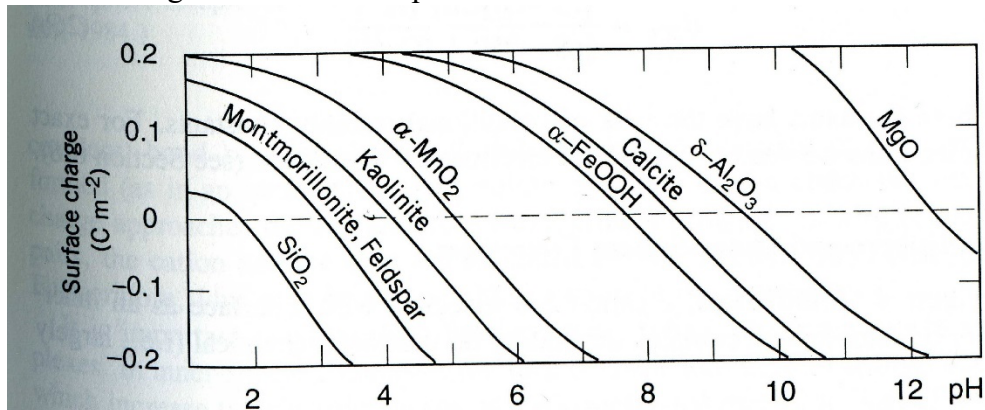


*here, $[H^+]$ indicates the activity of H^+ at the surface of the solid which is different from the bulk solution due to attraction/repulsion with charged surface

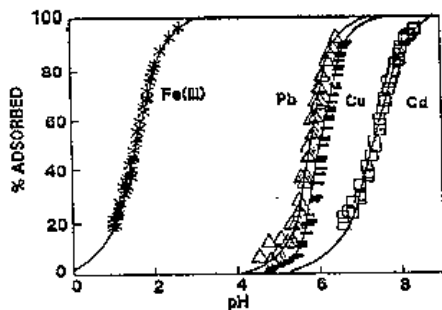
Zero Point Charge (PZC)

- the pH where the net charge on a surface is zero (aka *isoelectric point*)
- At pH_{PZC} , sum of (+) sites = sum of (-) sites

Surface charge as a function of pH for various minerals:



pH-dependent surface charge drives ion adsorption:



Reactions at mineral surfaces

Topographic and chemical variability (interfaces) create high energy surface sites where reactions can occur due to interactions between forces

1. chemical forces (covalent bonds)
2. electrostatic interactions
3. dipole-dipole interactions
4. van der Waals forces
5. hydrogen bonding

Sorption – the processes by which solutes partition onto solid surfaces or into solid matrices (see diagram in notes)

Absorption – solute is incorporated into the solid matrix of the particle

Adsorption – attachment of a solute to the surface of a solid or the accumulation of solutes in the near vicinity of a surface

1. *Physical adsorption* – weak interactions, e.g. van der Waals forces
2. *Electrostatic adsorption* – ions are attracted to a surface of the opposite electrical charge (e.g. **outer-sphere complex**)
3. *Chemical adsorption* – chemical bonding between the solute and atoms on the solid surface (e.g. **inner-sphere complex**)

The concentration and chemistry of sorption sites determines what kind and how much of a solute can bind to a surface

Concentration of sorption sites can be calculated as:
$$\Gamma_{SOH} = \frac{N_S SSA C_S}{N_A}$$

Where Γ_{SOH} = Concentration of sorption sites (mol sites/L solution)

N_S = Surface site density (sites/m²)

SSA = Specific surface area (m²/g) = surface area (S_A) divided by the sorbent mass

C_S = concentration of sorbent (g sorbent/L solution)

N_A = Avogadro's number (sites per mole) = 6.022×10^{23}

How do we measure surface area, S_A ?

- Geometrically, approximating each particle as a sphere: S_A (sphere) = $4\pi r^2$
- BET (Brunauer-Emmett-Teller) surface area – experimentally measure how much gas (e.g., N_2) adsorbs to a surface; more accurate; better able to fill in nooks and crannies

S_A generally increases with decreasing grain size (see diagram in slides)

Specific surface area (SSA; m²/g): the total surface area per unit mass of solid material

How do we measure surface site density, N_S ? Adsorption of a reactive solute (or sorbate) to a surface:

- Protons (H^+ , e.g. mineral titration)
- Fluoride ions (F^-)

Sorption Isotherms

Sorption of a solute to mineral surface *at constant temperature* can be modeled as a function of solution chemistry using simple equations

- Data is experimentally collected and modeled with different equations to find a best fit
- Each point on an isotherm represents an *equilibrium condition* where the solute has reached an equilibrium between the amount in solution and the amount adsorbed to the surface
- The isotherms we will discuss:
 1. Linear distribution coefficient
 2. Freundlich Isotherm
 3. Langmuir Isotherm

Linear distribution coefficient

$$m_{i,ads} = K_d m_{i,soln}$$

- $m_{i,ads}$ = concentration of a solute i sorbed to a surface (mol/kg)
- K_d = linear distribution coefficient; the value of K_d depends on the properties of the surface and solution; determined experimentally for each system and not easily transferred to other systems
- $m_{i,soln}$ = concentration of solute i that remains in solution at equilibrium (mol/L)

Freundlich Isotherm

$$m_{i,ads} = K_d m_{i,soln}^n$$

- $m_{i,ads}$ = concentration of a solute i sorbed to a surface (mol/kg)
- K_d = Freundlich distribution coefficient
- $m_{i,soln}$ = concentration of solute i that remains in solution at equilibrium (mol/L)
- n = Exponent (< 1) that limits adsorption at higher concentrations

Langmuir Isotherm

Expresses sorption as a function of available binding sites ($m_{i,max}$)

$$m_{i,ads} = m_{i,max} \frac{K_{Lang} m_{i,soln}}{1 + K_{Lang} m_{i,soln}}$$

- $m_{i,ads}$ = concentration of a solute i sorbed to a surface (mol/kg)
- $m_{i,max} = m_{i,ads} + m_{vacant}$
- K_{Lang} = Langmuir adsorption coefficient
- $m_{i,soln}$ = concentration of solute i that remains in solution at equilibrium (mol/L)

Linear form of the equation (plotted as $m_{i,soln}/m_{i,ads}$ (y-axis) vs $m_{i,soln}$ (x-axis)):

$$\frac{m_{i,soln}}{m_{i,ads}} = \frac{1}{K_{Lang} m_{i,max}} + \frac{m_{i,soln}}{m_{i,max}}$$

The isotherm flattens at high concentrations because surface sites become gradually saturated

- Cation exchange reactions are well approximated by Langmuir isotherms because the adsorbed ions can never be greater than the number of exchange sites

Factors that influence adsorption

1. Surface charge – f(pH, mineralogy, surface site density)
2. Solute charge – f(pH, solute)
3. Surface area
 - Small particles → high SA → more adsorption