Answers – problem set 7.

(32)

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

$$\underbrace{\qquad\qquad}_{[\text{in lecture } nRT(x_1 \ln x_1 + x_2 \ln x_2)]}$$

a)

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

$$G_{unmixed} = \underset{\uparrow \text{ pure 1}}{G_1^*} + \underset{\uparrow \text{ pure 2}}{G_2^*}$$

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

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

$$\Rightarrow \mu_1 = \frac{\partial}{\partial n_1}(G_1^* + G_2^*) + RT \frac{\partial}{\partial n_1}\left(\overbrace{n_1 \ln n_1 - n_1 \ln n}^{n_1 \ln x_1} + \overbrace{n_2 \ln n_2 - n_2 \ln n}^{n_2 \ln x_2}\right)$$

$$\underbrace{\qquad}_{\left(\frac{\partial G_1^*}{\partial n_1}\right) = \mu_1^* \; \& \; \left(\frac{\partial G_2^*}{\partial n_1}\right) = 0}$$

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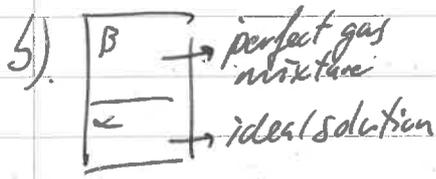
use: $\dfrac{\partial \ln n}{\partial n_1} = \dfrac{1}{n}\dfrac{\partial n}{\partial n_1} = \dfrac{1}{n}\dfrac{\partial}{\partial n_1}(n_1 + n_2) = \dfrac{1}{n}$

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

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

$$\boxed{\mu_1 = \mu_1^* + RT \ln x_1}$$

(so little fiddly).

5)

β → perfect gas mixture

α → ideal solution

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

sub in ⟵
$$\mu_i^\alpha = \mu_i^* + RT \ln X_i \quad \text{(ideal solution)}$$
$$\mu_i^\beta = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus} \quad \text{(perfect gas)}$$

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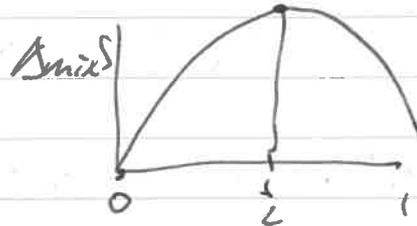
reference state
$X_i = 1$
$$\mu_i^* = \mu_i^\ominus + RT \ln \frac{P_i^*}{P^\ominus} \quad (2)$$

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

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

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

i) $\frac{n_{hex}}{n_{hep}} = \frac{\left(\frac{n_{hex}}{n}\right)}{\left(\frac{n_{hep}}{n}\right)} =$

$$= \frac{X_{hex}}{X_{hep}} = \frac{1/2}{1/2} = 1$$

ii) in terms of masses → you need molar masses:

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

(33) $\Delta T = \dfrac{RT^{*2}}{\Delta_{vap}H} \cdot x_2$

* $\Delta_{vap}H = 30.8 \text{ kJ/mol}^{-1}$

* $T^* = 80.15 + 273.15$
$= 353.30 k$

* $\Delta T = 80.95 - 80.15 =$
$= 0.80 k$

Sub all th 8 unknown $= x_2$

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

$= \dfrac{n_2}{n_{benzene} + n_2}$

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

$n_2 = \dfrac{10 g}{M_2}$

$x_2 = \dfrac{\frac{10}{M_2}}{\frac{100}{78.11} + \frac{10}{M_2}}$

$x_2 = \Delta T \cdot \dfrac{\Delta_{vap}H}{RT^{*2}} = 0.80 \cdot \dfrac{30.8 \cdot 10^3}{8.314 \cdot (353.30)^2} = 0.0237$

$x_2 = \dfrac{\frac{10}{M_2} \cdot M_2}{\left(\frac{100}{78.11} + \frac{10}{M_2}\right) M_2} = \dfrac{10}{\alpha \cdot M_2 + 10}$
$\left(\alpha = \dfrac{100}{78.11}\right)$

$M_2 = \dfrac{10}{\alpha}\left(\dfrac{1}{x_2} - 1\right) = \left(\dfrac{10}{100} \cdot 78.11\right) \cdot \left(\dfrac{1}{0.0237} - 1\right) =$

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

Exercise 33

$$m = \frac{m}{M}$$

$m_2 = 10g \rightarrow \text{solid}$

$m_1 = 100g$

$T^* = 80.95°C = 353.30K$

$T_{b.p} (\text{benzene}) = 80.15°C$

$\Delta T = 80.95 - 80.15 = 0.80K$

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

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

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

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

$M_2 = ?$

$$X_2 = \Delta T \cdot \frac{\Delta_{vap}H}{RT^{*2}} = \frac{0.80 \cdot 30.8 \cdot 10^3}{8.314 \cdot (353.3)^2} = \underline{0.0237}$$

$$X_2 = \frac{n_2}{n_1 + n_2} \qquad n_1 = \frac{m_1}{M_1} = \frac{100 \, g}{78.11 \, g/mol}$$

$X_2(n_1 + n_2) = n_2$

$X_2 n_1 + X_2 n_2 = n_2 \Rightarrow X_2 n_2 - n_2 = -X_2 n_1 \, / \cdot (-1)$

$$n_2 - X_2 n_2 = X_2 n_1$$

$$n_2(1 - X_2) = X_2 n_1 \implies n_2 = \frac{X_2 n_1}{1 - X_2}$$

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

$$M_2 = \frac{m_2}{n_2} = \frac{10g}{0.031078 \, mol} :$$

$$\boxed{M_2 = 321 \, g/mol}$$

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

$[B] = 0.282 \text{ mol dm}^{-3}$ $\Big\}$ $\pi = 0.282 \cdot 10^{+3} \cdot 8.314 \cdot 293 =$

$T = 293 \text{ k}$

$\qquad = 6.877 \cdot 10^5 \text{ Pa}$

$\qquad = 6.87 \text{ bar}.$

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

π: osmotic pressure

μ_i: chemical potential of component 1
$\qquad$ (comp 1 = typically the solvent)
μ_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

in general - for non-ideal solutions -: $\mu_i = \mu_i^* + RT \ln a_i$ activity $\downarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad$ sub, in:

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

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

$V_{i,m}$ for water @ 20°C: $V_{i,m} = \dfrac{M_{H2O}}{\rho_{H2O}} = \dfrac{18.015}{0.998} = 18.05 \dfrac{cm^3}{mol}$

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

$\boxed{a_i = 0.9943}$ activity coeff: $a_i = X_i f_i$

$f_i = \dfrac{a_i}{X_i} = a_i \cdot \dfrac{n_{H2O} + n_z}{n_{H2O}} \Rightarrow$ $n_z = 0.300 \text{ mol per kg } H2O \; (b_z)$

$\qquad\qquad\qquad\qquad\qquad\qquad$ $n_{H2O} = \dfrac{1000}{M_{H2O}} = \dfrac{1000}{18.015}$

$\rightarrow f_i = 0.9943 \cdot \dfrac{\left(\frac{1000}{18.015} + 0.300\right)}{(1000/18.015)} = 0.9943/0.9946 = 0.9997.$

(35) $n=1$ vdw: $p = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$

a): a: parametrises the attractive interactions

b: " " " repulsive "

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

$pV = nRT$

$\downarrow$

$p = \dfrac{nRT}{V} \longrightarrow \left(\dfrac{\partial p}{\partial V}\right)_T = \dfrac{-nRT}{V^2} \xrightarrow{n=1} \dfrac{-RT}{V^2} = 0$

· condition $\left(\dfrac{\partial p}{\partial V}\right)_T = 0$ only met as $V \to \infty$ (or $T \to 0$)

$\Longrightarrow$ no critical point in perfect gas.

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

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

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

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

$\Downarrow$

$\dfrac{3}{V} = \dfrac{2}{V-b} \longrightarrow 2V = 3(V-b) = 3V - 3b$

$-V = -3b \rightarrow \boxed{V_c = 3b}$

Sub back in (1):

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

Alternative answer 35c

1. $\left(\dfrac{\partial p}{\partial V}\right)_T = \dfrac{-RT}{(V-b)^2} + \dfrac{2a}{V^3} = 0$ -> $\dfrac{2a}{V^3} = \dfrac{RT}{(V-b)^2}$ -> $a = \dfrac{RTV^3}{2(V-b)^2}$

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

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

$\dfrac{1}{1} = \dfrac{2V}{3(V-b)}$ -> $2V = 3(V-b) = 3V - 3b$

$-V = -3b$ -> $V_c = 3b$

Exercise 35

c) $P = \dfrac{RT}{V-h} - \dfrac{a}{V^2}$

$\left(\dfrac{\partial P}{\partial V}\right)_T = -\dfrac{RT}{(V-h)^2} + \dfrac{2a}{V^3} = 0$

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

$\underline{a = \dfrac{RT\,V^3}{2(V-h)^2}}$

$\left(\dfrac{\partial^2 P}{\partial V^2}\right)_T = \dfrac{2RT}{(V-h)^3} - \dfrac{6a}{V^4} = 0$

$\dfrac{2RT}{(V-h)^3} = \dfrac{6a}{V^4} = \dfrac{6}{V^4}\left(\dfrac{RT\,V^3}{2(V-h)^2}\right)$

$\dfrac{2RT}{(V-h)^3} = 3\left(\dfrac{RT}{V(V-h)^2}\right) \Bigg/ \cdot \dfrac{(V-h)^2}{RT}$

$\dfrac{2}{(V-h)} = \dfrac{3}{V} \Rightarrow 3(V-h) = 2V$

$3V - 3h = 2V$

$3V - 2V = 3h$

$\boxed{V = 3h}$

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

$\boxed{T_c = \dfrac{8a}{27Rh}}$

d). $V_c = 3b$
$T_c = \dfrac{8a}{27Rb}$ $\Big\}$ in vdw: $p = \dfrac{RT_c}{3b-b} - \dfrac{a}{(3b)^2}$

$$p = \dfrac{\cancel{R}\cdot\left(\dfrac{8a}{27\cancel{R}b}\right)}{2b} - \dfrac{a}{9b^2} = \dfrac{8a}{27\cdot 2b^2} - \dfrac{a}{9\cdot b^2} =>$$

$$p = \dfrac{8a}{27\cdot2b^2} - \dfrac{2\cdot3\,a}{2\cdot3\cdot9\,b^2} = \dfrac{8a}{27\cdot2b^2} - \dfrac{6a}{27\cdot2\,b^2} =$$

$$= \dfrac{(8a-6a)}{27\cdot2b^2} = \dfrac{2a}{27\cdot2\cdot b^2} => \boxed{p_c = \dfrac{a}{27\,b^2}.}$$

e). $a = 0.361\ Jm^3\,mol^{-2}$

$b = 42.9\cdot10^{-6}\ m^3\,mol^{-1}$

$V_c = 3\cdot b = 3\cdot 42.9\cdot10^{-6} = 3\cdot42.9\cdot10^{-6}\ m^3\,mol^{-1} = 1.29\cdot10^{-4}\ \dfrac{m^3}{mol}$

$T_c = \dfrac{8\cdot a}{27\cdot R\cdot b} = \dfrac{8\cdot0.361}{27\cdot0.314\cdot42.9\cdot10^{-6}} = \dfrac{8\cdot0.361}{27\cdot0.314\cdot42.9\cdot10^{-6}} = 299.9\ k$

$P_c = \dfrac{a}{27\,b^2} = \dfrac{0.361}{27\cdot(42.9\cdot10^{-6})^2} = 7.26\cdot10^6\ Pa$

$= 72.6\ atm.$

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

✗