

# Answers - problem set 7.

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

a)

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

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

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

[in lecture  $nRT (x_1 \ln x_1 + x_2 \ln x_2)$ ]

$$G_{unmixed} = \underbrace{\sigma_1^*}_{\text{pure 1}} + \underbrace{\sigma_2^*}_{\text{pure 2}}$$

$$\Rightarrow \mu_i = \frac{\partial}{\partial n_i} (\sigma_1^* + \sigma_2^*) + RT \frac{\partial}{\partial n_i} \left( \overbrace{n_1 \ln x_1} + \overbrace{n_2 \ln x_2} - n_1 \ln n - n_2 \ln n \right)$$

$\left( \frac{\partial \sigma_1^*}{\partial n_1} \right) = \mu_1^*$  &  $\left( \frac{\partial \sigma_2^*}{\partial n_1} \right) = 0$

$$\Rightarrow \mu_i = \mu_i^* + RT \left\{ \ln n_1 + \frac{n_1}{n_1} - \ln n - n_1 \left( \frac{\partial \ln n}{\partial n_1} \right) - n_2 \left( \frac{\partial \ln n}{\partial n_1} \right) \right\} =$$

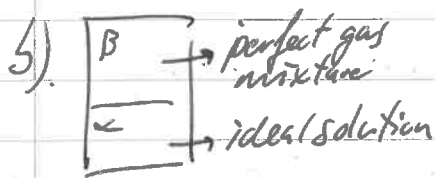
use:  $\frac{\partial \ln n}{\partial n_1} = \frac{1}{n} \frac{\partial n}{\partial n_1} = \frac{1}{n} \frac{\partial}{\partial n_1} (n_1 + n_2) = \frac{1}{n}$

$$\Rightarrow \mu_i = \mu_i^* + RT \left\{ \ln n_1 + 1 - \ln n - \frac{n_1}{n} - \frac{n_2}{n} \right\} =$$

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

$$\boxed{\mu_i = \mu_i^* + RT \ln x_i}$$

(so little fussy).



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

sub in  $\left\{ \begin{array}{l} \mu_i^\alpha = \mu_i^* + RT \ln X_i \quad (\text{ideal solution}) \\ \mu_i^\beta = \mu_i^G + RT \ln \frac{P_i}{P^G} \quad (\text{perfect gas}) \end{array} \right.$

$$\therefore \mu_i^* + RT \ln X_i = \mu_i^G + RT \ln \frac{P_i}{P^G} \quad (1)$$

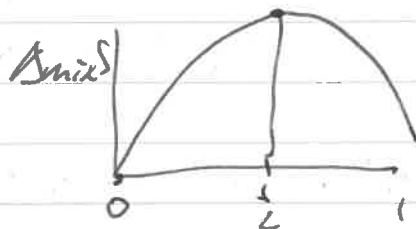
reference state  $X_i = 1$ :  $\mu_i^* = \mu_i^G + RT \ln \frac{P_i^*}{P^G} \quad (2)$

$$(1) - (2): RT \ln X_i = RT \ln \left( \frac{P_i}{P^G} \cdot \frac{P^G}{P_i^*} \right)$$

$$X_i = \frac{P_i}{P_i^*} \rightarrow P_i = X_i P_i^*$$

c) largest entropy of mixing:  $X_1 = X_2 = \frac{1}{2}$

$$\begin{aligned} \text{i)}: \frac{n_{hex}}{n_{hep}} &= \frac{\left(\frac{n_{hex}}{n}\right)}{\left(\frac{n_{hep}}{n}\right)} = \\ &= \frac{X_{hex}}{X_{hep}} = \frac{1/2}{1/2} = 1 \end{aligned}$$



ii) in terms of masses  $\rightarrow$  you need molar masses:

$$\frac{m_{hex}}{m_{hep}} = \frac{n_{hex} M_{hex}}{n_{hep} M_{hep}} = 1 \cdot \frac{86 \text{ g mol}^{-1}}{100 \text{ g mol}^{-1}} = 0.86$$

33  $\Delta T = \frac{RT^{*2}}{\Delta_{\text{vap}}H} \cdot X_2$

\*  $\Delta_{\text{vap}}H = 30.0 \text{ kJ mol}^{-1}$

\*  $T^* = 80.15 + 273.15 = 353.30 \text{ K}$

\*  $\Delta T = 80.95 - 80.15 = 0.80 \text{ K}$

sub all in & unknown =  $X_2$

$$X_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_{\text{benzene}} + n_2}$$

$\Rightarrow n_{\text{benzene}} = \frac{100 \text{ g}}{M_{\text{benzene}}} = \frac{100}{78.11}$

$n_2 = \frac{10 \text{ g}}{M_2}$

$$X_2 = \frac{\frac{10}{M_2}}{\frac{100}{78.11} + \frac{10}{M_2}}$$

$$X_2 = \Delta T \cdot \frac{\Delta_{\text{vap}}H}{RT^{*2}} = 0.80 \cdot \frac{30.0 \cdot 10^3}{8.314 \cdot (353.30)^2} = 0.0237$$

$$X_2 = \frac{\frac{10}{M_2} \cdot M_2}{\left(\frac{100}{78.11} + \frac{10}{M_2}\right) M_2} = \frac{10}{\alpha \cdot M_2 + 10} \quad \left(\alpha = \frac{100}{78.11}\right)$$

$$M_2 = \frac{10}{\alpha \left(\frac{1}{X_2} - 1\right)} = \left(\frac{10}{100} \cdot 78.11\right) \cdot \left(\frac{1}{0.0237} - 1\right) =$$

$M_2 = 321 \text{ g mol}^{-1}$

### Exercise 33

$$\mu_2 = 10g \rightarrow \text{solid}$$

$$n = \frac{\mu}{M}$$

$$\Delta T = \frac{RT^{*2}}{\Delta_{\text{vap}}H} \cdot x_2$$

$$m_1 = 100g$$

$$T^* = 80.95^\circ\text{C} = 353.30\text{K}$$

$$T_{\text{u.p.}}(\text{benzene}) = 80.15^\circ\text{C}$$

$$\Delta T = 80.95 - 80.15 = 0.80\text{K}$$

$$M_1(\text{benzene}) = 78.11\text{ g/mol}$$

$$\Delta_{\text{vap}}H = 30.8\text{ kJ/mol}$$

$$x_2 = \Delta T \cdot \frac{\Delta_{\text{vap}}H}{RT^{*2}}$$

$$M_2 = ?$$

$$x_2 = \Delta T \cdot \frac{\Delta_{\text{vap}}H}{RT^{*2}} = \frac{0.80 \cdot 30.8 \cdot 10^3}{8.314 \cdot (353.3)^2} = 0.0237$$

$$x_2 = \frac{n_2}{n_1 + n_2}$$

$$n_1 = \frac{\mu_1}{M_1} = \frac{100\text{ g}}{78.11\text{ g/mol}}$$

$$x_2(n_1 + n_2) = n_2$$

$$x_2 n_1 + x_2 n_2 = n_2 \Rightarrow x_2 n_2 - n_2 = -x_2 n_1 \quad | \cdot (-1)$$

$$n_2 - x_2 n_2 = x_2 n_1$$

$$n_2(1 - x_2) = x_2 n_1 \Rightarrow n_2 = \frac{x_2 n_1}{1 - x_2}$$

$$n_2 = \frac{0.0237 \cdot \frac{100}{78.11}}{1 - 0.0237} = 0.031078\text{ mol}$$

$$M_2 = \frac{\mu_2}{n_2} = \frac{10g}{0.031078\text{ mol}}$$

$$M_2 = 321\text{ g/mol}$$

34 a)  $\pi = [B]RT$

$$\left. \begin{aligned} [B] &= 0.282 \text{ mol dm}^{-3} \\ T &= 293 \text{ K} \end{aligned} \right\} \begin{aligned} \pi &= 0.282 \cdot 10^3 \cdot 8.314 \cdot 293 = \\ &= 6.877 \cdot 10^5 \text{ Pa} \\ &= 6.87 \text{ bar} \end{aligned}$$

b)  $\pi = - \frac{\mu_i - \mu_i^*}{V_{i,m}}$

$\pi$ : osmotic pressure  
 $\mu_i$ : chemical potential of component 1  
 (comp 1 = typically the solvent)  
 $\mu_i^*$ : chem. pot. of pure comp. 1  
 $V_{i,m}$ : molar volume of solvent.

for ideal solution:  $\mu_i = \mu_i^* + RT \ln x_i$ , but activity  
 in general - for non-ideal solutions - :  $\mu_i = \mu_i^* + RT \ln a_i$

$$\pi = - \frac{\mu_i^* + RT \ln a_i - \mu_i^*}{V_{i,m}} = - \frac{RT}{V_{i,m}} \ln a_i$$

c)  $\pi = 7.61 \text{ atm} = 101325 \cdot 7.61 = 7.71 \cdot 10^5 \text{ Pa}$

$V_{i,m}$  for water @ 20°C:  $V_{i,m} = \frac{M_{H_2O}}{\rho_{H_2O}} = \frac{18.015}{0.998} = 18.05 \frac{\text{cm}^3}{\text{mol}}$

$$\Rightarrow \ln a_i = - \frac{\pi \cdot V_{i,m}}{RT} = - \frac{7.71 \cdot 10^5 \cdot 18.05 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}}{8.314 \cdot 293.2} = -5.71 \cdot 10^{-3}$$

$a_i = 0.9943$

activity coeff:  $a_i = x_i \cdot f_i$

$f_i = \frac{a_i}{x_i} = a_i \cdot \frac{n_{H_2O} + n_2}{n_{H_2O}} \Rightarrow n_2 = 0.300 \text{ mol per kg H}_2\text{O (b}_2\text{)}$   
 $n_{H_2O} = \frac{1000}{M_{H_2O}} = \frac{1000}{18.015}$

$\Rightarrow f_i = 0.9943 \cdot \frac{(\frac{1000}{18.015} + 0.300)}{(\frac{1000}{18.015})} = 0.9943 / 0.9946 = 0.9997$

35)  $n=1$  vdW:  $p = \frac{RT}{v-b} - \frac{a}{v^2}$

a):  $a$ : parametrises the attractive interactions  
 $b$ : " " repulsive "

b).  $\left(\frac{\partial p}{\partial v}\right)_T = 0$  &  $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$

$pV = nRT$

$p = \frac{nRT}{v} \rightarrow \left(\frac{\partial p}{\partial v}\right)_T = -\frac{nRT}{v^2} \xrightarrow{n=1} -\frac{RT}{v^2} = 0$

• condition  $\left(\frac{\partial p}{\partial v}\right)_T = 0$  only met as  $v \rightarrow \infty$  (or  $T \rightarrow 0$ )  
 $\Rightarrow$  no critical point in perfect gas.

c).  $p = \frac{RT}{v-b} - \frac{a}{v^2}$

(1)  $\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \rightarrow \frac{2a}{v^3} = \frac{RT}{(v-b)^2}$

(2)  $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = +\frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \rightarrow \frac{2a}{v^3} \cdot \frac{3}{v} = \frac{2RT}{(v-b)^3}$

combine:  $\frac{RT}{(v-b)^2} \cdot \frac{3}{v} = \frac{2RT}{(v-b)^3}$

$\Downarrow$   
 $\frac{3}{v} = \frac{2}{v-b} \rightarrow 2v = 3(v-b) = 3v - 3b$   
 $-v = -3b \rightarrow \boxed{v_c = 3b}$

Sub back in (1):

$\frac{2a}{(3b)^3} = \frac{RT}{(3b-b)^2} \rightarrow \frac{2a}{27b^3} = \frac{RT}{4b^2} \rightarrow \boxed{T_c = \frac{8a}{27Rb}}$

### Alternative answer 35c

$$\begin{aligned} 1. \quad \left(\frac{\partial p}{\partial V}\right)_T &= \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0 & \rightarrow \frac{2a}{V^3} &= \frac{RT}{(V-b)^2} \rightarrow a = \frac{RTV^3}{2(V-b)^2} \\ 2. \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T &= \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 & \rightarrow \frac{6a}{V^4} &= \frac{2RT}{(V-b)^3} \rightarrow a = \frac{2RTV^4}{6(V-b)^3} \end{aligned}$$

$a = a$ , so:  $\frac{RTV^3}{2(V-b)^2} = \frac{2RTV^4}{6(V-b)^3}$  some terms cancel each other out,  $\frac{RTV^3}{2(V-b)^2}$  resulting in:

$$\begin{aligned} \frac{1}{1} &= \frac{2V}{3(V-b)} \rightarrow 2V = 3(V-b) = 3V - 3b \\ -V &= -3b \rightarrow V_c = 3b \end{aligned}$$

## Exercise 35

$$c) p = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$\frac{RT}{(V-b)^2} = \frac{2a}{V^3} \Rightarrow 2a(V-b)^2 = V^3 \cdot RT$$

$$a = \frac{RTV^3}{2(V-b)^2}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$

$$\frac{2RT}{(V-b)^3} = \frac{6a}{V^4} = \frac{6}{V^4} \left( \frac{RTV^3}{2(V-b)^2} \right)$$

$$\frac{2RT}{(V-b)^3} = 3 \left( \frac{RT}{V(V-b)^2} \right) \quad \left| \cdot \frac{(V-b)^2}{RT} \right.$$

$$\frac{2}{(V-b)} = \frac{3}{V} \Rightarrow 3(V-b) = 2V$$

$$3V - 3b = 2V$$

$$3V - 2V = 3b$$

$$\boxed{V = 3b}$$

$$\frac{2a}{V^3} = \frac{RT}{(V-b)^2} \Rightarrow \frac{2a}{(3b)^3} = \frac{RT_c}{(3b-b)^2} \Rightarrow \frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$



$$d) \left. \begin{array}{l} V_c = 3b \\ T_c = \frac{pa}{27Rb} \end{array} \right\} \text{in vdw: } p = \frac{RT_c}{3b-b} - \frac{a}{(3b)^2}$$

$$p = \frac{R \cdot \left( \frac{pa}{27Rb} \right)}{2b} - \frac{a}{9b^2} = \frac{pa}{27 \cdot 2b^2} - \frac{a}{9 \cdot b^2} \Rightarrow$$

$$p = \frac{pa}{27 \cdot 2b^2} - \frac{2 \cdot 3a}{2 \cdot 3 \cdot 9b^2} = \frac{pa}{27 \cdot 2b^2} - \frac{6a}{27 \cdot 2b^2} =$$

$$= \frac{(pa - 6a)}{27 \cdot 2b^2} = \frac{2a}{27 \cdot 2 \cdot b^2} \Rightarrow \boxed{p_c = \frac{a}{27b^2}}$$

$$e) a = 0.361 \text{ J m}^3 \text{ mol}^{-2}$$

$$b = 42.9 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$V_c = 3b = 3 \cdot 42.9 \cdot 10^{-6} = 3 \cdot 42.9 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1} = 1.29 \cdot 10^{-4} \frac{\text{m}^3}{\text{mol}}$$

$$T_c = \frac{p \cdot a}{27 \cdot R \cdot b} = \frac{p \cdot 0.361}{27 \cdot 8.314 \cdot 42.9 \cdot 10^{-6}} = \frac{p \cdot 0.361}{27 \cdot 8.314 \cdot 42.9 \cdot 10^{-6}} = 299.9 \text{ K}$$

$$p_c = \frac{a}{27b^2} = \frac{0.361}{27 \cdot (42.9 \cdot 10^{-6})^2} = 7.26 \cdot 10^6 \text{ Pa}$$

$$= 72.6 \text{ atm.}$$

Comparison is not too bad given the simplicity of vdw eq. of state

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