LECTURE-21

GIBBS – DUHEM EQUATION [PARTIAL & INTEGRAL MOLAR PROPERTIES]

Relations amongst partial molar properties:

Imagine a very large quantity of solution, add 1 gm-mole of pure i into it. Upon dissolution, the total quantity of solution increase by 1 gm – mole. As a result without effective the composition so much the Q get increases. For constant pressure & temperature the increase in Q' is equal to $\overline{Q_i}$. Therefore, $\overline{Q_i}$ .is the value of Q per mole of i in the solution

Again, we know

$$\overline{\mathrm{Q}_\mathrm{i}}^{\mathrm{m}} = \overline{Q_i} - Q_i^0 \qquad (194)$$

[Where $Q_i^0 = Q$ per mole for pure i

$\overline{Q_i^m}$ = Partial molar value of Q of mixture of i in the solution

$\overline{Q_i}$ = Partial molar value of Q of component in the solution

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So for Gibbs free energy per gm. mole of component i, we have

$$\overline{\mathrm{G_i}}^{\mathrm{m}} = \bar{G}_i - G_i^0 \tag{195}$$

Again in general,

$$\overline{dH_i} = T\,\overline{ds_i} + \bar{V}_i dP \tag{196}$$

$$\overline{dG_i} = -\overline{S_i}\,dT + \bar{V}_i\,dP \tag{197}$$

$$\overline{dH_m} = T\,\overline{dS_i^m} + \overline{V_i^m}\,dP \tag{198}$$

$$\overline{dG_i^m} = -\overline{S_i^m}dT + \overline{V_i^m}dP \tag{199}$$

So, we have

$$\bar{G}_i = \overline{H_i} - T\bar{S}_i \tag{200}$$

$$G_i^0 = H_i^0 - TS_i^0 \tag{201}$$

$$\overline{G_i^m} = \overline{H_i^m} - T\overline{S_m} \tag{202}$$

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Using equation (200) and (201) in equation (195), we will get equation (203) as follows

$$\overline{G_i^m} = \overline{G_i} - \mathrm{G}_\mathrm{i}^0 = (\overline{H_i} - T\,\overline{S_i}) - \left(\mathrm{H}_\mathrm{i}^0 - \mathrm{T}S_i^0\right) \qquad (203)$$

$$\overline{\mathrm{G}_\mathrm{i}^\mathrm{m}} = \left(\overline{H_i} - H_i^0\right) - \left(T\overline{S_i} - TS_i^0\right) = \overline{H_i^0} - T\overline{S_i^0} \qquad (204)$$

So considering some common extensive properties, we can write

$$\overline{\mathrm{G}}_\mathrm{i}' = \left(\frac{\partial \mathrm{G}'}{\partial \eta_\mathrm{i}}\right)\text{T, P, } n_1, n_2\text{.... except } n_i \qquad (205)$$

$$\overline{\mathrm{S}}_\mathrm{i} = \left(\frac{\partial \mathrm{S}'}{\partial \eta_\mathrm{i}}\right)\text{T, P, } n_1, n_2\text{.... except } n_i \qquad (206)$$

$$\overline{\mathrm{H}_\mathrm{i}} = \left(\frac{\partial \mathrm{H}'}{\partial \eta_\mathrm{i}}\right)\text{T, P, } n_1, n_2\text{.... except } n_i \qquad (207)$$

$$\overline{\mathrm{V}}_\mathrm{i} = \left(\frac{\partial \mathrm{V}'}{\partial \eta_\mathrm{i}}\right)\text{T, P, } n_1, n_2\text{.... except } n_i \qquad (208)$$

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Again, using equation (194), we can get the following equations

$$\overline{S_i^m} = \bar{S_i} - S_i^0 \tag{209}$$

$$\overline{H_i^m} = \overline{H_i} - H_i^0 \tag{210}$$

$$\overline{V_i^m} = \bar{V_i} - V_i^0 \tag{211}$$

Common symbols that are used

Q – Extensive property of solution, it can refer as U, H, V, S, G etc.

$\overline{Q_i}$ - Partial molar value of Q of component i in the solution.

Q_i^0 - Q per mole for pure i.

$\overline{Q_i^m}$ - Partial molar value of mixing of component i in the solution.

Q' - Value of quantity in the entire solution

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Gibb’s – Duhem Equation:

Since we know, at constant T, P we have got

$$dQ' = \overline{Q_1}\,dn_1 + \overline{Q_2}\,dn_2 + ---- + \overline{Q_n}\,dn_n \qquad (212)$$

$$\Rightarrow dQ' = \sum_i \overline{Q_i}\,dn_i \qquad (213)$$

By adding small quantities of component $(\partial n_{1,}\partial n_2, \ldots, \partial n_i)$ at constant T, P such that overall composition of the solution remains same in all stages. Since $\overline{Q_1}$, $\overline{Q_2}$, ………., $\overline{Q_i}$ are functions of T, P & compositions. So these are remained constant. Therefore after the additions are complete, we get

$$Q' = \overline{Q_1}n_1 + \overline{Q_2}n_2 + \ldots\ldots\ldots\ldots + \overline{Q_n}n_n \qquad (214)$$

Differentiating equation (214), we will get

$$dQ' = (\overline{Q_1}dn_1 + n_1\overline{dQ_1)} + (\overline{Q_2}dn_2 + n_2\overline{dQ_2)} + \ldots\ldots\ldots\ldots\ldots + \overline{(Q_n}dn_n + n_n\overline{dQ_n)} \qquad (215)$$

Continued…

$$dQ' = \sum_i \overline{Q_i} dn_i + \sum_i n_i \overline{dQ_i)} \qquad (216)$$

Equating equation (213) and (216), we will get

$$\sum_i n_i \overline{dQ_i} = 0 \qquad (217)$$

Dividing the equation (217) by the total no. of moles(n_T), we will get

$$\sum_i X_i \overline{dQ_i} = 0 \qquad \text{(Since, } \frac{n_i}{n_T} = X_i) \qquad (218)$$

[Where, Total no of moles $(n_T) = n_1 + n_2 + \ldots\ldots\ldots. + n_i$]

In the above, equation (217) and (218) are the alternative forms of **Gibb's-Duhem equation (G-D equation)**, which provide the principal foundation to thermodynamic solutions.

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For Gibb’s free energy, the G-D equation can be written as

$$\sum_i n_i \overline{dG_i} = 0 \qquad \text{or} \qquad \sum_i X_i \overline{dG_i} = 0 \qquad (219)$$

For pure component the values of Q such as $Q_1^0, Q_2^0, \ldots\ldots\ldots, Q_i^0$ are constants at constant T & P.

So $dQ_1^0, dQ_2^0, \ldots\ldots\ldots\ldots, dQ_i^0$ are zero. Hence we have

$$\sum_i n_i\, dQ_i = 0 \qquad \text{or} \qquad \sum_i X_i\, dQ_i = 0 \qquad (220)$$

Since we know that

$$\left.\begin{aligned} &\sum_i n_i \overline{dQ_i^m} = \sum_i n_i d(\overline{Q_i^m} - Q^0) = 0 \\ &\quad \text{Or} \\ &\sum_i X_i \overline{dQ_i^m} = \sum_i X_i d(\overline{Q_i^m} - Q^0) = 0 \end{aligned}\right\} \qquad (221)$$

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The G-D equation is usually applied to describe the effect temperature and pressure changes on free energy that well-known as Clausius-Clapeyron equation.

Consider a phase transformation of an element or compound (designated as A)

A (phase I) = A (phase II)

For phase I: $dG_A(I) = V_A(I)dP - S_A(I)dT$ (I)

For phase II: $dG_A(II) = V_A(II)dP - S_A(II)dT$ (II)

At equilibrium phase transformation temp (T_{tr}) and pressure (P_{tr})

$$\Delta G = G_A(II) - G_A(I) = 0 \qquad \text{(III)}$$

So, due change the system have achieved new state of equilibrium where pressure is $P_{tr} + dP$, temp is $T_{tr} + dT$ and also Gibb's free energy change to $G_A(I) \rightarrow G_A(I) + dG_A(I)$ & $G_A(II) \rightarrow G_A(II) + dG_A(II)$.

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Since, $\Delta G = G_A(II) - G_A(I) = 0$ from equation (III),

So $G_A(II) = G_A(I) \Rightarrow V_A(I)dP - S_A(I)\,dT = V_A(II)dP - S_A(II)\,dT$ (IV)

$$\Rightarrow [S_A(II) - S_A(I)]\,dT = [V_A(II) - V_A(I)]dP \qquad \text{(V)}$$

$$\Rightarrow \left(\frac{dT}{dP}\right)_{eqlbm} = \frac{V_A(II) - V_A(I)}{S_A(II) - S_A(I)} \qquad \text{(VI)}$$

$$\Rightarrow \boxed{\left(\frac{dT}{dP}\right)_{eqlbm} = \frac{\Delta V_{tr}}{\Delta S_{tr}} = \frac{\Delta V_{tr}\,T_{tr}}{\Delta H_{tr}}} \qquad \text{(VII)}$$

So it can be written as

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_{\Delta G=0} = \frac{\Delta S_{tr}}{\Delta V_{tr}} = \frac{\Delta H_{tr}}{\Delta V_{tr} T_{tr}}}$$

Note: tr stands for transformation

Clausius-Clapeyron equation