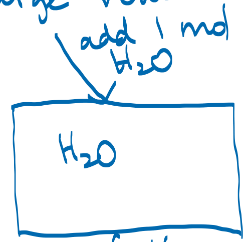
Lecture 13

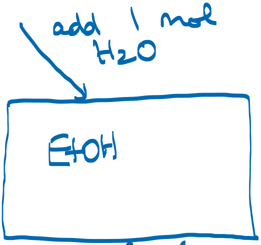
Thursday, October 26, 2023 11:35

Topic 5A : Thermodynamic Description of Mixtures

- binary mixtures

partial molar volume : change in volume per mole of A add to a large volume of the mixture

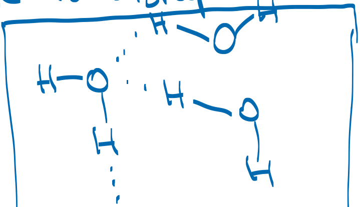


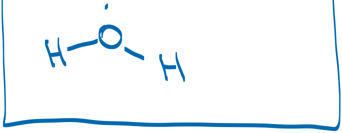


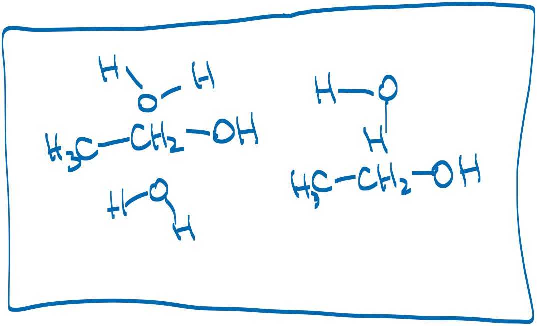
$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$ $\qquad$ $V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$

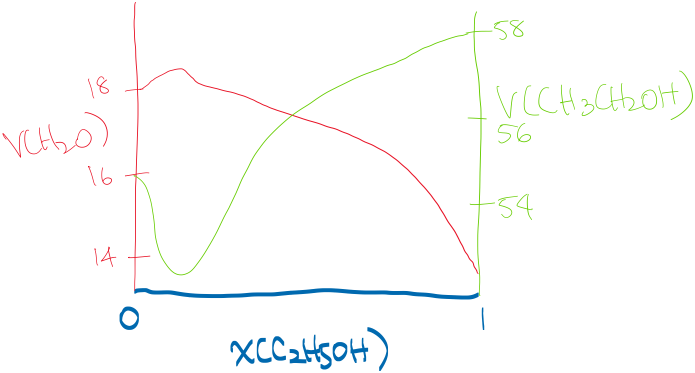
$V_J = 18\ \text{cm}^3$ $\qquad$ $V_J = 14\ \text{cm}^3$

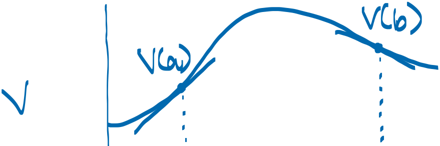
H_2O in EtOH is packed more tightly due to disruption in H-bond network

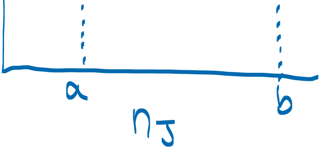












$V(a) > 0$, $v(b) < 0$

adding J at point b decreases the total volume of the sample

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

$$dV = V_A dn_A + V_B dn_B$$

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} v_B dn_B$$

ratio of A and B is kept constant

$$V = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B$$

$$\boxed{V = V_A n_A + V_B n_B}$$

Partial molar Gibbs energies

for a single substance:

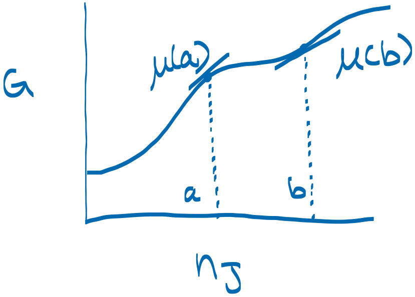
$$\mu = \frac{G}{n} = G_m$$

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

chemical potential of a substance in a mixture

$$\boxed{G = n_A\mu_A + n_B\mu_B}$$

total Gibbs energy in a binary mixture



$$\boxed{dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots}$$

fundamental equation of chemical thermodynamics

$$\boxed{dG = \mu_A dn_A + \mu_B dn_B} + \cdots$$

at constant pressure and temperature

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

$$G = U + pV - TS$$

$$U = G - pV + TS$$

$$dU = dG - d(pV) + d(TS)$$

$$= \cancel{Vdp} - \cancel{SdT} + \mu_A dn_A + \mu_B dn_B + \cdots$$

$$- \cancel{Vdp} - pdV + TdS + \cancel{SdT}$$

$$\boxed{dU = TdS - pdV + \mu_A dn_A + \mu_B dn_B + \cdots}$$

at constant entropy and volume,

$$dU = \mu_A dn_A + \mu_B dn_B + \cdots$$

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$$

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}$$

$$\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{T,V,n'}$$

∴ all extensive thermodynamic properties depend on the composition.

Gibbs-Duhem equation

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

$$dG = d(n_A \mu_A) + d(n_B \mu_B)$$

$$dG = n_A d\mu_A + \mu_A dn_A + \mu_B dn_B + n_B d\mu_B$$

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$n_A d\mu_A + \cancel{\mu_A dn_A} + n_B d\mu_B + \cancel{\mu_B dn_B}$$

$$= \cancel{\mu_A dn_A} + \cancel{\mu_B dn_B}$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\boxed{\sum_J n_J d\mu_J = 0}$$

Gibbs-Duhem equation

i.e. the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components

$$\boxed{d\mu_B = -\frac{n_A}{n_B} d\mu_A}$$

$$\sum_J n_J dV_J = 0$$

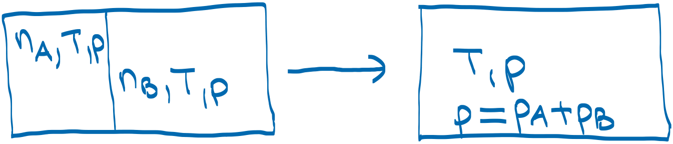
$$dV_B = -\frac{n_A}{n_B} dV_A$$

The thermodynamics of mixing

Intuitively, we know that mixing is spontaneous

initial

final



write chemical potentials for the pure substances

$$G_m(p) = G_m^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)$$

$$\mu = \mu^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)$$

1 bar

$\mu^\ominus$: standard chemical potential, chemical potential of the pure gas at 1 bar

$$\mu = \mu^\ominus + RT\ln p$$

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

Before mixing :

$$G_i = n_A(\cancel{\mu_A^\ominus} + RT\ln p) + n_B(\cancel{\mu_B^\ominus} + RT\ln p)$$

After mixing:

$$G_f = n_A(\cancel{\mu_A^\ominus} + RT \ln p_A) + n_B(\cancel{\mu_B^\ominus} + RT \ln p_B)$$

Gibbs energy of mixing:

$$\Delta_{mix}G = G_f - G_i$$

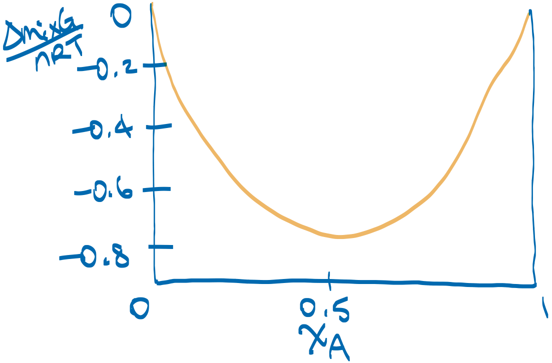
$$\Delta_{mix}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

Topic 1A: $p_J = x_J p$

$$\frac{p_J}{p} = x_J$$

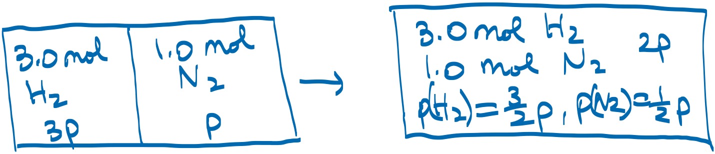
$$\boxed{\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)}$$

$x_A \leq 1$, $x_B \leq 1$



perfect gases mix spontaneously in all proportions

Calculating a Gibbs energy of mixing:



Write the initial Gibbs energy:

$$G_i = (3.0\,\text{mol})\left[\cancel{\mu^\ominus(H_2)} + RT\ln 3p\right]$$
$$+ (1.0\,\text{mol})\left[\cancel{\mu^\ominus(N_2)} + RT\ln p\right]$$

$$G_f = (3.0\ \text{mol})\left[\cancel{\mu^\ominus(H_2)} + RT \ln \tfrac{3}{2}p\right]$$

$$+(1.0\ \text{mol})\left[\cancel{\mu^\ominus(N_2)} + RT \ln \tfrac{1}{2}p\right]$$

$$\Delta_{mix} G = (3.0\ \text{mol})\,RT \ln \frac{3/2\,p}{3p}$$

$$+(1.0\ \text{mol})\,RT \ln \frac{1/2\,p}{p}$$

$$= -(3.0\ \text{mol})\,RT \ln 2$$

$$-(1.0\ \text{mol})\,RT \ln 2$$

$$= -(4.0\ \text{mol})(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

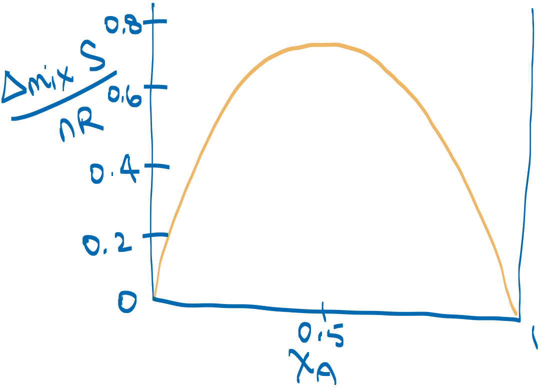
$$\cdot(298\ \text{K})\cdot 0.693$$

$$\boxed{\Delta_{mix} G = -6.9\ \text{kJ}}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\Delta_{mix} S = -\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_p$$

$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B)$$



$$G = H - TS$$

$$H = G + TS$$

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

$$= nRT(x_A \ln x_A + x_B \ln x_B)$$

$$- nRT(x_A \ln x_A + x_B \ln x_B)$$

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

no interactions between the molecules

A ⋯ A A ⋯ B B ⋯ B