Systems with Variable Composition

In a closed system, there can be no change in the mass of the system. The change of state of such a system can be considered to be due to change in *T* and *P* only.

In an open system containing two or more components, there can be change in the number of mole of various components due to interchange of matter with the surroundings or to irreversible chemical reaction or to irreversible interphase transport of matter within the system. The thermodynamic properties *U*, *H*, *S*, *A* and *G* are extensive properties. Therefore, they may be written as

$$U = f(T, p, n_1, n_2, \dots \dots \dots ., n_j)$$

$$G = f(T, p, n_1, n_2, \dots \dots \dots ., n_j)$$

$$V = f(T, p, n_1, n_2, \dots \dots \dots ., n_j)$$

$$H = f(T, p, n_1, n_2, \dots \dots \dots ., n_j)$$

Partial Molar quantities: For any thermodynamic property *X*, of an open system, the partial molar property $\overline{X_J}$ of a substance *j* is defined as

$$\overline{X_J} = \left(\frac{\delta X}{\delta n_j}\right)_{T,p,n'} \quad \dots \dots \dots \dots (1)$$

where n_j is the number of moles of *j* and n' signifies that the amounts of all other substances present are constant.

In other words, any partial molar property $\overline{X_J}$ of a substance *j* in a mixture is the change in the property X on addition of 1 mol of *j* to a large excess of the mixture at constant *T* and *P*.

Partial molar properties are intensive properties. Corresponding to any extensive property *U*, *V*, *S*, *H*, *A*, *G*, etc, there are partial molar properties $\overline{U_J}, \overline{V_J}, \overline{S_J}, \overline{H_J}, \overline{A_J}, \overline{G_J},$ defined as

$$\overline{U_J} = \left(\frac{\delta U}{\delta n_j}\right)_{T,p,n'}$$

$$\overline{V_J} = \left(\frac{\delta V}{\delta n_j}\right)_{T,p,n'}$$

$$\overline{S_J} = \left(\frac{\delta S}{\delta n_j}\right)_{T,p,n'}$$

$$\overline{H_J} = \left(\frac{\delta H}{\delta n_j}\right)_{T,p,n'}$$

$$\overline{A_J} = \left(\frac{\delta A}{\delta n_j}\right)_{T,p,n'}$$

$$\overline{G_J} = \left(\frac{\delta G}{\delta n_j}\right)_{T,p,n'}$$

Partial Molar Volume: The partial molar volume of a substance j in a mixture is the change in volume on the addition of 1 mol of j to a large excess of the mixture at constant T and P. Mathematically,

$$\overline{V_J} = \left(\frac{\delta V}{\delta n_j}\right)_{T,p,n'}$$

and n' signifies that the amounts of all other substances present are constant.

The definition implies that when the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, the total volume of the mixture changes by

$$dV = \left(\frac{\delta V}{\delta n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\delta V}{\delta n_B}\right)_{T,p,n_A} dn_B$$

$$\Rightarrow dV = \overline{V_A} dn_A + \overline{V_B} dn_B$$

When n_A moles of A and n_B moles of B are present in a mixture, the total volume V is obtained by integrating the above equation given by

$$\int dV = \overline{V_A} \int dn_A + \overline{V_B} \int dn_B$$

$$\Rightarrow V = \overline{V_A} n_A + \overline{V_B} n_B$$

where $\overline{V_A}$ and $\overline{V_B}$ are partial molar volumes of A and B respectively.

In general,

$$V = \sum_j n_j \overline{V_J}$$

When 1 mol of H_2O is added to a huge volume of pure water at 25°C, the volume increases by 18 cm^3. Thus, 18 cm^3mol^{-1} is the molar volume of pure water. However, when 1 mol H_2O is added to a huge volume of pure ethanol, the volume increases by only 14 cm^3. The reason for the difference in increase in volume is as follows: The volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules. The stronger forces acting between H_2O and ethanol molecules result in better packing for which the volume increases only by $14 cm^3$. The quantity $14\ cm^3mol^{-1}$ is the partial molar volume of water in pure ethanol.

Prob: At 25°C, the density of a 50% by mass ethanol/water solution is 0.914 $g\ cm^{-3}$. Given that the partial molar volume of water in the solution is 47.4 cm^3mol^{-1}, what is the partial molar volume of ethanol?

Fundamental equation of Thermodynamics for an open system:

Let us consider a one-plane system that is in thermal and mechanical equilibrium but not in material equilibrium.

At any instant during a chemical process in the system, the Gibbs energy is given by

$$G = f(T, p, n_1, n_2, \dots\dots\dots, n_j) \dots\dots\dots\dots (1)$$

Total differential of (1) is

$$dG = \left(\frac{\delta G}{\delta T}\right)_{p,n_j} dT + \left(\frac{\delta G}{\delta p}\right)_{T,n_j} dp + \left(\frac{\delta G}{\delta n_1}\right)_{T,p,n'} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,p,n'} dn_2 + \cdots\cdots\cdots\cdots (2)$$

where n' signifies that all the components except the one are kept constant.

For a reversible process where no change in composition occurs, considering only $P{-}V$ work,

$$dG = -SdT + Vdp \dots\dots\dots\dots\dots\dots (3)$$

It follows from (3) that

$$\left(\frac{\delta G}{\delta T}\right)_{p,n_j} = -S \dots\dots\dots\dots\dots\dots (4a)$$

$$\left(\frac{\delta G}{\delta p}\right)_{T,n_j} = V \dots\dots\dots\dots\dots\dots (4b)$$

Putting (4a) and (4b) in equation (2), we get

$$dG = -SdT + Vdp + \left(\frac{\delta G}{\delta n_1}\right)_{T,p,n'} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,p,n'} dn_2 + \cdots\dots\dots\dots (5)$$

Now partial molar Gibbs free energy or chemical potential of a substance j is defined as

$$\overline{G_j} = \mu_j = \left(\frac{\delta G}{\delta n_j}\right)_{T,p,n'} \dots\dots\dots\dots\dots\dots (6)$$

Using (6) in (5), we get

$$dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \cdots \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Equation (7) is a fundamental equation of thermodynamics for open system.

At constant T and P equation (7b) simplifies to

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots\cdots\cdots\cdots = \sum_j \mu_j \, dn_j \cdots\cdots\cdots\cdots\cdots (8)$$

Under same conditions

$$dG = dw_{e,max} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (9)$$

Therefore,

$$dw_{e,max} = \sum_j \mu_j \, dn_j \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (10)$$

i.e. non-expansion work can arise from the changing composition of a system.

From equation (8), Gibbs-free energy of a mixture is given by

$$G = \sum_j n_j \mu_j \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (11)$$

New from,

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS$$

We get

$$U = H - PV$$

$$\Rightarrow U = G + TS - PV \ldots\ldots (12a)$$

and

$$H = G + TS \ldots\ldots\ldots\ldots\ldots\ldots (12b)$$

$$A = G - PV \ldots\ldots\ldots\ldots\ldots\ldots (12c)$$

Differentiating 12a, 12b and 12c

$$dU = dG + TdS + SdT - pdV - Vdp$$

$$dH = dG + TdS + SdT$$

$$dA = dG - pdV - Vdp$$

Substituting the value of dG from eqn (7) in the above equations

$$dU = TdS - pdV + \sum_j \mu_j \, dn_j \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (13a)$$

$$dH = TdS + Vdp + \sum_j \mu_j \, dn_j \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (13b)$$

$$dA = -SdT - pdV + \sum_j \mu_j\, dn_j \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .(13c)$$

Equations (13a), (13b)) and (13c) are called fundamental equations for open system (including equation (7). These equations are also known as Gibbs equations.

Partial Molar Gibbs free energy or chemical potential:

The quantity μ_j defined as $\mu_j = \left(\frac{\delta G}{\delta n_j}\right)_{T,p,n'}$ is known as the chemical potential of the j^{th} component. Thus, chemical potential is the increase in *G* per mole that results when a small amount dn_j moles are added to the system keeping temperature, pressure and all other compositions constant.

Chemical potential is a measure of escaping tendency. It is the chemical potential of a component in a system is high, the component has a large escaping tendency, while if the chemical potential is low, the component has a small escaping tendency. Matter flows spontaneously from a region of high chemical potential to a region of low chemical potential.

Chemical potential of a component in a mixture of ideal gases

Desired expression can be obtained using the relation between μ_j and $\overline{V_j}$ given by

$$\left(\frac{\delta \mu_j}{\delta P}\right)_{T,n_1,n_2\ldots\ldots} = \overline{V_j} \ldots\ldots\ldots\ldots\ldots (1)$$

where *P* is the total pressure of a system consisting of a number of ideal gases. Let $n_1, n_2, \ldots\ldots..$ be the number of moles of each constituent present in the mixture.

Hence,

$$PV = (n_1 + n_1 + \cdots\cdots + n_1 + \cdots\cdots)RT$$

$$\Rightarrow V = \left(n_1 + n_1 + \cdots\cdots + n_1 + \cdots\cdots\right)\frac{RT}{P}$$

where *P* is the total pressure of the mixture.

Therefore,

$$\overline{V_j} = \left(\frac{\delta V}{\delta n_j}\right)_{T,p,n'} = \frac{RT}{P}$$

Using this (1) becomes.

$$\therefore \left(\frac{\delta \mu_j}{\delta P}\right)_{T,n_1,n_2\ldots\ldots} = \frac{RT}{P} \ldots\ldots\ldots\ldots .. (2)$$

So,

$$d\mu_j = RT\frac{dP}{P}$$

Integrating this from pressure $p^0 = 1\ bar$ to any pressure of interest p, we get

$$\int_{p^0=1\ bar}^{p} d\mu_j = RT\int_{p^0=1\ bar}^{p}\frac{dP}{P}$$

$$\Rightarrow \mu_j(p) - \mu_j(p^0) = RT\int_{p^0}^{p} dlnP$$

$$\Rightarrow \mu_j - \mu_j^0 = RT\int_{p^0}^{p} dlnP \ldots\ldots..(3)$$

Let p_j be the partial pressure of the *j*th component, then

$$p_j = \frac{n_j}{n}P$$

$$\therefore dlnp_j = dlnP \qquad \left[\frac{n_j}{n}\ is\ a\ constant\right]$$

Using this equation (3) becomes

$$\mu_j - \mu_j^0 = RT\int_{p^0}^{p_j} dlnp_j \ldots\ldots..(3)$$

$$\Rightarrow \mu_j - \mu_j^0 = RTln\frac{p_j}{p^0}$$

This expression gives the chemical potential of the *j*th component in a mixture of ideal gases.

Gibbs-Duhem equation

Let us consider a mixture of components 1, 2, 3,……….., j,……….., etc. having mole numbers $n_1,\ n_2, n_3\ \ldots\ldots.., n_j, \ldots\ldots\ldots, etc.$ If $\mu_{1,}\ \mu_{2,}\ \mu_{3,}\ \ldots\ldots\ldots etc$ be the chemical potential of the components in the open system, then at constant *T* and *P,* total Gibbs free energy is given by additivity rule

$$G = n_1\mu_1 + n_2\mu_2 + \cdots\cdots\cdots + n_j\mu_j + \cdots\cdots$$

$$\Rightarrow G = \sum_{j=1} n_j\mu_j \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

Again,

$$G = f(T, p, n_1, n_2, \dots\dots\dots, n_j)$$

$$dG = \left(\frac{\delta G}{\delta T}\right)_{p,n_j} dT + \left(\frac{\delta G}{\delta p}\right)_{T,n_j} dp + \left(\frac{\delta G}{\delta n_1}\right)_{T,p,n'} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,p,n'} dn_2 + \cdots\cdots\cdots\cdots$$

$$\Rightarrow dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots\cdots\cdots\cdots$$

At constant T and p,

$$(dG)_{T,p} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots\cdots\cdots\cdots \sum_{j=1} \mu_j \, dn_j \cdots\cdots (2)$$

From (1),

$$(dG)_{T,p} = (n_1 d\mu_1 + \mu_1 dn_1) + (n_2 d\mu_2 + \mu_2 dn_2) + \cdots\cdots\cdots\cdots\cdots$$

$$\Rightarrow (dG)_{T,p} = (n_1 d\mu_1 + n_2 d\mu_2 + \cdots\cdots) + (\mu_1 dn_1 + \mu_2 dn_2 + \cdots\cdots)$$

$$\Rightarrow (dG)_{T,p} = \sum_{j=1} n_j \, d\mu_j + \sum_{j=1} \mu_j \, dn_j \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

Comparing (2) and (3),

$$\sum_{j=1} n_j \, d\mu_j = 0$$

This equation is known as Gibbs-Duhem equation.

Significance:

Gibbs-Duhem equation for a binary solution of components 1 and 2 can be written as

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

$$\Rightarrow d\mu_1 = -\frac{n_2}{n_1} d\mu_2$$

This implies that chemical potential of the components of a mixture cannot change independently. In a binary mixture if chemical potential of one component increases then chemical potential for the other component must decrease.

Change in thermodynamic functions in mixing of ideal gases

The Gibbs energy of mixing, $\Delta_{mix}G$

Let the amounts of two perfect gases in two containers be n_A and n_B ; both are at a temperature T and pressure P.

At this stage, the free energy of the total system is given by the additivity rule

$$G_i = n_A\mu_A + n_B\mu_B$$

Again, the chemical potentials of the ideal gas A and B are given by

$$\mu_A = \mu_A^0 + RTln\left(\frac{P}{p^0}\right)$$

$$\mu_B = \mu_B^0 + RTln\left(\frac{P}{p^0}\right)$$

$$\therefore G_i = n_A\left\{\mu_A^0 + RTln\left(\frac{P}{p^0}\right)\right\} + n_B\left\{\mu_B^0 + RTln\left(\frac{P}{p^0}\right)\right\}$$

After mixing, the partial pressures of the gases are p_A and p_B with total pressure

$$P = p_A + p_B$$

Again, the chemical potential of the component ideal gases in the mixture is given by

$$\mu_A = \mu_A^0 + RTln\left(\frac{p_A}{p^0}\right)$$

$$\mu_B = \mu_B^0 + RTln\left(\frac{p_B}{p^0}\right)$$

The total Gibbs energy changes to

$$G_f = n_A\left\{\mu_A^0 + RTln\left(\frac{p_A}{p^0}\right)\right\} + n_B\left\{\mu_B^0 + RTln\left(\frac{p_B}{p^0}\right)\right\}$$

Gibbs energy of mixing is given by

$$\begin{aligned}\Delta_{mix}G &= G_f - G_i \\ &= n_ARTln\left(\frac{p_A}{p^0}\right) - n_ARTln\left(\frac{P}{p^0}\right) + n_BRTln\left(\frac{p_B}{p^0}\right) - n_BRTln\left(\frac{P}{p^0}\right) \\ &= n_ARTln\left(\frac{p_A}{P}\right) + n_BRTln\left(\frac{p_B}{P}\right)\end{aligned}$$

Now, mole fraction of A,

$$x_A = \frac{n_A}{n}$$

and, mole fraction of B,

$$x_B = \frac{n_B}{n}$$

And, partial pressures

$$p_A = x_A P$$

$$\Rightarrow x_A = \frac{p_A}{P}$$

And

$$p_B = x_B P$$

$$\Rightarrow x_B = \frac{p_B}{P}$$

With these modifications

$$\Delta_{mix} G = nRT(x_A ln x_A + x_B \, ln x_B)$$

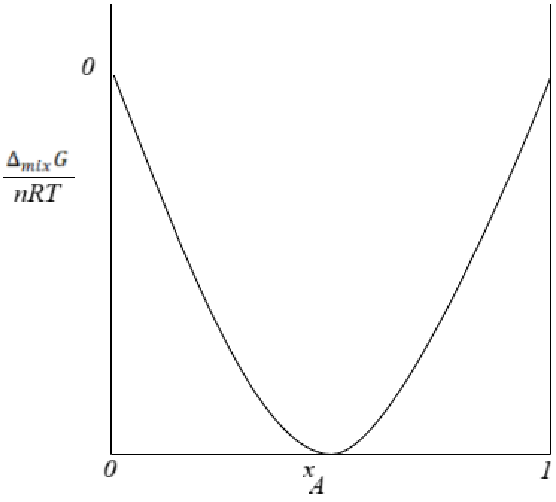
Because $x_A < 1$ and $x_B < 1$, the logarithms in this equation are negative, and $\Delta_{mix} G < 0$.

∴ Perfect gases mix spontaneously in all proportions.

If there are more than two components of the mixture, the above equation becomes

$$\Delta_{mix} G = nRT(x_A ln x_A + x_B ln x_B + x_C ln x_C + \cdots\cdots\cdots)$$

$$= nRT \sum x_j ln x_j \cdots\cdots\cdots (1)$$



Entropy of mixing, $\Delta_{mix} S$

Because

$$\left(\frac{\delta G}{\delta T}\right)_{p,n_j} = -S$$

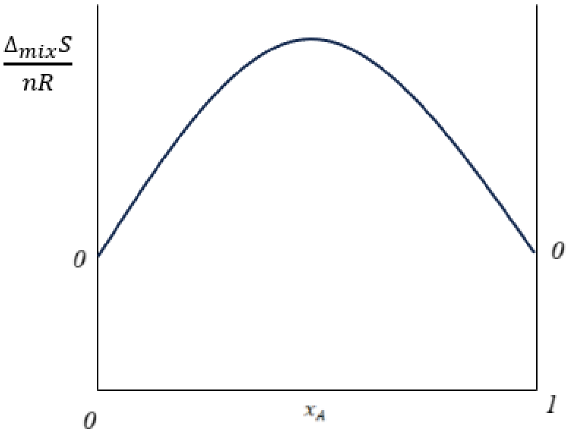
for a mixture of perfect gases

$$\left(\frac{\delta \Delta_{mix} G}{\delta T}\right)_{p,n_j} = -\Delta_{mix} S$$

$$\Rightarrow \Delta_{mix}S = -\left(\frac{\delta \Delta_{mix}G}{\delta T}\right)_{p,n_j}$$

$$\Rightarrow \Delta_{mix}S = -nR\sum x_j ln x_j \cdots\cdots\cdots (2)$$

Because $ln x_j < 0$, it follows that $\Delta_{mix}S > 0$ for all compositions. This increase in entropy is expected because when one gas disperses into the other the system becomes more chaotic.



Enthalpy of mixing, $\Delta_{mix}H$

This can be calculated by

$$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$$

From (1) and (2)

$$nRT\sum x_j ln x_j = \Delta_{mix}H + nRT\sum x_j ln x_j$$

$$\Rightarrow \Delta_{mix}H = 0$$

There is no heating effect associated with the formation of an ideal gas mixture because in an ideal system there are no interactions between particles. The whole of the driving force for mixing comes from the increase in entropy of the system. The mixing is entirely an entropy effect. Gibbs free energy of mixing stems from the change in disorder of the system that arises from the mingling of the molecules of the gases.

Prob: Show that the molar free energy of mixing in a binary ideal gas mixture is minimum when

$$x_1 = x_2 = \frac{1}{2}$$