

**Q.1 Question 1**

The van der Waals equation of state (vdW EOS) is given by,

$$P = \frac{RT}{V-b} - \frac{a}{V^2},$$

- (a) Show that the vdW EOS can be expressed as a cubic polynomial equation in  $Z$  (compressibility coefficient),

$$Z^3 - (1+B)Z^2 + AZ - AB = 0,$$

with  $B = bP/(RT)$ ,  $A = aP/(RT)^2$  and  $R \left( = 8.314 \times 10^{-5} \frac{\text{bar.m}^3}{\text{mol.K}} \right)$  is the molar gas constant [7 marks]

**Solution:**

[2/7] We can rearrange the vdW EOS,

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \implies \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RTV} = \frac{1}{1 - \frac{b}{V}} - \frac{a}{RTV}$$

[1/7] Eliminating  $V$  as  $V = ZRT/P$ ,

$$Z = \left( 1 - \frac{bP}{ZRT} \right)^{-1} - \frac{aP}{Z(RT)^2} = \frac{ZRT}{ZRT - bP} - \frac{aP}{Z(RT)^2}$$

[3/7] Manipulating this expression,

$$\begin{aligned} Z^2 R^2 T^2 (ZRT - bP) &= Z^2 (RT)^3 - aP (ZRT - bP) \\ Z^3 - \frac{bP}{RT} Z^2 - Z^2 - \frac{aP}{(RT)^2} Z + ab \frac{P^2}{(RT)^3} &= 0 \end{aligned}$$

[1/7] with  $B = bP/(RT)$ ,  $A = aP/(RT)^2$ ,

$$Z^3 - (1+B)Z^2 + AZ - AB = 0$$

- (b) Calculate the fugacity of gaseous  $\text{CO}_2$  at 310 K and 1.4 MPa using the vdW EOS, with  $a = 0.3658 \text{ Pa.m}^6.\text{mol}^{-2}$ ,  $b = 4.286 \times 10^{-5} \text{ m}^3.\text{mol}^{-1}$ . Given,

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{b}{V} \right) - \frac{a}{RTV} - \ln Z + (Z-1).$$

Use the largest real root of the cubic polynomial equation in  $Z$  to represent the gaseous phase. [13 marks]

**Solution:**

Solving the cubic polynomial in  $Z$ ,

$$Z^3 - (1+B)Z^2 + AZ - AB = 0 \implies Z = 0.9436$$

**[2/13]**

*with  $B = bP/(RT) = 2.3281 \times 10^{-2}$  and  $A = aP/(RT)^2 = 7.7095 \times 10^{-2}$ , leads to  $Z = 0.9436$ . Now for the fugacity equation, either*

**[3/13]**

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{b}{V} \right) - \frac{a}{RTV} - \ln Z + (Z - 1)$$

*or*

$$\ln \left( \frac{f}{P} \right) = -\ln \left( 1 - \frac{B}{Z} \right) - \frac{A}{Z} - \ln Z + (Z - 1)$$

**[8/13]**

*leads to  $f = 1.3250 \times 10^6 \text{ Pa} = 1.3250 \text{ MPa}$ . . If the first equation was used to calculate  $f$ , then one needs to calculate the molar volume of the gaseous  $\text{CO}_2$  through*

$$V = \frac{ZRT}{P} = 1.7371 \times 10^{-3} \text{ m}^3.\text{mol}^{-1}$$

**Total Question Marks:20**

**Q.2 Question 2**

In a saturated liquid mixture of benzene and toluene containing 45 mol% of benzene, determine:

- (a) Temperature and composition of the first bubble at 200 kPa. [10 marks]

**Solution:**

[1/10] *The molar constraint of vapour composition is*

$$\sum_{i=1}^2 y_i = y_1 + y_2 = 1,$$

[1/10] *and replacing the Raoult law,  $y_i = \frac{x_i P_i^{\text{sat}}}{P}$ , in the constraint relation,*

$$\begin{aligned} P &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} \\ &= x_1 \exp\left(A_1 - \frac{B_1}{T + C_1}\right) + x_2 \exp\left(A_2 - \frac{B_2}{T + C_2}\right) \end{aligned}$$

[3/10] *Solving this non-linear equation we obtain the bubble temperature of the benzene-toluene mixture as  $T = 391.79 \text{ K}$ . In order to calculate the compositions, we should*  
 [1/10] *use the Raoult's relation with  $P_1^{\text{sat}} = 289.01 \text{ kPa}$ ,*

[4/10] 
$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = 0.6503 \implies y_2 = 0.3497$$

- (b) Pressure and composition of the first bubble at 400 K. [10 marks]

**Solution:**

[1/10] *The molar constraint of vapour composition is*

$$\sum_{i=1}^2 y_i = y_1 + y_2 = 1,$$

[1/10] *and replacing the Raoult law,  $y_i = \frac{x_i P_i^{\text{sat}}}{P}$ , in the constraint relation,*

$$\begin{aligned} P &= x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} \\ &= x_1 \exp\left(A_1 - \frac{B_1}{T + C_1}\right) + x_2 \exp\left(A_2 - \frac{B_2}{T + C_2}\right) \end{aligned}$$

[3/10] *Solving this equation for  $T = 400 \text{ K}$  results in  $P = 245.28 \text{ kPa}$ . In order to calculate*  
 [1/10] *the compositions, we should use the Raoult's relation with  $P_1^{\text{sat}} = 352.16 \text{ kPa}$ ,*

[4/10] 
$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P} = 0.6461 \implies y_2 = 0.3539$$

For this problem, benzene and toluene mixtures may be considered as ideal and you should use,

$$\ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C}$$

with [P] = kPa, [T] = K, [B] = K and [C] = K.

<b>Species</b>	<b>A</b>	<b>B</b>	<b>C</b>
Benzene (1)	14.1603	2948.78	-44.5633
Toluene (2)	14.2515	3242.38	-47.1806

**Total Question Marks:20**

**Q.3 Question 3**

Consider the following chemical reaction representing the chemical equilibrium between dinitrogen tetroxide,  $N_2O_4(g)$ , and nitrogen dioxide,  $NO_2(g)$  at  $25^\circ C$  and 1 atm,



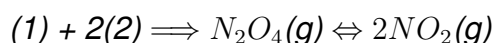
Determine:

- (a) Equilibrium constant of this reaction.

[8 marks]

**Solution:**

The reaction  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  may be obtained by combining the linearly independent chemical reactions (1) and (2), i.e.,



Thus, the standard free Gibbs energy change of the mixture at  $25^\circ C$  can be obtained from the

$$\Delta G_{298}^\circ = \Delta G_1^\circ + 2\Delta G_2^\circ = 4478.86 \text{ J.mol}^{-1}$$

The equilibrium constant at  $25^\circ C$  is given by

$$K_{eq,298} = \exp \left[ -\frac{\Delta G_{298}^\circ}{RT} \right] = 0.1641$$

- (b) Equilibrium composition of  $N_2O_4(g)$ .

[12 marks]

**Solution:**

The equilibrium constant can also be obtained as a function of the species' activities,

$$K = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{\left( \frac{\bar{f}_{NO_2}}{f_{NO_2}^\circ} \right)^2}{\left( \frac{\bar{f}_{N_2O_4}}{f_{N_2O_4}^\circ} \right)}$$

Assuming ideal gas behaviour,  $\bar{f}_i = P_i$ ,  $f_i^\circ = P_{NO_2}^\circ = P_{N_2O_4}^\circ = 1 \text{ atm}$ ,

$$K = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{\left( \frac{\bar{f}_{NO_2}}{f_{NO_2}^\circ} \right)^2}{\left( \frac{\bar{f}_{N_2O_4}}{f_{N_2O_4}^\circ} \right)} = \frac{\left( \frac{P_{NO_2}}{P_{NO_2}^\circ} \right)^2}{\left( \frac{P_{N_2O_4}}{P_{N_2O_4}^\circ} \right)} = \frac{\left( \frac{P \cdot y_{NO_2}}{1 \text{ atm}} \right)^2}{\left( \frac{P \cdot y_{N_2O_4}}{1 \text{ atm}} \right)}$$

As  $P = 1 \text{ atm}$ ,

$$K = \frac{\left( \frac{P \cdot y_{NO_2}}{1 \text{ atm}} \right)^2}{\left( \frac{P \cdot y_{N_2O_4}}{1 \text{ atm}} \right)} = \frac{y_{NO_2}^2}{y_{N_2O_4}}$$

Assuming that initially there are 1 mole of  $N_2O_4$  and 0 mole of  $NO_2$ , the gaseous composition during the equilibrium is expressed by

$$y_i = \frac{n_i}{n} = \frac{n_{i,0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon},$$

[1/12]

with  $n_{N_2O_4,0} = 1$ ,  $n_{NO_2,0} = 0$ ,  $\nu_{N_2O_4} = -1$ ,  $\nu_{NO_2} = 2$  and  $\nu = 1$ . Thus, the compositions in equilibrium are

[2/12]

$$y_{N_2O_4} = \frac{1 - \varepsilon}{1 + \varepsilon} \quad \text{and} \quad y_{NO_2} = \frac{2\varepsilon}{1 + \varepsilon}$$

Here any initial conditions are acceptable (i.e., any initial number of moles for both species), however this would change the expressions for  $y_{N_2O_4}$  and  $y_{NO_2}$ . Replacing these expressions in the previous equation with  $K_{eq,298} = 0.1641$  (from (a))

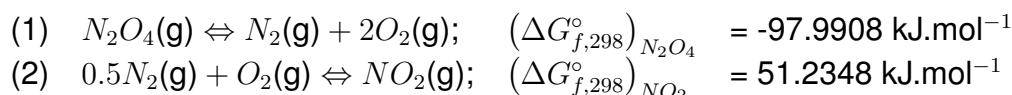
[2/12]

$$K = \frac{y_{NO_2}^2}{y_{N_2O_4}} = \frac{\left(\frac{2\varepsilon}{1 + \varepsilon}\right)^2}{\frac{1 - \varepsilon}{1 + \varepsilon}} = 0.1641 \implies \varepsilon = 0.1985$$

[2/12]

The equilibrium composition is  $y_{N_2O_4} = 0.6688$  and  $y_{NO_2} = 0.3312$ .

For this problem, you should consider the following reaction data:



where  $G_{f,298}^\circ$  is the standard molar free Gibbs energy of formation. Also, the equilibrium constant at 25°C is given by

$$K_{298} = \exp \left[ -\frac{\Delta G_{298}^\circ}{RT} \right]$$

where  $R \left( = 8.314 \frac{\text{J}}{\text{mol.K}} \right)$  is the molar gas constant and  $\Delta G_{298}^\circ$  is the standard free Gibbs energy change of the mixture. Assume ideal gas behaviour.

**Total Question Marks:20**

**Q.4 Question 4**

- (a) Two litres of an anti-freezing solution is needed for a cooling process. The solution is prepared by mixing 30%-mol of methanol in water. What are the volumes of pure methanol and water at 25°C necessary to prepare solution? Partial molar volumes ( $\bar{V}$ ) for methanol and water in a 30%-mol of methanol solution and their pure species molar volumes ( $V$ ), both at 25°C are: [8 marks]

	$\bar{V}_i$ (cm <sup>3</sup> .mol <sup>-1</sup> )	$V_i$ (cm <sup>3</sup> .mol <sup>-1</sup> )
Methanol (1)	38.6320	40.7270
Water (2)	17.7650	18.0680

**Solution:**

- [2/8] *The molar volume of the 30%-mol of methanol solution is given by,*

$$V = \frac{V^T}{n_T} = \frac{\sum_{i=1}^2 n_i \bar{V}_i}{n_T} = \sum_{i=1}^2 x_i \bar{V}_i = x_1 \bar{V}_1 + x_2 \bar{V}_2$$

$$= (0.3)(38.6320) + (0.7)(17.7650) = 24.0251 \text{ cm}^3.\text{mol}^{-1}$$

- [2/8] *The total number of moles are:*

$$n_T = \frac{V^T}{V} = \frac{2000}{24.0251} = 83.2463 \text{ mol}$$

- [4/8] *The volume of pure methanol and water for the solution are:*

$$V_1^{\text{pure}} = x_1 n_T V_1 = 1017.1116 \text{ cm}^3$$

$$V_2^{\text{pure}} = x_2 n_T V_2 = 1052.8759 \text{ cm}^3$$

- (b) In generating expressions from  $G^E/RT$  from VLE data, a convenient approach is to plot values of  $G^E/(x_1 x_2 RT)$  vs  $x_1$  and fitting results with an appropriate function. Consider if such data were fit by the expression,

$$\frac{G^E}{x_1 x_2 RT} = A + B x_1^2.$$

From the expression  $G^E/(x_1 x_2 RT)$ , provide equations for the activity coefficient,  $\ln \gamma_i$ , as a function of  $A$ ,  $B$ ,  $x_1$  and  $x_2$ , given [12 marks]

$$\ln \gamma_i = \frac{\bar{G}_i^E}{RT}.$$

**Solution:**

- [2/12] *For a binary mixture, the partial molar property,  $\bar{M}$  can be defined as,*

$$\overline{M}_1 = M + x_2 \frac{dM}{dx_1} \quad \text{and} \quad \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

**[3/12]**

thus with  $\overline{M}_i = \frac{\overline{G}_i^E}{RT}$ ,

$$\ln \gamma_1 = \frac{\overline{G}_1^E}{RT} = \frac{G^E}{RT} + x_2 \frac{d(G^E/RT)}{dx_1} \quad \text{and} \quad \ln \gamma_2 = \frac{\overline{G}_2^E}{RT} = \frac{G^E}{RT} - x_1 \frac{d(G^E/RT)}{dx_1}.$$

**[5/12]**

Replacing  $x_2 = 1 - x_1$  in  $\frac{G^E}{RT} = x_1 x_2 (A + Bx_1^2)$  and differentiating  $G^E/(RT)$  w.r.t.  $x_1$ ,

$$\frac{d(G^E/RT)}{dx_1} = (1 - 2x_1) A + (3 - 4x_1) Bx_1^2$$

**[2/12]**

The activity coefficient (as a function of  $A, B, x_1$  and  $x_2$ ) is then given by,

$$\ln \gamma_1 = x_1 x_2 (A + Bx_1^2) + x_2 [(1 - 2x_1) A + (3 - 4x_1) Bx_1^2]$$

$$\ln \gamma_2 = x_1 x_2 (A + Bx_1^2) - x_1 [(1 - 2x_1) A + (3 - 4x_1) Bx_1^2]$$

Alternatively, one could also further develop/simplify the equations above considering  $x_2 = 1 - x_1$ .

**Total Question Marks:20**



**Q.5 Question 5**

- (i) A concentrated binary solution containing mainly species 2 (though  $x_2 \neq 1$ ) is in equilibrium with a vapour phase containing both species 1 and 2. Pressure and temperature of this two-phase system are 1 bar and 298.15 K. Given  $\mathcal{H}_1 = 200$  bar (Henry constant) and  $P_2^{\text{sat}} = 0.10$  bar, calculate  $x_1$  and  $y_1$ . [10 marks]

**Solution:**

Assuming that at 1 bar the vapour phase behaves as an ideal gas. The vapour phases fugacities are then equal to the partial pressures. Assume the Lewis-Randall rule applies to the concentrated species 2 and that Henry's law applies to the diluted species 1, therefore,

$$y_1 P = \mathcal{H}_1 x_1; \quad \text{and} \quad y_2 P = x_2 P_2^{\text{sat}}$$

**[5/10]**

with  $x_1 + x_2 = 1$  and  $y_1 + y_2 = 1$ . As  $P = \sum_{i=1}^2 y_i P = y_1 P + y_2 P$ ,

$$P = \mathcal{H}_1 x_1 + (1 - x_1) P_2^{\text{sat}} \implies x_1 = 4.5023 \times 10^{-3}$$

**[5/10]**

$$\text{and } y_1 = \frac{\mathcal{H}_1 x_1}{P} = 0.9005.$$

- (ii) Chemical species A and B are in vapour-liquid equilibrium at 298.15 K. The following conditions are applied to this system:

	$P_i^{\text{sat}}$ (bar)	$\ln \gamma_i$
<b>A</b>	1.24	$1.8 x_B^2$
<b>B</b>	0.89	$1.8 x_A^2$

Assuming that  $y_i P = x_i \gamma_i P_i^{\text{sat}}$  (where  $\gamma_i$  is the activity coefficient of species  $i$ ) is valid, calculate the pressure  $P$  and the vapour mole fraction  $y_A$  for a liquid mole fraction of  $x_A = 0.65$ . [10 marks]

**Solution:**

With  $x_A = 0.65$  and  $x_B = 0.35$ , we can calculate the activity coefficients,  $\gamma_A = 1.2467$  and  $\gamma_B = 2.1393$ , and apply in

**[2/10]****[3/10]**

$$P = x_A \gamma_A P_A^{\text{sat}} + x_B \gamma_B P_B^{\text{sat}} = 1.6712 \text{ bar.}$$

**[5/10]**

The vapour mole fraction is obtained from

$$y_A = \frac{x_A \gamma_A P_A^{\text{sat}}}{P} = 0.6013$$

**Total Question Marks:20****END OF PAPER****Total Paper Marks:100**