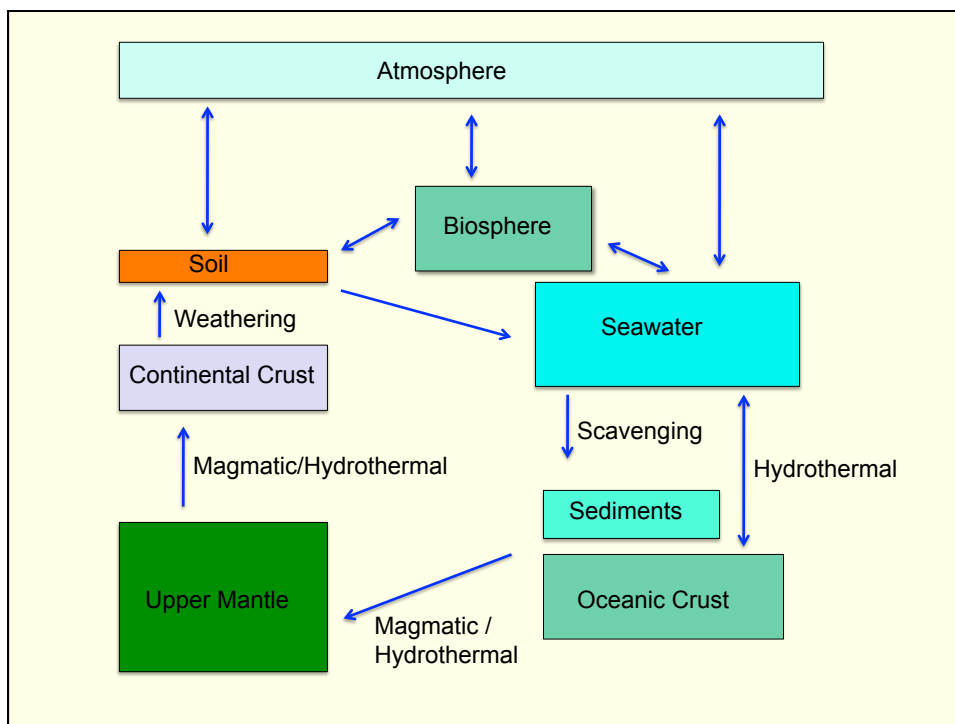


# Introduction and Review of Chemical Equilibrium

Advanced Aqueous Geochemistry  
DM Sherman, University of Bristol



## Open vs. Closed Systems

**Open Systems** can exchange matter with the surroundings.

An open system will evolve to *steady state*.

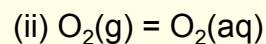
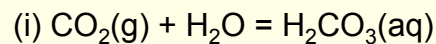
**Closed Systems** cannot exchange matter and have constant composition.

A closed system will evolve to *chemical equilibrium*.

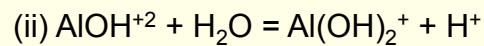
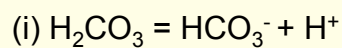
No geochemical system is closed; however we can say a system is approximately closed on a particular time-scale.

## Types of Chemical Reactions

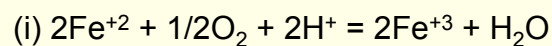
### Gas Dissolution:



### Acid-base reactions:

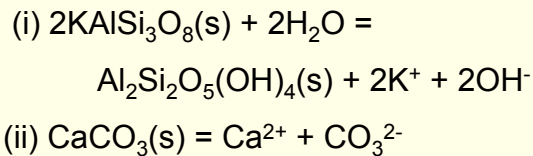


### Redox reactions:

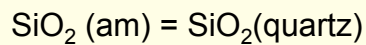


## Types of Chemical Reactions (cont.)

### Mineral dissolution:

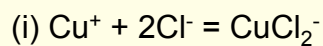


### Mineral recrystallization:

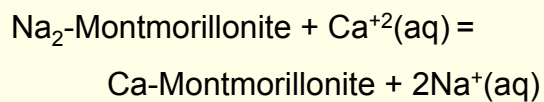


## Types of Chemical Reactions (cont.)

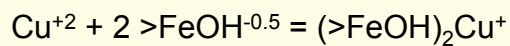
### Complexation:



### Ion Exchange:



### Surface Complexation:



## Thermodynamic Quantities

**Gibbs Free Energy** (G) = a measure of driving force of a process or chemical reaction:

$$\Delta G = \Delta H - T\Delta S$$

If  $\Delta G < 0$ , the process is spontaneous. If  $\Delta G > 0$ , process unfavoured.  $\Delta G$  is also the amount of non-PV work that can be done by a process.

## Chemical Equilibrium

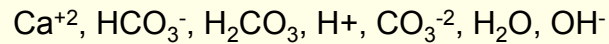
A chemical process will eventually run down so that the free energy difference between products and reactants is zero. The system can no longer do work.

$$\Delta G = \Delta H - T\Delta S = 0$$

We call this state “chemical equilibrium”. The goal of thermodynamics is to predict what the system will be like at chemical equilibrium.

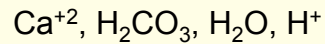
## Species vs. Components

The **chemical species** of a system are the atoms/ molecules/complexes etc. that form in the system.

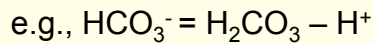


The **chemical components** of a system are the minimum set of chemical species needed to define all the other chemical species in the system:

These chemical components:

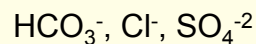
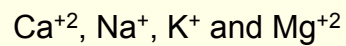


can define other chemical species in the list above

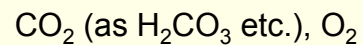


## Chemical Components in Natural Waters

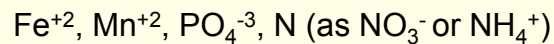
**Major components:**



**Dissolved Gases:**



**Important trace components:**



## Free Energy of Mixtures

Define the **chemical potential** of species  $i$  as

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (n_i \text{ is the number of moles of } i)$$

Using the chemical potential, we can define the free energy of a mixture:

$$G = G(P, T, n_1, \dots, n_i)$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

## Chemical Potential and Activity

The free energy of a species in a phase is called its **chemical potential** ( $\mu_i$ )

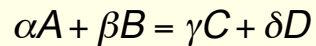
$$\mu_i = \mu^0 + RT \ln(a_i)$$

$\mu_i^0$  is the free energy/mole of species  $i$  in its **standard state**.

$a_i$  is the **activity** of species  $i$  in the phase.

## The Equilibrium Constant

Consider a chemical reaction where A and B reversibly transform to C and D:



Eventually, this reaction will go to equilibrium so that  $\Delta G = 0$ . At equilibrium, we will find that

$$K = \left( \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \right) \quad \text{with } \ln K = -\Delta G^0 / RT$$

$$\Delta G^0 = (\delta\mu_D^0 + \gamma\mu_C^0) - (\alpha\mu_A^0 + \beta\mu_B^0)$$

Prove this yourself!

## The Equilibrium Constant (cont.)

$$K = \left( \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} \right) \quad \text{with } \ln K = -\Delta G^0 / RT$$

where  $a_i$  is the **activity** of species  $i$ .

$\Delta G^0$  is the change in free energy when all components are in their **standard state**.

## Standard States

- For **solid solutions**, we can define a standard state of a component as being the solid phase made of the pure component.
- For **ions in aqueous solution**, we usually define the standard state as being a 1 m solution with the properties of infinite dilution (!). **The activity of an ion in a dilute aqueous solution will be its molal concentration.**
- For **components in a gas phase**, the standard state is a pure gas (ideal) at 1 bar pressure.

## Concentration Units

**Molality**: moles of species/component per kg of water.

**Normality**: equivalents of species per kg of water (usually based on charge)

**Molarity**: moles of species/component per litre of water

**ppm**: mg of component per kg of water

**ppb**:  $\mu\text{g}$  of component per kg of water



## Minerals in Equilibrium with Natural Waters

### Sulphates, Carbonates:

Calcite  $\text{CaCO}_3$ , Gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

### Clay Minerals:

Smectites, Kaolinite, Illite, Chlorite

### Secondary Oxides:

Goethite ( $\alpha\text{-FeOOH}$ ), Birnessite ( $\delta\text{-MnO}_2$ )

*Note: primary igneous and metamorphic minerals (except for quartz) will almost never be in equilibrium with an aqueous solution at low P,T.*

## The Phase Rule

$$f = c - p + 2$$

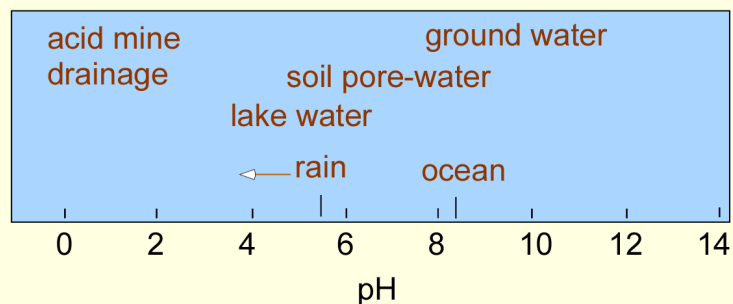
- A **phase** is something that can be mechanically separated from the other phases (e.g., ice, water).
- A **component** is one of the smallest number of chemical species needed to define the compositions of the phases in the system (e.g.,  $\text{H}_2\text{O}$ ).
- A **degree of freedom** is a property that can be independently varied (e.g., P, T).

## Applications

- Understanding how the lithosphere is coupled to the hydrosphere/atmosphere (weathering, soil formation).
- How ore-deposits form and how to process the ore.
- Fate of contaminants in soil and groundwater.
- Chemical effects of deep-well injection schemes.
- Generation and fate of acid-mine drainage.
- Chemistry and treatment of mine pit lakes.

## pH values in the Environment

The pH of natural waters are usually buffered by reactions with rocks or with the atmosphere:

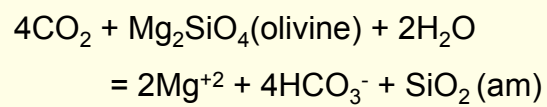


## Alkalinity

Defined as:

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Reaction of  $\text{CO}_2$  with rock produces excess  $\text{HCO}_3^-$  over  $\text{H}^+$ :



For waters reacting with a given rock type, the alkalinity will increase with the degree of weathering.