Equilibrium & Pressure

With gases it is usually more useful to express the equilibrium expression in terms of pressure instead of concentration.

$$P = \left(\frac{n}{V}\right) RT \qquad PV = nRT \qquad P = CRT$$

If we look at the equilibrium expression from a generic equation we can see how the K_p is related to K.

$$j\mathrm{A} + k\mathrm{B} \iff l\mathrm{C} + m\mathrm{D}$$

$$K_p = \frac{{\mathrm{P_C}}^l {\mathrm{P_D}}^m}{{\mathrm{P_A}}^j {\mathrm{P_B}}^k} = \frac{(\mathrm{C_C} \cdot \mathrm{RT})^l (\mathrm{C_D} \cdot \mathrm{RT})^m}{(\mathrm{C_A} \cdot \mathrm{RT})^j (\mathrm{C_B} \cdot \mathrm{RT})^k} = \frac{C_C^l C_D^m}{C_A^j C_B^k} \cdot \frac{(\mathrm{RT})^{l+m}}{(\mathrm{RT})^{j+k}} = K(RT)^{(l+m)-(j+k)}$$

$$K_p = K(RT)^{\Delta n}$$

Heterogeneous Equilibria

We need to consider how solids and liquid concentrations can be dealt with in the equilibrium expression. When pure solids or liquids are part of a chemical reaction their concentrations are not included in the equilibrium expression.

$$\mathrm{CaCO_{3(s)}} \iff \mathrm{CaO_{(s)}} + \mathrm{CO_{2(g)}}$$

$$K' = \frac{[\mathrm{CO_2}][\mathrm{CaO}]}{[\mathrm{CaCO_3}]} \qquad K' = \frac{[\mathrm{CO_2}]C_1}{C_2} \qquad \frac{C_2 K'}{C_1} = K = [CO_2]$$

Reaction Quotient

The first thing we need to be able to calculate is which direction does a system need to move to establish equilibrium. To do this we calculate the reaction quotient (Q) and compare it to the equilibrium constant.

$$N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)} \qquad Q = \frac{{[NH_3]_o}^2}{[N_2]_o{[H_2]_o}^3}$$

There are three possibilities for the relationship of Q and K:

1- Q=K, the system is at equilibrium and no change in concentrations will take place.

2- Q>K, the ratio is too large. The concentration of products is too large. The system will shift to the left. The concentration of reactants will increase.

3- Q<K, the ratio is too small. The concentration of reactants is too large. The system will shift to the right. The concentration of products will increase.

Equilibrium Calculations

A common procedure for organizing equilibrium calculations uses the acronym ICE(Initial, Change, Equilibrium) to set up a chart to track the values.

A 1.0L tank has 1.00 mol each of CO, H_2O, CO_2, and H_2. What will be the equilibrium concentration of each species?

$$CO_{(g)} + H_2O_{(g)} \iff CO_{2(g)} + H_{2(g)}$$

I	1.0	1.0		1.0	1.0
C	-x	-x		+x	+x
E	1.0-x	1.0-x		1.0+x	1.0+x

$$K = \frac{[1.0+X][1.0+X]}{[1.0-X][1.0-X]} = 5.10$$

$$5.10 = \frac{[1.0+X]^2}{[1.0-X]^2}$$

$$\sqrt{5.10} = \frac{[1.0+X]}{[1.0-X]}$$

$$2.26 = \frac{[1.0+X]}{[1.0-X]}$$

$$2.26[1.0-X] = [1.0+X]$$

$$2.26 - 2.26X = 1.0 + X$$

$$\frac{1.26}{3.26} = X = 0.39$$