Lecture 6
Free energy and its uses

$$\int dG = \int VdP$$

$$G - G^o = \int_{P_o}^{P} VdP$$

$$G = G^o(T) + RT \ln P/P^o \quad \text{for gases}$$

and

$$G = G^o(T) + V(P-P^o) \quad \text{for solids and liquids}$$

$$\mu = \mu^o + RT \ln P \quad \text{(for one mole)}$$

$$\Delta G = \Delta G^o + RT \ln Q \quad \text{(for a reaction)}$$

$$\Delta G^o = -RT \ln K \quad \text{(at equilibrium)}$$

Equilibrium constant and ΔG

$\mu_i = \mu_i^o + RT \ln P_i$ i is a component gas, for one mole

Consider the reaction (for an ideal gas), $aA + bB \rightarrow cC + dD$ (1)

ΔG of the reaction can be given in terms of equation (1)

Assume, $\Delta G^0 = c\,\mu_C^o + d\,\mu_D^o - (a\,\mu_A^o + b\,\mu_B^o)$

So, $\Delta G = \Delta G^0 + RT \ln [P_C^c P_D^d / P_A^a P_B^b]$ or $\Delta G = \Delta G^0 + RT \ln Q$

$[P_C^c P_D^d / P_A^a P_B^b]_e = K$, equilibrium constant

At equilibrium, $0 = \Delta G^0 + RT \ln [P_C^c P_D^d / P_A^a P_B^b]$

$$\Delta G^0 = - RT \ln [P_C^c P_D^d / P_A^a P_B^b]$$

Standard free energy, ΔG°

ΔG° refers to the standard free energy change Accompanying the reaction when all the products and reactants are in their standard states. In this condition, for ideal gases each of the constituent will be present at a partial pressure of 1 atm.

The sign of the standard free energy gives an indication of the feasibility of the reaction.

Properties of standard free energy

1. It has a definite value at a temperature, for a reaction.
    It is related to the equilibrium constant. Thus a tabulation of standard Free energy is equivalent to a tabulation of equilibrium constants.
2. Standard free energy depends only on the state of the system.
    Thus it is possible to add and subtract free energy changes.
    Reversal of a reaction merely changes the sign of the free energy.
3. ΔG° values of some reactions which are difficult to study experimentally can be obtained indirectly.

$\Delta G°$ values of some reactions which are difficult to study experimentally can be obtained indirectly.

Example:

1. $2H_2O \text{ (g)} = 2H_2 + O_2 \text{ (g)}, \Delta G° = 109.28 \text{ kcal}$
2. $CO_2 \text{ (g)} + H_2 \text{ (g)} = H_2O \text{ (g)} + CO \text{ (g)}, \Delta G° = 6.82 \text{ kcal}$

2 x 2 + 1 gives

$2CO_2 \text{ (g)} = 2CO \text{ (g)} + O_2 \text{ (g)}$
$\Delta G° = 2 \times 6.82 + 109.28 = 122.92 \text{ kcal}$

Since $\Delta G°$ is the negative logarithm of the equilibrium constant ($-RT\ln K_p$), addition and subtraction of free energies is like multiplication and division of equilibrium constants.
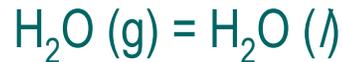
If standard free energy of a substance in one state is known, it is possible to determine it for another state.
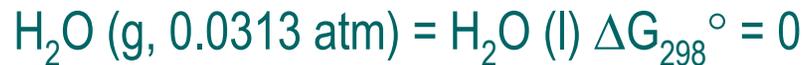
H_2 (g) + ½ O_2 (g) = H_2O (l)

We want to know this from

H_2 (g) + ½ O_2 (g) = H_2O (g), ΔG = – 54.64 kcal

The difference between the two reactions is,

H_2O (g) = H_2O (l)

Standard state of water is liquid and the standard state as vapour is at a pressure of 1 atm. At 25°C, water liquid is in equilibrium with vapour at a pressure of 23.76 mm Hg. Pressure = 23.76 / 760 = 0.0313 atm. This means that,

H_2O (g, 0.0313 atm) = H_2O (l) $\Delta G_{298}°$ = 0

The process we want to know is,

H_2O (g) (1 atm) = H_2O (l) is, equivalent to

H_2O (g, 1 atm) = H_2O (g, 0.0313 atm)

ΔG = RT ln P_2/P_1

ΔG = RT ln 0.0313/1 = – 2.05 kcal

Thus the standard free energy change for the formation of 1 mole of liquid water is –54.64 – 2.05 = –56.69 kcal

The process is more negative in free energy, it will happen.

Water vapour will condense to give you liquid water.

Standard free energy of reactions can be studied by a number of ways. Study of equilibrium constant is one way. If the reaction goes to completion, equilibrium constant cannot be determined and so the result has to be derived from a combination of two or more reactions. For reactions taking place in an electrochemical cell, standard free energy can be derived from emf measurements.

Standard free energy and measurements

The equilibrium constant varies with temperature and similarly standard free energy also varies with temperature.

$\Delta G^\circ = - RT \ln K_P$

$-RT \ln K_P = \Delta H^\circ - T \Delta S^\circ$

$\Delta G = \Delta G^\circ + RT \ln Q = \Delta H - T \Delta S$

$\Delta G^\circ = -RT \ln Q + (\Delta H - T \Delta S)$

Here ΔH is treated as a constant. In a range of temperatures, it can be taken as a mean value

As we know, $\Delta H = \Delta H^\circ + \Delta a T + \Delta b/2 \, T^2 + \ldots$

$\Delta G^\circ = -RT \ln Q + (\Delta H^\circ + \Delta a T + \Delta b/2 \, T^2 + \ldots) - T \Delta S$

ΔH°, Δa, Δb, etc. can be known from heats of reaction and heat capacities of substances.

Standard free energies and equilibrium constant

Molar free energies can be tabulated. For gases this refers to 1 atm,
and for liquids and solids it refers to pure state. We need to know relative
changes, it is not necessary to obtain absolute free energies.
The free energies of elements in their standard state are taken as zero.
Thus the free energy values can be used the same way as enthalpy values.

$G°$ will be negative when K is greater than unity.
Thus at equilibrium, products exceed the reactants.
$\Delta G°$ will be positive when K is less than unity.
A reaction with $\Delta G°$ positive can still occur if Q term is small
such that ΔG is negative.

$$\Delta G = \Delta G° + RT \ln Q$$

If $\Delta G°$ highly positive, the conditions under which
ΔG is negative will have Q very small, the yield of products at
equilibrium will be very small to make the process worthless.
 In general if $\Delta G°$ exceeds +10 kcal the reaction will not have much utility.

Effect of Temperature on Chemical Equilibrium

The equilibrium constant of a chemical reaction is constant at a given temperature, but varies considerably with changes in temperature.

A quantitative relation can be found with van't Hoff's equation.

$$\Delta G^0 = - RT \ln K_a \qquad \text{K in terms of activities}$$

or

$$\ln K_a = - \Delta G^0/RT$$

On differentiating equation with respect to T at constant pressure we get, why constant P?

$$d \ln K_a/dT = -1/R[d(\Delta G^0/T)/dT]_P$$

$$\{As \quad [d(\Delta G^0/T)/dT]_P = -\Delta H^0/T^2\} \rightarrow \textbf{G-H equation}$$

$$d \ln K_a/dT = -1/R \ (-\Delta H^0/T^2)$$
or
$$d \ln K_a/dT = \Delta H^0/RT^2$$

For gaseous reactions, $K_a = K_P$ and hence equation becomes,

$$d \ln K_P/dT = \Delta H^0/RT^2$$

This result represents the variation of equilibrium constant with temperature and is generally known as the van't Hoff's equation.

In order to integrate the equation, ΔH^0 must be known as a function of temperature. Assuming ΔH^0 to be constant over a small range of temperatures integration of equation yields.

$$\int_{KP1}^{KP2} d \ln K_P = \int \Delta H^0/RT^2 \, dT$$

$$[\ln K_P] = \Delta H^0/R \, [-1/T]$$

$$\ln K_{P2}/K_{P1} = \Delta H^0/R[-1/T_2 + 1/T_1]$$

$$= \Delta H^0/R \, [T_2 - T_1/T_1T_2]$$

$$\log K_{P2}/K_{P1} = \Delta H^0/2.303R[T_2 - T_1/T_1T_2]$$

Equation helps in calculating K_{P_2} at T_2 provided the enthalpy of the reaction at constant pressure ΔH^0, K_{P_1} and T_1 are known.

Alternatively,

ΔH^0 can be determined if K_P is known at two temperatures.

Integrating equation without using limits, we get

$$\int d \ln K_P - = \int \Delta H^0/RT^2 \, dT$$

$$\ln K_P = - \Delta H^0/RT + \text{constant}$$

Or

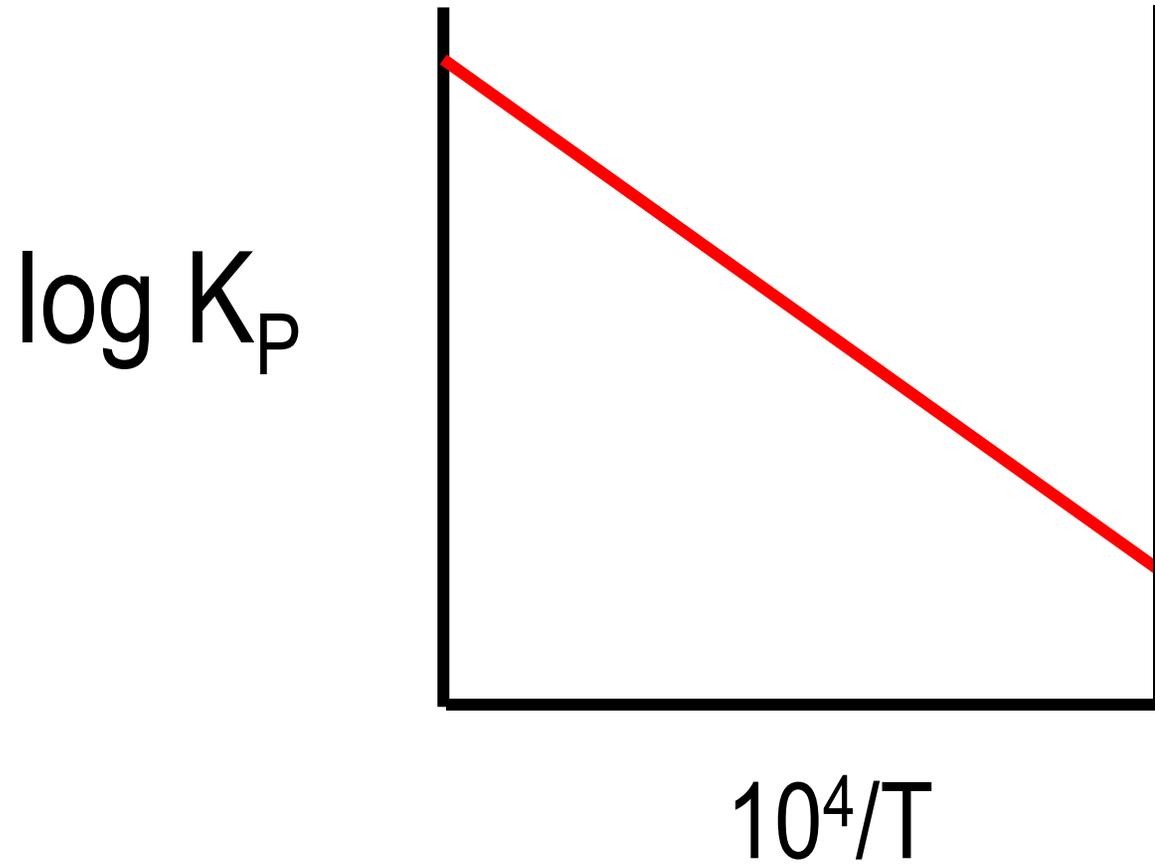$$\log_{10} K_P = - \Delta H^0/2.303 \, RT + \text{constant}$$

One can get ΔH^0.

In a number of cases, ΔH^0 varies with temperature.

$\Delta H^0 = \Delta H^0_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots$ where the coefficients are determined by the heat capacities of the substances involved in the reactions.

We can get,

$d \ln K_a/dT = \Delta H^0_0/RT^2 + \alpha/RT + \beta/R + (\gamma/R)T + \cdots$

Plot of log K_P against $1/T$

What one does is to get ΔH^0 from the above plot and calculate ΔS^0 from the relation, $\Delta G^o = \Delta H^0 - T\Delta S^0$

This also means that,

In Kp = $-\Delta H^0/RT + \Delta S^0/R$

This relation is always true.

If ΔH^0 is constant, ΔS^0 is also constant.

If not, it can be represented as,

$\Delta H^0 = \Delta H^0_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots$

But, integration has to be done with this ΔH^0

Additional reading

Chemical potential

$dG = VdP$

$\int_{Pi}^{Pf} dG = \int_{Pi}^{Pf} VdP$

For an ideal gas,

$$\int_{Pi}^{Pf} = nRT\int_{Pi}^{Pf} dP/P$$

$G(P) = G(Pi) + nRT \ln P_f/P_i$

If we set, $P_i = P^0$ (the standard pressure, 1 bar)

$$G(P) = G^0 + nRT \ln(P/P^0)$$

For one mole of a gas,

$$\mu = \mu^0 + RT\ln P/P^0$$

μ is the **chemical potential**.

Although this appears more like a new system of nomenclature, the significance is much more.
Chemical potential shows how extensive quantities such as U, A, H and G depend on concentration.

Implications of this can be traced to an equation called,
Gibbs-Duhem equation:

$$\sum_J n_J d\mu_J = 0$$

Fugacity

In real gases, the pressure P has to be taken as an effective pressure called, fugacity (f).

$$\mu = \mu^0 + RT\ln f/P^0$$

f = ΦP

Φ is the dimensionless fugacity coefficient.

$\mu = \mu^0 + RT\ln P/P^0 + RT\ln \Phi$

Gases become ideal when pressure approaches zero.

f → P as P → 0

Φ → 1 as P → 0

Partial molar quantities

Properties such as, U, H, S, G, A, etc. depend upon the number of moles, n, in addition to P, V and T.

$$U = f(P, V, T, n_1, n_2, \ldots n_i)$$

$n_1, n_2, \ldots n_i$ represent the number of moles of each constituent in volume, V.

$$U = f(P, T, n_1, \ldots n_i)$$

$$dU = (\partial U/\partial P)_{T, n1, \ldots ni,} \, dP + (\partial U/\partial T)_{P, n1, \ldots ni,} \, dT + (\partial U/\partial n_{i) \, P, T, n1, \ldots n,i} \, dni$$

$(\partial U/\partial n_i) \, P, T, n_1, \ldots n_{i-1}$ is the partial molar internal energy $\bar{U}i$. Similarly Si, Hi, etc can be defined. $\partial U/\partial n_i$ refers to the change in U with the addition of one mole of the ith component keeping all the other variables constant. Thus the system should be dilute such that the addition of a mole of one constituent does not change the concentration appropriately.

The quantity,

$(\partial G/\partial n_i)P, T, n_1, \dots = \mu_i$ is called the chemical potential.

$dG = -SdT + VdP + \Sigma_i \mu_i dn_i$

$(dG)_{T, P} = \Sigma_i \mu_i dn_i$

$G_{T, \rho} = \mu_1 n_1 + \mu_2 n_2 + \dots$

Partial molar free energy is the contribution per mole
of that constituent to the free energy of the system.
For a one component system, $\mu = G/n$, partial molar
free energy is the chemical potential for a pure substance.