❖ Gibb's-Duhem Equation

In order to derive the expression for Gibbs's-Duhem equation, consider a system that comprises of *n* types of constituents with n_1, n_2, n_3, n_4 … moles. So, being an extensive property, the partial molar free energy depends upon not only the temperature and pressure but also on the number of moles of different components. Mathematically, we can say that

$$G = f(T, P, n_1, n_2, n_3 \dots) \tag{179}$$

Now let us assume a small change in the temperature, pressure and amount of different components, this would impart a variation in partial molar free energy as given below.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \cdots \tag{180}$$

The first term on the right-hand side gives the change in the free energy with the temperature at constant pressure and compositions; while the second term gives the change in the free energy with pressure at constant temperature and compositions. The terms afterward represent the variation in free energy with the amount of one component while the temperature, pressure and all other compositions are kept constant.

However, if the temperature and pressure of the system are kept constant, i.e., $dT = 0$, $dP = 0$, the equation (180) takes the form

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 \dots \tag{181}$$

Every term on the right-hand side of the equation (181) is partial molar free energy or simply the "chemical potential" i.e.

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} \tag{182}$$

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} \tag{183}$$

$$\mu_3 = \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} \tag{184}$$

$$\mu_4 = \left(\frac{\partial G}{\partial n_4}\right)_{T,P,n_1,n_2\dots} \tag{185}$$

$$\mu_5 = \left(\frac{\partial G}{\partial n_5}\right)_{T,P,n_1,n_2\dots} \tag{186}$$

After putting the values from equations like (182 – 186) in equation (181), we get

$$(dG)_{T,P} = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \mu_4\, dn_4 + \mu_5\, dn_5 \ldots \tag{187}$$

Now, if the system composition is definite, the integration of the above equation gives

$$G_{T,P,N} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \mu_4\, dn_4 + \mu_5\, dn_5 \ldots \tag{188}$$

The differentiation of equation (188) at constant temperature and constant pressure but changing composition gives the following relation

$$\begin{aligned}(dG)_{T,P} = (n_1 d\mu_1 + \mu_1 dn_1) + (n_2 d\mu_2 + \mu_2 dn_2) + (n_3 d\mu_3 + \mu_3 dn_3)\\ + (n_4 d\mu_4 + \mu_4 dn_4) + (n_5 d\mu_5 + \mu_5 dn_5) \ldots\end{aligned} \tag{189}$$

or

$$\begin{aligned}(dG)_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \mu_4 dn_4 + \mu_5 dn_5 \ldots)\\ + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + n_4 d\mu_4 + n_5 d\mu_5 \ldots)\end{aligned} \tag{190}$$

After comparing the equation (187) and (190), we can conclude that the content included in the second bracket must be equal to zero. Mathematically, we can say that

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 \ldots = 0 \tag{191}$$

or

$$\sum n_i d\mu_i = 0 \tag{192}$$

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Which is the popular Gibbs-Duhem equation, and is applicable to the systems under constant temperature-pressure conditions.

The physical significance of the Gibbs-Duhem equation can be understood by taking the example of binary solutions i.e. a system of two components only. The Gibbs-Duhem equation for such systems is

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{193}$$

or

$$n_1 d\mu_1 = -n_2 d\mu_2 \tag{194}$$

or

$$d\mu_1 = -\frac{n_2}{n_1}\, d\mu_2 \tag{195}$$

Hence, the chemical potential of one constituent is not independent of another component in binary solutions. In other words, the chemical potentials or partial molar free energies of two components of the binary system are mutually dependent; and if the one increases the other one decreases.

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It is also worthy to note that if the number of moles of different constituents remains constant (closed system), i.e., $dn_i = 0$; equation (180) reduces to the following.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \tag{196}$$

Also, for a closed system, we know that

$$dG = VdP - SdT \tag{197}$$

Which means that

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad and \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \tag{198}$$

Which is the variation of free energy with temperature and pressure in closed systems. These two relations can further be used to deduce the variations of chemical potentials with temperature and volume.

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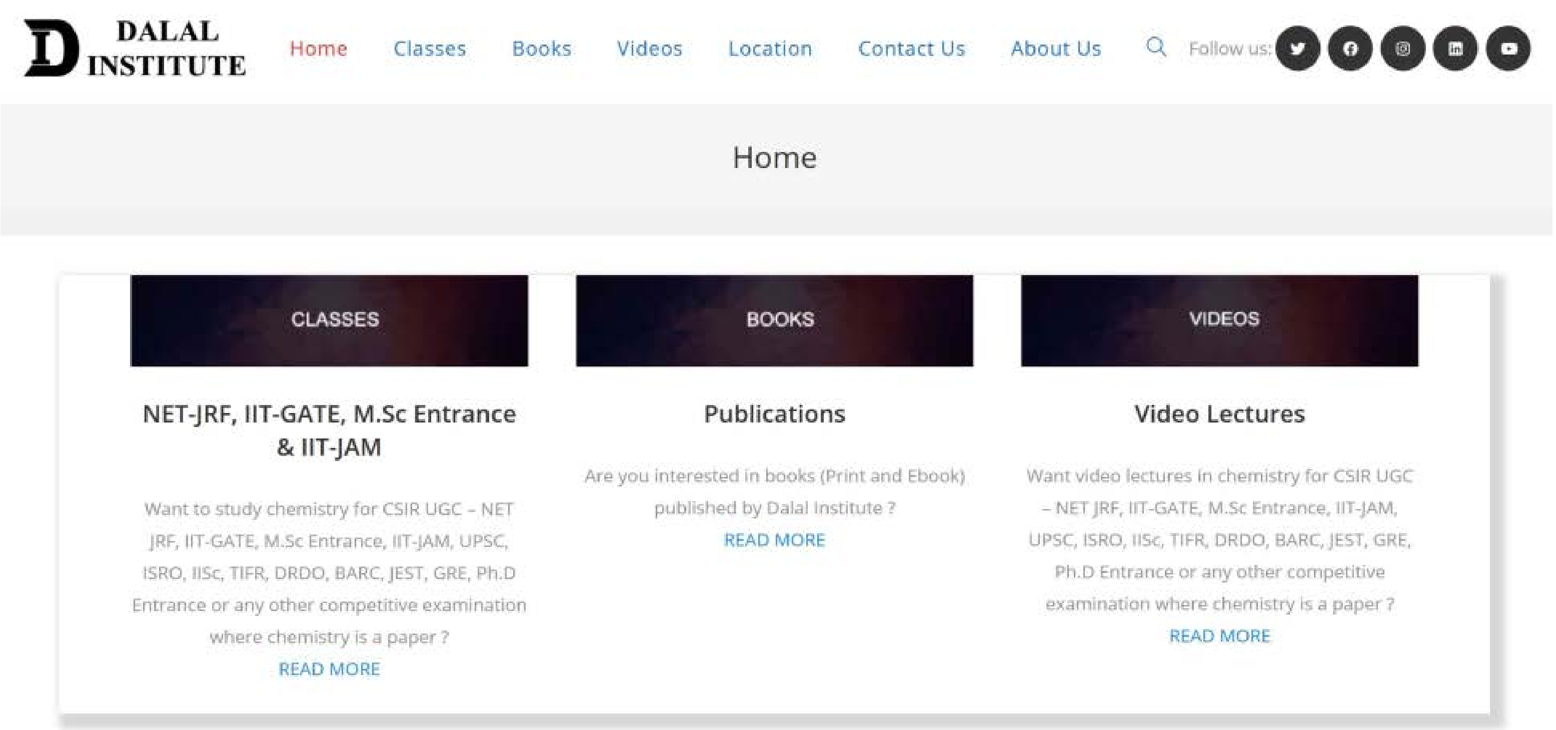

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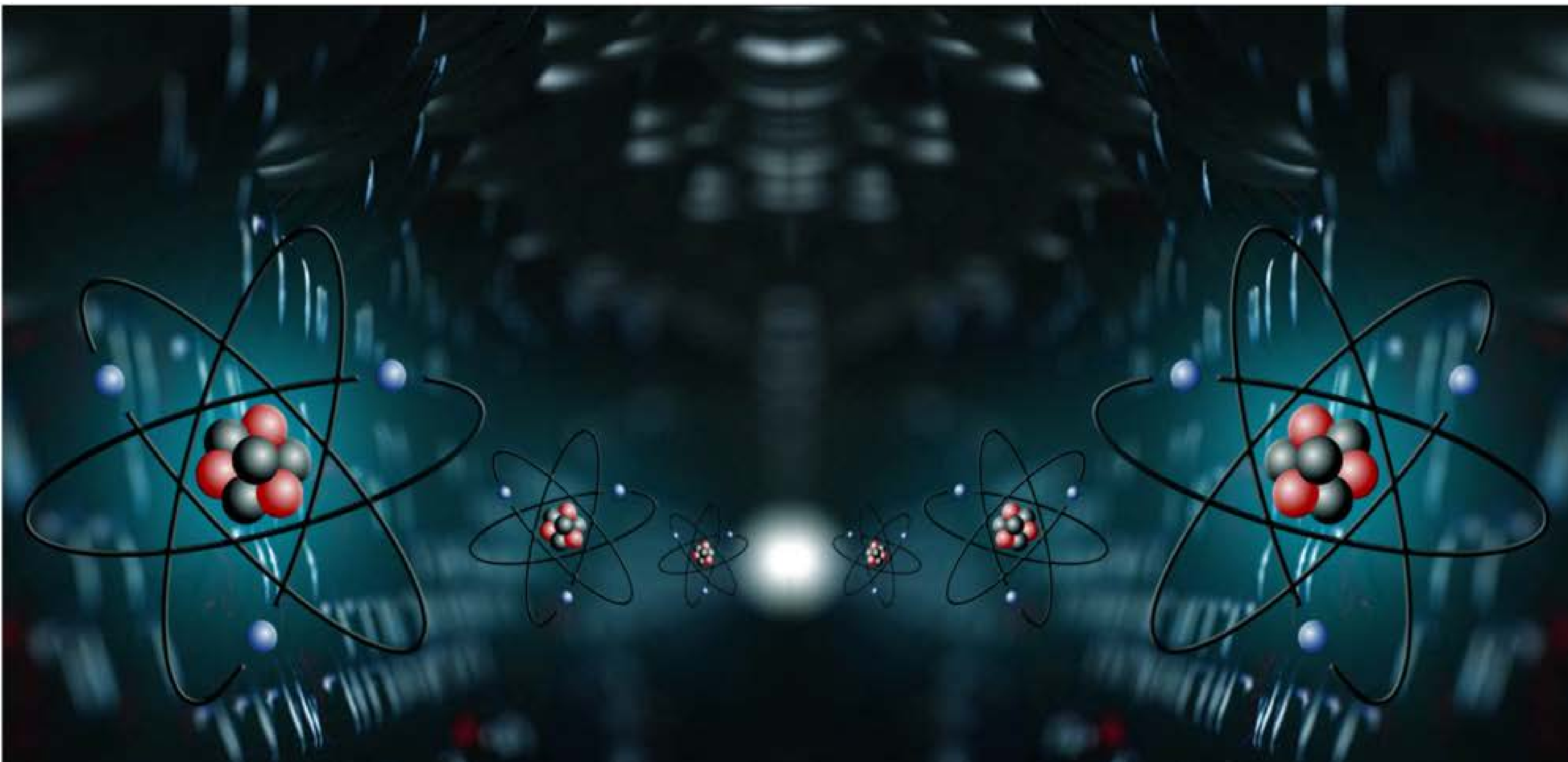

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