

Thermodynamics tutorhour 7

December 20th 2023

Questions about the lecture or course matter?

Colligative properties

Some definitions

Partial pressure: $p_i = \frac{p_{\text{component } i}}{p_{\text{total}}}$

Molar fraction: $x_i = \frac{\text{\#moles}_{\text{component } i}}{\text{\#moles}_{\text{total}}} = \frac{n_i}{n_{\text{total}}}$

Gasses mix ideal: $p_i = x_i \cdot p_{\text{total}}$

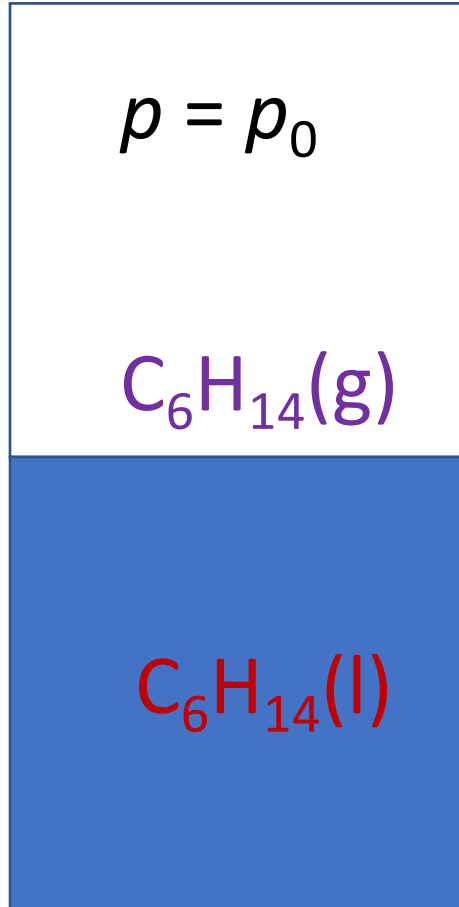
When liquids mix ideal: $\Delta_{\text{mix}}G = nRT(x_1 \ln x_1 + x_2 \ln x_2) < 0$

Non-ideal behaviour: use activity (a_i) instead of fraction (x_i)

At equilibrium: $\mu_{\text{phase 1}} = \mu_{\text{phase 2}}$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$$

Elevation of boiling point



At equilibrium:

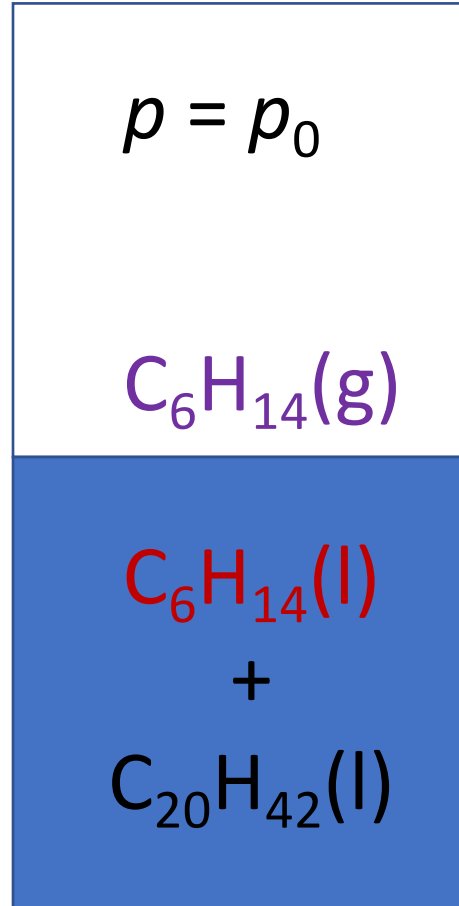
$$\mu_g = \mu_l$$

At $T = T_{vap}^*$ (69 °C):

$$\mu_g^* = \mu_l^*$$

* means: pure substance!

Elevation of boiling point

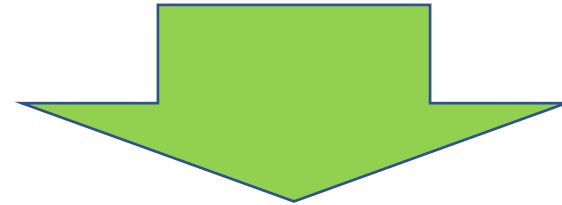


At equilibrium:

$$\mu_g = \mu_l$$

Dissolving eicosane in liquid phase:

$$\mu_g^* = \mu_l^* + \text{correction for dissolving}$$

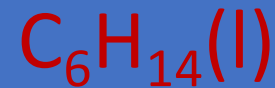


$$\Delta T = \left(\frac{RT_{vap}^*}{\Delta_{vap}H} \right)^2 x_B$$

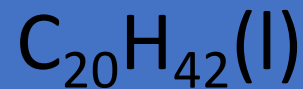
$p = p_0$, ideal dilute solution (low concentration)

Elevation of boiling point

$$p = p_0$$



+



$$\Delta T = \left(\frac{RT_{vap}^*}{\Delta_{vap}H} \right)^2 x_B$$

ΔT : elevation of boiling point ($T - T_{vap}^*$)

T_{vap}^* : boiling point of pure hexane

$\Delta_{vap}H$: enthalpy of vaporization of hexane

x_B : mole fraction of eicosane

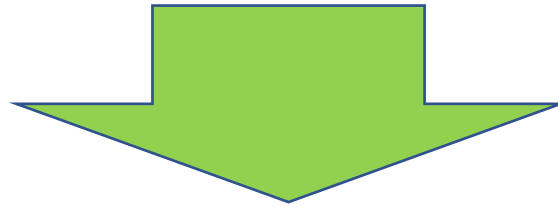
$$x_B = \frac{\# \text{ mol eicosane}}{\# \text{ mol hexane} + \# \text{ mole eicosane}}$$

$p = p_0$, ideal dilute solution

Boiling point **elevation** and freezing point **depression**

$$\Delta T = \left(\frac{RT_{vap}^*{}^2}{\Delta_{vap}H} \right) x_B$$

$$\Delta T = - \left(\frac{RT_{fus}^*{}^2}{\Delta_{fus}H} \right) x_B$$



$$\Delta T = \left| \left(\frac{RT_{trs}^*{}^2}{\Delta_{trs}H} \right) x_B \right|$$

Need to know!

trs = transition
 $p = p_0$, ideal dilute solution

Question 1:

How many grams of salt (sodium chloride), do you have to dissolve in 1.0 kg of water to lower the freezing point to 271 K?

Given is: molar mass NaCl = 58.44 g mol⁻¹ and $\Delta_{fus}H = 6.01$ kJ/mol

Assume $n_{\text{NaCl}} \ll n_{\text{H}_2\text{O}}$

$$\Delta T = - \left(\frac{RT_{fus}^*{}^2}{\Delta_{fus}H} \right) x_B \quad \text{so} \quad x_B = - \frac{\Delta T \cdot \Delta_{fus}H}{RT_{fus}^*{}^2} \quad x_B = - \frac{(271-273) \cdot 6.01 \cdot 10^3}{8.3145 \cdot 273^2} = 0.0194$$

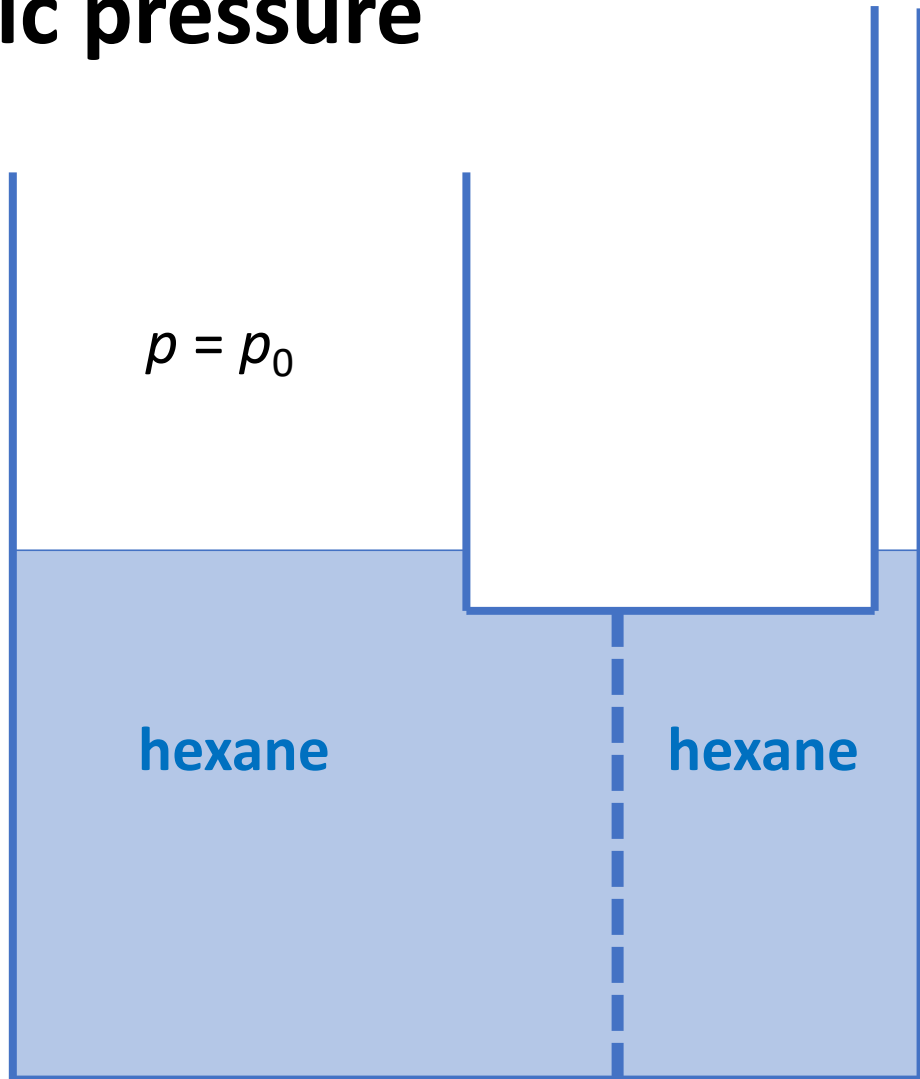
$$x_B = \frac{n_{\text{Na}^+} + n_{\text{Cl}^-}}{n_{\text{Na}^+} + n_{\text{Cl}^-} + n_{\text{H}_2\text{O}}} \approx \frac{n_{\text{Na}^+} + n_{\text{Cl}^-}}{n_{\text{H}_2\text{O}}} = \frac{2 \cdot n_{\text{Na}^+}}{n_{\text{H}_2\text{O}}}$$

$$n_{\text{Na}^+} = \frac{1}{2} x_B \cdot n_{\text{H}_2\text{O}} = \frac{1}{2} x_B \cdot \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{1}{2} 0.0194 \cdot \frac{1000}{18.02} = 0.538 \text{ mol}$$

You need 0.538 moles of Na⁺ and therefore you have to dissolve 0.538 moles NaCl.

So 31 grams of NaCl is needed (or 32 g if you didn't use the simplification).

Osmotic pressure

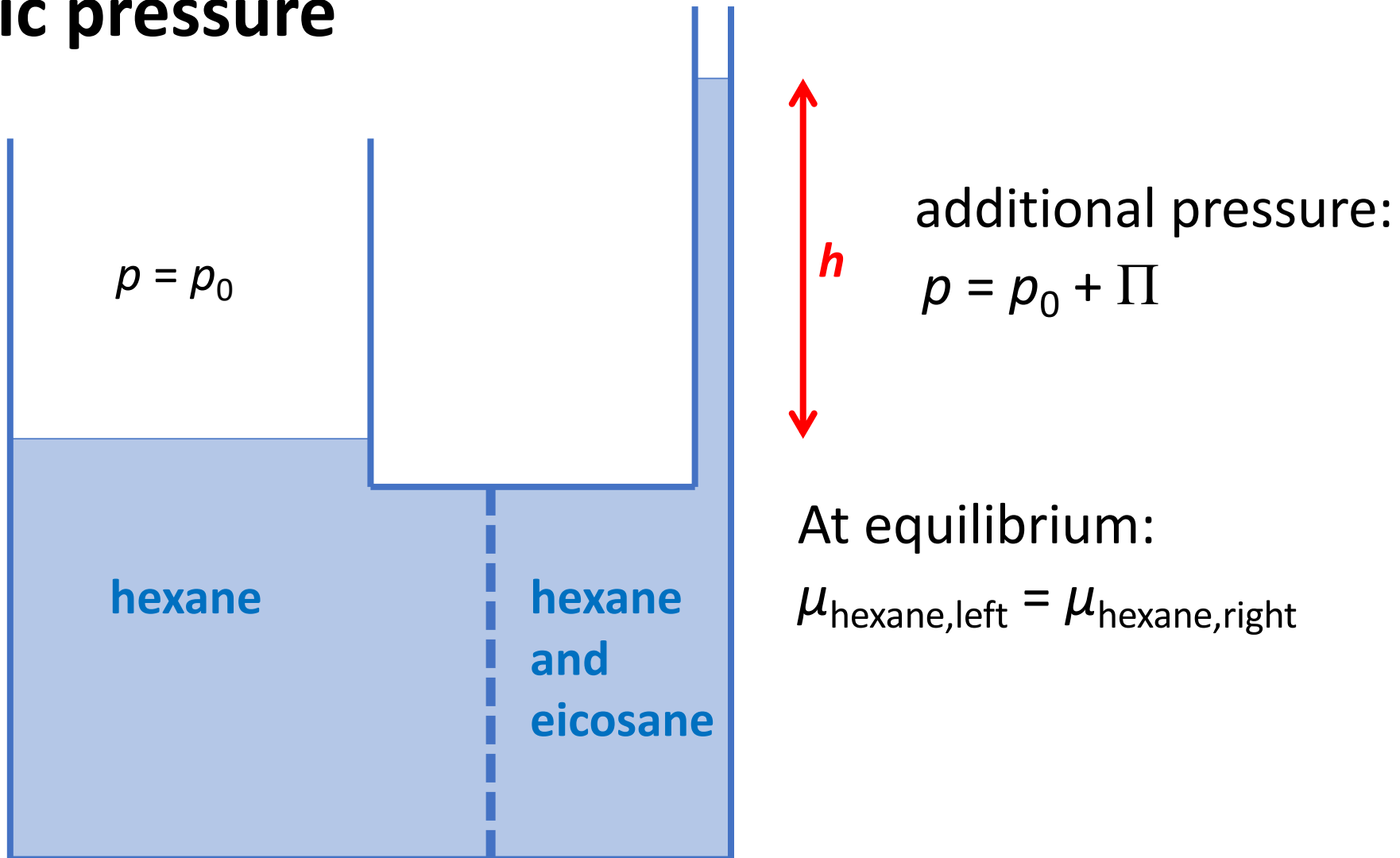


At equilibrium:

$$\mu_{\text{hexane, left}} = \mu_{\text{hexane, right}}$$

$$\mu^*_{\text{hexane}} = \mu^*_{\text{hexane}}$$

Osmotic pressure



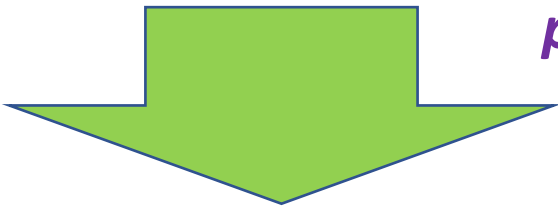
$$\mu^*(p_0)_{\text{hexane}} = \mu(p_0 + \Pi)_{\text{mixture}}$$

$$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}} + \text{correction for dissolving} + \text{additional pressure}$$

Osmotic pressure

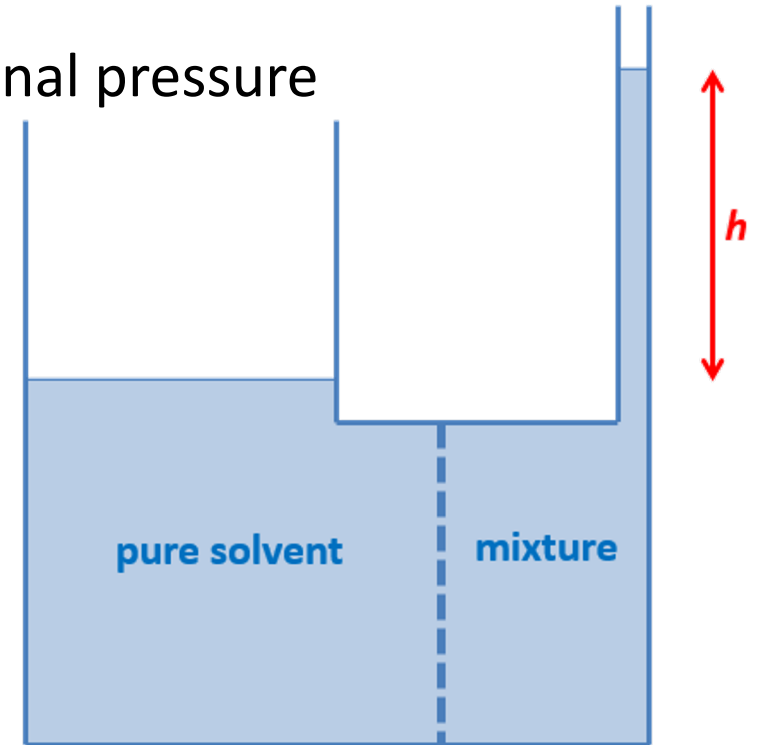
$$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}} + \text{correction for dissolving} + \text{additional pressure}$$

$p = p_0$, ideal dilute solution


$$\Pi = [B]RT = \frac{n_B}{V}RT$$

Note: [B] in **mol/m³**

$$\Pi = \rho \cdot g \cdot h = [B] \cdot R \cdot T$$



Question 2:

c [g/L]	2.042	6.613	9.521	12.602
h [cm]	0.592	1.910	2.750	3.600

Osmotic pressure: $\Pi = \rho \cdot g \cdot h = [B] \cdot R \cdot T$

The osmotic pressure of solutions of polystyrene in toluene at 25 °C is measured; see the table above (h is the pressure in terms of the height of a fluid column with density $\rho = 1.004 \text{ g cm}^{-3}$)

- From these data a graph (h as a function of c) can be constructed. For this graph we can incorporate the point $h(c_B = 0) = 0$. Determine the slope of this graph by using data from the table.
- Determine the molar mass of the polymer.

Question 2:

c [g/L]	2.042	6.613	9.521	12.602
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The osmotic pressure of solutions of polystyrene in toluene at 25 °C is measured; see the table above (h is the pressure in terms of the height of a fluid column with density $\rho = 1.004 \text{ g cm}^{-3}$)

- a. From these data a graph (h as a function of c) can be constructed. For this graph we can incorporate the point $h(c_B = 0) = 0$. Determine the slope of this graph by using data from the table.

$$\text{slope} = \frac{\Delta h}{\Delta c} = \frac{3.600 - 0}{12.602 - 0} = 0.29 \text{ cm} \cdot \text{L} \cdot \text{g}^{-1} = 0.29 \cdot 10^{-2} \text{ m}^4 \cdot \text{kg}^{-1}$$

Question 2:

c [g/L]	2.042	6.613	9.521	12.602
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Osmotic pressure: $\Pi = \rho \cdot g \cdot h = [B] \cdot R \cdot T$

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$$\text{slope} = \frac{\Delta h}{\Delta c} = 0.29 \cdot 10^{-2} \text{ m}^4 \cdot \text{kg}^{-1}$$

b. Determine the molar mass of the polymer.

$$h = \frac{[B]RT}{\rho g} \quad \text{and } [B] \text{ is in mol m}^{-3}, \quad \text{so } [B] \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{c \left(\frac{\text{kg}}{\text{m}^3} \right)}{M_B \left(\frac{\text{kg}}{\text{mol}} \right)}$$

$$h = \frac{cRT}{\rho g M_B} \rightarrow \text{slope} = \frac{\Delta h}{\Delta c} = \frac{RT}{\rho g M_B} = 0.29 \cdot 10^{-2} \text{ m}^4 \cdot \text{kg}^{-1}$$

$$M_B = \frac{RT}{\rho g \cdot 0.29 \cdot 10^{-2}} = \frac{8.314 \cdot 298.15}{1.004 \cdot 10^3 \cdot 9.81 \cdot 0.29 \cdot 10^{-2}} = 87 \frac{\text{kg}}{\text{mol}} = 87 \cdot 10^3 \text{ g/mol}$$

Extra info for exercise 35

Perfect gas (for 1 mole: $n=1$) : $pV = RT$

Molecules behave like billiard balls without volume

Real gas (still 1 mole): $p = \frac{RT}{V-b} - \frac{a}{V^2}$ (vd Waals equation)

Molecules have a volume (b) and attract each other (a)

Exercise 32 a)

$$G = G_{unmixed} + RT(n_1 \ln x_1 + n_2 \ln x_2)$$

$$G_{unmixed} = G_1^* + G_2^*$$

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n} \quad x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n}$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$$

$$\mu_1 = \frac{\partial}{\partial n_1} (G_1^* + G_2^*) + RT \frac{\partial}{\partial n_1} (n_1 \ln n_1 - n_1 \ln n + n_2 \ln n_2 - n_2 \ln n)$$

$$\mu_1 = \frac{\partial}{\partial n_1} (G_1^* + G_2^*) + RT \frac{\partial}{\partial n_1} (n_1 \ln n_1 - n_1 \ln(n_1 + n_2) + n_2 \ln n_2 - n_2 \ln(n_1 + n_2))$$

$$\left(\frac{\partial G_1^*}{\partial n_1} \right) = \mu_1^* \text{ en } \left(\frac{\partial G_2^*}{\partial n_1} \right) = 0$$

$$\mu_1 = \mu_1^* + 0 + RT \left\{ \left(1 \cdot \ln n_1 + \frac{n_1}{n_1} \right) - \left(1 \cdot \ln n + n_1 \frac{1}{n_1 + n_2} \right) + 0 - \left(0 + n_2 \frac{1}{n_1 + n_2} \right) \right\}$$

$$\mu_1 = \mu_1^* + RT \left(\ln n_1 + 1 - \ln n - \left(\frac{n_1}{n} + \frac{n_2}{n} \right) \right)$$

$$\mu_1 = \mu_1^* + RT \left(\ln \frac{n_1}{n} + 1 - (x_1 + x_2) \right)$$

$$\mu_1 = \mu_1^* + RT (\ln x_1)$$

b)

$$\mu_i^\alpha = \mu_i^\beta$$

$$\mu_i^\alpha = \mu_i^* + RT \ln x_i$$

$$\mu_i^\beta = \mu_i^\theta + RT \ln \frac{p_i}{p^\theta}$$

$$\mu_i^* + RT \ln x_i = \mu_i^\theta + RT \ln \frac{p_i}{p^\theta} \quad (1)$$

Reference state $x_i = 1$

$$\mu_i^* + 0 = \mu_i^\theta + RT \ln \frac{p_i}{p^\theta} \quad (2)$$

$$(1) - (2) = RT \ln x_i = RT \ln \frac{p_i p^\theta}{p^\theta p_i^*}$$

$$x_i = \frac{p_i}{p_i^*} \text{ so } p_i = x_i p_i^*$$

c)

$$\Delta_{mix}S = -nR(x_1 \ln x_1 + x_2 \ln x_2) = -nR(x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1))$$

$$\frac{d\Delta_{mix}S}{dx_1} = 0 = -nR \left(\ln x_1 + \frac{x_1}{x_1} - \ln(1 - x_1) - \frac{1-x_1}{1-x_1} \right) = -nR \ln \frac{x_1}{1-x_1}$$

$$\frac{x_1}{1-x_1} = 1, \quad \text{so} \quad x_1 = \frac{1}{2}$$

$$n_{hexane} = n_{heptane}$$

$$\frac{m_{hexane}}{m_{heptane}} = \frac{n_{hexane}M_{hexane}}{n_{heptane}M_{heptane}} = 1 \cdot \frac{86.17}{100.20} = 0.8600$$