Ion (Ad)sorption

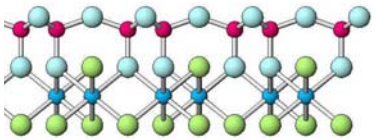
- Interaction between ion and surface
  - Ion Exchange
    - Reversible
  - Chemisorption (Specific adsorption)
    - Largely irreversible
  - Precipitation
  - Absorption (partitioning)

Ion Exchange

- Extremely rapid
- "Outer sphere"
- Reversible
- Stoichiometric
- Depends on:
  - Characteristics of ions
  - Characteristics of surface
  - Ionic strength of solution
  - Relative concentrations of competing ions

Charge dependent on mineralogy

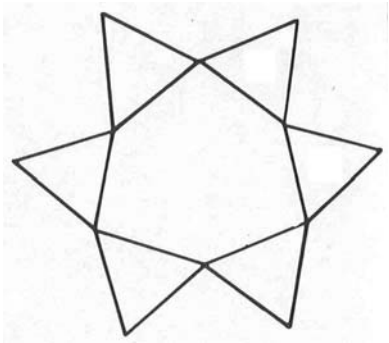
- Alumino-silicates
  - Permanent charge
    - Isomorphic substitution
  - Variable charge
    - Charge varies with pH
    - "Broken edges"



In clay minerals, the magnitude of variable charge much smaller than permanent charge

Siloxane surface

- Distorted hexagonal hole in Si sheet
- "ditrigonal"
- Surface O (3) have partial negative charge
- Stronger when iso' substitution is close to surface



Variable charge

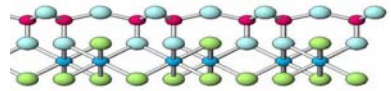
- PDI—potential determining ion
  - usually H^+ and OH^-
  - adsorption of phosphate could result in an increase in negative charge
- Increasing the pH will increase dissociation of H^+ and increase negative charge.
- Increasing the ionic strength will also increase dissociation and increase the charge.
- The charge in forest soils and tropical soils is predominantly variable in nature.

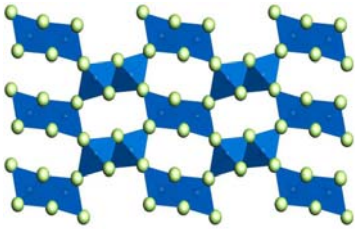
Development of charge on oxides

- Bond strength
  - Metal valence (IV for Si and Ti, III for Al and Fe)
  - Coordination (tetrahedral (4) or octahedral (6))
- Electronegativity of the metal
  - > indicates > covalency in bond with O and > acidity
  - Less likely to take on another H^+
- Relative hardness of the metal
  - Harder again indicates greater acidity

Types of variable charge

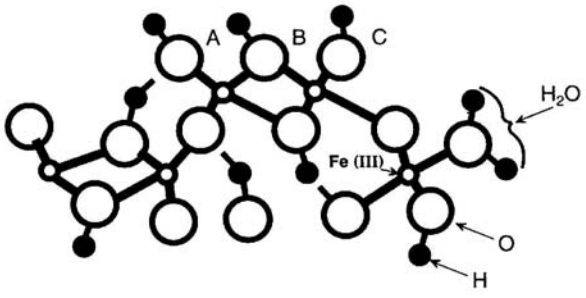
- Phyllosilicate edges
- Oxides
  - Surface hydroxyls
- Organic matter
  - Carboxylic
  - Phenolic





Ramsdellite (MnO_2)

Three types of surface hydroxyl groups on goethite



Goethite (FeOOH)

A: single
C: double
B: triple

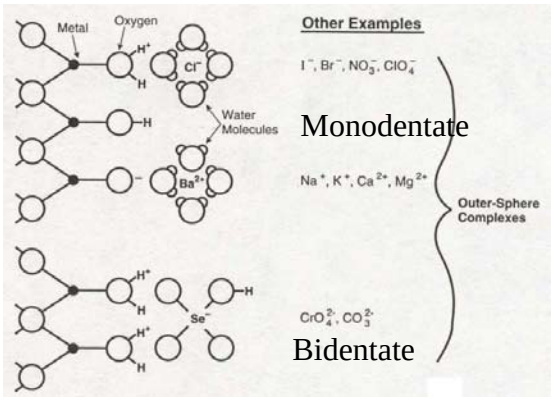
Only type A (single) will accept another proton.

Ion Sorption

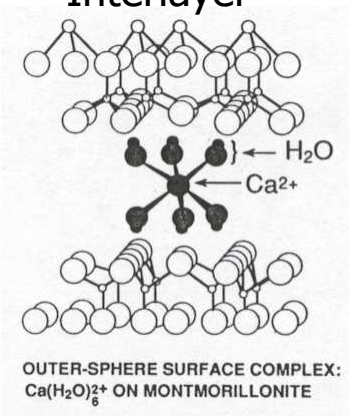
Outer Sphere	Inner Sphere
electrostatic interaction	ionic or covalent bond
rapid	slower
reversible	not reversible
affected by ionic strength	not affected by ionic strength
surface charge dependant	surface charge independant
	affects surface charge

Ion Exchange

Surface

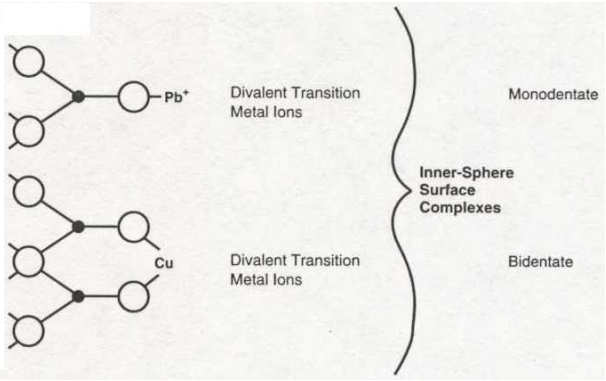


Interlayer

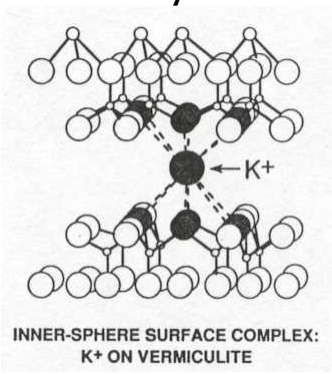


Chemisorption

Surface



Interlayer



Chemisorption (specific adsorption)

- High degree of specificity
- Tendency toward irreversibility
- Can change the charge of the surface
  - Adsorbed metal becomes part of the surface

Chemisorption

- For the most part, chemisorption occurs at sites were a valence-unsatisfied OH^- or H_2O ligand is bound to a metal ion (Fe^{3+}, Al^{3+}, Mn^{3+}, Mn^{4+}).
  - "Broken edges"
  - Allophanes (non-crystalline aluminosilicates)
  - Oxides and hydroxides of Al, Fe, Mn
- Silanol (SiOH) and aluminol (AlOH) groups

Components of surface charge

- σ_o – isomorphic substitution, permanent
- σ_H – surface plane, variable charge
- σ_{is} – inner sphere complexes
- σ_{os} – outer sphere complexes
- σ_d – diffuse ion swarm
- σ_p – sum of all but diffuse ion swarm

New Terms

- PZC: Point of zero charge
  - $\sigma_p = 0$; mineral surface has no charge
- PZNC: Point of zero net charge
  - CEC = AEC; soil has no net charge
- PZNPC: Point of zero net proton charge
  - $\sigma_H = 0$; variable charged surface at 0
- PZSE: Point of zero salt effect
  - effect of ionic strength is minimal

PZC - minerals

α-Al_2O_3	9.1	δ-MnO_2 (vernadite)	2.8
α-$Al(OH)_3$	5.0		
γ-AlOOH	8.2	β-MnO_2 (pyrolusite)	7.2
CuO	9.5		
Fe_3O_4	6.5		
α-FeOOH	7.8		
α-Fe_2O_3	6.7		
"$Fe(OH)_3$"	8.5		

AEC vs CEC (PZNC)