The concept of equilibrium

- Chemical reactions often involve a series of processes that may oppose each other.
- At some point the *rate* at which one process takes place will be equal to the *rate* at which another takes place. Thus there is no **net** change in the system, but changes are still happening!
  - Dynamic equilibrium (vs. static equilibrium)
- These reactions are usually indicated with two arrows to imply (microscopic) reversibility

Descriptions of dynamic equilibrium

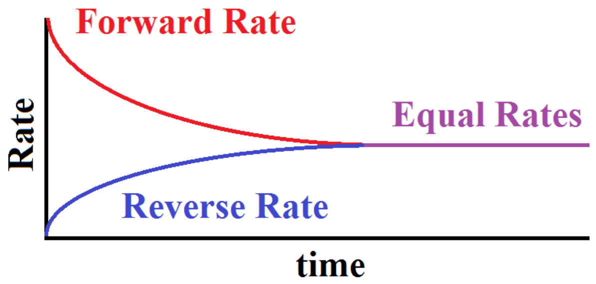
- In general we represent this as

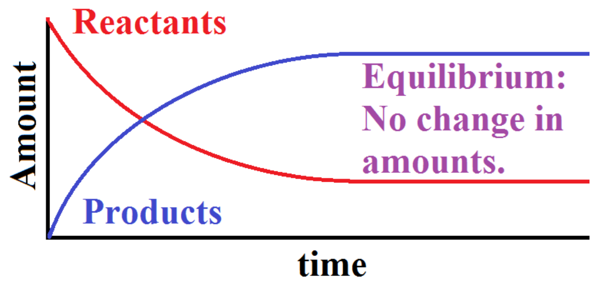
$$\text{Reactants} \rightleftharpoons \text{Products}$$

- Mathematically the reaction rate is related to the rate of change of the concentration of a product or reactant

$$rate = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

- Graphically we can represent the change in reaction rate or amount





http://www.chem.queensu.ca/people/faculty/mombourquette/firstyrchem/equilibrium/

The equilibrium constant

- It turns out that the *ratio* of products to reactants in a reversible reaction is indicative of the state of equilibrium
- For a chemical reaction $aA + bB \rightleftharpoons cC + dD$

  The equilibrium constant K (K_{eq}, K_c) is defined as $K = \frac{a(C)^c a(D)^d}{a(A)^a a(B)^b}$ where a represents the activity. Typically the activities are replaced with concentrations in *M* (this assumes the concentrations are fairly dilute)

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Notes on the equilibrium constant

- K is meant to give an impression of “how well” a reaction proceeds.
  – Large value of K means the reaction proceeds nearly to completion (products far outweigh reactants)
  – Small value of K means the reaction barely happens at all
- ALL reactions are really reversible, but practically reactions with very large K values ($>10^{10}$) are said to proceed irreversibly
- K is dimensionless because each term is really divided by a reference activity, which is equal to 1.

More notes on the equilibrium constant

- K is a measure of the thermodynamic stability of the products in comparison to the reactants.
- It says NOTHING about the speed of a chemical reaction, just which side (products or reactants) are favored. To understand the effects of concentration on the rates of a reaction, we have to look at kinetics
- Often there is a delicate interplay between kinetics and thermodynamics

Heterogeneous Equilibria

- Often chemical processes occur where various phases are present simultaneously.
- Although the amounts of liquids and solids may change throughout the course of a reaction, typically the activities for PURE liquids and solids are very close to one, which means that the concentration of a solid or liquid is close to one. Thus we ignore it in an equilibrium expression.
- The only quantities that appear in an expression for K are gases and concentrations in a solution.

Le Châtelier's Principle (1888)

- When a system already at equilibrium is disturbed, the system will respond in such a way as to relieve the stress that was imposed on it.
- The disturbances include varying the concentration, pressure, and temperature.
- *Except for temperature, all disturbances are temporary and the system will revert back to the original equilibrium point!*

Effects of disturbances on the system

- Concentration
  - If the concentration of one of the reactants is increased, then the corresponding reaction quotient will decrease, meaning that the reaction will go forward to try to achieve equilibrium.
  - Conversely, if the concentration of one of the products is decreased (done by removing the product continuously as it is being formed), then Q will still decrease, so the reaction will still go forward!
  - Generally high concentrations of reactants are favored, but this may not be possible (economics, availability, safety, etc.)

Effects of disturbances on the system

- Volume of the container (gases only)
  - For a reaction involving gases, the volume is inversely related to the concentration. Thus decreasing the volume is akin to increasing the concentration, and vice versa.
  - Thus we can treat volume changes in an equivalent fashion to concentration changes.
  - Typically as small a container as possible is best – though this will also mean the pressure will increase… so it must still be safe and able to withstand this!

Effects of disturbances on the system

- Pressure (gases only)
  - Liquids and solids are fairly incompressible so reactions involving these are not typically affected by pressure.
  - If the total pressure is increased by decreasing the volume, then this has already been explained (effect of volume and concentration)
  - If the total pressure is increased by increasing the partial pressure of one of the components, then the reaction will shift in the direction of less moles of gas.
    - Higher P_i means greater number of moles, which need to occupy the same volume as before. The system would prefer to have as few moles as possible in the same volume (since $V \alpha n$) and so will shift to alleviate this stress.
  - If the total pressure is increased by adding an inert gas, then the equilibrium will be unaffected
    - The partial pressures of the components remain unchanged so K_p is the same!

Effects of disturbances on the system

- Catalyst
  - A catalyst helps to accelerate the course of a reaction by providing an alternate pathway. Although the kinetics (rate) of the reaction may be altered drastically, this will have **no effect** on the thermodynamics (stabilities) of the reactants and products (only the intermediates throughout the course of the reaction)

Effects of disturbances on the system

- Temperature
  - The effect of altering the temperature will be based upon the enthalpy change (ΔH) for the reaction.
    - If $\Delta H<0$ then increasing the temperature will cause the reaction to shift to the left
    - If $\Delta H>0$ then increasing the temperature will cause the reaction to shift to the right
  - This is the only factor that will **permanently** affect K since K=K(T)

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

Equilibria can be expressed in different ways

- For gases, sometimes it is more convenient to express quantities in terms of pressures than in terms of concentrations.
- Let K_c be the equilibrium constant for the reaction $aA + bB \rightleftharpoons cC + dD$ (using concentrations) and K_p be the equilibrium constant for the same reaction (using partial pressures).
- It can be shown that $K_p = K_c(RT)^{\Delta n}$ where $\Delta n = n_{gas}(\text{products}) - n_{gas}(\text{reactants})$

Convert the value of K_P to a value of K_c.

(d) $H_2O(l) \rightleftharpoons H_2O(g)$ K_P = 0.122 at 50 °C

Quantitative Aspects of the Equilibrium Constant

- The equilibrium constant is useful because it establishes a relationship between the initial concentrations and equilibrium (“final”) concentrations of chemical species in a chemical reaction
- Fundamentally this approach can be used for ANY equilibrium process
  - Homogeneous/Heterogeneous reaction
  - Acid-Base
  - Solubility
  - Complexation

Quantitative Aspects of the Equilibrium Constant

- The key to all these problems is to set up a systematic relationship between the concentrations of all the reactants and products.
- This is most easily done using the "ICE" box.

$$aA + bB \rightleftharpoons cC + dD$$

Initial	A_o	B_o	C_o	D_o
Change	-ax	-bx	+cx	+dx
Equilibrium	A_o-ax	B_o-bx	C_o+cx	D_o+dx

$$K = \frac{[C_0 + cx]^c [D_0 + dx]^d}{[A_0 - ax]^a [B_0 - bx]^b}$$

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures:

$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?