Free Energy Functions

An irreversible change is always spontaneous and in an isolated system the entropy must increase and should be maximum at equilibrium. All the natural processes are spontaneous and rarely occur in isolated systems. In selecting entropy as a criterion of spontaneity is not convenient. So it desirable to introduce new functions as criteria of spontaneity. These functions are the Helmholtz free energy or the work function denoted by A and the Gibbs free energy or Gibbs potential represented by G. They are defined as:

$$A = U - TS$$

$$G = H - TS$$

The values of A and G are defined by the state of the system and are independent of the path followed for the change in the state of the system, both are single-valud thermodynamic functions of the system. dA and aG are exact differentials and the cyclic integrals are zero. They are extensive properties of the system and depend on the quantity of the matter and nature of the system.

$$\oint dA = 0 \quad , \quad \oint dG = 0$$

Relation between A and G

From the definition of enthalpy $H = U + PV$

$$G = H - TS$$

$$G = U + PV - TS$$

$$as \quad A = U - TS$$

$$G = A + PV$$

Changes in A and G in isothermal processes

The change in A for an isothermal process is given by:

$$\Delta A = A_2 - A_1$$

$$\Delta A = (U_2 - TS_2) - (U_1 - TS_1)$$

$$\Delta A = (U_2 - U_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta U - T\Delta S$$

For infinitesimal change

$$dA = dU - TdS$$

Similarly, the change in Gibbs free energy for isothermal process is given by:

$$\Delta G = G_2 - G_1$$

$$\Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S$$

For infinitesimal change

$$dG = dH - TdS$$

Significant of A and G

For a system of fixed composition:

$$dA = dU - TdS - SdT$$

$$dU = TdS + W_{rev}$$

W_{rev}: reversible work done by the system and include both mechanical and non mechanical work.

$$dA = TdS - TdS - SdT + W_{rev} = -SdT + W_{rev}$$

If the process is isothermal dT=0

$$d(A)_T = -P(dV)_T$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad , P = \frac{nRT}{V}$$

$$\int_{A_1}^{A_2} dA = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$\Delta A = A_2 - A_1 = -nRT\, ln \frac{V_2}{V_1}$$

$$= nRT\, ln \frac{V_1}{V_2} = \boldsymbol{n}RT\, ln \frac{P_2}{P_1}$$

$$dG = dH - TdS - SdT$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = TdS - PdV + VdP + PdV - TdS - SdT$$

$$dG = VdP - SdT$$

At constant T, -SdT =0

$$\Delta G = VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad , \qquad V = \frac{nRT}{P}$$

$$\int_{G_1}^{G_2} dG = -\int_{P_1}^{P_2} \frac{nRT}{P} =$$

$$\Delta \boldsymbol{G} = \boldsymbol{n}RT\, ln \frac{P_2}{P_1} = nRT\, ln \frac{V_1}{V_2}$$

We show that ΔG=ΔA in isothermal process.

If the change from G^0 to G and from P^0 to P , where G^0 is Gibbs energy at standard state.

$$\int_{G^0}^{G} dG = nRT \int_{P^0}^{P} \frac{dP}{P}$$

$$G = G^0 + RT \ln \frac{P}{P^0}$$

Maxwell's Relation

The four fundamental thermodynamics equation are:

$$dU = TdS - PdV \;\ldots\ldots(1)$$

$$dH = TdS + VdP \;\ldots\ldots(2)$$

$$dA = -SdT - PdV \;\ldots\ldots(3)$$

$$dG = -SdT + VdP \;\ldots.(4)$$

From these relations we can be derived four relations known as Maxwell's relation as follow:

$$U = f(S,V) \qquad , \qquad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$H = f(S,P) \qquad , \qquad dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$A = f(T,V) \qquad , \qquad dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$G = f(T,P) \qquad , \qquad dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T \qquad , \qquad \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = V \qquad , \qquad \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$Z = f\,(x, y)$$

$$dZ = MdX + NdY$$

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y = M \quad , \quad \left(\frac{\partial Z}{\partial Y}\right)_X = N$$

Since the mixed partial derivatives

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial \boldsymbol{T}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{S}} = -\left(\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{S}}\right)_{\boldsymbol{V}} \ldots\ldots(\boldsymbol{a})$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial \boldsymbol{T}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{S}} = \left(\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{S}}\right)_{\boldsymbol{P}} \ldots\ldots..(\boldsymbol{b})$$

$$dA = -SdT - PdV$$

$$-\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{V}}\right)_{\boldsymbol{T}} = -\left(\frac{\partial \boldsymbol{P}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{V}} \ldots\ldots..(\boldsymbol{c})$$

$$dG = -SdT + VdP$$

$$-\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{P}}\right)_{\boldsymbol{T}} = \left(\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{P}} \ldots\ldots\ldots.(\boldsymbol{d})$$

A, b, c and d are called **Maxwell's relation**.

Variation of Gibbs energy with Temperature at constant pressure

$$dG = -SdT + VdP$$

At constant pressure dP=0

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \dots\dots..(1)$$

From the definition: $G = H - TS$

$$S = \frac{H-G}{T} \dots\dots\dots\dots.(2)$$

Substitute eq(2) in eq(1) yields:

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = \frac{H}{T} \dots\dots\dots(3)$$

The left side of eq (3) is simplified as:

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\frac{d}{dT}\frac{1}{T}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}$$

$$= \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right] \dots\dots..(4)$$

Substitute eq (3) in (4) we get:

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{1}{T}\left[-\frac{H}{T}\right]$$

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{H}{T^2}$$

This is Gibbs-Helmholtz equation.

For change between final and initial state:

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{\partial T}\right)_P = -\frac{H}{T^2}$$

If we can determine ΔG for reactions, we can calculate ΔH without using a calorimetry.

If ΔH and ΔG are known at one temperature, we can calculate ΔG at another temperature assuming ΔH is independent on T.

Chemical Potential of an Ideal gas

The quantity μ_i defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n}$$

$\mu_i$is known as the chemical potential of the I component.

" The increase in G per mole that results when a small amount dn_i moles are added to the system keeping temperature, pressure and all other compositions constant.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

For pure substance G= nḠ , Ḡ is the molar Gibbs energy.

$$\mu_i = \left(\frac{\partial nG}{\partial n_i}\right)_{T,P}$$

From equation: $G = G^0 + RT\ln\frac{P}{P^0}$

$$\mu = \mu^0 + RT\ln\frac{P}{P^0} \quad , \quad \mu^0 : \text{chemical potential in the standard state}$$

In a mixture of ideal gases, chemical potential of the ith component is given by:

$$\mu_i = \mu^0{}_i + RT\ln P_i \quad , \quad P_0 = 1\ atm$$

$$P_i = X_i\,P \quad , \quad P = total\ pressure, \quad X_i = mole\ fraction$$

$$\mu_i = \mu^0{}_i + RT\ln X_i\,P$$

$$\mu_i = \mu^0{}_i + RT\ln P + RT\ln X_i$$

$$\boldsymbol{\mu^0{}_i + RT\ln P} : \quad is\ the\ chemical\ potential\ of\ pure\ substance$$

Thermodynamics of Mixing of Ideal Gases

$$\Delta G_{mix} = RT\sum_i X_i\, lnX_i$$

$$\Delta S_{mix} = -R\sum_i X_i\, lnX_i$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = RT\sum_i X_i\, lnX_i - RT\sum_i X_i\, lnX_i = \mathbf{0}$$

$$\Delta V_{mix} = 0 \;\; , no\ change\ in\ volume\ occurs\ when\ ideal\ gases\ were\ mixed$$

The Clapeyron Equation

For a pure substance present in two phase 1 and 2 at a pressure P and temperature T, the condition of equilibrium:

$$G_{m,1} = G_{m,2} \quad , \quad \Delta G = 0$$

Where $G_{m,1}$ and $G_{m,2}$ are the free energies per mole in phase 2 and 1, respectively.

If the pressure of the system is changed to P+dP and temperature to T+dT, the value of G will changed to G_m+dG_m :

$$G_1 + dG_1 = G_2 + dG_2$$

$$G_1 = G_2 \quad , \quad dG_1 = dG_2$$

$$dG_1 = V_1 dP - S_1 dT$$

$$dG_2 = V_2 dP - S_2 dT$$

$$S_2 - S_1 = dT = (V_2 - V_1)dP$$

$$\frac{dT}{dP} = \frac{(V_2 - V_1)}{(S_2 - S_1)} = \frac{\Delta V}{\Delta S}$$

This is known as the **Clapeyron equation** and holds for the equilibrium between two phases of a substance.

i) For liquid- vapour equilibrium: the molar entropy of a gas are higher than those for the liquids, therefore ΔS_m and ΔV_m are always positive for liquid vapour transformation and the quantity dP/dT will be positive. A rise in temperature increases the equilibrium vapour pressure of the liquid.

(ii) For solid- vapour transformation: for solid –vapour transformation

$$\Delta S_m = S_{m,g} - S_{m,s} = \frac{\Delta H_{sub}}{T} = positive$$

$$\Delta V_m = V_{m,g} - V_{m,s} = positive \quad , \quad \frac{dP}{dT} = positive$$

Increase in temperature increase the equilibrium vapour of the solid. Further

$$\Delta H_{sub,m} = \Delta H_{fus,m} + \Delta H_{vap,m}$$

$$\Delta H_{sub,m} > \Delta H_{vap,m}$$

(iii) For solid- liquid equilibrium: in this case

$$\Delta S_m = S_{m,l} - S_{m,s} = \frac{\Delta H_{fus,m}}{T} = positive$$

For most of the substance $\Delta V_m = V_{m,l} - V_{m,s} = positive \;,\; \frac{dP}{dT} = positive$

Clausius- Clapeyron Equation

In solid-vapour or liquid-vapour equilibrium if $V_{m,\,l}$ or $V_{m,\,S}$ can be neglected in comparison to $V_{m,\,g}$, then the calpeyron equation becomes:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_{vap,m}}{TV_{m,g}}$$

$$\Delta S_m = \frac{\Delta H_{vap,m}}{T}$$

If the vapours are assumed to behave ideally, then $V_{m,g}$ can be replaced by $\frac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta H_{vap,m}\,P}{T.RT}$$

$$\frac{dP}{P} = \frac{\Delta H_{vap,m}}{RT^2}dT$$

For small temperature variation, $\Delta H_{vap,m}$ may be assumed to be constant. Integration of the above equation then yields Clausius- Clapeyron Equation:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap,m}}{R}\frac{(T_2 - T_1)}{T_1T_2}$$

Solved Examples

Example 1: the entropy and enthalpy changes for the reaction :

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$$

At 300 K and 1 atm pressure are respectively -42.4 JK^{-1} and -41.2 kJ. Calculate the free energy change for the reaction, predict if the reaction is feasible and the temperature at which the reaction will go in the opposite direction.

Solution: the free energy of the reaction is given by:

$$\Delta G = \Delta H - T\Delta S$$

$$= (-41.2 + 300 \times 42.4) = -28.48\,kJ$$

Since ΔG < 0 , the reaction is spontaneous.

It will go in the opposite direction as soon as ΔG start changing its sign, so the minimum temperature at which ΔG becomes zero can be calculated as:

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S} = \frac{41.2 \times 10^3}{42.4} = 971.7K$$

Example 2: It is found that ΔH= -2810 kJ mol^{-1} and ΔS= 182.4JK^{-1} when glucose is oxidized at 300 K according to the reaction: Calculate the free energy.

$$C_6H_2O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-2810) - (300)(182.4 \times 10^{-3})kJ\,mol^{-1}$$

$$\Delta G = (-2810) - 54.72)\,kJmol^{-1} = -2864.72kJmol^{-1}$$

Example 3: one mole of an ideal gas expands isothermally and reversibly from5 dm^3 to 10 dm^3 at 300K. Calculate q, W, ΔU, ΔH, ΔS , ΔA, and ΔG.

For isothermal process ΔT=0, ΔU=0, ΔH=0

$$q = -W_{rev} = nRT\ln\frac{V_2}{V_1} = 1729Jmol^{-1}$$

$$\Delta S = nR\ln\frac{V_2}{V_1} = 1 \times 8.314 \times ln\frac{10}{5} = 5.76\,JK^{-1}mol^{-1}$$

$$\Delta G = \ \Delta A = \ -nRT\ln\frac{V_2}{V_1} = \ -1729Jmol^{-1}$$

Example 4: the boiling point of water is 373K at 1atm pressure. Calculate q, W, ΔU, ΔH, ΔS , ΔA, and ΔG when a mole of steam is compressed isothermally and reversibly. The heat of vaporization of water is 40.67 kJmol^{-1}.

$$-W = P\Delta V = P\left(V_l - V_g\right) = -PV_g = \ -RT = \ -8.314 \times 373 = -3100Jmol^{-1}$$

$$q_P = \Delta H = -40.67\ kJmol^{-1}$$

$$\Delta U = \Delta H - P\Delta V = \ -40.67kJmol^{-1} + 3.1kJmol^{-1} = \ -37.57kJmol^{-1}$$

$$\Delta A = W = 3.1kJmol^{-1}$$

$$\Delta S = \frac{q_{rev}}{T} = -\frac{40.67}{373} = \ -109\,J\,K^{-1}mol^{-1}$$

Unsolved Problems

1- Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

2- Calculate Δ*G* and Δ*A* when 4 moles of an ideal gas are expanded isothermally and reversibly from 5 atm to 1 atm at 323K.

3- 1mole of perfect gas molecules at 27°C is expanded isothermally and reversibly from an initial pressure of 3.00 atm to a final pressure of 1.00 atm. determine the values of *q*, *w*, Δ*U*, Δ*H*, Δ*S*, Δ*A* and Δ*G*.

4- Assuming that He and N_2 form an ideal gaseous mixture, calculate Δ*U*, Δ*H*, Δ*S*, Δ*V*, Δ*A* and Δ*G* when 5 moles of He and 3 moles of N_2 are mixed at 298K.

5- 1 mole of an ideal gas (C_v= 30J K^{-1}mol^{-1}) initially at 300 K and 1 atm is heated at constant pressure until the final volume is doubled. Calculate of *q*, *w*, Δ*U*, Δ*H*, Δ*S*, and Δ*G* for the process.

6- For the reaction below Δ*H* is -562.59 kJ and Δ*S* is -194.75 JK^{-1} at 298K, show that the reaction is non-spontaneous and calculate the minimum temperature at which the reaction will be reversed.

$$H_2S_{(g)} + \frac{3}{2}O_{2(g)} = \ H_2S_{(l)} + SO_{2(g)}$$