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Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof. A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr. Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof. A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi	**Dr. Geetika Bhalla** Asst Professor Hindu College University of Delhi **Dr. Aditi Gupta** Asst Professor S.G.T.B. Khalsa College University of Delhi	**Prof. A.K.Bakhshi** Sir Shankar Lal Professor, Department of Chemistry University of Delhi

Anchor Institute : SGTB Khalsa College, University of Delhi

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1. Learning outcomes

After studying this module you shall be able to:

- Know about free energy functions i.e. Gibb's free energy and work function
- Know the dependence of Gibbs free energy on temperature and pressure
- Learn about Gibb's Helmholtz equation
- Learn different Maxwell relations
- Derive Gibb's Duhem equation
- Determine partial molar volume through intercept method

2. Introduction

Thermodynamics is used to determine the feasibility of the reaction, that is , whether the process is spontaneous or not. It is used to predict the direction in which the process will be spontaneous. Sign of internal energy alone cannot determine the spontaneity of a reaction. The concept of entropy was introduced in second law of thermodynamics. Whenever a process occurs spontaneously, then it is considered as an irreversible process. For such a process the entropy change of the universe is positive. The change in entropy of universe is the sum of entropy change of the system and the surroundings, viz., $\Delta S_{sys} + \Delta S_{surr}$. It serves as a criterion of spontaneity of a reaction. If the total entropy change of the universe is positive, then the process is considered to be feasible. If the total entropy change is zero, then the system is considered to be in a state of equilibrium. Thus for determining the feasibility of the reaction, the entropy change of system as well as entropy change of the surroundings should be known. But the entropy change of the surroundings is not easy to determine. For most of the spontaneous processes it is observed that the system either tries to attain the state of minimum energy or maximum entropy. Thus it is necessary to define a new function which takes into account both the properties, i.e., energy and entropy. Gibb's free energy (G) is a function that takes into account the effect of both energy change as well as entropy change of the system.

3. Free energy functions

Two functions which define the effect of entropy as well as energy are work function (A) and the free energy (G). These functions are defined by following equations:

Work function: $A = U - TS$ or $A = E - TS$ ...(1)

Free energy: $G = H - TS$ ...(2)

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Since, H, U, T and S all are state functions (depend on the state of the system), therefore G and A must also be state functions. Considering the work function at two different states but at same temperature, then we get:

$$A_1 = U_1 - TS_1 \qquad \qquad \text{...(3)}$$

$$A_2 = U_2 - TS_2 \qquad \qquad \text{...(4)}$$

Subtracting equation (3) from (4) we get

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1) \text{ or } \Delta A = \Delta U - T\Delta S \qquad \text{...(5)}$$

where ΔA stands for change in work function, ΔU stands for change in internal energy and ΔS is the entropy change. Since $\Delta S = q_{rev}/T$ thus substituting in equation (5) we get:

$$\Delta A = \Delta U - q_{rev} \qquad \qquad \text{...(6)}$$

From the first law of thermodynamics i.e. $\Delta U = q + w$, we get

$$w_{rev} = \Delta U - q_{rev} \qquad \qquad \text{...(7)}$$

If system does the work, then work will be negative. Accordingly,

$$-w_{rev} = \Delta U - q_{rev} \qquad \qquad \text{...(8)}$$

On comparing equation (6) and (8) we get,

$$-\Delta A = w_{rev} \qquad \qquad \text{...(9)}$$

Here, w is the maximum work done by the system. Thus decrease in work function increases the work done by the system. Therefore the function A is regarded as the work function and also Helmholtz free energy. Similarly considering the change in free energy by making use of equation (2) we get,

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S \qquad \text{...(10)}$$

Also the change in enthalpy at constant pressure is known:

$$\Delta H = \Delta U + P\Delta V \qquad \qquad \text{...(11)}$$

Substituting equation (11) in equation (10):

$$\Delta G = \Delta U + P\Delta V - T\Delta S \qquad \qquad \text{...(12)}$$

Using equation (5) in equation (12), we get:

$$\Delta G = \Delta A + P\Delta V \qquad \qquad \text{...(13)}$$

Substituting equation (9) in equation (13), we get:

$$\Delta G = -w + P\Delta V \quad \text{or} \quad -\Delta G = w - P\Delta V \qquad \text{...(14)}$$

In the above equation $P\Delta V$ gives the work done by the gas on expansion against constant external pressure P.

Thus in equation $-\Delta G$ gives the maximum amount of work done by the system other than the work obtain due to change of volume at constant pressure and temperature.

But the amount of work done due to change of volume is:

$$w - P\Delta V = -\Delta G \qquad \qquad \text{...(15)}$$

The term G is known as Gibb's free energy.

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4. The effect of temperature and pressure on Free energy

Considering the equation (2)

$G = H - TS$

And also $H = U + PV$ …(16)

Substituting equation (16) in equation (2) we get:

$G = U + PV - TS$ …(17)

Differentiating the above equation,

$dG = dU + PdV + VdP - TdS - SdT$ …(18)

For infinitesimal small change, the first law equation can be written as:

$dq = dU - dw$ …(19)

As $- dw = PdV$ substituting this in equation (19)

$dq = dU + PdV$ …(20)

Making the use of equation

$dS = dq/T$ or $TdS = dq = dU + PdV$ …(21)

Combining equation (18) and (21)

$dG = VdP - SdT$ …(22)

The above equation gives the change in free energy on variation of temperature and pressure.

If pressure of the system kept constant then $dP = 0$, thus equation (22) becomes:

$dG = -SdT$ …(23)

Rearranging the above equation:

$(\partial G / \partial T)_P = -S$ …(24)

Similarly if temperature of the system is kept constant then, $dT = 0$,

Thus equation (22) becomes:

$dG = VdP$

$(\partial G / \partial P)_T = V$ …(25)

5. Maxwell's Relations

The expressions or equations which relate internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy with parameters like entropy, pressure, etc., are called Maxwell's relations. Some of these are:

i. $dU = TdS - PdV$

ii. $dH = TdS + VdP$

iii. $dA = -SdT - PdV$

iv. $dG = -SdT + VdP$

If volume of the system remains constant, i.e., $dV=0$ then equation (i) becomes;

$(\partial U / \partial S)_V = T$ …(26)

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If entropy of the system does not change, i.e., dS=0, then equation (i) becomes,

$$(\partial U / \partial V)_S = -P \qquad \qquad \ldots(27)$$

Now on differentiating equation (26) with respect to V keeping S as constant and differentiating equation (27) with respect to S keeping V constant, we get

(from equation 26): $\partial^2 U / (\partial S)(\partial V) = (\partial T / \partial V)_S \qquad \qquad \ldots(28)$

(from equation 27) : $\partial^2 U / (\partial S)(\partial V) = -(\partial P / \partial S)_V \qquad \qquad \ldots(29)$

On comparing equation (28) and (29) we get,

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V \qquad \qquad \ldots(30)$$

Similarly by following the same procedure some following relations were also derived:

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P \qquad \qquad \ldots(31)$$

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V \qquad \qquad \ldots(32)$$

$$(\partial S / \partial P)_T = -(\partial V / \partial T)_P \qquad \qquad \ldots(33)$$

The above relations are known as Maxwell's relations. Some more relations are:

$$(\partial U / \partial S)_V = (\partial H / \partial S)_P \qquad \text{from (i) and (ii)} \qquad \ldots(34)$$

$$(\partial U / \partial V)_S = (\partial A / \partial V)_T \qquad \text{from (i) and (iii)} \qquad \ldots(35)$$

$$(\partial H / \partial P)_S = (\partial G / \partial P)_T \qquad \text{from (ii) and (iv)} \qquad \ldots(36)$$

$$(\partial A / \partial T)_V = (\partial G / \partial T)_P \qquad \text{from (iii) and (iv)} \qquad \ldots(37)$$

Some relations are derived as as follows:

Helmholtz free energy (work function A) is given by:

A = E – TS

Differentiation gives:

dA= dE – TdS – SdT

But the combined first and second laws of thermodynamic reads:

TdS = dE + PdV

Therefore, dA = -SdT- PdV $\qquad \qquad$ as A= f (T,V)

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

On comparing the coefficients of dT in above two equations, we get:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and}$$

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

6. Gibbs Helmholtz equation

The variation of Gibbs free energy change with temperature is known as Gibbs Helmholtz equation. This relation is derived as follows:

Taking equation (24)

$(\partial G / \partial T)_P = -S$

For a small change from one state to another the above equation can be written as:

$(\partial(\Delta G) / \partial T)_P = -\Delta S$ …(38)

Now taking the expression of Gibbs free energy, i.e.,

G= H-TS

Differentiating it keeping the temperature constant we get,

$\Delta G= \Delta H - T \Delta S$ …(39)

$\Delta S = \frac{\Delta H - \Delta G}{T}$ …(40)

Substituting this in equation (38) and then on rearranging we get,

$\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{T} = -\frac{\Delta H}{T}$ …(41)

From differential calculus

$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = \frac{1}{T}\frac{\partial \Delta G}{\partial T} - \frac{\Delta G}{T^2}$ …(42)

So equation (41) can be written as

$T\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P$

Thus we can write this as:

$T\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T}$ …(43)

Or

$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = -\frac{\Delta H}{T^2}$ …(44)

This equation is known as **Gibbs-Helmholtz equation.** It is valid for all processes which occur at constant pressure. The enthalpy change can also be calculated using this equation provided that the values of free energy changes at two different temperatures are known.

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7. Partial Molar properties

Some thermodynamic properties like entropy, enthalpy, internal energy, etc., are known as extensive properties because their values change by varying mass of the system. In many thermodynamic equations, the change of state was due to variation of temperature and pressure only. Accordingly, it was assumed that in the case of a closed system there is no change in mass of the system, while in the case of an open system containing two or more components, the number of moles of various components can also be changed. In such case, the extensive property (X) must be function of number of moles of various components of the system, in addition to temperature and pressure of the system.

Expression of Partial molar quantity

Suppose the temperature of the system be T and pressure be P and n_1, n_2, n_3, ... n_j be the corresponding number of moles of the components 1, 2, 3, ..., j. Thus accordingly the property X must be the function of temperature, pressure and the number of moles of the various components of the system, i.e.,

$$X = f(T, P, n_1, n_2, n_3, ... n_j) \qquad \qquad \text{...(45)}$$

The total number of moles $N = n_1 + n_2 + n_3 + ... + n_j$

Thus change in property dX when the temperature, pressure and number of moles change will be:

$$dX = (\partial X / \partial T)_{P,N,} dT + (\partial X / \partial P)_{T,N,} dP + (\partial X / \partial n_1)_{T,P,n_2....n_j,} dn_1$$
$$+ (\partial X / \partial n_2)_{T,P,n_1,n_3....n_j,} dn_2 + (\partial X / \partial n_i)_{T,P,n_1,n_2....n_j,} dn_i$$
$$+ (\partial X / \partial n_j)_{T,P,n_1,n_2,n_3....n_i......n_j,} dn_j \qquad \qquad \text{...(46)}$$

This quantity $(\partial X / \partial n_i)_{T,P,n_1,n_2....n_j}$ is called the **partial molar property** of the ith component. This is also represented as $\bar{X}_i$.

Thus partial molar property may be defined as a thermodynamic quantity, which shows that an extensive property of a solution or mixture changes with the change in the molar composition of the solution, while keeping the temperature and pressure constant. It is a partial derivative of the extensive property with respect to the amount of the component of interest. Each extensive property of a mixture has its corresponding partial molar property. Thus for any component (say i[th]) component of a system:

Partial molar Gibbs energy: $(\partial G / \partial n_i)_{T,P,n_1,n_2,n_3,.......} = \bar{G}_i$

Partial molar internal energy: $(\partial U / \partial n_i)_{T,P,n_1,n_2,n_3,.......} = \bar{U}_i$

Partial molar enthalpy: $(\partial H / \partial n_i)_{T,P,n_1,n_2,n_3,.......} = \bar{H}_i$

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Partial molar entropy: $(\partial S / \partial n_i)_{T,P,n_1,\,n_2,\,n_3,\,\ldots\ldots} = \bar{S}_i$

Partial molar volume: $(\partial V / \partial n_i)_{T,P,n_1,\,n_2,\,n_3,\,\ldots\ldots} = \bar{V}_i$ …(47)

Physical significance of Partial molar quantity

The quantity $\bar{X}_i$ represents the actual value of X per mole of the ith component of the system.

This value may be same or different from the actual molar value X^* in the pure state. These two values i.e. partial molar value and actual molar value are same in the case of ideal systems. While in the case of non-ideal systems, these two values are different because of the interactions between the constituents, i.e., actual molar value get modified to partial molar value. This partial molar value may not be same throughout the whole solution since the extent of interactions vary according to the amount of the constituents in the system. Hence the partial molar value is dependent on the composition of the system. Therefore, the partial molar quantities are meant for the individual components of the system, but their values are not only dependent on the nature of the particular component in consideration but also on the nature and amounts of the other components of the system. Now taking some partial molar properties in detail in next section.

7.1 Partial molar volume

The partial molar volume of a substance (say i[th] component) in a mixture is the change in volume per mole of substance 'i' added to a large volume of the mixture. In the case of ideal solution, the partial molar volume of the ith component will be equal to its molar volume in the pure state, whereas in the case of non-ideal solution the partial molar volume is the molar volume actually occupied by the substance in a solution of known composition. The partial molar volume of constituents of the mixture changes with the composition. As the partial molar volume is the actual molar volume of the component present in the solution of known composition therefore the total volume of solution will be given as:

$$V_{total} = n_1 V_{1,pm} + n_2 V_{2,pm} \qquad \text{…(48)}$$

Determination of Partial Molar Volumes (For two component system)

The values of partial molar volumes of the components of the solution can be determined by various methods. A direct method to measure $V_{1,pm}$ (partial molar volume of component 1) is to measure the volume of the solutions which is formed by adding different amount of component 1 in a definite amount of component 2. Then a graph is plotted between volume of solution and amount of component 1. At the given composition of the solution, the slope of the line at that composition gives partial molar volume of the component 1.

But better method for determining the partial molar volumes is the intercept method.

Intercept method

Assuming $V_{m,\,mix}$ be the volume of mixture consisting of total of one mole of the two components. Thus, we can write it as

$$V_{m.mix} = \frac{V}{n_1 + n_2}$$

In the above expression, V stands for the volume of the mixture consisting the amounts n_1 and n_2 of the corresponding components 1 and 2. Under constant temperature and pressure the partial molar volume can be written as:

$$V_{1,pm} = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = \left(\frac{\partial(n_1+n_2)V_{m,mix}}{\partial n_1}\right)_{n_2} \qquad \ldots(49)$$

After undergoing the differentiation, the expression becomes:

$$= V_{m,mix} + (n_1 + n_2)\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} \qquad \ldots(50)$$

Since the total mole fraction of the system is equal to 1, i.e., $x_1 + x_2 = 1$, thus the total molar volume $V_{m,\ mix}$ at specified temperature and pressure will be the function of only one of the mole fraction terms.

$$V_{m,mix} = f(x_2)$$

Taking differential of the above expression:

$$dV_{m,mix} = \left(\frac{dV_{m,mix}}{dx_2}\right)dx_2 \qquad \ldots(51)$$

Now dividing the equation by dn_1, and taking n_2 be constant, we get:

$$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} = \left(\frac{dV_{m,mix}}{dx_2}\right)\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} \qquad \ldots(51.1)$$

Since the mole fraction is given by

$$x_2 = \frac{n_2}{n_1+n_2} \qquad \ldots(52)$$

Thus for the expression $\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2}$, we can write

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{n_2}{(n_1+n_2)^2} \qquad \ldots(53)$$

Substituting equation (52) in equation (53):

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{x_2}{(n_1+n_2)} \qquad \ldots(54)$$

Substituting the equation (54) in equation (51.1), we get:

$$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} = \left(\frac{dV_{m,mix}}{dx_2}\right)\left(-\frac{x_2}{n_1+n_2}\right) \qquad \ldots(55)$$

Putting this expression in equation (50), we get:

$$V_{1,pm} = V_{m,mix} - x_2\left(\frac{dV_{m,mix}}{dx_2}\right) \qquad \ldots(56)$$

Or

$$V_{m,mix} = V_{1,pm} + x_2\left(\frac{dV_{m,mix}}{dx_2}\right) \qquad \ldots(57)$$

Similarly for second component, the partial molar volume will be given by:

$$V_{m,mix} = V_{2,pm} + x_1\left(\frac{dV_{m,mix}}{dx_1}\right) \qquad \ldots(58)$$

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The above equations represent tangent line drawn to the plot of $V_{m,mix}$ versus x_2 (taking equation 57) with the intercept equal to $V_{1,pm}$ and accordingly the slope of the line is $\left(\frac{dV_{m,mix}}{dx_2}\right)$. Similarly the plot is drawn between $V_{m,mix}$ and x_1 in which the intercept becomes $V_{2,pm}$ and slope is $\left(\frac{dV_{m,mix}}{dx_1}\right)$. Both the equations given above represent a single plot because $x_1 + x_2 = 1$. This plot is shown in the figure given below:
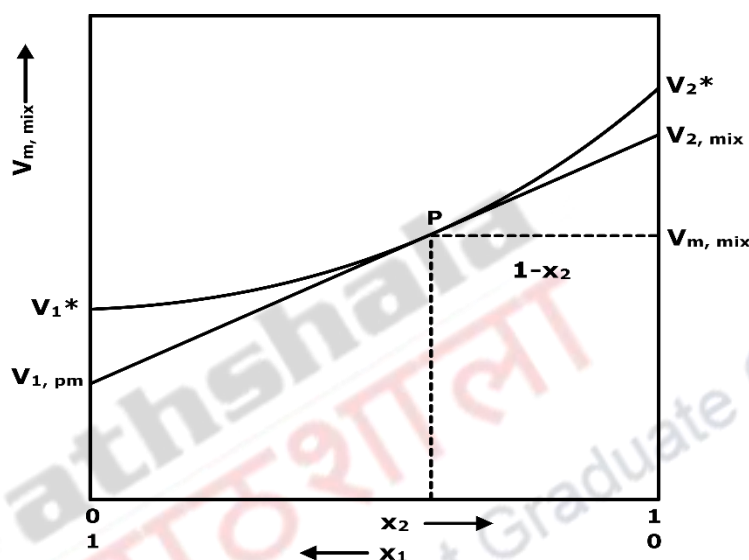

Figure: The method of intercepts to determine the partial molar volumes of components of a binary solution

In Figure: Intercepts are: $V_{1,pm}$ at $x_2 = 0$ (or $x_1 = 1$)

$$V_{2,pm} \text{ at } x_2 = 1 \ (\text{or } x_1 = 0)$$

The equations (57) and (58) are valid for any extensive property Y (V, G, U, S, A, H) of the mixture.

Thus the generalized equation is can be written as:

$$Y_{m,mix} = Y_{1,pm} + x_2 \left(\frac{dY_{m,mix}}{dx_2}\right) \qquad \qquad \dots(59)$$

$$Y_{m,mix} = Y_{2,pm} + x_1 \left(\frac{dY_{m,mix}}{dx_1}\right) \qquad \qquad \dots(60)$$

Determination of partial molar volume for system containing more than two components

Suppose the solution is consisting of more than two components (let m), then from equations (49) to (54) we come to the conclusion that:

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$$V_{i,pm} = V_{m,mix} + n_{total}\left(\frac{\partial V_{m,mix}}{\partial n_i}\right)_{n_j\ (j\neq i)} \qquad \text{...(61)}$$

$$V_{m,mix} = f(x_1, x_2, \ldots x_{i-1}, x_{i+1}, \ldots, x_m) \qquad \text{...(62)}$$

$$dV_{m,mix} = \sum_{k\neq i}\left(\frac{\partial V_{m,mix}}{\partial x_k}\right)_{x_l\ (l\neq k,i)} dx_k \qquad \text{...(63)}$$

$$\left(\frac{\partial V_{m,mix}}{\partial n_i}\right)_{n_j\ (j\neq i)} = \sum_{k\neq i}\left(\frac{\partial V_{m,mix}}{\partial x_k}\right)_{x_l\ (l\neq k,i)}\left(\frac{\partial x_k}{\partial n_i}\right)_{n_j} \qquad \text{...(64)}$$

$$\left(\frac{\partial x_k}{\partial n_i}\right)_{n_j\ (j\neq i)} = -\frac{x_k}{n_{total}} \qquad \text{...(65)}$$

Now substituting equation (64) and (65) in equation (61), we get :

$$V_{i,pm} = V_{m,mix} - \sum_{k\neq i} x_k\left(\frac{\partial V_{m,mix}}{\partial x_k}\right)_{x_l\ (l\neq k,i)} \qquad \text{...(66)}$$

The above equation gives the partial molar volume in a solution consisting of more than two components.

7.2 Partial molar Gibb's energy

The partial molar free energy $G_{i,pm}$ is the most important partial molar quantity in the physical chemistry. It is known as Chemical Potential and is represented as

$$(\partial G / \partial n_i)_{T,P,n_1,n_2,n_3,\ldots} = \bar{G}_i = \mu_i \qquad \text{...(67)}$$

Thus, chemical potential is the change in the free energy of the system which results on the addition of one mole of that particular substance to a very large system such that the overall composition of the system does not change, while keeping the temperature and pressure constant,

Now writing the free energy change by an infinitesimal amount:

$$dG = (\partial G / \partial T)_{P,N} dT + (\partial G / \partial P)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j \qquad \text{...(68)}$$

In which μ_1, μ_2 ...... and μ_j are the chemical potentials of corresponding constituents 1,2 …. and j.

Assuming temperature and pressure to be constant, then free energy change will be:

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots + \mu_j dn_j \qquad \text{...(69)}$$

Let the system has definite composition having n_1, n_2, …. n_j moles of components 1,2,3…j respectively, then integrating equation (69), we get:

$$(G)_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots n_j\mu_j \qquad \text{...(70)}$$

Thus, by looking at above equation, chemical potential may be defined as the contribution to the total free energy of the system by one mole of each component of the mixture while

keeping temperature and pressure constant. And Gibb's free energy of the system is the sum of $n\mu$ terms of the individual constituent of the system.

Gibb's Duhem equation

Chemical potential is dependent on the composition of the system. To understand this, take the total differential of the equation (70):

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots \mu_j dn_j + n_j d\mu_j \qquad \ldots(71)$$

Separating differential of chemical potential and differential of number of moles terms :

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j)(n_1 d\mu_1 + n_2 d\mu_2 + \ldots n_j d\mu_j) \qquad \ldots(72)$$

But from equation (69) we know that at constant temperature and pressure,

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_j dn_j \qquad \ldots(73)$$

Therefore,

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots n_j d\mu_j = 0$$

It is concluded that at constant temperature and pressure the system has definite composition i.e.

$$\sum n_j d\mu_j = 0 \qquad \ldots(74)$$

The above equation is **Gibb's Duhem equation.** The significance of the Gibb's Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potential of the other components.

For a two component system, this equation can be written as:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Or rearranging the above equation:

$$d\mu_1 = -\left(\frac{n_2}{n_1}\right) d\mu_2 \qquad \ldots(75)$$

Thus, by looking at the above equation we can say that the variation in chemical potential of one component of system can bring the variation in chemical potential of second component of the system.

Some important results obtained after Gibb's Duhem equation:
If the number of moles of the components of a system remain constant, that is, the terms dn_1, dn_2, ... dn_j are zero then the equation (5) becomes:

$$dG = (\partial G / \partial T)_{P,\,N} dT + (\partial G / \partial P)_{T,\,N} dP \qquad \ldots(76)$$

But for closed system it is known that $dG = VdP - SdT$ $\qquad \ldots(77)$

Thus by equating the coefficients of dT and dP in equations (76) and (77), we get:

$$(\partial G / \partial T)_{P,\,N} = -S \qquad \ldots(78)$$

$$(\partial G / \partial P)_{T,\,N} = V \qquad \ldots(79)$$

By the results obtained above, the variation of chemical potential with temperature and pressure can be obtain thus these results are important.

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8. Question

For an ideal gas undergoing isothermal reversible expansion, show that $\Delta G = \Delta A$.

Solution:

The free energy functions G and A are given by:

G = H - TS

And

A = U - TS

Also enthalpy is given by:

H = U + pV

Substituting this enthalpy in the expression of free energy G, we get:

G = (U + pV) – TS = (U – TS) + pV

Or G = A + pV

Thus, for a process

$\Delta G = \Delta A + \Delta(pV)$

Thus for an isothermal expansion of an ideal gas, we have:

$\Delta(pV) = \Delta(nRT) = 0$ since $\Delta T = 0$ for an isothermal process.

Thus giving.

$\Delta G = \Delta A$.

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9. Summary

- The two work energy functions are
  Free energy: G = H – TS
  Work function: A = U – TS

- The expression for variation of Gibbs free energy with temperature, keeping the pressure constant is:

  $(\partial G / \partial T)_P = -S$

  Similarly, the expression for variation of Gibbs free energy with pressure, keeping temperature constant is:

  $(\partial G / \partial P)_T = V$

- Maxwell's relations are the expressions connecting internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G) with parameters like volume, pressure, entropy etc. Some of these are:

  i. $dU = TdS - PdV$

  ii. $dH = TdS + VdP$

  iii. $dA = -SdT - PdV$

  iv. $dG = -SdT + VdP$

- Gibb's Helmholtz equation is the variation of Gibb's free energy with temperature and is given by:

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

- The quantity $(\partial X / \partial n_i)_{T,P,n_1, n_2 \dots n_j}$ is called the **partial molar property** of the ith component. This is also represented as $\bar{X}_i$.

- The partial molar volume is represented by:

$$V_{i,pm} = V_{m,mix} - \sum_{k \neq i} x_k \left(\frac{\partial V_{m,mix}}{\partial x_k}\right)_{x_l \ (l \neq k, i)}$$

- Gibb's Duhem equation is given by:

$$\sum n_j d\mu_j = 0$$

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