

MARKS

Q.1 Question 1

- (a) Assuming
- $S = S(P, V)$
- and taking into consideration that,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Prove that

$$dS = \frac{C_V}{T} \left(\frac{\partial T}{\partial P}\right)_V dP + \frac{C_P}{T} \left(\frac{\partial T}{\partial V}\right)_P dV$$

[8 marks]

Solution:

As entropy is expressed as a function of pressure and molar volume, we can write it in differential form as,

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

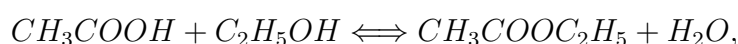
We can rewrite this equation as

$$dS = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$\text{As } \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \text{ and } \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T},$$

$$dS = \frac{C_v}{T} \left(\frac{\partial T}{\partial P}\right)_V dP + \frac{C_P}{T} \left(\frac{\partial T}{\partial V}\right)_P dV$$

- (b) In the esterification reaction of acetic acid with ethanol at 100°C,



calculate the mass fraction of ethyl acetate given that initially there was 1 mole of acetic acid and ethanol. The reaction enthalpy and Gibbs energy at standard state (25°C and 1 atm) are $\Delta H_{298}^\circ = -3640$ J and $\Delta G_{298}^\circ = -4650$ J. Given the van't Hoff equation, [12 marks]

$$\frac{d}{dT} (\ln K) = -\frac{\Delta H_{298}^\circ}{RT^2}$$

Solution:

Initially we have 1 mol of acetic acid (HAc) and 1 mol of ethanol (EtOH). We can calculate the mole fractions for all species as a function of the reaction coordinate, ϵ

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$$\begin{aligned}
 x_{EtAc} &= \frac{\epsilon}{2 + 0.\epsilon} = \frac{\epsilon}{2} = x_{H_2O} \\
 x_{HAc} &= \frac{1 - \epsilon}{2} = x_{EtOH}
 \end{aligned}$$

[2/12] Assuming ideal solution,

$$\prod_{i=1}^{c=4} x_i^\nu = K = x_{HAc}^{-1} x_{EtOH}^{-1} x_{EtAc} x_{H_2O} \implies K = \frac{\epsilon^2}{(1 - \epsilon)^2}$$

[2/12] Thus, by calculating K , we can obtain ϵ and then x_{EtAc} . K (temperature-dependent) can be obtained from the Gibbs free energy,

$$\ln K_{298} = -\frac{\Delta G_{298}^\circ}{RT} = \frac{4650.0}{8.314 \times 298.15} = 1.8759$$

[2/12] Now, in order to calculate K at 373.15 K, we can integrate the van't Hoff equation from 298.15 K to 373.15 K

$$\int_{K_{298}}^{K_{373}} d(\ln K) = - \int_{298.15}^{373.15} \frac{\Delta H_{298}^\circ}{RT^2} dT \implies K_{373} = 4.8586$$

Now we can calculate the reaction coordinate,

$$K_{373} = \frac{\epsilon^2}{(1 - \epsilon)^2} \implies \epsilon = 0.6879$$

[2/12] Thus

$$x_{EtAc} = \frac{\epsilon}{2} = 0.3440$$

Total Question Marks:20

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Q.2 Question 2

- (a) Show that the van der Waals equation of state (vdW EOS),

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

can be expressed as a cubic polynomial equation in Z (compressibility coefficient),

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

with $B = bP/(RT)$ and $A = aP/(RT)^2$. [7 marks]**Solution:**[3/7] *We can rearrange the vdW EOS,*

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

$$Z = \frac{1}{1 - \frac{b}{V}} - \frac{a}{RTV} \quad \text{since } V = \frac{ZRT}{P}$$

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

[2/7] *Defining $B = bP/(RT)$ and $A = aP/(RT)^2$ and replacing in the above expression*
[2/7] *leads to,*

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

- (b) Calculate the fugacity of
- CO_2
- at 310 K and
- 1.4×10^6
- Pa using the van der Waals equation of state (EOS), with
- $a = 0.3658 \text{ Pa}\cdot\text{m}^6/\text{mol}^2$
- ,
- $b = 4.286 \times 10^{-5} \text{ m}^3/\text{mol}$
- . Given, [13 marks]

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

Solution:[5/13] *Solving the cubic polynomial in Z , with $B = bP/(RT)$ and $A = aP/(RT)^2$,*

$$Z^3 - (1+B)Z^2 + AZ - AB = 0 \Rightarrow A = 7.7095 \times 10^{-2}; B = 2.3281 \times 10^{-2}$$

$$\Rightarrow Z = 0.9436$$

[8/13] *Now for the fugacity equation:*

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

$$\ln\left(\frac{f}{P}\right) = -\ln\left(1 - \frac{B}{Z}\right) - \frac{A}{Z} - \ln Z + (Z - 1) \Rightarrow f = 1.26 \times 10^6 \text{ Pa}$$

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Q.3 Question 3

An ideal liquid mixture of 25 mol-% n-pentane (nC_5), 45 mol-% n-hexane (nC_6) and 30 mol-% n-heptane (nC_7), initially at 69°C and high pressure, is partially vaporised by isothermally lowering the pressure to 1.013 bar. Calculate the relative amounts of vapour and liquid in equilibrium and their compositions. [20 marks]

Solution:

[3/20] From the Antoine equation, we can calculate the saturation pressure of the species $P_{C_5}^{sat} = 2.721$ bar, $P_{C_6}^{sat} = 1.024$ bar, $P_{C_7}^{sat} = 0.389$ bar. Assuming ideal solution,

$$\frac{y_i}{x_i} = K_i = \frac{P_i^{sat}}{P}$$

[3/20] Thus $K_{C_5} = 2.6861$, $K_{C_6} = 1.0109$ and $K_{C_7} = 0.3840$, therefore

[2/20]

$$y_{C_5} = x_{C_5} K_{C_5}, \quad y_{C_6} = x_{C_6} K_{C_6}, \quad y_{C_7} = x_{C_7} K_{C_7}$$

$$\sum_{i=1}^3 x_i = x_{C_5} + x_{C_6} + x_{C_7} = 1$$

$$\sum_{i=1}^3 y_i = y_{C_5} + y_{C_6} + y_{C_7} = 1 = K_{C_5} x_{C_5} + K_{C_6} x_{C_6} + K_{C_7} x_{C_7}$$

[1/20] The mass balance is,

$$L + V = 1$$

$$x_i L + y_i V = z_i$$

[3/20] with $z_i = (0.25 \ 0.45 \ 0.30)^T$. Rearranging this set of equations lead to a non-linear expression in L ,

$$\frac{0.25}{(1 - K_{C_5}) L + K_{C_5}} + \frac{0.45}{(1 - K_{C_6}) L + K_{C_6}} + \frac{0.30}{(1 - K_{C_7}) L + K_{C_7}} = 1$$

[2/20] Solving this equation leads to $L = 0.5748$ and $V = 0.4252$. Calculating the molar fractions of the species:

[6/20]

	n-C ₅	n-C ₆	n-C ₇
x_i	0.1456	0.4479	0.4065
y_i	0.3911	0.4528	0.1561

For this problem, use

$$\ln P_i^{sat} = A_i - \frac{B_i}{RT}$$

with [P] = bar and [T] = K, and

$$\begin{array}{lll} A_{nC_5} = 10.422 & A_{nC_6} = 10.456 & A_{nC_7} = 11.431 \\ B_{nC_5} = 26799 & B_{nC_6} = 29676 & B_{nC_7} = 35200 \end{array}$$

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Q.4 Question 4

- (a) A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is obtained through a single-stage liquid/vapour separator. Specifications on the equilibrium composition are: $x_1 = 0.002$ and $y_1 = 0.950$. Assuming that the modified Raoult's law applies,

$$y_i P = x_i \gamma_i P_i^{\text{sat}}$$

Determine T and P for the separator. Given the activity coefficients for the liquid phase,

$$\ln \gamma_1 = 0.93x_2^2 \quad \text{and} \quad \ln \gamma_2 = 0.93x_1^2,$$

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad \text{with } [P] = \text{bar and } [T] = \text{K},$$

with $A_1 = 10.08$, $B_1 = 2572.0$, $A_2 = 11.63$ and $B_2 = 6254.0$. [13 marks]

Solution:

Given,

$$x_1 = 0.002 \implies x_2 = 0.998$$

$$y_1 = 0.950 \implies y_2 = 0.050$$

[2/13] Calculating the activity coefficient, ,

$$\ln \gamma_1 = 0.93x_2^2 \implies \gamma_1 = 2.5251$$

$$\ln \gamma_2 = 0.93x_1^2 \implies \gamma_2 = 1.0000$$

[4/13] The modified Raoult's law,

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \implies P = \frac{x_i \gamma_i P_i^{\text{sat}}}{y_i}$$

$$\frac{P_1^{\text{sat}}}{P_2^{\text{sat}}} = \frac{x_2 \gamma_2 y_1}{x_1 \gamma_1 y_2} = 3754.7028 = \frac{\exp\left(A_1 - \frac{B_1}{T}\right)}{\exp\left(A_2 - \frac{B_2}{T}\right)}$$

[3/13] Solving this equation results in $T = 376.45 \text{ K}$. The pressure can now be obtained,

[4/13]
$$P = \frac{x_i \gamma_i P_i^{\text{sat}}}{y_i} = 0.1368 \text{ bar}$$

- (b) Determine the temperature and composition of the first bubble created from a saturated liquid mixture of benzene and toluene containing 45 mole percent of benzene at 200 kPa. Benzene and toluene mixtures may be considered as ideal. Given

$$\ln P^{\text{sat}} = A - \frac{B}{T + C} \quad \text{with } [P] = \text{kPa and } [T] = \text{K}.$$

And

[7 marks]

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	A	B	C
Benzene	14.1603	2948.78	-44.5633
Toluene	14.2514	3242.38	-47.1806

Solution:*From Raoult's law,*

$$y_i = \frac{x_i P_i^{sat}}{P}$$

[1/7] *with benzene (1) and toluene (2),*

$$P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

[3/7] *leading to the bubble point temperature of the mixture benzene-toluene*

$$P = x_1 \exp\left(A_1 - \frac{B_1}{T + C_1}\right) + x_2 \exp\left(A_2 - \frac{B_2}{T + C_2}\right) \implies T = 391.73 \text{ K}$$

[3/7] *Calculating the saturation pressure and mole fraction of benzene in the vapour phase,*

$$P_1^{sat} = \exp\left(A_1 - \frac{B_1}{T - C_1}\right) = 289.01 \text{ kPa}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P} = 0.6503 \text{ and } y_2 = 1 - y_1 = 0.3497$$

Total Question Marks:20

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Q.5 Question 5

The molar volume (in $\text{cm}^3 \cdot \text{mol}^{-1}$) of a binary liquid mixture at T and P is given by:

$$V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$$

(a) Find expressions for the partial molar volumes of species 1 and 2 at T and P . [7 marks]

Solution:

[1/7] *Eliminating $x_2 = 1 - x_1$ in the molar volume expression,*

$$\begin{aligned} V &= 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2 \\ &= 70 + 58x_1 - x_1^2 - 7x_1^3 \end{aligned}$$

The Gibbs-Duhem equation at constant T and P can be expressed as,

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

[2/7] *and are used to obtain \overline{V}_1 and \overline{V}_2 . However we first need to calculate*

$$\frac{dV}{dx_1} = 58 - 2x_1 - 21x_1^2$$

[4/7] *Thus*

$$\begin{aligned} \overline{V}_1 &= 128 - 2x_1 - 20x_1^2 + 14x_1^3 \\ \overline{V}_2 &= 70 + x_1^2 + 14x_1^3 \end{aligned}$$

(b) Show that these expressions satisfy the Gibbs-Duhem equation, $\sum_i x_i d\overline{M}_i = 0$, where M is an intensive thermodynamic property. [5 marks]

Solution:

[1/5] *From this relation,*

$$x_1 d\overline{V}_1 + x_2 d\overline{V}_2 = 0 \implies x_1 \frac{d\overline{V}_1}{dx_1} + x_2 \frac{d\overline{V}_2}{dx_1} = 0$$

[2/5] *Differentiating \overline{V}_i with respect to x_1 ,*

$$\frac{d\overline{V}_1}{dx_1} = -2 - 40x_1 + 42x_1^2 \quad \text{and} \quad \frac{d\overline{V}_2}{dx_1} = 2x_1 + 42x_1^2$$

[2/5] *Now applying it into the original equation,*

$$\begin{aligned} x_1(-2 - 40x_1 + 42x_1^2) &= (1 - x_1)(2x_1 + 42x_1^2) \\ 0 &= 0 \end{aligned} \tag{1}$$

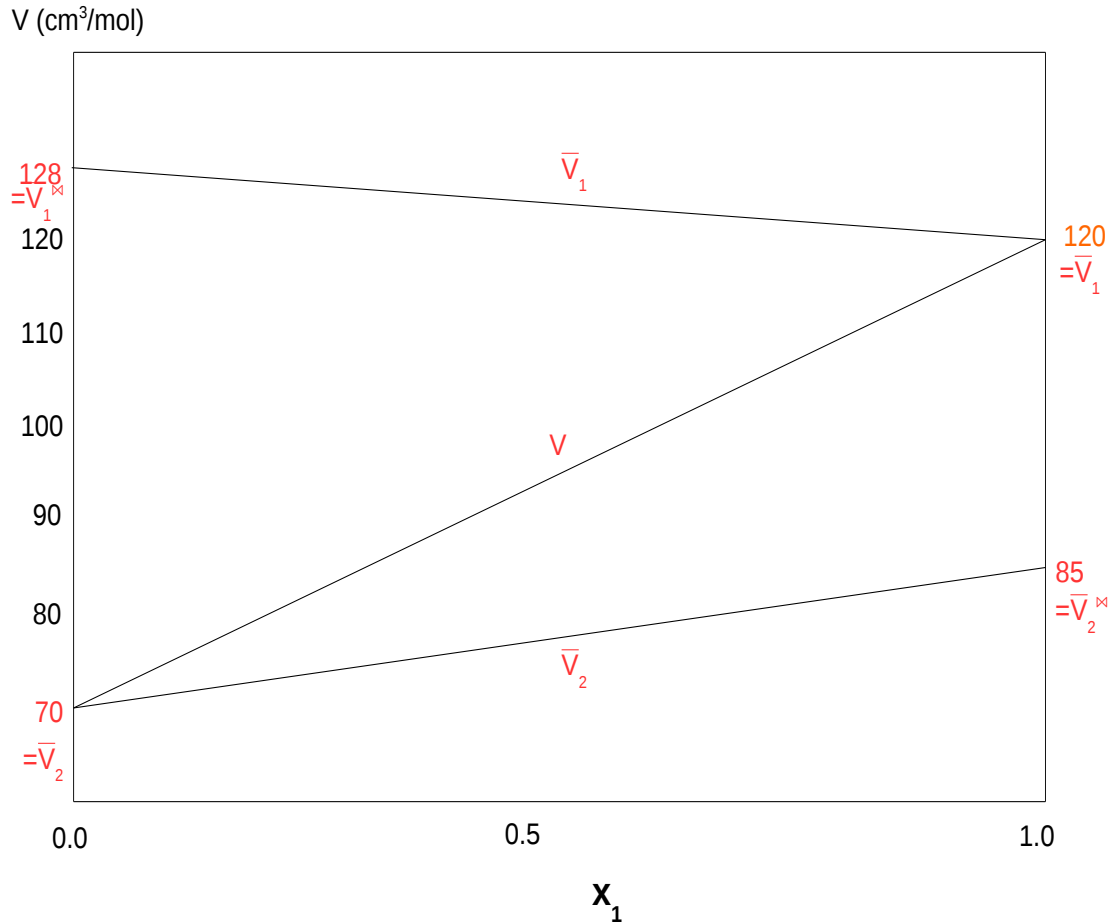
This demonstrates the validity of the Gibbs-Duhem equation.

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- (c) Plot values of V , \bar{V}_1 and \bar{V}_2 calculated by the given equation for V and by the equations developed in (a) *vs* x_1 . Label points \bar{V}_1^∞ and \bar{V}_2^∞ and show their values. [8 marks]

Solution:*The plot is*

[2/8]



[6/8]

where

	$x_1 = 0.0$	$x_1 = 1.0$
V	70	120
\bar{V}_1	128	120
\bar{V}_2	70	85

Total Question Marks:20