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 :

$B = -2{\cdot}19 \times 10^{-4}$ m^3/mol

$C = -1{\cdot}73 \times 10^{-4}$m^6/mol^2

$T_c = 512 \cdot 6$ K, $P_c = 81$ bar. 5

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 :

$B = -207{\cdot}5$ cm^3/mol

$C = 18200$ cm^3/mol^2

$T_c = 416 \cdot 3$ K, $P_c = 66{\cdot}8$ bar. 5

c) Justify the relation between entropy an probability. 4

2 a) Calculate the compressibility factor of a methane (i) – n butane (ii) vapour mixture at $2 \cdot 76 \times 10^6$ Pa and $310 \cdot 93$ K using virial equation of state : $Z = 1 + BP/RT$.

Data given :

$y_1 = 0 \cdot 8942$

For methane

$T_c = 190 \cdot 58$ K, $P_c = 46 \cdot 04$ bar, $Z_c = 0 \cdot 288$, $V_c = 99 \cdot 1$ cm^3/mol, w (acentric factor) = $0 \cdot 011$

For n-butane

$T_c = 425 \cdot 18$ K, $P_c = 37 \cdot 97$ bar., $Z_c = 0 \cdot 274$, $V_c = 255 \cdot 1$ cm^3/mol, $w = 0 \cdot 193$. 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 :

$ln\ \phi = \sum y_i \ \overline{}\phi_i$ 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. $CO + 0 \cdot 5\, O_2 \rightarrow CO_2$.

Initially a mixture of 1 mol of CO an 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

${C_p}^o = a + bT + cT^2 + dT^3$, ${C_p}^o$ 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	$\Delta H^{\circ}{}_{f,298\cdot15}$ (kcal/mol)	$\Delta G^{\circ}{}_{f,298\cdot15}$ $\Delta H^{\circ}{}_{f,298\cdot15}$ (kcal/mol)
CO(g)	– 26·416	– 32·808
$CO_2(g)$	– 94·052	– 94260

10

Module III

5. a) Excess Gibbs free energy of a binary liquid mixture is given by $\dfrac{G^E}{RT} = x_1 \, x_2 \, [A + B \, (x_1 - x_2) \,]$ where, A an 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. 4

6. a) Calculate the activity coefficients of the components in the liquid mixture of acetone (i) water (ii) at 60°C and $x_1 = 0{\cdot}3$ using Wilson and NTRL equations. The molar volume of pure components at 60°C are $V_1 = 74{\cdot}05\ cm^3/mol$. For Wilson equation, $a_{12} = 291{\cdot}27$ cal/mol and $a_{21} = 1448{\cdot}01$ cal/mol and for NRTL, $b_{12} = 631{\cdot}05$ cal/mol, $b_{21} = 1197{\cdot}41$ cal/mol and $\alpha = 0{\cdot}5343$. 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