

Exercise 2

The volume of a binary mixture has a molar volume, V , that depends on its composition:

$$V_m = 75x_1 + 95x_2 + 3.7x_1x_2 \quad \left(\frac{\text{cm}^3}{\text{mol}}\right)$$

For a mixture with $x_1 = 0.60$, determine

- the molar volume of the mixture
- the partial molar volume of component 1.

Solution 2

a. ($x_1 = 0.60 \rightarrow x_2 = 0.4$ then, $V = 83.9 \text{ cm}^3/\text{mol}$)

b. $\bar{V}_1 = V_m + x_2 \left(\frac{\partial V_m}{\partial x_1}\right)_{P,T,n_1}$

$$V_m = 75x_1 + 95(1 - x_1) + 3.7x_1(1 - x_1) = 95 - 16.3x_1 - 3.7x_1^2$$

$$\left(\frac{\partial V_m}{\partial x_1}\right)_{P,T,n_1} = -16.3x_1 - 7.4x_1 = -16.3x_1 - 7.4(0.6) = -20.7$$

$$\bar{V}_1 = 83.9 + 0.4(-20.7) = 75.6 \text{ cm}^3/\text{mol}$$

Exercise 3

The molar enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is represented by the following equation:

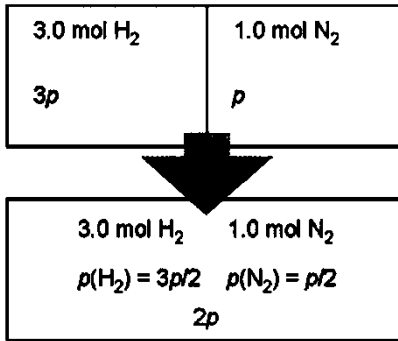
$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J/mol

- determine expressions for \bar{H}_1 and \bar{H}_2 as functions of x_1
- Numerical values for the pure species enthalpies H_1^* and H_2^*
- Find the expression of (H^E)
- Numerical values for the partial enthalpies at infinite dilution \bar{H}_1 and \bar{H}_2

Exercise 4

A container is divided into two equal compartments (figure below). One contains 3.0 mol H_2 at $25^\circ C$; the other contains 1.0 mol N_2 at $25^\circ C$. Calculate the *Gibbs energy of mixing* when the partition is removed. Assume perfect gas behavior. $P^0 = 1bar$



Solution

The Gibbs energy of mixing : so we have to consider both states initial and final

Two perfect gases in two identical containers with amounts n_A and n_B , both at the same T and P

We first calculate the initial Gibbs energy from chemical potentials. We need the pressure of each gas.

$$G_{initial} = n_A \bar{G}_A + n_B \bar{G}_B = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^\circ + RT \ln \frac{f_A}{f_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{f_B}{f_B^\circ} \right) = n_A \left(\mu_A^\circ + RT \ln \frac{P_A}{P_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{P_B}{P_B^\circ} \right)$$

$$G_{initial} = n_A \bar{G}_A + n_B \bar{G}_B = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^\circ + RT \ln \frac{f_A}{f_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{f_B}{f_B^\circ} \right) = n_A \left(\mu_A^\circ + RT \ln \frac{P_A^i}{P_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{P_B^i}{P_B^\circ} \right) \\ = n_A (\mu_A^\circ + RT \ln 3P) + n_B (\mu_B^\circ + RT \ln P) =$$

$$P_1 V_1 = P_2 V_2 \rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1} = 2 \rightarrow P_{Af} = \frac{3P}{2} \text{ and } P_B = \frac{P}{2}$$

$$G_{final} = n_A \bar{G}_A + n_B \bar{G}_B = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^\circ + RT \ln \frac{P_{Af}}{P_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{P_{Bf}}{P_B^\circ} \right) \\ = n_A \left(\mu_A^\circ + RT \ln \frac{P_{Af}}{P_A^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{P_{Bf}}{P_B^\circ} \right) = n_A \left(\mu_A^\circ + RT \ln \frac{3P}{2} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{P}{2} \right)$$

$$\Delta G = G_f - G_i = n_A RT \ln \frac{1}{2} + n_B RT \ln \frac{1}{2} = 4(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln \frac{1}{2} = -6900 \text{ J} \cdot \text{mol}^{-1}$$

Exercise 5

<https://www.youtube.com/watch?v=bof3vwEBdc0&t=1s>

For a mixture contains 75% H_2 and 25% N_2 (molar basis) estimate the pseudo critical Temperature and pressure (P_{pc} and T_{pc}) using Kay's rule.

We give:

For N_2 : $T_C = 126.2K$ and $P_C = 33.5atm$

For H_2 $T_C = 33 + 8 = 41K$ and $P_C = 12.8 + 8 = 20.8 atm$

Solution

$$T_{pc} = y_{H_2} T_{cH_2} + y_{N_2} T_{cN_2} = 62.3K \quad P_{pc} = 24atm$$

