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Total No. of Pages : 03

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B.Tech.(Petroleum Refinary Engineering) (2013 Batch) (Sem.–4)

CHEMICAL ENGINEERING THERMODYNAMICS

Subject Code : BTPC-404/BTCH-305

Paper ID : [72427]

Time : 3 Hrs. Max. Marks : 60

INSTRUCTIONS TO CANDIDATES :

1. **SECTION-A is COMPULSORY consisting of TEN questions carrying TWO marks each.**
2. **SECTION-B contains FIVE questions carrying FIVE marks each and students have to attempt any FOUR questions.**
3. **SECTION-C contains THREE questions carrying TEN marks each and students have to attempt any TWO questions.**

SECTION A

1. Answer briefly :

a. State the third law of thermodynamics and its application.

b. Prove that multiple phases at the same T and P are in equilibrium when chemical potential of each species is same in all the phases.

c. Explain the theory of corresponding states.

d. A piston-cylinder arrangement contains 0.02 m^3 of air at 50°C and 400 kPa. Heat is added in the amount of 50 kJ and work is done by a paddle wheel until the temperature reaches 700°C. If the pressure is held constant how much paddle-wheel work must be added to the air? Assume constant specific heats.

e. Water exists at the critical point in a rigid container. The container and water are cooled until a pressure of 10 psia is reached. Calculate the final quality.

f. Show that the efficiency of a Carnot engine operating between two reservoirs is independent of the working substance used by the engine.

g. What is reaction coordinate? What is its significance in chemical reaction?

h. A heat engine operates on a Carnot cycle with an efficiency of 75 percent. What COP would a refrigerator operating on the same cycle have? The low temperature is 0°C.

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i. Show that the slope of a constant-pressure line on a T-v diagram of an ideal gas increases with temperature.

j. What is the significance of Poynting pressure correction factor in a vapour-liquid equilibrium?

SECTION B

2. What is the influence of temperature on equilibrium constant? In light of this, derive Vant's Hoff's equation.

3. The excess enthalpy (heat of mixing) for a liquid mixture of species 1 and 2 at fixed T and P is represented by the equation :

$$H^E = x_1x_2(40\ x_1 + 20\ x_2)$$

where H^E is in J mol^{-1}. Determine the expression for partial molar excess enthalpy of species 1 and 2 as function of x_1.

4. The system acetone (1)/acetonitrile (2)/nitromethane (3) at 80°C and 110 KPa has an overall composition $z_1 = 0.45$, $z_2 = 0.35$, $Z_3 = 0.20$. Assuming that Raoult's law is appropriate to the system, determine L, V, {xi} and {yi}. The vapour pressures of the pure species at 353.15 K are :

P_1^{sat}= 195.75 KPa,

P_2^{sat} = 97.84 KPa

P_3^{sat} = 50.32 KPa

5. The excess Gibbs free energy of a binary liquid at T and P is given by

$$G^E/RT = (-2.6x_1-1.8x_2)x_1.x_2$$

Find the expression for $\ln\gamma_1$ and $\ln\gamma_2$. Show that expression satisfies the Gibbs-Duhem equation.

6. What is the Fundamental excess property relation? Prove that activity coefficient and excess Gibbs energy are correlated.

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SECTION C

7. A binary system of species 1 and 2 consists of vapour and liquid phases in equilibrium at temperature T. The overall mole fraction of species 1 in the system is Z1 = 0.65. At temperature T,

   $\ln \gamma_1 = 0.67\ x_2^2$ $\ln \gamma_2 = 0.67\ x_1^2$

   $P_1^{sat} = 32.27$ KPa $P_2^{sat} = 73.14$ KPa

   Assuming the validity of modified Raoult's law,

   a. Over what range of pressure can this system exist as two phase at given T and Z_1.

   b. For a liquid phase mole fraction $X_1 = 0.75$, what is the pressure P and what molar fraction V of the system is vapour.

   c. Show whether or not the system exhibits an azeotrope.

8. A cylinder/piston contains 3 kg of water at 500 kPa, 600°C. The piston has a cross-sectional area of 0.1 m^2 and is restrained by a linear spring with spring constant 10 kN/m. The setup is allowed to cool down to room temperature due to heat transfer to the room at 20°C. Calculate the total (water and surroundings) change in entropy for the process.

9. a. What do you mean by property change of mixing? Derive an expression for the free energy change due to mixing in solution.

   b. Show that in a binary solution, if the solute obeys Henry's law, the solvent obeys the Lewis Randall rule.

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