

Surface Chemistry and Ion Exchange

1. Importance of surface processes

Surface chemistry is a fundamental part of aqueous geochemistry – there is no such thing as rock-water interactions, there are only water-surface interactions. Everything is really happening on a mineral surface, including

- Dissolution and Precipitation
- Adsorption
- Ion Exchange
- Isotopic exchange
- Mineral redox (oxidative and reductive dissolution)

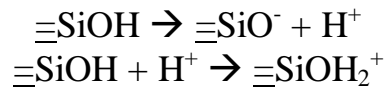
There are many types of surfaces that react with solutes, and include::

- Inorganic Colloids
- Organic Colloids
- microbes
- Mineral surfaces

2. Atomic Nature of the Oxide Surface

An oxide mineral surface, such as silicates, can be thought of as a surface of hydroxyls that participate in acid-base reactions and ion exchange. This surface is formed by:

1. When an oxide mineral is cleaved, it exposes dangling bonds to metals and oxygen wherever the fracture cut a chemical bond.
2. Water reacts with this surface, adding hydrogen to the oxygen atoms, and hydroxyls to the metals, resulting in a surface of metal-hydroxides, and bridging oxygens.
3. Each of these hydroxides can accept or donate a proton similar to the behavior of water, for example with quartz or silica:



These sites are amphoteric, and each of these reactions can be characterized by an equilibrium expression, e.g.::

$$K_0 = \frac{[\equiv \text{SiO}^-]}{[\equiv \text{SiOH}][\text{H}^+]}$$

where K_0 is the dissociation equilibrium constant analogous to the K_a used in acid base chemistry. For most oxides, the K_0 is very similar to the K_a for the analogous solution hydroxo or aquo complex of that metal, except Quartz.

3. Zero Point of Charge

1. The zero point of charge is a fundamental description of a mineral surface, and is more or less the point where the total concentration of surface anionic sites is equal to the total concentration of surface cationic sites, and most (but not all) of the sites are as the neutral hydroxide, i.e.:

$$ZPC = \left\langle [\equiv SiOH_2^+] = [\equiv SiO^-] \right\rangle$$

2. At pH values above the ZPC, the surface has a net negative or anionic charge, and the surface would participate in cation attraction, and cation exchange reactions.
3. At pH values below the ZPC, the surface has a net positive charge, and the surface will attract anions, and participate in anion exchange reactions.
4. Each mineral, and even mineral crystal structure has a ZPC, although the measurement of this property is difficult, and values and even names for the property vary, including *point of zero charge*, *point of zero net proton charge*.

| Material | pH _{pznpc} | Material | pH _{pznpc} |
|----------------------------------|---------------------|-------------------------|---------------------|
| α-Al ₂ O ₃ | 9.1 | δ-MnO ₂ | 2.8 |
| Corundum | | Birnessite | |
| α-Al(OH) ₃ | 5.0 | β-MnO ₂ | 7.2 |
| γ-AlOOH | 8.2 | SiO ₂ | 2.0 |
| CuO | 9.5 | ZrSiO ₄ | 5.0 |
| Magnetite | 6.5 | Feldspars | 2-2.4 |
| α-FeOOH | 7.8 | Kaolinite | 4.6 |
| Goethite | | | |
| α-Fe ₂ O ₃ | 8.5 | Montmorillonite | 2.5 |
| Hematite | | Hydroxyapatite | 7.6 |
| Fe(OH) _{3am} | 8.5 | Albite | 2.0 |
| MgO | 12.4 | Chrysotile | >10 |
| Calcite | 9.5 | Rutile TiO ₂ | 5.8 |

5. The charge developed on oxide surfaces is called the *temporary* or *variable* charge, because it depends on the pH. As pH increases above the ZPC, the anionic charge density increases, and the amount of exchange increases. The variable charge however is relatively weak overall, and is always less than the permanent charge of a clay mineral.

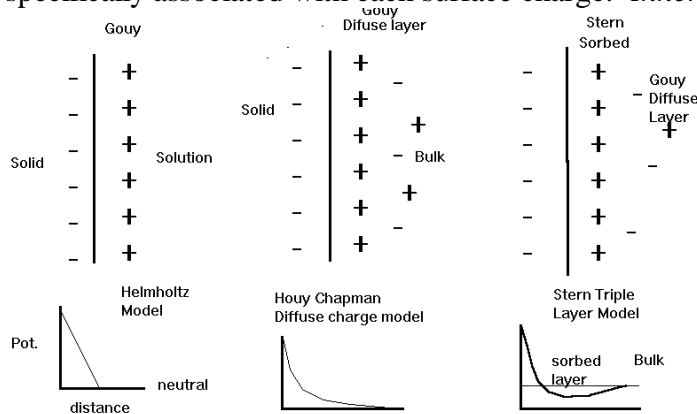
4. Electrical Double Layer

1. The electrical double layer is a continuum description of the nature of a charged mineral surface that tries to account for the charge density and the thermodynamics of ion exchange and charge attraction at the surface.
2. The double layer model reflects an unequal distribution of charges at the mineral-water boundary, and depends on the distribution of ions at the surface.
3. **Hydration Spheres:** All ions in water are hydrated to some extent, as the water dipole is attracted to the charged ion, and forms a structure with it, and with the surrounding water. Close to a charged ion or surface, the water is highly structured and closely

associated with the charge. Away from that charge the water is more and more like a bulk liquid with continuum properties.

| Ion | Ionic Radius (pm) | Hydrated Radius |
|------------------------|-------------------|-----------------|
| Li⁺ | 68 | 600 |
| Na⁺ | 97 | 450 |
| K⁺ | 133 | 300 |
| Rb⁺ | 147 | 250 |
| Cs⁺ | 167 | 200 |
| Mg²⁺ | 66 | 800 |
| Ca²⁺ | 99 | 600 |
| Sr²⁺ | 112 | 500 |
| Ba²⁺ | 134 | 450 |
| Fe²⁺ | 74 | 600 |
| Fe³⁺ | 64 | 900 |

- The inner layer is the fixed or variable charge on the mineral surface. For most silicates at environmental pH values the fixed layer is usually anionic. The outer layer can be composed of two types of sorbing ions:
 - Inner Sphere Complexes:** These are solution complexes that closely associate with the charged mineral surface (*chemisorption*), often forming specific bonds with the mineral surface. *Structure Breaker* ions form inner sphere complexes
 - Outer Sphere Complexes:** These complexes are formed as hydrated ions approach a mineral surface – the ion has charge, but the hydration sphere prevents the close approach of the ion to the hydrated surface, precluding the formation
- There are 3 general layer models with increasing complexity that describe surface charge:
 - Helmholtz Model:** A simple electrostatic interaction at the surface with 2 charged layers, an inner fixed charge layer and an outer solution charge layer that is specifically associated with each surface charge. *Inner sphere only.*



- Gouy Chapman Diffuse charge model:** A fixed charge is countered by a diffuse charged zone (Gouy layer), reflecting thermal forces. *Outer Sphere only.*
 - Stern Triple Layer Model:** The fixed layer is countered by a inner sphere sorbed layer of opposite charges (Stern Layer). This sorbed layer is countered by a diffuse Gouy layer.

5. Ion Exchange

- Oxides and clay minerals all exhibit ion exchange behavior to some degree, as different ions exchange places at the sorbed layer. Minerals with fixed charge, such as the clays, have high degrees of ion exchange.
- In every double layer one type of counterion can be exchanged for another type of the same sign.

a) Cation Exchange Capacity:

| Mineral | CEC (meq/100g) |
|-----------------------------|-------------------|
| Kaolinite | 3-15 |
| Montmorillonite | 80-120 |
| Chlorite | 10-40 |
| Vermiculite (Trioctahedral) | 100-200 |
| Vermiculite (Dioctahedral) | 10-150 |
| Allophane | 3-100 |
| Gibbsite | 4 |
| Goethite & Hematite | 4-100 |
| Illite | 20-50 |
| Glauconite | 5-40 |

- Can be defined as the excess of counterions that can be exchanged with other cations.
- The Gouy layer counterions exchange very quickly, Stern layer cations are sorbed, so they react much slower.
- Operationally defined by the uptake and release of ammonium ions from a 1m ammonium acetate solution at pH 7, and expressed in units of meq/100g.
- CEC of a bulk soil can be estimated from the formula:

$$\text{CEC (meq/100g)} = (0.7 \times \% \text{ clay}) + (3.5 \times \% \text{ OC})$$

For typical soils, CEC are:

| Soil | CEC | pH |
|-----------|-------|------|
| Ultisols | 3.5 | 5.6 |
| Alfisols | 9.0 | 6.0 |
| Spodosols | 9.3 | 4.93 |
| Vertisols | 35.6 | 6.72 |
| Aridisols | 15.2 | 7.26 |
| Entisols | 11.6 | 7.32 |
| Histosols | 128.0 | 5.50 |

b) Selectivity

- Gouy theory predicts that multivalent ions are concentrated in the double layer to a much larger extent than the monovalent ions, due to charge density:

So $\frac{(\text{Ca}^{++})}{(\text{Na}^{+})}$ is much greater on the anionic mineral surface than in the bulk solution

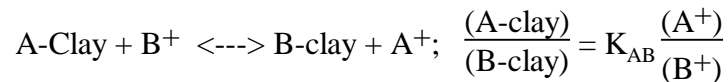
- This preference for the divalent cation decreases with increasing ionic strength, i.e. in dilute waters, the dominant exchangeable cation is calcium.
- In seawater, the dominant exchangeable cation is sodium.
- Gouy theory does not predict selectivity between cations of similar valence. This is done by the The Eisenmann Affinity series, which predicts selectivity of like charged cations based on fixed charge AND interaction with water (Hydration spheres),
- Where ion-dipole forces dominate, (Usually) the Hofmeister series is seen, and

$$\text{Cs} > \text{K} > \text{Na} > \text{Li}$$

$$\text{Ba} > \text{Sr} ? \text{Ca} > \text{Mg}$$
- Where the ion with the larger *hydrated* radius is displaced by the smaller ion. So Li is displaced by sodium and Na is displaced by Ca
- Where Coulombic interactions dominate, the reverse is seen, and preference is given to the decreasing *crystal* radius.

4. Ion Exchange Equilibria:

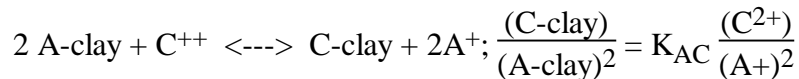
a) Exchange of like charged cations:



Where: K_{AB} is the exchange constant when written as activities.

- When written as mole fractions and concentrations, this is the selectivity coefficient. This is not a constant because the activity-mole correction will vary as a function of the ratio of A to B on the solid.

b) Exchange between a monovalent and divalent cation:



- The squared term is important:
 - the ratio of C on the exchanger to that of A (in meq) at 1 molar is 0.61
 - in a 1 millimolar solution, the X_c/X_a ratio is 31!
 - The divalent cation has almost completely displaced the monovalent cation on the exchange sites.

Selectivity of ions relative to Na, using equivalent fractions.

| Ion I ⁺ | $K_{Na/I}$ | Ion I ²⁺ | $K_{Na/I}$ | Ion I ³⁺ | $K_{Na/I}$ |
|------------------------------|------------|---------------------|------------|---------------------|------------|
| Li ⁺ | 1.2 | Mg ²⁺ | 0.5 | Al ³⁺ | 0.6 |
| K ⁺ | 0.2 | Ca ²⁺ | 0.4 | Fe ³⁺ | |
| NH ₄ ⁺ | 0.25 | Sr ²⁺ | 0.35 | | |
| Rb ⁺ | 0.1 | Ba ²⁺ | 0.35 | | |
| Cs ⁺ | 0.08 | Mn ²⁺ | 0.55 | | |
| | | Fe ²⁺ | 0.6 | | |
| | | Co ²⁺ | 0.6 | | |
| | | Ni ²⁺ | 0.5 | | |
| | | Cu ²⁺ | 0.5 | | |