Lecture No: 3

3.4 Heterogeneous Equilibrium

If the substances are in more than one phase, the equilibrium is heterogeneous. In heterogeneous equilibrium, K_p contains only the pressures of the gaseous substances, pure solids and liquids are not included.

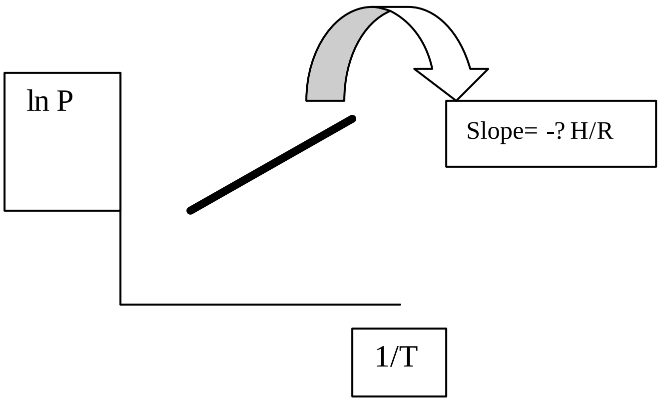
An important example is the equilibrium between a pure liquid and its vapor.

$$A(\ell) \rightarrow A(g) \qquad\qquad K_p = P$$

Using van't Hoff's equation we may obtain;

$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

This is the Clausius-Clapeyron equation. It relates the vapor pressure to the temperature. A plot of ln P versus 1/T is linear with a slope equal to $-\Delta H_v$/R.



3.5 The LeChatelier Principle

A chemical system at equilibrium has a certain T and P. If any one of these properties is changed, the equilibrium is destroyed. Then, the system shifts either to the right or to the left, in order to establish a new equilibrium state.

The LeChatelier principle shows how a change in temperature or pressure affects the degree of extent of a reaction.

$$\frac{dx}{dT} = \frac{\Delta H}{T.G''}$$

If the reaction is endothermic, $\Delta H > 0$ then an increase in temperature shifts the equilibrium to the right. Conversely, if the reaction is exothermic $\Delta H < 0$, then an increase in temperature shifts the equilibrium to the left. In other words, if T is increased, the equilibrium will shift to the high enthalpy side, or if T is decreased it shifts to the low enthalpy side.

$$\frac{dx}{dP} = -\frac{\Delta V}{G''}$$

If the pressure is increased, the equilibrium shifts to the low-volume side in order to decrease it. Conversely, if the pressure is decreased, it shifts to the high-volume side in order to increase it.

Concentration change also destroys equilibrium. If the concentration of the products is increased, then the reaction shifts to the left, to the reactants side. If the concentration of the products is decreased then the reaction shifts the equilibrium to the right, to the products side.

3.6 Application of the Equilibrium Constant

The equilibrium constant for the reaction:

$$N_2O_4(g) \leftrightarrow NO_2(g)$$

may be expressed in terms of the concentrations as:

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63x10^{-3}$$

For any chemical reaction:

$$aA + bB \rightarrow gC + dD$$

$$K = \frac{[C]^g [D]^d}{[A]^a [B]^b}$$ Law of Mass Action

Equilibrium will :

K>1 favor the PRODUCTS
K<1 favor the REACTANTS

The reaction quotient Q at any time during the reaction may be written in a similar form. It is used to determine the direction of the reaction :

If Q > K the reaction proceeds from right to left to reach equilibrium
If Q = K the reaction is at equilibrium
If Q < K the reaction proceeds from left to right to reach equilibrium

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

A + B $\rightarrow$ $\cancel{C + D}$ $\quad K_1 = \frac{[C][D]}{[A][B]}$

$\cancel{C + D}$ $\rightarrow$ E + F $\quad K_2 = \frac{[E][F]}{[C][D]}$

A + B $\rightarrow$ E + F $\quad K = K_1 K_2$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

A + B $\rightarrow$ C + D $\quad K_1 = \frac{[C][D]}{[A][B]}$

C + D $\rightarrow$ A + B $\quad K_2 = \frac{[A][B]}{[C][D]} = \frac{1}{K_1}$

Example #1

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^{0}C are [CO] = 0.012 *M*, [Cl_2] = 0.054 *M*, and [$COCl_2$] = 0.14 *M*. Calculate the equilibrium constants *Kc* and *Kp*.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_C = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{(0.012)(0.054)} = 220$$

$$K_P = K_C (RT)^{\Delta n}$$

? n = 1 – 2 = -1 $K_P = 220(0.082 * 347)^{-1} = 7.7$

Example #2

At 1280^{0}C the equilibrium constant (K_c) for the reaction;

$$Br_2(g) \rightarrow 2Br(g)$$

is 1.1 x 10^{-3}. If the initial concentrations are [Br_2] = 0.063 *M* and [Br] = 0.012 *M*, calculate the concentrations of these species at equilibrium.

Let *x* be the change in concentration of Br_2, then ;

Initial # of moles ………………..	0.063	0.012
Changes in the # of moles ……	- x	+2x
Equilibrium # of moles………..	0.063 – x	0.012 + 2x

$$K_C = \frac{[Br]^2}{[Br_2]} = \frac{(0.012 + 2x)^2}{(0.063 - x)} = 1.1x10^{-3}$$

4x^2 + 0.0491x + 0.0000747 = 0

x = - 0.0105 x = -0.00178

At equilibrium;

$$[Br] = 0.012 + 2x = -\cancel{0.009}............or.........0.00844$$

$$[Br_2] = 0.062 - x = 0.060$$