# CHEMICAL ENGINEERING THERMODYNAMICS (CHEN 2203)

**Time Allotted : 3 hrs** **Full Marks : 70**

***Figures out of the right margin indicate full marks.***

***Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.***

***Candidates are required to give answer in their own words as far as practicable.***

## Group – A
## (Multiple Choice Type Questions)

1. Choose the correct alternative for the following: **10 × 1 = 10**

(i) Two moles of an ideal gas is expanded reversibly and isothermally form 1 L to 10 L. The enthalpy change of the process is
(a) 11.4 kJ (b) -11.4 kJ (c) 0 kJ (d) 4.8 kJ.

(ii) The enthalpy of a binary liquid system at a fixed T and P is represented by the equation
$H = 600 - 180x_1 - 20x_1^3$ j / mol
The partial molar enthalpy of the component 1 is given by
(a) $420 - 60x_1^2 -+ 40x_1^3$ (b) $420 + 60x_1^2 - - 40x_1^3$
(c) $40 - 60x_1^2 -+ 420x_1^3$ (d) $60 - 40x_1^2 -+ 20x_1^3$.

(iii) The residual Gibbs free energy change ( $\Delta G^{R}{}_{0}$ ) of hydrogen gas at 35$^0$C and 1 atm is
(a) 0 (b) 1 (c) Always positive (d) Always negative.

(iv) For a real solution comprising of two components A and B, the activity coefficient of A ($\gamma_A$)
(a) is zero (b) may be positive or negative
(c) is always positive (d) is always negative.

(v) An aqueous solution of ethanol contains 60 mole % ethanol. If the partial molar volumes of ethanol and water are 57.5ml/mole and 16.0 ml/mole respectively, the molar volume of the mixture is
(a) 40.9 ml /mole (b) 73.5 ml / mole
(c) 41.5 ml / mole (d) none of the above.

(vi) For minimum boiling azeotrope the deviation from ideality
(a) is positive and large (b) is negative and large
(c) may be either positive or negative (d) none of the above.

(vii) Mollier diagram is a plot of
(a) temperature vs enthalpy (b) temperature vs entropy
(c) temperature vs humidity (d) enthalpy vs entropy.

(viii) In any spontaneous process
(a) entropy remains constant (b) enthalpy remains constant
(c) gibbs energy increase (d) entropy increases.

(ix) During melting of a single component system
(a) enthalpy remains constant (b) gibbs energy remains constant
(c) entropy remains constant (d) internal energy remains constant.

(x) Degree of freedom of the system ice-water-vapour will be
(a) 0 (b) 1 (c) 2 (d) 3.

## Group – B

2. (a) Why heat capacity at constant pressure is higher than heat capacity at constant volume? For a constant volume reversible process show that the heat transferred is equal to the internal energy change of the system.

(b) The Berthelot equation of state is given by

$$\left(P+\frac{a}{Tv^2}\right)(v-b)=RT$$

Develop necessary relation to determine the parameter 'a' and 'b' in terms of critical constant $T_c$ and $P_c$ and then convert the equation in reduced form where compressibility factor, Z is only function of reduced pressure, $P_r$ and reduced temperature, $T_r$

**(1 + 3) + 8 = 12**

3. (a) A mass of 1 kg gaseous ammonia ($T_c$ = 405.6K, $P_c$ = 111.3 bar) is contained in a 50 L container immersed in a constant temperature bath at 30$^0$C. Calculate the pressure of the gas in cylinder using any real gas equation of state. ($\omega$ = 0.25)





(b) Estimate the standard free energy change and equilibrium constant at 700 K for the reaction
$N_2$ (g) + 3 $H_2$ (g) = 2 $NH_3$(g)
Given that the standard heat of reaction and standard free energy of reaction at 298 K
$\Delta H^0$ = -92200 J / mole and $\Delta G^0$ = - 33000 J / mole
The heat capacity (J/mole K) data are given below as function of temperature (K)
$C_P$ = A + B T

| Component | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| A | 27.27 | 27.01 | 29.75 |
| B × $10^3$ | 4.93 | 3.51 | 25.11 |

9. (a) Deduce Lewis and Randall equation.

(b) A mixture of CO (g), $H_2O$(g) and $H_2$(g) in the mole ratio 1:1 : 0.5 is fed to a reactor which is maintained at 10 bar and 1000 K. Given that the equilibrium constant for the reaction
CO (g) + $H_2O$ (g) $\rightleftharpoons$ $CO_2$ (g) + $H_2$ (g)
at 1000 K is 1.5. Estimate the composition of the gas that leaves the reactor. Assume that the reaction mixture behaves like an ideal gas.

**5 + 7 = 12**

(b) A gas obeying the Clausius equation of state is isothermally compressed from 5 MPa to 15 MPa in a closed system at 400K. The Clausius equation of state is $P = \dfrac{RT}{v - b(T)}$ where P is the pressure, T is the temperature, v is the molar volume and R is the universal gas constant. The parameter b in the above equation varies with temperature as $b(T) = b_0 + b_1 T$ with $b_0 = 4\times10^{-5}\, m^3 mol^{-1}$ and $b_1 = 1.35\times10^{-7}\, m^3 mol^{-1} K^{-1}$. The effect of pressure on the molar enthalpy (h) at a constant temperature is given by $\left(\dfrac{\partial h}{\partial P}\right)_T = v - T\left(\dfrac{\partial v}{\partial T}\right)_P$. Determine the change in molar enthalpy for this process.

**6 + 6 = 12**

## Group – C

4. (a) Derive Clausius-Clapeyron equation from fundamental property relation. Write the assumption needed to derive the equation.

(b) It is proposed to produce 1000 kg of ice per hour from water at 0 $^0$C when the atmospheric temperature is 27 $^0$C. It is planned to use a heat engine coupled with a refrigerator to achieve the objective. The work generated by the heat engine is supplied to the refrigerator. Hot water at 60 $^0$C is to be used as a source to supply energy as heat to the heat engine which uses ambient atmosphere as sink. Calculate the power required by the refrigerator unit and the rate of heat rejection to the atmosphere. The latent heat of fusion of ice at 0 $^0$C is 335 kJ/kg.

**5 + 7 = 12**

5. (a) Discuss with a schematic diagram the working principle of absorption refrigeration cycle. Determine the efficiency of an ideal absorption refrigeration cycle.

(b) A rigid insulated tank of volume 3m$^3$ is divided into two compartments by a removable partition. One compartment of volume 1m$^3$ contains ideal gas A at 500 K and 10 bar while the other compartment contains ideal gas B at 800 K and 20 bar. The partition is removed and the gas is allowed to mix. After mixing, calculate the total change in entropy of the process. Given, specific heat capacity ratio of both ideal gases is 1.4.

**6 + 6 = 12**

## Group – D

6. (a) At atmospheric pressure ethyl alcohol and water form azeotrope at 78.15$^0$C and contains 89.43 mol % alcohol. Find the composition of ethyl alcohol vapour in equilibrium with a liquid analysing 60 mol % alcohol at this temperature. Vapour pressures of ethyl alcohol and water at 78.15$^0$C are respectively 755mm Hg and 329 mm Hg.

(b) From the following compressibility data for carbon dioxide gas at100$^0$C and 50 atm, determine the fugacity of carbon dioxide gas at 50 atm.

| P (atm) | 0 | 14 | 22 | 30 | 44 | 58 | 68 |
|---|---|---|---|---|---|---|---|
| Z | 1.00 | 0.95 | 0.92 | 0.89 | 0.84 | 0.79 | 0.76 |

**7 + 5 = 12**

7. (a) For a binary liquid mixture at constant temperature and pressure excess Gibbs energy is given by

$G^E / RT = (0.198\ x_1 + 0.372\ x_2)\ x_1 x_2$

Find the value of $\ln \gamma_1$ at infinite dilution. Does it follow Gibbs-Duhem equation?

(b) It is required to prepare 3 m$^3$ of a 60 mole% ethanol – water mixture. Determine the volumes of ethanol and water to be mixed in order to prepare the required solution. Given:

| Component | Partial molar volume, m$^3$/mole | Molar volume of pure component, m$^3$/mole |
|---|---|---|
| Ethanol | 57.5 x 10$^{-6}$ | 57.9 x 10$^{-6}$ |
| Water | 16.0 x 10$^{-6}$ | 18.0 x 10$^{-6}$ |

**5 + 7 = 12**

## Group – E

8. (a) Calculate the equilibrium constant for the vapour phase hydration of ethylene at 145$^0$C from the given data:

$C_P / R = A + BT + CT^2 + DT^{-2}$

$\Delta A = -1.376,\ \Delta B = 4.157 \times 10^{-3},\ \Delta C = -1.610 \times 10^{-6}, \Delta D = -0,121 \times 10^5$

$\Delta H^0_{298} = -45792 J/mol$ , $\Delta G^0_{298} = -8348 J/mol$

The reaction is: $C_2H_{4(g)} + H_2O_{(g)} = C_2H_5OH_{(g)}$