EQUILIBRIUM CONTANTS

MEANING OF VALUES

$$2H_2(g) + O_2(g) \iff 2H_2O(g)$$

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{9.1 \times 10^{80}}{1}$$

Very little reactant relative to product.

Requires 200,000L of water vapor to locate 2 H₂ and 1 O₂ molecules.

$$N_2(g) + O_2(g) \iff 2NO(g)$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31} = \frac{4.8}{10^{31}}$$

Very little product relative to reactant.

In general for either K_c or K_p

K value very large Reaction far toward completion

K value close to 1 Reactant and product concentrations nearly same

K value very small Hardly any products formed

EQUILIBRIUM EXPRESSION

Equilibrium Expression for General Reaction

$$aA + bB \iff cC + dD$$
 $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

Also termed "mass action quotient" or "reaction quotient"

For reverse reaction
$$cC + dD \ll aA + bB$$
 $K_c^{-1} = \frac{[A]^a [B]^b}{[C]^c [D]^d}$

If double reaction, all coefficients are twice original value so $\left(K_c\right)^2$ If ½ reaction, all coefficients are ½ original value so $\left(K_c\right)^{1/2}$

$$2A \iff C$$

$$K_1 = \frac{[C]}{[A]^2}$$

$$3B \iff 3D$$

$$2A + B \iff C + 3D$$

$$K_2 = \frac{[D]^3}{[B]}$$

$$K = K_1 K_2 = \frac{[C]}{[A]^2} x \frac{[D]^3}{[B]} = \frac{[C][D]^3}{[A]^2 [B]}$$

EQUILIBRIUM EXPRESSIONS

Relationship of K_p and K_c

For a gaseous reaction the ratio of products to reactants in terms of pressure (atm) is K_p

$$aA + bB \ll cC + dD$$

$$K_{c} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$
 and $K_{p} = \frac{P_{C}^{c} P_{D}^{d}}{P_{A}^{a} P_{B}^{b}}$

$$PV = nRT$$
 so $P = \frac{n}{V}RT = MRT$

$$K_{p} = \frac{P_{C}^{\ c} P_{D}^{\ d}}{P_{A}^{\ a} P_{B}^{\ b}} = \frac{(M_{C}RT)^{c} (M_{D}RT)^{d}}{(M_{A}RT)^{a} (M_{B}RT)^{b}}$$

Factor out RT

$$K_p = (RT)^{\Delta n_{gas}} \left(\frac{M_C^c M_D^d}{M_A^a M_B^b} \right)$$

Therefore

$$K_p = (RT)^{\Delta n_{gas}} K_c$$
 where $\Delta n_{gas} = (c+d) - (a+b)$

EQUILIBRIUM EXPRESSIONS

For the reaction: $2NO(g) + Cl_2(g) \iff 2ClNO(g)$, write the K_c and K_p equilibrium expressions.

$$K_{C} = \frac{[\text{ClNO}]^2}{[\text{NO}]^2[\text{Cl}_2]}$$
$$K_{P} = \frac{P_{\text{ClNO}}^2}{P_{\text{NO}}^2 P_{\text{Cl}2}}$$

At 500K, an equilibrium mixture contained 0.242 atm NO, 0.605 atm Cl_2 , and 1.38 atm ClNO. Determine the K_p and K_c values.

To calculate K_c the relationship $K_p = K_c(RT)^{\Delta n}$ is used.

$$K_{P} = \frac{P_{ClNO}^{2}}{P_{NO}^{2}P_{Cl2}} = \frac{(1.38atm)^{2}}{(0.242atm)^{2}(0.605atm)} = 53.7atm^{-1}$$

$$K_{P} = K_{C}(RT)^{\Delta n \text{ gas}}$$

$$53.7atm^{-1} = K_{C}(0.08206 \text{ L} \bullet atm/mol \bullet K * 500K)^{-1}$$

$$K_{C} = 2.20 \times 10^{3} \text{ M}^{-1}$$

HETEROGENEOUS EQUILIBRIA

Pure solids or pure liquids do not appear in equilibrium expression since their concentration is constant.

$$\begin{split} \text{EXAMPLE:} & \text{CaCO}_3(s) \\ \text{density} &= 2.71 \text{g/cm}^3 \end{split} <=> \frac{\text{CaO}(s)}{\text{density}} + \frac{\text{CO}_2(g)}{\text{cm}^3} \\ \text{[CaCO}_3] &= \left(\frac{2.71 \text{g}}{\text{cm}^3}\right) \left(\frac{1 \text{mol}}{100.1 \text{g}}\right) \left(\frac{1000 \text{ cm}^3}{1 \text{L}}\right) = 27.1 \text{ mol/L} \end{split}$$

[CaO] =
$$\left(\frac{3.25g}{cm^3}\right)\left(\frac{1mol}{56.1g}\right)\left(\frac{1000 \text{ cm}^3}{1\text{L}}\right) = 57.9 \text{ mol/L}$$

$$K = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$$\frac{K * [CaCO_3]}{[CaO]} = [CO_2]$$
So $K_c = [CO_2]$ and $K_p = P_{CO2}$