Name : .....

Roll No. : .....

Invigilator's Signature : .....

CS/M.Tech (CHE)/SEM-2/CHE-11/2011

2011

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* questions. 5 × 14 = 70

1. The gases from the pyrites burner of a contact sulphuric acid plant have the following composition by volume :

   $SO_2 = 8 \cdot 1\%,\ O_2 = 10 \cdot 5\%,\ N_2 = 81 \cdot 4\%$

   The gaseous mixture is passed into a converter where in presence of a catalyst the SO_2 is oxidized to SO_3. The temperature is maintained at 520° C and the pressure at 760 mm Hg. Calculate the composition of the gases leaving the converter, assuming that equilibrium conditions are reached. It may be assumed that the fugacity coefficient $K_v = 1 \cdot 0$

   The reaction is : $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

   The equilibrium constant $K = 84 \cdot 0$.

2. A vapour mixture containing 25 mole per cent *n*-hexane, 30 per cent *n*-heptane and 45 per cent *n*-octane is partially condensed at atmospheric pressure. Assuming ideal gas and ideal solution, compare the composition of the residual vapour for the case of condensation of 75 per cent of the total moles when the condensation is

   a) integral

   b) differential

   Data : Vapour pressure may be calculated from the equation $\log$ (mm) = $A - B/T$ (kelvin)

	A	***B***
Hexane :	7·7215	1654·6
Heptane :	7·5917	1750·0
Octane :	7·7503	1941·4

3. 4·0 mole of steam is reacted with 1·0 mole of CH_4 at 570° C and one atmospheric pressure to produce hydrogen. The following reactions take place :

   i) $CH_4 = C + 2H_2$; $K_1 = 2 \cdot 10$

   ii) $C + H_2O = CO + H_2$; $K_2 = 0 \cdot 27$

   iii) $CH_4 + H_2O = CO + 3H_2$; $K_3 = 0 \cdot 57$

   iv) $CO + H_2O = CO_2 + H_2$; $K_4 = 2 \cdot 20$

   v) $CO_2 = CO + \frac{1}{2}O_2$; $K_5 = 4 \cdot 9 \times 10^{-13}$

   vi) $2CH_4 = C_2H_6 + H_2$; $K_6 = 5 \cdot 8 \times 10^{-5}$

   It is desired that no carbon should be present in the product. It should be noted that only traces of C_2H_6 and O_2 are found in the product. Calculate the composition equilibrium mixture. Assume $K_v = 1 \cdot 0$.

4. Discuss any *four* of the following briefly :

   a) Fanno lines

   b) Shock waves

   c) Thrust of open jets and on curved blade

   d) Minimum work of separation by distillation

   e) Partial molal free energy and chemical potential.

5. a) Excess Gibbs free energy of binary liquid mixture is given by

$$\frac{G^E}{RT} = x_1 x_2 \cdot \left[A + B(x_1 + x_2)\right]$$

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 expression satisfies the Gibbs-Duhem equation. 4 + 2 + 4

b) Discuss the steps in preparing p-x-y diagram for the system where the vapour phase is ideal. 4

6. a) Starting with Van Larr activity coefficient equations $ln\gamma_1 = \frac{A}{\left[1 + \frac{Ax_1}{Bx_2}\right]^2} \cdot ln\gamma_2 = \frac{B}{\left[1 + \frac{Bx_2}{Ax_1}\right]^2}$, show that the parameters A and B of Van Larr equation are given by

$$A = \left[1 + \frac{x_2 ln\gamma_2}{x_1 ln\gamma_1}\right]^2 ln\gamma_1 \text{ and } B = \left[1 + \frac{x_1 ln\gamma_1}{x_2 ln\gamma_2}\right]^2 ln\gamma_2 .$$ 6

b) Ethyl alcohol and hexane form an azeotrope containing 33·2 mol% ethanol at 58·7° C and 1 atm pressure. Calculate the distribution coefficient k at $x_1 = 0 \cdot 5$ and 58·7° C for the more volatile component. Assume the system to follow modified Raoult's law. Use Van Larr method to calculate activity coefficients. The Antoine equations are :

For ethyl alcohol (1) $ln\ P_1^{sat} = 16 \cdot 758 - \frac{3774 \cdot 49}{t + 226 \cdot 45}$

For hexane (2) $ln\ P_2^{sat} = 13 \cdot 8216 - \frac{2697 \cdot 5}{t + 224 \cdot 37}$

where, t is in °C and P_i^{sat} in kPa. 8

7. a) With a flow diagram and corresponding p-h diagram, describe a two stage vapour compression refrigeration system. 6

   b) In an aqua-ammonia absorption refrigerator system, heat is supplied to the generator by condensing steam at 0·2 MPa, 90% quality. The temperature to be maintained in the refrigerator is 10° C and the ambient temperature is 30° C. Estimate the maximum COP of the refrigerator. If the actual COP is 40% of the maximum and the refrigeration load is 20 tonnes, what will the required steam flow rate be ? 4

   c) What is the principle of the Linde-Hampson system for liquefaction of air ? 4

8. a) Show that the fugacity of a gas obeying van der Waals equation of state is given by $\ln f = \frac{b}{v-b} - \frac{2a}{RTV} + \ln \frac{RT}{v-b}$; a, b are Van der Waals constants. 4

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

   c) What are the different types of compressors and expansion devices used in vapour compression refrigeration plants ? 3

   d) Mention different standard states used in thermodynamics. 3