

Name :

Roll No. :

Invigilator's Signature :

CS/M.Tech(CHE)/SEM-2/CHE-11/2013

2013

**ADVANCED CHEMICAL ENGINEERING
THERMODYNAMICS**

Time Allotted : 3 Hours

Full Marks : 70

The figures in the margin indicate full marks.

*Candidates are required to give their answers in their own words
as far as practicable.*

Answer any five taking at least one from each Module.

Module I

1. a) Calculate molar volume, V for methanol vapour at 500 K and 10 bar using the following truncated form of Virial equation :

$$Z = 1 + (B/V) + (C/V^2)$$

Data given :

$$B = -2.19 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$C = -1.73 \times 10^{-4} \text{ m}^6/\text{mol}^2$$

$$T_c = 512.6 \text{ K}, P_c = 81 \text{ bar.}$$

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- b) Calculate the work of mechanically reversible compression if one mole of methyl chloride undergoes a pressure change from 1 bar to 60 bar at 125°C, if the species follows the following equation :

$$Z = 1 + (BP/RT) + ((C - B^2) \times P^2) / (RT)^2$$

Data given :

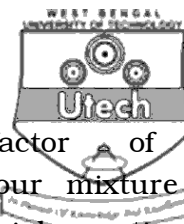
$$B = -207.5 \text{ cm}^3/\text{mol}$$

$$C = 18200 \text{ cm}^3/\text{mol}^2$$

$$T_c = 416.3 \text{ K}, P_c = 66.8 \text{ bar.}$$

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- c) Justify the relation between entropy and probability. 4



- 2 a) Calculate the compressibility factor of a methane (i) – n butane (ii) vapour mixture at 2.76×10^6 Pa and 310.93 K using virial equation of state : $Z = 1 + BP/RT$.

Data given :

$$y_1 = 0.8942$$

For methane

$$T_c = 190.58 \text{ K}, P_c = 46.04 \text{ bar}, Z_c = 0.288, \\ V_c = 99.1 \text{ cm}^3/\text{mol}, w (\text{acentric factor}) = 0.011$$

For n-butane

$$T_c = 425.18 \text{ K}, P_c = 37.97 \text{ bar.}, Z_c = 0.274, \\ V_c = 255.1 \text{ cm}^3/\text{mol}, w = 0.193. \quad 8$$

- b) Using partition function, find out the expression of entropy for a monatomic gas. 6

Module II

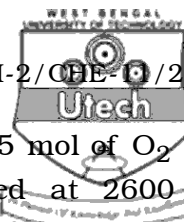
3. a) Show that, for the binary gas mixture following the virial gas equation of state, the fugacity coefficient satisfies the following relation :

$$\ln \phi = \sum y_i \bar{\phi}_i \quad 7$$

- b) Discuss the procedure to calculate the activity coefficients as per UNIQUAC and UNIFAC method. 7

4. a) Derive an expression for a binary system to show that the region where Henry's law is valid for component 1, Lewis Randal rule is valid for component 2. 4

- b) Determine the equilibrium constant at 2600 K for the reaction. $\text{CO} + 0.5 \text{O}_2 \rightarrow \text{CO}_2$.



Initially a mixture of 1 mol of CO and 0.5 mol of O_2 are placed in a container and maintained at 2600 K. Determine the equilibrium composition of the mixture at 1 atm. Standard molar heat capacity is given as

$C_p^0 = a + bT + cT^2 + dT^3$, C_p^0 is in cal/mol.K and T is in K. a , b , c values of different components are given in the table below :

| Species | a | $b \times 10^2$ | $c \times 10^5$ | $d \times 10^9$ |
|-----------|-------|-----------------|-----------------|-----------------|
| CO(g) | 6.726 | 0.04001 | 0.1283 | -0.5307 |
| $O_2(g)$ | 6.085 | 0.3631 | -0.1709 | 0.3133 |
| $CO_2(g)$ | 5.316 | 1.4285 | -0.8364 | 1.784 |

Standard enthalpy and standard Gibbs free energy of formation are given below :

| Species | $\Delta H_f^{\circ}, 298.15$ (kcal/mol) | $\Delta G_f^{\circ}, 298.15$ (kcal/mol) |
|-----------|---|---|
| CO(g) | -26.416 | -32.808 |
| $CO_2(g)$ | -94.052 | -94.260 |

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Module III

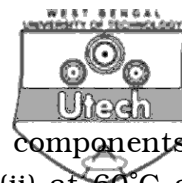
5. a) Excess Gibbs free energy of a binary liquid mixture is given by $\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 - x_2)]$ where, A and B are functions only of temperature and are dimensionless. Obtain the expression of activity coefficients of components 1 and 2. From expressions of these activity coefficients, calculate the expression of excess Gibbs free energy. Do you get the above given expression ?

Check that the activity coefficient expressions satisfy the Gibbs-Duhem equation.

4 + 2 + 4

- b) Discuss the step by step procedure in preparing T - x - y diagram of a binary VLE mixture.

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6. a) Calculate the activity coefficients of the components in the liquid mixture of acetone (i) water (ii) at 60°C and $x_1 = 0.3$ using Wilson and NRTL equations. The molar volume of pure components at 60°C are $V_1 = 74.05 \text{ cm}^3/\text{mol}$. For Wilson equation, $a_{12} = 291.27 \text{ cal/mol}$ and $a_{21} = 1448.01 \text{ cal/mol}$ and for NRTL, $b_{12} = 631.05 \text{ cal/mol}$, $b_{21} = 1197.41 \text{ cal/mol}$ and $\alpha = 0.5343$. 7
- b) Construct equilibrium curves (x vs y) for ethyl alcohol-water system at a total pressure of 760 mm Hg. The data needed (Van Laar method) are :
- (i) Ethanol-water system forms an azeotrope at 71.15° C and corresponding ethanol composition is 89.43 mole %.
- (ii) At 78.15 °C vapour pressure of water and ethanol are 329 mm Hg and 755 mm Hg respectively. 7

Module IV

7. a) Describe Claude system of air liquefaction. 5
- b) With the help of flow and $P-h$ diagram, explain how dry ice is produced. 5
- c) Derive the expression for the maximum COP of an absorption refrigeration system. 4
8. a) With a flow diagram at corresponding $P-h$ diagram, describe a two stage vapour compression refrigeration system. 7
- b) With schematic diagram describe Linde-Hampson air liquefaction cycle. 7

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