

Thermodynamics

Aqueous Geochemistry

What to learn from this lecture:

1. **Thermodynamic systems:** What are thermodynamics? How do we describe thermodynamic systems?
2. **Chemical Energy:** How do we calculate whether a chemical reaction will occur spontaneously? How much energy does a chemical reaction use or release?
3. **Chemical equilibrium:** What is chemical equilibrium? What is the composition of a given system at equilibrium?
4. **Temperature:** How do chemical reactions respond to changes in temperature?

Open systems exchange mass and energy with their environment



What if we cut the system off from external influences?

Chemical equilibrium is used to understand chemical reactions in a ***closed system*** at constant temperature and pressure

- No mass moves into or out of the system (energy can be transferred)
- Good approximation for systems where chemical reactions occur more quickly than the chemical species are transported out of the system

SYSTEM



If there are no external inputs, a system will move towards a state of equilibrium...

Equilibrium

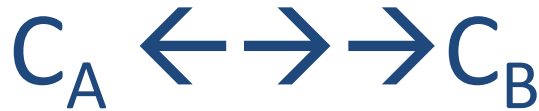
- concentrations of components in a system are constant
- the rate of a forward reaction is equivalent to the rate of a backwards reaction



If there are no external inputs, a system will move towards a state of equilibrium...

Disequilibrium

- concentrations of components in a system are changing
- the rate of a forward reaction is NOT equivalent to the rate of a backwards reaction
- System moves towards the equilibrium state



WHAT WE LEARNED TODAY:

1. Chemical reactions result in the transfer of energy between a system and its surroundings, and reactions occur spontaneously when energy is lost from a system to its surroundings.
2. Gibbs free energy of a reaction at standard state (ΔG^0_{rxn}) can be calculated from changes in enthalpy, ΔH^0_{rxn} (heat), and entropy, S^0_{rxn} (disorder)
3. The Gibbs free energy of a reaction (ΔG_{rxn}) depends on the activities (or fugacities) of the reaction components, i.e. how far away the system is from equilibrium
4. A system is at equilibrium when the energy of the system is minimized, $\Delta G_{\text{rxn}} = 0$ and the $a_{\text{products}}/a_{\text{reactants}} = K_{\text{eq}}$ (the equilibrium constant)