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Total number of printed pages – 3

B. Tech  
PCCH 4401

**Seventh Semester Examination – 2011**  
**CHEMICAL ENGINEERING THERMODYNAMICS**

Full Marks – 70

Time : 3 - Hours

Answer Question No. 1 which is compulsory and any **five** from the rest.

The figures in the right-hand margin indicate marks.

1. Answer the following questions : 2×10
- (a) Write mathematical expression of first law of thermodynamics for close system and open system.
- (b) What is degree of freedom? The degree of freedom for invariant system is \_\_\_\_\_.
- (c) Define reaction coordinate. For mole of reaction the change in reaction coordinate is \_\_\_\_\_.
- (d) Define entropy. For isentropic process the value of entropy is \_\_\_\_\_.
- (e) What is Raoult's law and write its limitation ?
- (f) What is the effect of temperature on equilibrium value of reaction coordinate for gas phase reaction ?
- (g) What is the significance of Virial coefficient ?
- (h) What do you mean by intensive and extensive property ? Give one example of each.
- (i) For a chemical reaction at equilibrium the total Gibb's energy is \_\_\_\_\_ and its differential value is \_\_\_\_\_.
- (j) What do you mean by state function ?

P.T.O.

2. (a) Derive the phase rule for reacting system. 4  
 (b) Determine the number of degree of freedom for the system consisting of gases CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> in chemical equilibrium. 6
3. Air at 1 bar and 25°C having molar volume 0.02479 m<sup>3</sup>mol<sup>-1</sup> is compressed to 5 bar and 25°C by two different mechanically reversible processes :  
 (a) Cooling at constant pressure followed by heating at constant volume.  
 (b) Heating at constant volume followed by cooling at constant pressure  
 Calculate Q, W, ΔU, ΔH for of the air for each path. The following heat capacities for air may be assumed independent of temperature :  
 $C_V = 20.78$  and  $C_P = 29.10 \text{ J mol}^{-1}\text{K}^{-1}$   
 Assume also for air that PV/T is a constant. 10
4. (a) Write the Maxwell relations. 2  
 (b) Show that
- (i)  $dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_p \right] dP$  4
- (ii)  $dS = C_p \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right) dP$  4
5. 2 kg of air (ideal gas) is first compressed from state 1 at 13.75 N/cm<sup>2</sup> and 5°C to state 2 at 48 N/cm<sup>2</sup> and 283°C. It is then expanded isothermally to a pressure 13.75 N/cm<sup>2</sup>. Finally it is cooled at constant pressure to state 4 until its volume is half of that before the cooling process. Determine the change in entropy of the whole process by drawing the P-V diagram. Also verify state 4 is same as that of state 1. 10
6. Reported values of the virial coefficients of isopropanol at 200°C are :  
 $B = -388 \text{ cm}^3 \text{ mol}^{-1}$        $C = -26000 \text{ cm}^6 \text{ mol}^{-2}$   
 Calculate V and Z for isopropanol vapor at 200°C and 10 bar by 10
- (a) Ideal gas equation  
 (b)  $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$   
 (c)  $Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$



7. Benzene (1) and toluene (2) form an ideal solution. The vapor pressures of benzene and toluene are adequately represented by the Antoine equation

$$\log_{10} P = A - \frac{B}{t + C}$$

Where P is in Torr and t is in °C

- (a) Prepare a P-x-y diagram at 95°C
- (b) Prepare a T-x-y diagram 760 Torr

Antoine constants are

Component	A	B	C
Benzene(1)	6.87987	1196.760	219.161
Toluene(2)	6.95087	1342.310	219.187

10

8. Write short notes on :

2.5×4

- (a) Fugacity and fugacity coefficient
- (b) Activity and activity coefficient
- (c) Lewis and Randal rule
- (d) Mathematical statement of Second law of thermodynamics.