CHAPTER 4 LECTURE NOTES

Chemical Equilibrium Involving Ideal Gases (Replaces Sections 4.1):

Consider a reaction of the type

$$n_A A(g) + n_B B(g) \rightleftharpoons n_C C(g) + n_D D(g),$$

where A, B, C, and D all behave ideally. During the reaction, the partial pressure of each gas changes. The resulting free energy change for each gas can be expressed as

$$\Delta G_A = n_A RT \ln\left(\frac{P_{A,2}}{P_{A,1}}\right),$$

$$\Delta G_B = n_B RT \ln\left(\frac{P_{B,2}}{P_{B,1}}\right), \text{ and so on.}$$

If we assume that the reaction starts with each gas at the standard pressure, denoted as $P°$, we may write

$$G_A = G_A^\circ + n_A RT \ln\left(\frac{P_A}{P^\circ}\right),$$

$$G_B = G_B^\circ + n_B RT \ln\left(\frac{P_B}{P^\circ}\right), \text{ and so on.}$$

It is important to remember that the free energies in the expressions above are NOT molar quantities, i.e., we need to keep in mind that $G_A = n_A G_{m,A}$, $G°_A = n_A G°_{m,A}$, etc.. Now, the free energy change for the reaction may be written as

$$\boxed{\Delta_r G = \Delta_r G^\circ + RT \ln\left[\frac{(P_C/P^\circ)^{n_C}(P_D/P^\circ)^{n_D}}{(P_A/P^\circ)^{n_A}(P_B/P^\circ)^{n_B}}\right],}$$

where

$$\Delta_r G = (G_C + G_D) - (G_A + G_B)$$

$$= (n_C G_{m,C} + n_D G_{m,D}) - (n_A G_{m,A} + n_B G_{m,B}),$$

and $\Delta_r G°$ is similarly defined.

Now, at equilibrium, $\Delta_r G = 0$ and so, we get

$$\boxed{\Delta_r G^\circ = -RT\ln\left[\frac{(P_C/P^\circ)^{n_C}(P_D/P^\circ)^{n_D}}{(P_A/P^\circ)^{n_A}(P_B/P^\circ)^{n_B}}\right]_{eq}.}$$

The partial pressures that enter into this expression are the values measured at equilibrium and, therefore, is a constant at a given temperature. <u>Note that, because of the division of each pressure term by the standard pressure, the quantity within the square brackets is dimensionless</u>.

In other words,

$$\boxed{\begin{aligned}&\Delta_r G^\circ = -RT\ln K_P^\circ, \text{ or}\\ &\quad K_P^\circ = \exp\left[-\Delta_r G^\circ/(RT)\right].\end{aligned}}$$

This is the *thermodynamically correct* definition of the equilibrium constant with respect to pressure. <u>Note that, because of the division of each pressure term by the standard pressure, this is a dimensionless quantity</u>.

For real gases, the partial pressures must be replaced by the partial fugacities.

The equilibrium constant can also be expressed in terms of concentrations by substituting $P_A = n_A RT/V$, etc., and recognizing that $n_A/V = [A]$, etc., to get

$$\boxed{\begin{aligned}&K_P^\circ = K_C\left(\frac{RT}{P^\circ}\right)^{n_C+n_D-n_A-n_B}, \text{ where}\\ &K_C = \frac{[C]^{n_C}[D]^{n_D}}{[A]^{n_A}[B]^{n_B}}.\end{aligned}}$$

Also, by recalling that $P_A = x_A P$, where x_A is the mole fraction of A and P is the total pressure at equilibrium, we can express the equilibrium constant in terms of mole-fractions K_x:

$$\boxed{\begin{aligned}&K_P^\circ = K_x\left(\frac{P}{P^\circ}\right)^{n_C+n_D-n_A-n_B}, \text{ where}\\ &K_x = \frac{x_C^{n_C}x_D^{n_D}}{x_A^{n_A}x_B^{n_B}}.\end{aligned}}$$

Chemical Equilibria in Solution:

Consider the aqueous reaction

$$n_P\mathrm{P}(aq) + n_Q\mathrm{Q}(aq) \rightleftharpoons n_R\mathrm{R}(aq) + n_S\mathrm{S}(aq).$$

If the standard state is taken to be a concentration of 1 mol dm^{-3} of solution (i.e., a 1 **molar** solution), the equilibrium constant used is K_C, defined as follows:

$$\boxed{K_C^\circ = \frac{(c_R/c^\circ)^{n_R}(c_S/c^\circ)^{n_S}}{(c_P/c^\circ)^{n_P}(c_Q/c^\circ)^{n_Q}},}$$

where the standard concentration, $c^\circ = 1$ mol dm^{-3}, is included only to ensure that K_C is dimensionless.

If the standard state is taken to be 1 mol kg^{-1} of solvent (i.e., a 1 **molal** solution), a more accurate representation is possible in terms of "activities." Activities are similar to fugacities in that their purpose is to make sure that the free energy calculated for nonideal solutions yield the correct result without changing the general form of the equation. Activities are denoted by the letter a, and is commonly expressed in terms of activity coefficients γ which, when multiplied by the molality of the species, yields the activity, i.e., $a = \gamma m$.

$$\boxed{K_a^\circ = \frac{a_R^{n_R} a_S^{n_S}}{a_P^{n_P} a_Q^{n_Q}} = \frac{\gamma_R^{n_R} \gamma_S^{n_S}}{\gamma_P^{n_P} \gamma_Q^{n_Q}} \times \frac{m_R^{n_R} m_S^{n_S}}{m_P^{n_P} m_Q^{n_Q}}.}$$

It is generally understood that in these equations, the units of the concentrations or activities are cancelled by a term-by-term division of the standard concentration. In order to keep the notation simple, we refrain from explicitly showing these terms as we have done in the case of K_C above.

Heterogeneous equilibrium:

The activity of pure solids and liquids is accepted to be exactly equal to 1.

Examples: 4.1 – 4.4,

Problems: 4.1 – 4.5, 4.7 – 4.12, 4.15, 4.16, 4.17, 4.19 – 4.21, 4.24, 4.29

Le Chatelier Principle:

If a system in dynamic equilibrium is disturbed, the system will adjust itself in such a way as to counteract, as far as possible, the effect of that change.

Types of disturbances to chemical equilibria we will consider are: (a) change in volume, (b) change in pressure, (c) change in temperature, (d) change in concentration or partial pressure.

(a) change in volume:

Consider the reaction $AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$. The equilibrium constant K_C (ignoring the standard concentration terms for simplicity) is given by:

$$K_C = \frac{c_{A^+} \times c_{B^-}}{c_{AB}} = \frac{(n_{A^+}/V) \times (n_{B^-}/V)}{(n_{AB}/V)} = \frac{n_{A^+} \times n_{B^-}}{n_{AB}} \times \frac{1}{V}.$$

So, if the number of moles of each species remained the same, as the system is diluted, the equilibrium constant decreases. Since this cannot happen (K_C is a constant at a given temperature), the number of moles of $A^+(aq)$ and $B^-(aq)$ must increase with increasing volume.

(b) change in pressure:

Consider the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Similar arguments as above can be made for K_P as pressure is changed. However, it is sufficient to note that there are 4 moles of gases on the reactant side and only two moles of gases on the product side. When pressure is increased holding temperature constant, the equilibrium shifts in the direction of the products so that the volume shrinks. When pressure is decreased, the equilibrium shifts in the direction of the reactants so that volume is increased.

(c) change in temperature:

If a reaction is exothermic in the forward direction, a decrease in temperature drives the reaction forward to counteract the decrease in temperature. An increase in temperature will drive the reaction in the reverse direction since the reverse reaction will be endothermic.

(d) change in concentration or partial pressure:

Adding reactants or removing products drives the equilibrium towards products, removing reactants or adding products drives the equilibrium towards reactants.

Temperature Dependence of Equilibrium Constants

From Chapter 4, we have

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right)\right]_P = -\frac{\Delta H^\circ}{T^2}. \tag{4.69}$$

Since $\Delta G^\circ = -RT\ln K_P^\circ$, substituting for ΔG°, we get

$$\left(\frac{\partial}{\partial T}\ln K_P^\circ\right)_P \simeq \frac{d}{dT}\ln K_P^\circ = \frac{\Delta H^\circ}{RT^2}. \tag{4.71}$$

On rearranging and integrating, we get

$$\ln K_P^\circ = -\frac{\Delta H^\circ}{RT} + const. \tag{4.75}$$

which implies that when $\ln(K^\circ_P)$ is plotted as a function of $1/T$, the slope will be equal to $-\Delta H^\circ/R$. However, we also know that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Therefore, we get

$$\ln K_P^\circ = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \tag{4.76}$$

Comparing Eqs. (4.75) and (4.76), we see that <u>if ΔH° is independent of temperature</u>, the intercept of the line will be equal to the entropy change for the process.

It is also possible to show that

$$\left(\frac{\partial}{\partial T}\ln K_C^\circ\right)_P \simeq \frac{d}{dT}\ln K_C^\circ = \frac{\Delta U^\circ}{RT^2}.$$

Problems 4.32, 4.34