

III B.Tech I Semester Regular Examinations, November 2006
CHEMICAL ENGINEERING THERMODYNAMICS-II
(Chemical Engineering)

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions
All Questions carry equal marks

- Pyrites are roasted in SO_2 plant to produce SO_2 . The gases leaving are at 500°C , have molar composition of $SO_2 = 7.055\%$, $O_2 = 10.55\%$, $SO_3 = 0.785\%$, $N_2 = 81.64\%$. Calculate the heat content of gas mixture (1 kmol) over 25°C .
 $C_{p,SO_2} = 6.147 + 13.844 \times 10^{-3}T - 91.03 \times 10^{-7}T^2$
 $C_{p,O_2} = 6.732 + 1.505 \times 10^{-3}T - 1.7913 \times 10^{-7}T^2$
 $C_{p,SO_3} = 6.077 + 23.53 \times 10^{-3}T - 96.7 \times 10^{-7}T^2$
 $C_{p,N_2} = 6.529 + 1.488 \times 10^{-3}T - 2.27 \times 10^{-7}T^2$. [16]
- Explain the Standard Heat of Combustion with suitable example.
 - Calculate the standard heat at 25°C for the following reaction,
 $4HCl_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + 2Cl_{2(g)}$
Standard heat of formation of $HCl_{(g)} = -92,307 \text{ J}$
Standard heat of formation of $H_2O_{(g)} = -241,818 \text{ J}$
 - Given that the latent heat of vaporization of water at 100°C is $2,257 \text{ J / gm}$. Estimate the latent heat at 300°C . The critical temperature is 647.1°K Do not use steam table. [6+5+5]
- Show that chemical potential of a component in all phases is same at thermodynamics equilibrium. [16]
- The following data for the VLE of a binary system at 45°C has been reported as follows. Assuming that the Margules equation adequately represents the VLE data of this system, determine the Margules parameters. Compare the experimental data with that calculated from the Margules equation.

P(Torr)	x_1	y_1
397.77	0.2152	0.4495
448.88	0.3970	0.5832
472.84	0.5300	0.6621
498.07	0.7128	0.7718
512.32	0.9090	0.9141

The Antoine constants are given by

Components	A	B	C
1	7.11714	1210.595	229.664
2	76.84083	1177.910	220576

The Antoine equation is given by $\log_{10} P = A - \frac{B}{t+C}$, P in torr, t in $^\circ\text{C}$. [16]

5. Elucidate the vapor-liquid equilibrium of binary systems with the help of p-x-y and t-x-y diagrams. [16]
6. Explain with flowchart for Flash calculations along with relevant equations. [16]
7. Prove: $\psi_i = \exp \int_{T_{m_i}}^T \frac{H_i^l - H_i^s}{RT^2} dT$ for SLE. All notations have their usual meaning. [16]
8. N_2O_4 at a low temperature is mixed with Air and heated to 25°C and 1 bar pressure. The mole fraction of N_2O_4 in the N_2O_4 – Air mixture before dissociation begins is 0.19. What is the extent of decomposition and what are the mole fractions of N_2O_4 and NO_2 present at equilibrium? The reaction equilibrium constant $K=0.154$. [16]

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- Explain how the Clausius-Clapeyron equation can be used for estimation of approximate value of mean molar heat of vaporization over a specified range of temperature.
 - The vapour pressure of liquid chlorine, in cm of Hg, can be expressed as $\log p = -\frac{1414.8}{T} + 9.91635 - 1.206 \times 10^2 T + 1.34 \times 10^{-5} T^2$. The specific volume of chlorine gas at its boiling point is $269.1 \text{ cc } g^{-1}$ and that of the liquid is $0.7 \text{ cc } g^{-1}$. Calculate the heat of vaporization of liquid chlorine in calories g^{-1} at its boiling point 239.05 K. [8+8]
- Explain the Standard Heat of Combustion with suitable example.
 - Calculate the standard heat at 25°C for the following reaction,
 $4HCl_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + 2Cl_{2(g)}$
 Standard heat of formation of $HCl_{(g)} = -92,307 \text{ J}$
 Standard heat of formation of $H_2O_{(g)} = -241,818 \text{ J}$
 - Given that the latent heat of vaporization of water at 100°C is 2,257 J / gm. Estimate the latent heat at 300°C. The critical temperature is 647.1 °K Do not use steam table. [6+5+5]
- State the equilibrium criteria usually applied by chemical engineers in the solution of phase-equilibrium problems.
 - Explain the term partial residual Gibbs Energy. With its help define fugacity coefficient of a species in solution and show that fugacity of a species 'i' in an ideal-gas mixture is equal to its partial pressure. [8+8]
- Derive an equation for VLE which is in thermodynamic consistency check.
 - Mixture of n-pentene
 - and n-heptane
 - conform to ideal solution behaviour. Prepare p –x-y diagram at 70 °C using the Antoine equation to calculate the vapor pressure $\log_{10} P = A - \frac{B}{t+C}$, P in torr, [8+8]

Component	A	B	C
n-Pentene	6.87632	1075.780	233.205
n-heptane	6.89386	1264.370	216.640

- Explain the bubble P calculation with neat flowchart along with relevant equations. [16]

6. Calculate the fraction of liquid, liquid composition and vapor composition in a two phase system consisting of acetone acetonitrile - nitromethane at 80°C and 110 Kpa. The overall composition of the mixture is $Z=0.45$, $Z=0.35$ and $Z=0.2$. The vapor pressures of the components (1), (2) and are 195.8 Kpa, 97.84 Kpa and 50.32 Kpa respectively. [16]
7. Develop equations that apply to the limiting case of binary LLE for which the α -phase is very dilute in species 1 and the β -phase is very dilute in species 2.. [16]
8. For the gas phase reaction $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ at 1000°C and at 500 bar pressure, calculate the equilibrium composition using the following data: $K=0.68$ at 1000°C .; The fugacity coefficients at this pressure: $\text{CO}_2=0.99$; $\text{H}_2=1.15$; $\text{CO}=1.08$; $\text{H}_2\text{O}=0.86$. [16]

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1. Calculate the amount of heat given off when $1m^3$ of air (at S.T.P.) cools from $(500^{\circ}C)$ to $(-100^{\circ}C)$ at constant pressure of 1 atmosphere. Heat capacity constants:

$$C_p = a + bT + cT^2 \text{ (cal/mol.K)}$$

	a	$b \times 10^3$	$b \times 10^6$
N_2	6.457	1.389	-0.069
O_2	6.117	3.167	-1.005

Write the important assumptions involved in the problem. [16]

2. The standard heat of combustion of graphite at 298(K) is -393.778 kJ/Mol . Determine the heat of combustion at 800K. The heat capacities are (J/mol.K):

$$\text{Carbon: } 11.19 + 1.096 \times 10^{-2} T - 4.894 \times 10^5 / T^2$$

$$\text{Oxygen: } 34.62 + 1.08 \times 10^{-3} T - 7.859 \times 10^5 / T^2$$

$$CO_2 : 43.29 + 1.147 \times 10^{-2} T - 8.185 \times 10^5 / T^2$$

Explain process steps and the thermodynamic principle involved. [16]

3. (a) Derive an expression for estimating fugacity of a liquid at a given T and P.
 (b) The partial molar volume of methanol in a methanol
 i. water
 ii. solution at $x_1(\text{mol.fraction}) = 0.3881$ is $39.176 \times 10^{-6} m^3 / \text{mol}$. The density of the mixture is $905.376 \text{ kg}/m^3$. Calculate the partial molar volume of water in the solution. [8+8]

4. (a) Derive an equation for VLE which is in thermodynamic consistency check.
 (b) Mixture of n-pentene
 i. and n-heptane
 ii. conform to ideal solution behaviour. Prepare p - x - y diagram at $70^{\circ}C$ using the Antoine equation to calculate the vapor pressure $\log_{10} P = A - \frac{B}{t+C}$, P in torr, [8+8]

Component	A	B	C
n-Pentene	6.87632	1075.780	233.205
n-heptane	6.89386	1264.370	216.640

5. Chloroform(1)-Methanol(2) forms an azeotrope at 760 mm Hg and $53.5^{\circ}C$ with $x_1=0.65$. Using the Margules equation, calculate the vapor-liquid equilibrium data (P-x, y) at $53.5^{\circ}C$ neglecting vapor phase non-ideality.

$$\begin{aligned}\text{Chloroform : } \log_{10} P^{sat} \text{ (mm Hg)} &= 6.9546 - 1170.966 / (t/ ^\circ\text{C} + 226.232) \\ \text{Methanol : } \log_{10} P^{sat} \text{ (mm Hg)} &= 8.0810 - 1582.271 / (t/ ^\circ\text{C} + 239.726).\end{aligned}\quad [16]$$

6. Determine expressions for G, H, S implied by the vander waals equations of state.

[16]

7. Show that the variation of chemical potential of a pure substance is given by $d\mu = [RT dn f]_T$. Hence deduce the fugacity of a pure substance. [16]

8. The reaction $N_2 + O_2 \rightleftharpoons 2NO$ takes place in the gas phase at 2700°C and 2000 K Pa. The reaction mixture initially 10 mole% oxygen, 70 mole% nitrogen and the rest inerts. The standard Gibb's free energy change for the reaction is 113.8 KJ/mol at this temperature. Assume ideal gas behavior, calculate the partial pressure of all species at equilibrium. [16]

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1. (a) Derive an expression, for Clapeyron equation to find the latent heat when volumetric data is not available.
 (b) Write three expressions used for rough estimation of latent heat, clearly mentioning the notation for which it stands. [8+8]
2. Carbon monoxide at 1000K is burned with air at 800K is used 90% excess air. The product of combustion leave the reaction chamber at 1250K. Calculate the heat evolved in the reaction chamber per kmol of CO burned. The standard heat of reaction at 298K is (-283.028) kJ/mol CO. The mean specific heat (temperature range of this problem) are 29.38, 49.91, 33.13 and 31.43 (J/mol.K) for CO, CO₂, O₂ and N₂ respectively. [16]
3. (a) Derive an expression for estimating fugacity of a liquid at a given T and P.
 (b) The partial molar volume of methanol in a methanol
 i. water
 ii. solution at $x_1(\text{mol.fraction}) = 0.3881$ is $39.176 \times 10^{-6} \text{ m}^3 / \text{mol}$. The density of the mixture is 905.376 kg/m^3 . Calculate the partial molar volume of water in the solution. [8+8]
4. (a) Show that the partial molar mass of a species in a solution is equal to its molar mass (molecular weight).
 (b) The excess Gibbs free energy of a binary liquid mixture at T and P is given by $\frac{G^E}{RT} = (-2.6 x_1 - 1.8 x_2) x_2 x_1$. For the given T and P, find $\ln \gamma_1$. and $\ln \gamma_2$.
 (c) Define activity and activity coefficient. [4+8+4]
5. Explain the bubble P calculation with neat flowchart along with relevant equations. [16]
6. Explain briefly the estimation procedure of thermodynamics properties from cubic equations of state along with equations. [16]
7. (a) What are the criteria for chemical reaction equilibrium. Discuss in detail?
 (b) For a system in which the following reaction occurs:

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$$
 Assume there are present initially 2 mol CH₄, 1mol H₂O, 1 mol CO and 4 mol H₂. Determine expressions for the mole fractions y_i as function of E. [8+8]

8. Moist silver carbonate is to be dried in an oven at 110°C and 1 atm. Will the silver carbonate decompose at this temperature? The possible reaction is $\text{Ag}_2\text{CO}_3(s) \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{CO}_2(g)$ [16]

The following data are given:

Substance	ΔS_f^0 at 25°C kca/kg mole $^{\circ}\text{K}$	ΔH_f^0 at 25°C kcal/kg mole	Specific heat (assumed constant) kcal/kg mole $^{\circ}\text{K}$
CO_2	51.08	-94036	9.6
$\text{Ag}_2\text{O}(s)$	29.09	-6950	16.5
$\text{Ag}_2\text{CO}_3(s)$	40.17	-119900	26.1
