

Solutions 7

1. For an ideal solution,

$$\mu_A - \mu_A^* = RT \ln x_A = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353.25 \text{ K}) \ln(0.30) = -3.536 \text{ kJ mol}^{-1}$$

$$a_A = p_A / p_A^* \quad \gamma_A x_A = p_A / p_A^* \quad p_A = \gamma_A x_A p_A^*$$

At the normal boiling point, $p_A^* = 1 \text{ atm} = 760 \text{ Torr}$

$$p_A = 0.93 \times 0.30 \times 760 \text{ Torr} = 212 \text{ Torr}$$

$$2. \quad \Delta_{\text{mix}} S = -nR(x_A \ln x_A + x_B \ln x_B) \quad x_B = 1 - x_A$$

$$\Delta_{\text{mix}} S = -nR(x_A \ln x_A + (1 - x_A) \ln(1 - x_A))$$

$$\frac{d\Delta_{\text{mix}} S}{dx_A} = -nR(\ln x_A + 1 - \ln(1 - x_A) - 1) = -nR \ln \frac{x_A}{1 - x_A}$$

The maximum $\Delta_{\text{mix}} S$ is reached when $\frac{d\Delta_{\text{mix}} S}{dx_A} = 0$, i.e. at $\frac{x_A}{1 - x_A} = 1$

Therefore, $x_A = x_B = 0.5$

(a) hexane and heptane should be mixed each with the mole fraction of 0.5.

(b) to have the same chemical amounts of hexane and heptane, their mass ratio should be equal to the ratio of their molar masses:

$$m(\text{hexane}) / m(\text{heptane}) = M(\text{C}_6\text{H}_{14}) / M(\text{C}_7\text{H}_{16}) = (86.17 \text{ g mol}^{-1}) / (100.2 \text{ g mol}^{-1}) = 0.86$$

3. For ideal mixing,

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

$$x_A = 0.25 \text{ (MCH)} \quad x_B = 0.75 \text{ (THF)}$$

$$\Delta_{\text{mix}} G (\text{ideal}) = (4.0 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (303.15 \text{ K}) \times \{0.25 \ln(0.25) + 0.75 \ln(0.75)\} = -5.67 \text{ kJ}$$

$$G^E = RTx(1 - x)\{0.4857 - 0.1077(2x - 1) + 0.0191(2x - 1)^2\} \quad x = 0.25$$

$$G^E = 0.1021RT = 0.257 \text{ kJ mol}^{-1} \text{ (note that } G^E \text{ is a molar quantity)}$$

$$\Delta_{\text{mix}} G (\text{real}) = \Delta_{\text{mix}} G (\text{ideal}) + nG^E = (-5.67 \text{ kJ}) + (4.0 \text{ mol}) \times (0.257 \text{ kJ mol}^{-1}) = -4.6 \text{ kJ}$$

4. Using the mole fraction in the vapor phase, we can calculate partial vapor pressure of each component:

$$y_A = p_A / (p_A + p_B) = p_A / 101.3 \text{ kPa} = 0.314 \quad p_A = 0.314 \times 101.3 \text{ kPa} = 31.8 \text{ kPa}$$

$$p_B = p - p_A = 101.3 \text{ kPa} - 31.8 \text{ kPa} = 69.5 \text{ kPa}$$

$$a_A = p_A / p_A^* = 31.8 \text{ kPa} / 73.0 \text{ kPa} = 0.436$$

$$a_B = p_B / p_B^* = 69.5 \text{ kPa} / 92.1 \text{ kPa} = 0.755$$

$$\gamma_A = a_A / x_A = 0.436 / 0.220 = 1.98$$

$$\gamma_B = a_B / x_B = 0.755 / (1 - 0.220) = 0.968$$

$$5. I = \frac{1}{2} \sum_i \left(\frac{b_i}{b^\ominus} \right) z_i^2$$

For an M_pX_q salt, $b_+/b^\ominus = pb/b^\ominus$, $b_-/b^\ominus = qb/b^\ominus$, so

$$I = \frac{1}{2} (pz_+^2 + qz_-^2) \frac{b_i}{b^\ominus}$$

$$I = I(K_3[Fe(CN)_6]) + I(KCl) + I(NaBr) = (1/2)(3 + 3^2)b(K_3[Fe(CN)_6])/b^\ominus + b(KCl)/b^\ominus + b(NaBr)/b^\ominus = 6 \times 0.040 + 0.03 + 0.05 = 0.320$$

6.

The extended Debye-Hückel law:
$$\log \gamma_{\pm} = - \frac{A |z_+ z_-| I^{1/2}}{1 + BI^{1/2}}$$

$$A = 0.509 \quad z_+ = +1 \quad z_- = -1 \quad I = \frac{1}{2} \sum_i z_i^2 (b_i/b^\ominus) = b/b^\ominus$$

$$\log \gamma_{\pm} = - \frac{0.509 (b/b^\ominus)^{1/2}}{1 + B(b/b^\ominus)^{1/2}} \quad B = - \left(\frac{1}{(b/b^\ominus)^{1/2}} + \frac{0.509}{\log \gamma_{\pm}} \right)$$

Construct the following table:

$b/\text{mmol kg}^{-1}$	5.00E-03	1.00E-02	2.00E-02
$(b/b^\ominus)^{1/2}$	0.070710678	0.1	0.141421356
$\gamma_{\pm}$	0.93	0.907	0.879
$\log \gamma_{\pm}$	-0.031517051	-0.042392713	-0.056011125
B	2.007852292	2.006780522	2.016412589

Thus, B is close to 2.01.

7. Denote the mole fraction of methylbenzene as x_M and mole fraction of dimethylbenzene as x_D .

$$x_D = 1 - x_M$$

According to Raoult's law,

$$p_M = x_M p_M^*$$

$$p_D = x_D p_D^*$$

When the mixture boils at 0.5 atm, the total vapor pressure should be 0.50 atm (380 Torr):

$$p = p_M + p_D = x_M p_M^* + x_D p_D^* = x_M p_M^* + (1 - x_M) p_D^*$$

$$x_M = (p - p_D^*) / (p_M^* - p_D^*) = (380 \text{ Torr} - 150 \text{ Torr}) / (400 \text{ Torr} - 150 \text{ Torr}) = 0.92$$

$$x_D = 1 - x_M = 0.08$$

Vapor composition (according to Dalton's law):

$$y_M = p_M/p = x_M p_M^*/p = 0.92 \times (400 \text{ Torr}) / (380 \text{ Torr}) = 0.968$$

$$y_D = 1 - y_M = 0.032$$

8. At the boiling point the total vapor pressure of solution should be 1 atm = 760 Torr. For an ideal solution, according to Raoult's law,

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = 0.6589 \times (957 \text{ Torr}) + (1 - 0.6589) \times (379.5 \text{ Torr}) = 760.01 \text{ Torr} \approx 760 \text{ Torr}$$

Therefore, the solution is very close to ideal.

$$y_A = p_A/p = x_A p_A^*/p = 0.6589 \times (957 \text{ Torr}) / (760 \text{ Torr}) = 0.830$$

$$y_B = 1 - y_A = 0.170$$

9. Retrace the argument given in the derivation of van't Hoff's equation for osmotic pressure in the text. At equilibrium,

$$\mu_A^*(p) = \mu_A(x_A, p + \Pi)$$

For a real solution, $\mu = \mu^* + RT \ln a$

$$\mu_A^*(p) = \mu_A^*(p + \Pi) + RT \ln a_A = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp + RT \ln a_A$$

Therefore, $\int_p^{p+\Pi} V_m dp = -RT \ln a_A$

For an incompressible solution, $\int_p^{p+\Pi} V_m dp = \Pi V_m$, so $\Pi V_m = -RT \ln a_A$

The osmotic coefficient is defined as $\phi = -\frac{x_A}{x_B} \ln a_A$

$$\Pi V_m = RT \phi \frac{x_B}{x_A} \approx RT \phi \frac{n_B}{n_A} \quad (\text{because } n_B \ll n_A)$$

$$\Pi V_m n_A \approx RT \phi n_B \quad V_m n_A \approx V \quad \Pi V \approx RT \phi n_B$$

$$\frac{n_B}{V} = [B] \text{ - molar concentration of solute. Therefore, we obtain}$$

$$\Pi = RT \phi [B]$$