

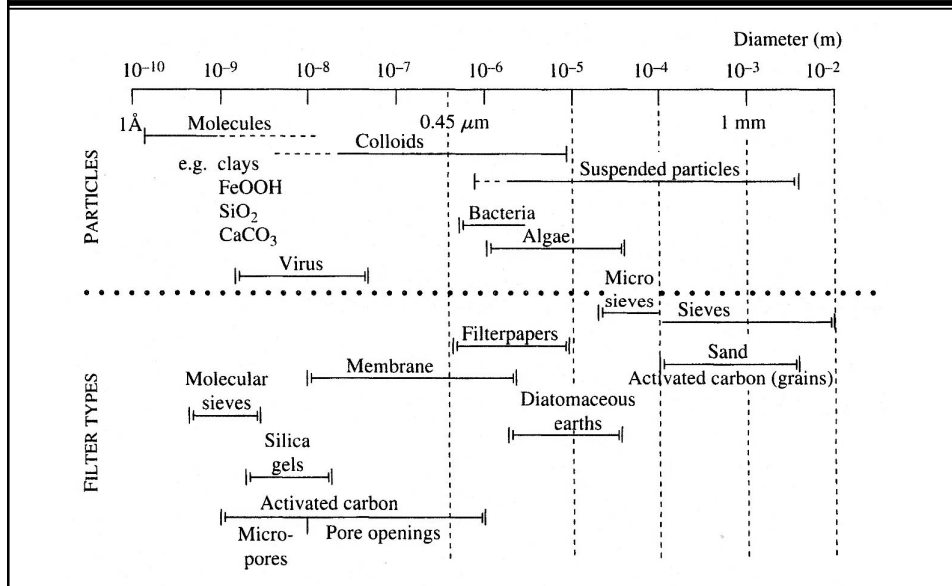
# GEOL 414/514

## ADSORPTION - DESORPTION REACTIONS

### Chapter 10

### Langmuir

## SIZES OF PARTICULATES & PORE SIZES OF FILTERS

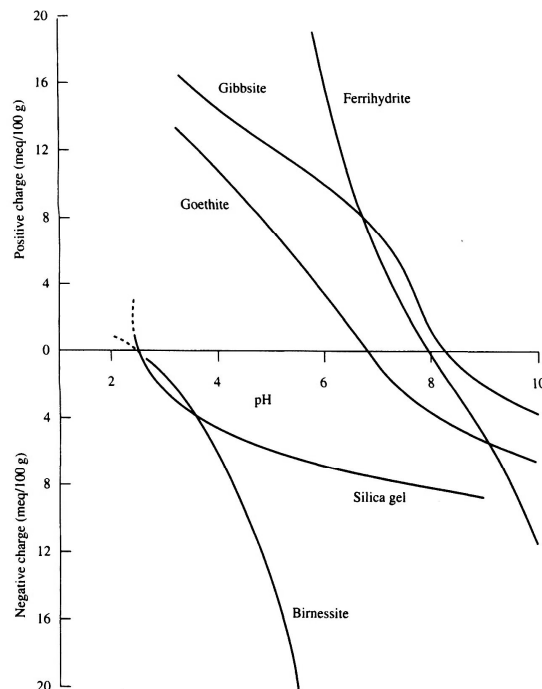


## NATURE OF THE INTERFACE

### Characteristics of particle surfaces:

- Irregular
- Possess electrical charges
  - permanent, from isomorphous substitution
  - pH dependent, from -Si-OH or -Al-OH groups
- Point of zero charge (PZC) or  $\text{pH}_{\text{PZC}}$  – the pH where the charge of a mineral (or amorphous compound) becomes zero. Above/below this point, there is a + or – charge.

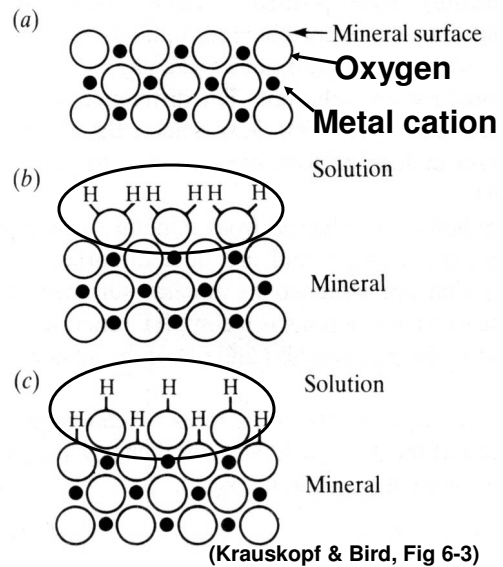
## SURFACE CHARGE OF SOME OXYHYDROXIDES



## NATURE OF THE INTERFACE-2

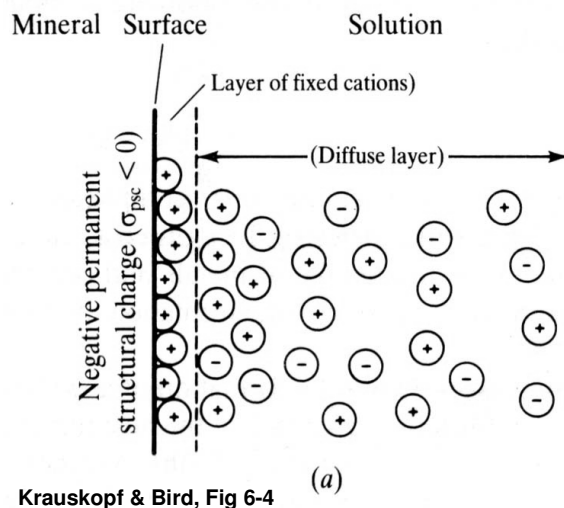
Water molecules orient with mineral surface as a function of surface charge expression (b).

Hydroxylated surface of  $\text{OH}^-$  forms from dissociation of  $\text{H}_2\text{O}$  (c).



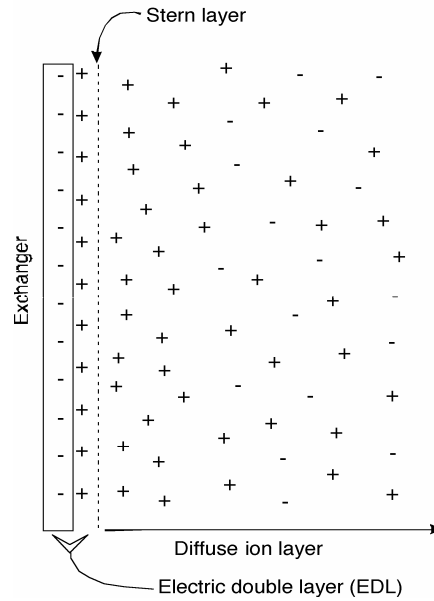
## NATURE OF THE INTERFACE-3

Counter-ions accumulate near the surface-solution interface to neutralize the net charge deficiency.

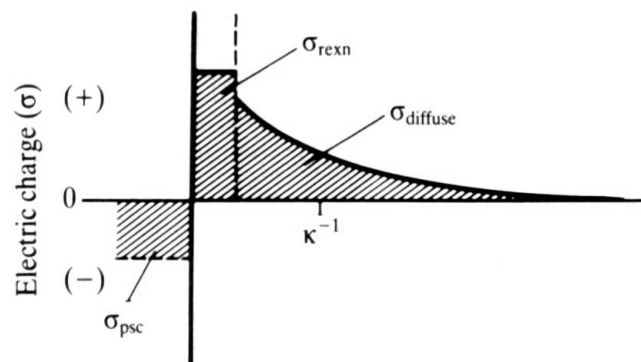


## NATURE OF THE INTERFACE-4

Distribution of ions near a charged surface.



## NATURE OF THE INTERFACE-5



(b) Krauskopf & Bird, Fig 6-4

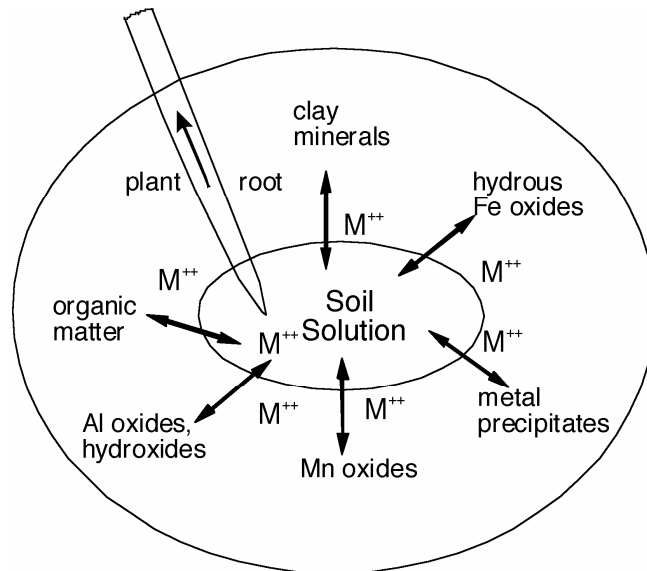
Net charge distribution at the solution-mineral interface

# SORPTION

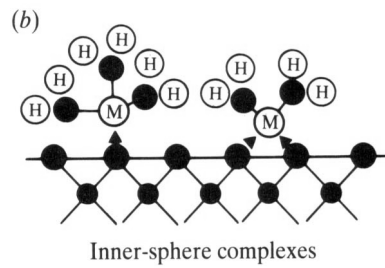
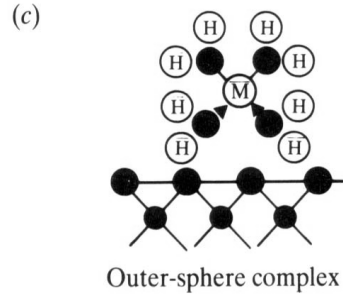
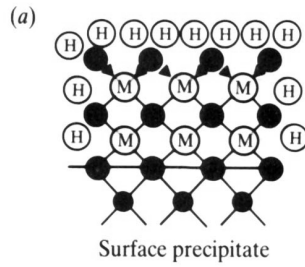
- Ions are attracted to mineral surfaces through a variety of mechanisms
- Sorption is a general term used to describe this attraction, which may be due to three processes:
  - formation of a surface precipitate via bonding with surface atoms of mineral (epitaxial overgrowth)
  - absorption or coprecipitation via diffusion or dissolution/reprecipitation
  - absorption which is an accumulation of an aqueous species on the mineral surface without 3-D bonding mechanism

## SORPTION - 2

Equilibrium of solution cations with different geochemical phases & plant roots.

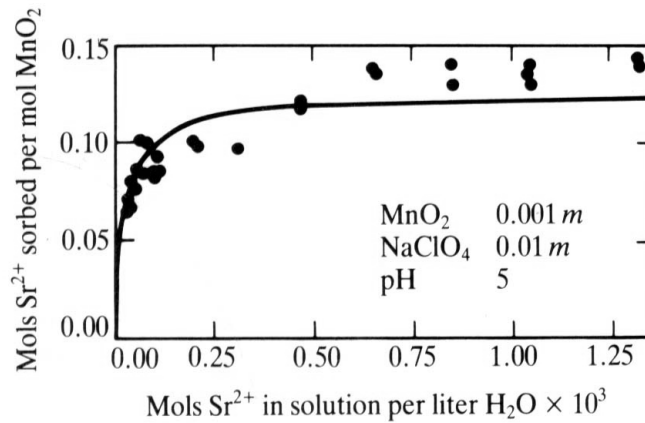


## SORPTION - 3



**Surface bonding of metals to a mineral surface (Krauskopf & Bird, Fig 6-5)**

## SORPTION - 4



**Sorption of Sr<sup>2+</sup> onto solid MnO<sub>2</sub> as a function of Sr<sup>2+</sup> conc in solution. This is an adsorption isotherm. (Krauskopf & Bird, Fig 6-6)**

## SORPTION - 5



$$K_{\text{eq}} = [\text{Sr}^{+2}_{\text{ads}}] / [\text{Sr}^{+2}_{(\text{sol'n})}][\text{Surface sites}] \quad (\text{K\&B,6-9})$$

- Defining the max sorption capacity & rearranging:

$$[\text{Sr}^{+2}_{\text{ads}}] = [\text{Sr}^{+2}_{\text{ads}}]^{\text{max}}[\text{Sr}^{+2}_{(\text{sol'n})}]K_{\text{eq}} / 1 + [\text{Sr}^{+2}_{(\text{sol'n})}]K_{\text{eq}} \quad (6-10)$$

- Eq. (6-10) is called the Langmuir equation and a curve for the equation (Fig 6-6) is called a Langmuir isotherm.
- The Langmuir equation describes sorption with increasing solution.

## SORPTION - 6

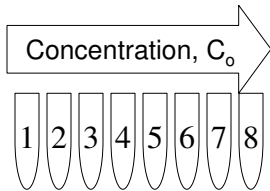
### Assumptions Necessary for Application of the Langmuir Adsorption Model

- Fixed number of identical sorption sites on a planar surface; each site can hold one molecule, only. Monolayer 2D process.
- Reversible Adsorption
- Adsorption energy is the same for all sites and is independent of surface coverage from the point of view of the next interaction.
- Linear Transform:  $C/q = 1/kb + C/b$ ; plot  $C(x)$  vs.  $C/q(y)$

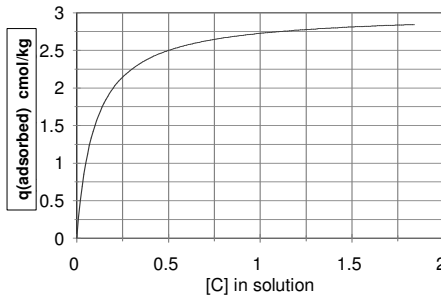
# SORPTION - 7

## Adsorption Isotherms - Experimental

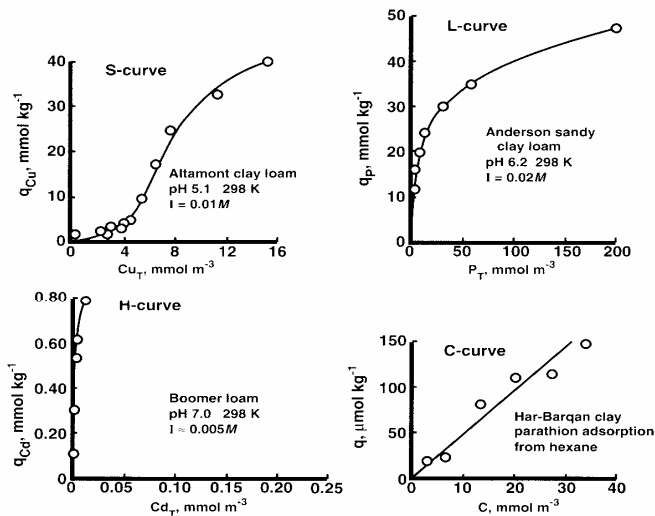
Batch Adsorption Isotherm is measured using multiple tubes with the same amount of solid and but with differing concentrations of solute molecules



$$q_i = (C_o - C_f) V_T / m_s$$



# SORPTION - 8

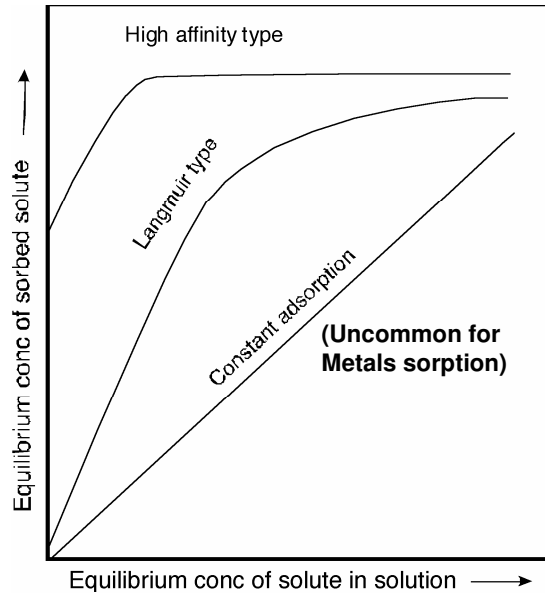


**FIGURE 5.6.** The four general categories of adsorption isotherms. From Sposito (1984), with permission.

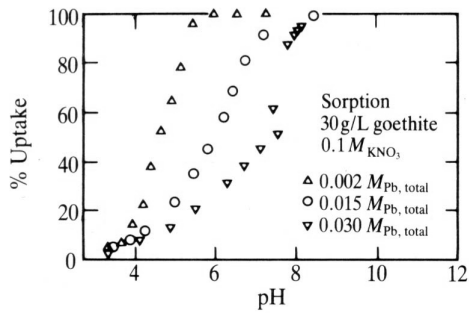


## SORPTION - 9

Three types of sorption isotherms

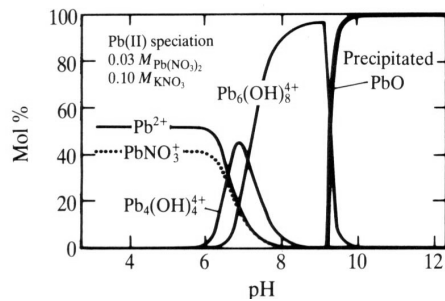


## SORPTION - 10

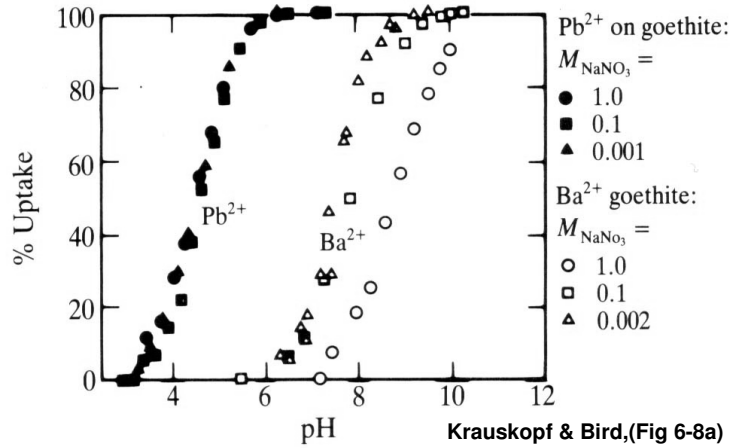


Sorption of Pb<sup>2+</sup> onto goethite (Krauskopf & Bird, Fig 6-7a)

Calculated distribution of aqueous Pb species from data in 0.030 m<sub>Pb</sub> in (a) (Krauskopf & Bird, Fig 6-7b).

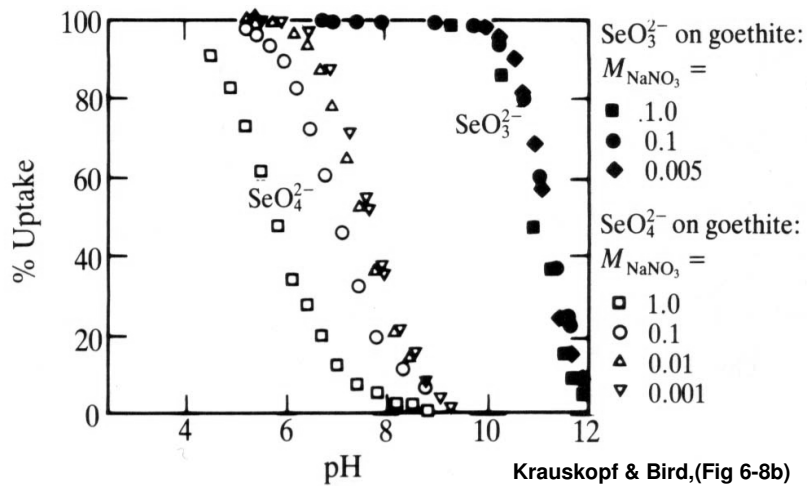


## SORPTION - 11



**Sorption of Pb<sup>2+</sup> and Ba<sup>2+</sup> onto goethite in background solutions of varying ionic strength**

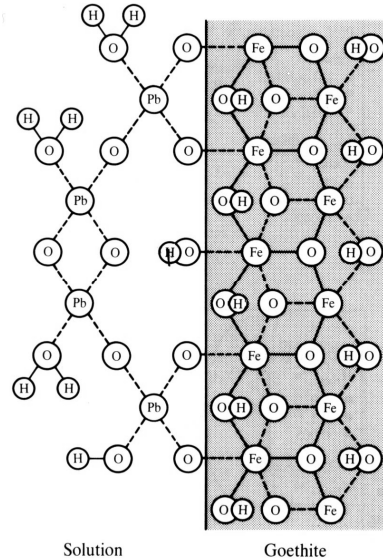
## SORPTION - 12



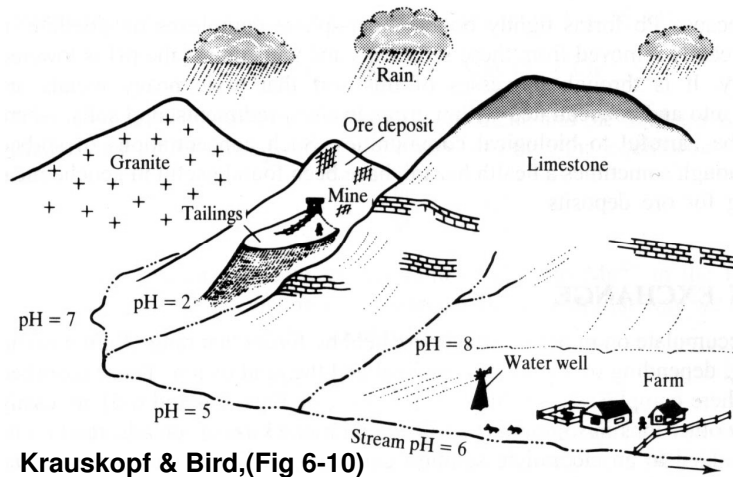
**Sorption of SeO<sub>3</sub><sup>-2</sup> & SeO<sub>4</sub><sup>-2</sup> onto goethite in background solutions of varying ionic strength**

## SORPTION - 13

Schematic two-dimensional representation of a multinuclear surface complex of Pb bound by two inner-sphere complexes to goethite (Krauskopf & Bird, Fig 6-9).



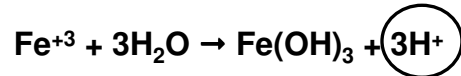
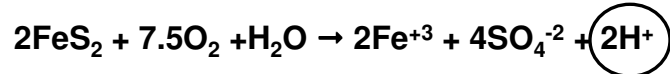
## SORPTION - 14



Schematic geologic setting illustrating trace metal transport & deposition in an acid mine drainage basin.

## SORPTION - 15

- Pyrite weathering, summary reaction:



Hence, acid mine drainage!

- $\text{Fe}(\text{OH})_3$  is colloidal and has a very high surface area
- $\text{Fe}(\text{OH})_3$  sorbs and coprecipitates other metals in surface waters and significantly affects sorption-desorption-transport of ions

## ION EXCHANGE

- Ions accumulate on surfaces & are held by forces ranging from weak to strong.
- Those sorbed by outer-sphere complexes or diffuse ion swarms (Fig 6-4, 6-5) are easily replaced by other ions in solution.
- The process of new ions replacing already sorbed ions is termed ion exchange.
- Ion exchange may also involve substitution of ions in a crystal, such as:  
$$\text{Na}_2\text{-zeolite} + \text{Ca}^{+2} \rightleftharpoons \text{Ca-zeolite} + 2\text{Na}^+$$
- This is the process utilized in water softening.

## ION EXCHANGE - 2

- Question: for ion exchange resins used for deionized water preparation, with which ions are they initially charged?
- Answer:  $H^+$  and  $OH^-$
- Other examples of ion exchange involving lattice structures are for carbonate minerals & alkali feldspars:  
$$CaCO_3 + Mg^{+2} \rightleftharpoons MgCO_3 + Ca^{+2}$$
$$NaAlSi_3O_8 + K^+ \rightleftharpoons KAlSi_3O_8 + Na^+$$
- These examples of ion exchange involve poorly understood complex processes

## ION EXCHANGE - 3

- Predictability's of ion behavior towards sorbents is very difficult and simple rules cannot be established
- It is noticed that when multiple ions are present in solution, a selectivity sequence can be established for different sorbents
- Sorbability should seemly follow:
  - 1 - inner-sphere complexes should have greater affinity than outer-sphere or diffuse-ion swarm
  - 2 - smaller ions held more firmly than larger
  - 3 - multivalent ion attached more firmly than univalent
  - 4 - ion whose bonds have strong covalent character more readily sorbed than those with mostly ionic

## ION EXCHANGE - 4

- Alkali cation selectivity sequence:

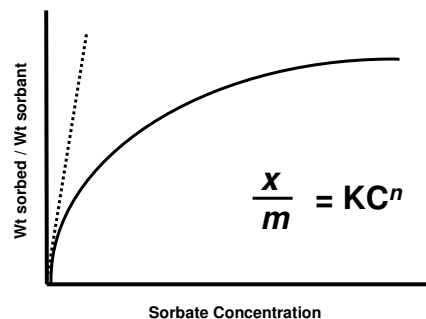


- This sequence contradicts the second rule on last slide
- The smallest ion,  $\text{Li}^+$ , is most highly hydrated & effectively largest in solution
- Hydrated radii and charge are important, but not only, properties related to sorption preference
- Importance of ion exchange:
  - redistribution of ions between solution & sediments - high  $\text{Na}^+$  in sea water due to sorption of  $\text{K}^+$  by soil clays
  - influence of ions on sorbents - Na-clays are sticky & dispersed; Ca-clays are aggregated

## ION EXCHANGE - 5

Typical adsorption isotherm. The slope equals the distribution coefficient,  $K_d$

The most simple sorption model, this is the Freundlich Adsorption Isotherm



A linearized form of the equation is generally used to test for Freundlich fit:

$$\log x/m = \log K + n \log C$$

## ION EXCHANGE - 6

- The  $K_d$  is frequently used to model the sorption of trace molecular organic species
- The amount of sorbed organic substances is a function of the amount of solid organic matter (humus).
- The sorption (distribution) coefficient for organic carbon,  $K_{OC}$  is defined as:

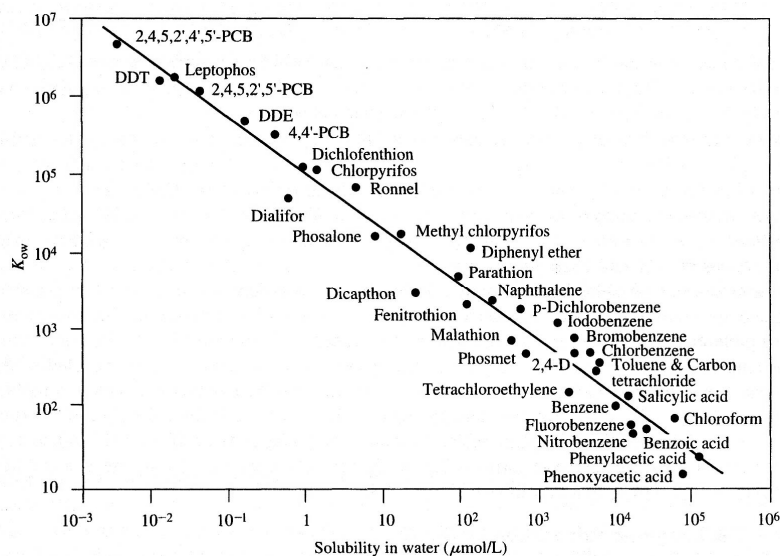
$$K_{OC} = [\mu\text{g sorbed} / \text{g organic C}] / [\mu\text{g/mL in sol'n}]$$

$$K_d = K_{OC} \times f_{OC}$$

Another useful entity is  $K_{OW}$ :

$$K_{OW} = [\text{conc in octanol phase}] / [\text{conc in water}]$$

## AQUEOUS SOLUBILITY VS OCTANOL-WATER PARTITION COEFFICIENT



## COLLOIDS

- Term “colloid” is from a period when a distinction was attempted between a “crystalloid” and a noncrystalline “colloid”
- We now define colloidal as a substance consisting of very tiny particles dispersed in another substance
- Size range is not universally agreed upon but generally agreed as from 0.01 - 10  $\mu\text{m}$
- In geologic systems we are concerned with solids dispersed in water
- An important exception is an emulsion, liquid-in-liquid, such as petroleum in  $\text{H}_2\text{O}$  or vice versa
- Aerosols are particles or liquids dispersed in atmos gas

## COLLOIDS - 2

### Properties of Colloids

- Solid-in-liquid systems may be prepared in two forms
- One that has liquid properties and appears to be a liquid solution - gelatin in warm water - termed a sol
- When gelatin sol is cooled and allowed to stand, it forms a transparent or translucent solid or gel
- Gelatin easily (spontaneously) disperses in water due to the attraction of water molecules to the gelatin. Such substances are said to be hydrophillic or “water loving.”
- Other substances do not disperse spontaneously due to their lack of adsorbed water and are termed hydrophobic or “water fearing.” (metallic Au,  $\text{Fe}(\text{OH})_3$ )



## **COLLOIDS - 3**

- Other substances are not clearly either hydrophobic or hydrophilic.
- Silica does not spontaneously disperse in water but dilute sols are infinitely stable and it readily forms a gel.
- Colloidal particles have sizes between that of true solutions ( $10^{-3}$   $\mu\text{m}$ ) and suspensions where particles quickly settle out ( $> 1-10$   $\mu\text{m}$ ).
- Colloids exhibit apparent homogeneity and stability.
- Colloids possess the ability to scatter light (Tyndall effect).
- Some exhibit an apparent milky, opalescence, due to light scattering.

## **COLLOIDS - 4**

- Colloids exhibit slowness in diffusion
- Particles cannot cross a semipermeable membrane, although there are now molecular sieves of variable pore size - use dialysis to purify colloids
- Have notable but unpredictable effect on b.p., m.p., v.p.
- Form a great variety of colored diffusion bands in gels, Liesegang bands. This can be accomplished by diffusing an electrolyte into a gel.
- The bands perhaps arise from supersaturation and depletion phenomena

## COLLOIDS - 5

### Surface chemistry of colloidal particles

- Colloids have a very high ratio of surface area to volume
- Particle surface charge is a determining factor in the stability of colloidal suspensions
- Surface charge also means that sorption & ion exchange play important role in migration of many elements
- Ion sorption & pH dependent surface reactions have strong influence on net surface charge
- Charge on colloidal particles is primary reason that they remain dispersed indefinitely
- When all particles have same charge, repulsion prevents settling

## COLLOIDS - 6

### Surface charges on various colloids

Substance	Charge
Silica (glass)	-
Al hydroxide (gibbsite)	+
Fe hydroxide	+
pH $\geq$ 7	-
MnO <sub>2</sub>	-
TiO <sub>2</sub>	+
ZrO <sub>2</sub>	+
ThO <sub>2</sub>	+
Sulfides	-
Carbonates	+ (usually)
Organic colloids	-
Plastics	+
Clay minerals	-

## CATION EXCHANGE CAPACITY OF SOME NATURAL MATERIALS

Substance	CEC(meq/100g)	pH dependence
Kaolinite	3 - 15	Strong
Glauconite	11 - 20	slight
Illite & chlorite	10 - 40	slight
Smectite-Montmorillonite	80 - 150	Absent/negligible
Vermiculite	100 - 150	negligible
Zeolites	100 - 400	negligible
Humic materials	100 - 500	strong
Mn & Fe oxyhydroxides	100 - 740 (???)	strong
Synth cation exch resins	290 - 1020	slight

## COLLOIDS - 7

### Flocculation by Electrolytes

- Concentrations of electrolytes above those necessary for stabilization may cause particles to flocculate (settle)
- $M^{+2}$  &  $M^{+3}$  ions much more effective than  $M^{+}$  ions  
 $Al^{+3} > Ca^{+2}, Mg^{+2} > K^{+} > Na^{+}$
- $H^{+}$  &  $OH^{-}$  especially effective in flocculation
- Flocculating ions must have sufficient charge to attract multiple particles to cause coagulation

## **COLLOIDS - 8**

### **Stability and Transport of Colloids**

- **Formation & stability of a metal compound sol determines the effectiveness of transport in surface or groundwaters**
- **Sols must be stable if metals are to be transported long distances**
- **Influence of electrolytes in transporting waters is obviously important**
- **Some colloids are stable in fresh water streams and coagulate upon entering saline water ( $\text{Fe}(\text{OH})_3$ )**
- **Effect of heat on stability is variable; enhances some, others not**

## **COLLOIDS - 9**

### **Stability and Transport of Colloids, continued**

- **Many colloids are more stable in the presence of a second colloid - a protective colloid**
- **Most protective colloids are hydrophilic**
- **A trace of gelatin will stabilize a copper sulfide sol**
- **Natural organic colloids will stabilize Fe & Mn oxide sols, an important consideration since these two oxides sometimes carry contaminant elements**
  - **this is of special concern in acid mine drainage**

## **COLLOIDS - 10**

### **Geologic evidences of former colloids**

- **Many amorphous or finely crystalline materials show evidences of once have being colloidal:**
  - smooth rounded surfaces (botryoidal)
  - indistinct color banding similar to Lesegang rings
  - chert has texture, banding & rounded surfaces
- **Problem is that solid materials have not been prepared from jels in the laboratory - jels always shrink, crack and form flakes upon dehydration**
- **Many natural materials that cannot be synthesized in lab show former colloidal characteristics**
- **Similar char shown by metallic ores in hydrothermal veins**