THE CONCEPT OF EQUILIBRIUM

Few physical and chemical changes proceed only in one direction. Fire is one chemical change that does. Once burned, a piece of paper cannot be restored.

The evaporation of water in a *closed* system is a ***reversible*** physical change that establishes a *dynamic equilibrium*. At equilibrium, when water seems to ceases evaporating, water is still evaporating but recondensing at the same rate. There is no net change, (therefore equilibrium)but molecules are continually shuttling between the liquid and vapor state (dynamic). Many chemical systems act in this manner where product is continually being formed and then back-reacting to form the reactants again.

THE EQUILIBRIUM CONSTANT

Weak acid dissociation in water is an example of a dynamic equilibrium. Acid molecules dissociate to anion and hydrogen ion, but the molecular acid reforms, keeping the acid concentration relatively high.

$$HA \leftrightarrow H^{+1} + A^{-1}$$

A value called the equilibrium constant can be assigned to the chemical system by measuring, at equilibrium, the concentrations of all the species.
The equilibrium constant, K can be taken as the product of the product molar concentrations divided by the reactant molar concentration

$$K_{eq} = [H^{+1}] \cdot [A^{-1}]/[HA]$$

The usefulness of K_{eq} is that remains *constant* for the system at one particular temperature. Its value does not change when any of the reactant or product concentrations are altered. The other concentrations adjust so that K_{eq} remains the same.

Ex: What happens to the system if $[H^{+1}]$ is changed? What happens if [HA] is changed? What happens if the temperature is changed?

In general, all chemical equilibrium systems obey the law of mass action. For the general equilibrium equation

$$aA + bB \leftrightarrow cC + dD$$

the equilibrium constant will be given by

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

The law of mass action can be extended to systems of any number or reactants and products. If K is much larger than unity, the reaction is said to lie on the right. If K is much smaller that one, then the equilibrium lies to the left.

As an example of the use of the exponents, note that if A is the same species as B and if D is not formed, in other words

$$1A + 1A \leftrightarrow cC + 0D \text{ or } 2A \leftrightarrow [C]^c$$

then the equilibrium expression becomes

$$K = [C]^c [D]^0/[A]^1 [A]^1 = [C]^c/[A]^2$$

EQUILIBRIUM CONSTANT EXPRESSIONS

Substances in solution will have their concentrations expressed in moles/liter or M. Gases require an expression to convert between M and pressure. Solids and liquids in heterogeneous systems will have their concentration expressed simply as unity, since their effective concentration will not change as long as some condensed phase remains.

HOMOGENEOUS EQUILIBRIA

All reactants and products are in the same liquid or gas phase.

$$A \leftrightarrow B$$

A can be (g) or (l) and B can be (g) or (l)

Concepts of K_c based on molar concentrations in gas or in solution and K_p, based on partial pressures of gaseous species.

$$K_c = [B]/[A]$$

whether A and B are in solution or in gas phase

$$K_p = P_B/P_A$$

In general $K_c \neq K_p$ unless the number of moles of gas does not change during the reaction.

If the equilibrium expression does not contain different powers of [A] or [B] in the numer denominator, the ration of [B]/[A] is the same as that of P_B/P_A. If there ore different pow [A] in the expression, then the ratio changes.
Text example of derivation of equation

$K_p = K_c (RT)^{\Delta n}$ calculation of the value of K_p requires the absolute temperature.

Ex: Write K_p and K_c for the decomposition of hydrogen peroxide.
Ex: Write K_p and K_c for the reaction of carbon dioxide gas with NaOH solution.