Name : ....

Roll No. : ....

Invigilator's Signature : ....

CS/B.TECH (CHE)OLD/SEM-4/CHE-401/2012

2012

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.

GROUP – A

(Multiple Choice Type Questions)

1. Choose the correct alternatives for any *ten* of the following : $10 \times 1 = 10$

i) Gibbs' free energy of a pure fluid approaches to .... as the pressure tends to zero at constant temperature.

a) infinity b) minus infinity

c) zero d) one.

ii) Chemical potential is

a) an extensive property b) an intensive property

c) a path property d) a reference property.

iii) The value of the activity coefficient for an ideal solution is

a) one

b) zero

c) equal to Henry's law constant

d) equal to vapour pressure.

iv) The phase rule for a system can be written as

a) F = C – P – 1 b) F = C – P + 1

c) F = C + P + 2 d) F = C – P + 2.

v) Fugacity and pressure are numerically not equal for gas

a) at low temperature and high pressure

b) at standard state

c) both (a) and (b)

d) in an ideal state.

vi) Which of the following is affected by temperature ?

a) Fugacity b) Activity coefficient

c) Free energy d) All of these.

vii) The rate of a chemical reaction is proportional to the product of active masses of the reacting substances. This is

a) Lewis-Randall rule b) van't Hoff equation

c) Le Chatelier's principle d) None of these.

viii) The efficiency of a Carnot engine between temperatures T_1 and T_2 $(T_1 < T_2)$ is

a) $\dfrac{T_2 - T_1}{T_1}$ b) $\dfrac{T_2 - T_1}{T_2}$

c) $\dfrac{T_1 - T_2}{T_2}$ d) $\dfrac{T_1 - T_2}{T_1}$.

ix) One ton of refrigeration capacity is equivalent to the heat removal rate of

a) 50 k.cal./hour b) 200 BTU/hour

c) 200 BTU/minute d) 200 BTU/day.

x) A system is said to be in mechanical equilibrium if the

a) composition of the system remains constant

b) temperature of the system remains constant

c) pressure of the system remains constant

d) none of these.

xi) In an ideal solution, the activity of a component is equal to its

a) fugacity b) mole fraction

c) vapour pressure d) partial pressure.

xii) The efficiency of an Otto engine compared to that of a diesel engine for the same compression ratio will be

a) more b) less

c) same d) data insufficient.

GROUP – B

(Short Answer Type Questions)

Answer any *three* of the following.

$3 \times 5 = 15$

2. Justify the statement with illustration —

'Violation of Kelvin-Planck statement leads to the violation of Clausius statement'.

3. Show that $\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\beta}{k} - P$, where, β = coefficient of volume expansion and k = isothermal compressibility.

4. A spherical balloon of 1 m diameter contains a gas at 120 k Pa. The gas inside the balloon is heated until the pressure reaches 360 kPa. During heating the pressure of the gas inside the balloon is proportional to the cube of the diameter of the balloon. Determine the work done by the gas inside the balloon.

5. Prove that van der Waals constants can be expressed in terms of T_c and P_c as $a = \frac{27\ R^2\ T_c^2}{64\ P_c}$ and $b = \frac{R\ T_c}{8\ P_c}$.

6. Derive the Maxwell's relation.

GROUP – C

(Long Answer Type Questions)

Answer any *three* of the following questions.

3 × 15 = 45

7. a) Two iron blocks of same size are at distinct temperatures T_1 and T_2 brought in thermal contact with each other. The transfer process is allowed to take place until the thermal equilibrium is attained. Suppose, after the attainment of equilibrium, blocks are at final temperature 'T'. Show that the change in entropy of the process is given by

$$\Delta S = C_p\, ln\left[\frac{(T_2 - T_1)^2}{4\, T_1\, T_2} + 1\right]$$ 5

b) Find the second and third virial coefficients of the van der Waals equation of state. 5

c) The total energy of a typical closed system is given by E = 50 + 25 T + 0·05 T^2 in joule. The amount of heat absorbed by the system can be expressed as Q = 4000 + 10 T in joule. Estimate the work done during the processes in which temperature rises from 400 K to 800 K. 5

8. a) Derive the relation between standard Gibbs' energy change ΔG° and equilibrium constant K. 8

b) The water gas shift reaction $CO\ (g) + H_2O\ (g) \rightarrow CO_2 + H_2$ is carried out under the following conditions described below :

The reactants are 2 moles of H_2O and 1 mole of CO. The temperature is 1100 K and pressure is 1 bar. Data given ln K = 0. Find the equilibrium composition of the components. 7

9. a) The following equations have been proposed to represent activity coefficient data for a system at fixed T and P.

$$ln\,\gamma_1 = x_2^{\,2}(0\cdot5 + 2x_1)$$

$$ln\,\gamma_2 = x_1^{\,2}(1\cdot5 - 2x_2)$$

Do these equations satisfy Gibbs/Duhem equation ? Determine an expression for G^E/RT for the system. 8

b) Express volumes ($cm^{-3}\ mol^{-1}$) for the system ethanol (i)/methyl butyl ether (ii) at 25°C are given by the equation

$$V^E = x_1 x_2 \left[-1\cdot026 = 0\cdot220(x_1 - x_2)\right]$$

If $V_1 = 58\cdot63$ and $V_2 = 118\cdot46\ cm^3\ mol^{-1}$, what volume of mixture is formed when $1000\,m^3$ each of pure species (i) and (ii) are mixed at 25°C ? 7

10. a) The heat capacity at 1 atm pressure of solid magnesium, in the temperature range of 0 to 560°C is given by the expression

$$C_p = 6\cdot2 + 1\cdot33\times10^{-3}T + 6\cdot78\times10^{4}T^{-2}\ \text{cal/deg. gm atom.}$$

Determine the increase of entropy, per gm atom, for an increase of temperature from 300 K to 800 K at 1 atm pressure. 5

b) A steam turbine developing 34 kW receives steam at 15 bar with an internal energy of 2720 kJ/kg and specific volume of $0 \cdot 17 \text{ m}^3/\text{kg}$ and velocity of 110 m/s. Steam is exhausted from turbine at 0·1 bar with internal energy 2177 kJ/kg, specific $15 \text{ m}^3/\text{kg}$ volume and velocity 320 m/s. The heat loss over the surface of the turbine is 20 kJ/kg. Neglecting change in potential energy, determine

i) Work done per kg of steam

ii) Steam flow through the turbine in kg/hr. 10

11\. a) State and prove Clausius inequality theorem. 5

b) Nitrogen is compressed from an initial state of 1 bar and 25°C to a final state of 5 bar and 25°C by three different reversible processes in a closed system.

i) Heating at constant volume followed by cooling at constant pressure

ii) Isothermal expansion

iii) Adiabatic compression followed by cooling at constant volume.

Nitrogen is assumed to behave an ideal gas with $C_V = \frac{5}{2}R, C_P = \frac{7}{2}R$ and the molar volume of nitrogen = 0·02479 m^3/mol. Estimate the heat, work requirement, ΔU and ΔH of nitrogen for the each process. 10