EQUILIBRIUM CONTANTS

MEANING OF VALUES

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

$$K_{c} = \frac{[H_{2}O]^{2}}{[H_{2}]^{2}[O_{2}]} = \frac{9.1 \times 10^{80}}{1}$$

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

If double reaction, all coefficients are twice original value so $(K_c)^2$ If $\frac{1}{2}$ reaction, all coefficients are $\frac{1}{2}$ original value so $(K_c)^{1/2}$ If add two reactions

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

$$\frac{3B \iff 3D}{2A + B \iff C + 3D} \qquad K_2 = \frac{[D]^3}{[B]}$$

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

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 <=> cC + dD

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

 $PV = nRT \quad so \qquad P = \frac{n}{V}RT = MRT$ $K_{p} = \frac{P_{C}^{\ c} P_{D}^{\ d}}{P_{A}^{\ a} P_{B}^{\ b}} = \frac{(M_{C}RT)^{c} \ (M_{D}RT)^{d}}{(M_{A}RT)^{a} \ (M_{B}RT)^{b}}$

Factor out RT

$$\mathbf{K}_{p} = \left(\mathbf{RT} \right)^{\Delta n_{gas}} \left(\frac{\mathbf{M}_{C}^{c} \ \mathbf{M}_{D}^{d}}{\mathbf{M}_{A}^{a} \ \mathbf{M}_{B}^{b}} \right)$$

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. 2

$$K_{\rm C} = \frac{[{\rm ClNO}]^2}{[{\rm NO}]^2 [{\rm Cl}_2]}$$
$$K_{\rm P} = \frac{P_{\rm ClNO}^2}{P_{\rm NO}^2 P_{\rm Cl2}}$$

At 500K, an equilibrium mixture contained 0.242 atm NO, 0.605 atm Cl₂, 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.

$$K_{P} = \frac{P_{C1NO}^{2}}{P_{NO}^{2}P_{C12}} = \frac{(1.38 \text{ atm})^{2}}{(0.242 \text{ atm})^{2}(0.605 \text{ atm})} = 53.7 \text{ atm}^{-1}$$

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

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

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

HETEROGENEOUS EQUILIBRIA

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

EXAMPLE:
$$CaCO_3(s) \iff CaO(s) + CO_2(g)$$

density = 2.71g/cm³ density = 3.25g/cm³

$$[CaCO_3] = \left(\frac{2.71g}{cm^3}\right) \left(\frac{1\text{mol}}{100.1g}\right) \left(\frac{1000 \text{ cm}^3}{1\text{L}}\right) = 27.1 \text{ mol/L}$$
$$[CaO] = \left(\frac{3.25g}{cm^3}\right) \left(\frac{1\text{mol}}{56.1g}\right) \left(\frac{1000 \text{ cm}^3}{1\text{L}}\right) = 57.9 \text{ mol/L}$$

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