For an ideal gas $\mu_i = \mu_i^0 + RT\ln x_i$

$$\left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P} = \frac{RT}{x_i} \quad , \quad V_{i,m} = \frac{RT}{P}$$

$$d\mu_i = -S_{i,m}\,dT + RT\frac{dP}{P} + \frac{RT\,dx_i}{x_i}$$

This equation was done on 7/3/2020

Thermodynamic Functions of Mixing

When two or more substances are mixed there will be changes in the properties of the various components of system.

To calculate thermodynamic function of mixing which is equal to the property of the mixture minus the total property of the pure components

(1) Free Energy of Mixing ΔG_{mix} : Let there be a vessel with three compartments and partition of compartment is movable. Each compartment contains a "known" amount of different pure gases which are at same T & P.

$G_{initial}$ = Free energy of gases before mixing

$$= n_1\mu_1^* + n_2\mu_2^* + n_3\mu_3^* = \sum_{i=1}^{3} n_i\mu_i^*$$

μ_i^* is chemical potential of pure gas

If gases are allowed to mixed by removing the partition then the free energy of each gas will be changed

Total free energy after mixing $G_{final} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3$

Free energy mixing = $\Delta G_{mix} = G_{final} - G_{initial}$

If the gases are ideal then $\mu_i = \mu_i^\circ + RT\ln x_i$

$\therefore \Delta G_{mix} = \sum n_i \mu_i^\circ + RT \sum n_i \ln x_i - \sum n_i \mu_i^\circ$

$= RT \sum n_i \ln x_i$

Since there were three gases considered

$\Delta G_{mix} = RT\,(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3)$ — ①

Divide eq ① by $\sum n_i = n$.

$$\Delta G_{mix,m} = \frac{\Delta G_{mix}}{n} = RT\left(\frac{n_1}{n}\ln x_1 + \frac{n_2}{n}\ln x_2 + \frac{n_3}{n}\ln x_3\right)$$

$$= RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3)$$

$$= RT \sum x_i \ln x_i \quad \text{— ②}$$

eq ② Shows that $\Delta G_{mix,m}$ is always −ve because because $x_i < 1$. always. $\therefore \ln x_i = -ve$

Since mixing is spontaneous (for gases & liquids) so it is accompanied by decrease of free energy

2) Entropy of Mixing ΔS_{mix}.

$S_{initial} = n_1 S^\circ_{1,m} + n_2 S^\circ_{2,m} + n_3 S^\circ_{3,m}$

$S_{final} = n_1 S_{1,m} + n_2 S_{2,m} + n_3 S_{3,m} = \sum n_i S_{i,m}$

$S^\circ_{i,m}$ is molar entropy of pure gas.

$S_{i,m}$ is " " of mixture of gases

$\Delta S_{mixing} = S_{Final} - S_{initial}$

$= \sum n_i S_{i,m} - \sum n_i S^\circ_{i,m}$ — ①

∵ Partial Molar entropy of gas can be determined from its chemical potential

$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -S_{i,m}$, $\mu_i = \mu_i^\circ + RT\ln x_i$

$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = R\ln x_i + \left(\frac{\partial \mu_i^\circ}{\partial T}\right)_{P,}$

$$-S_{i,m} = -S^{\circ}_{i,m} + R\ln x_i$$

$$S_{i,m} = S^{\circ}_{i,m} - R\ln x_i \quad \text{—②}$$

Sub. ② in eq ①

$$\Delta S_{mix} = \Sigma n_i S^{\circ}_{i,m} - \Sigma n_i R\ln x_i - \Sigma n_i S^{\circ}_{i,m}$$

$$= -n_i R\,\Sigma \ln x_i \quad \text{—③}$$

$$\Delta S_{mix,m} = \frac{\Delta S_{mix}}{n} = -n\Sigma \frac{n_i}{n} R\ln x_i = -Rn\Sigma x_i \ln x_i$$

$\because$ $\ln x_i$ is always negative ($\because x_i < 1$)

$\therefore$ ΔS_{mix} = +ve quantity.

Similarly $\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S$

$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{P,x_i} = -\frac{\partial}{\partial T}\left[RT\,\Sigma n_i \ln x_i\right)$$

$$= -R\Sigma n_i \ln x_i = -nR\Sigma x_i \ln x_i$$

(3) Volume of Mixing ΔV_{mix} : It is equal to the volume of mixture less the sum of the volumes of pure components. Let $V_{1,m}$, $V_{2,m}$, $V_{3,m}$ be partial molar volume of components 1, 2, 3 in the mixture and $V^{\circ}_{m,1}$, $V^{\circ}_{m,2}$, $V^{\circ}_{m,3}$ of molar volume of pure components

$$\Delta V_{mix} = (n_1 V_{1,m} + n_2 V_{2,m} + n_3 V_{3,m}) - (n_1 V^{\circ}_{1,m} + n_2 V^{\circ}_{2,m} + n_3 V^{\circ}_{3,m})$$

$$= \Sigma n_i V_{i,m} - \Sigma n_i V^{\circ}_i$$

For an ideal gas the partial molar of each component is same $= \frac{RT}{P}$ $\quad V_{i,m} = \frac{RT}{P}$

$$\Delta V_{mix} = \sum n_i \frac{RT}{P} - \sum n_i \frac{RT}{P} = 0$$

$$\Delta V_{mix} = 0$$

∴ There is no volume change when ideal gas are mixed at constt P & T.

(4) Enthapy of Mixing ΔH_{mixing} It is equal to the enthalpy of the mixture less the sum of the enthalpies of pure components

$$\Delta H_{mix} = \sum n_i H_{i,m} - \sum n_i H_i^\circ$$

$H_{i,m}$ = Partial Molar Enthalpy

H_i° = Molar Enthalpy of pure components

$\mu_i = H_{i,m} - TS_{i,m}$

$H_{im} = \mu_i + TS_{i,m}$ for the mixture.

$H_i^\circ = \mu_i^\circ + TS_{i,m}^\circ$ for pure component

$\mu_i = \mu_i^\circ + RT\ln x_i$

$S_{i,m} = S_{i,m}^\circ - R\ln x_i$

∴ $H_{i,m} = \mu_i^\circ + RT\ln x_i + TS_{i,m}^\circ - RT\ln x_i$

$= \mu_i^\circ + TS_{i,m}^\circ$

$H_{i,m} = H_{i,m}^\circ$

$\Delta H_{mix} = 0$. The partial molar enthalpy of an ideal gas is same as its value in pure state because there is no enthalpy change when ideal gas are mixed isothermally & isobarically.