# THERMODYNAMICS II
## (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) An ideal gas at temperature $T_1$ and pressure $P_1$ is compressed isothermally to a pressure $P_2$ ($>P_1$) in a closed system. Which of the following is true of the gas at two states?
(a) $U_1 = U_2$, $G_1>G_2$ (b) $H_1=H_2$, $G_1<G_2$ (c) $U_1 > U_2$, $G_1=G_2$ (d) $H_1<H_2$, $G_1=G_2$.

(ii) As pressure approaches zero, fugacity coefficient value tends to
(a) pressure (b) unity (c) zero (d) infinity.

(iii) In a throttling process, the pressure of a ideal gas reduces by 50%. The specific volume will change by a factor of (γ is specific heat capacity ratio)
(a) 2 (b) $2^{1/\gamma}$ (c) $2^{(\gamma-1)/\gamma}$ (d) 0.5.

(iv) The degrees of freedom of a binary azeotropic mixture under vapour liquid equilibrium is
(a) 0 (b) 1 (c) 2 (d) 3.

(v) The Gibbs free energy change of mixing for any binary system is
(a) zero (b) negative
(c) positive (d) depends on the type of system.

(vi) 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.

(vii) For an exothermic reaction, the increase in temperature results in
(a) increase of K (b) decrease of K
(c) no change of K (d) can't be predicted

Where K is reaction equilibrium constant.

(viii) Eutectic temperature is achieved at equilibrium between the following phases
(a) two liquids and one vapour phase
(b) one solid and one vapour phase
(c) two liquid phases
(d) two immiscible solids and one liquid phase.

(ix) For the equilibrium yield in a gas phase reaction, diluting the reaction mixture with an inert gas
(a) has the same effect as that of an increase in pressure
(b) has the same effect as that of an decrease in pressure
(c) has no correlation with change in pressure
(d) always produces unfavorable results.

(x) For an ideal solution the value of activity coefficient is
(a) 0 (b) 1 (c) undefined (d) infinity.

## Group - B

2. (a) An ideal gas at $P_i$ and $T_i$ enters a reversible and adiabatic nozzle with negligible inlet velocity and leaves at a pressure $P_e$. Derive an expression to estimate the exit velocity of the gas. [(CO1)Analyze/LOCQ]

(b) A boiler produces steam at 1 MPa and 300°C. The steam from the boiler is used to operate a turbine. The turbine exhausts steam into an evacuated tank of volume 100 $m^3$. The turbine operates till the pressure in the tank rises to 1 MPa at which point the temperature of steam in the tank is 250°C. Assuming that the turbine and the tank are adiabatic, determine the work delivered by the turbine.
Given, steam at 1MPa and 250°C: v = 0.232 $m^3$/kg; h = 2939.45 kJ/kg.
Steam at 1MPa and 300°C: h = 3052.1 kJ/kg. [(CO1)Evaluate/HOCQ]

**6 + 6 = 12**

3. (a) What is second law efficiency of a process? Derive the second law efficiency expression for a heat exchanger. [(CO1)(Understand/LOCQ)]

(b) Derive the following relation of $C_p$ and $C_v$ from the thermodynamic property relation: (Symbols bear usual significance)

$$C_p - C_v = \frac{\alpha^2 VT}{\beta}$$

where, $\alpha$ is isobaric thermal volume expansion coefficient and $\beta$ is isothermal compressibility coefficient. [(CO1)(Evaluate/HOCQ)]

**(2 + 4) + 6 = 12**

## Group - C

4. (a) Derive an expression to determine residual entropy of a real gas at low pressure range using virial equation of state truncated up to second virial coefficient. [(CO2)(Analyze/IOCQ)]

(b) Using the virial equation of state, estimate the residual entropy for propane at 60°C and 2.5 bar, given that $T_c$ = 370 K, $P_c$ = 42.57 bar and acentric factor, ω =0.153. [(CO2)(Apply/IOCQ)]

**7 + 5 = 12**

5. (a) Derive an expression to determine partial molar thermodynamic property of a component in a binary solution. [(CO3)Understand/LOCQ]

(b) Calculate the partial molar volume of methanol and water in a 40 mol% methanol solution given the following data at 1 bar and 298 K. (*x* is the mole fraction of methanol). [(CO3)Analyze/HOCQ]

| *x* | 0 | 0.114 | 0.197 | 0.249 | 0.495 | 0.692 | 0.785 | 0.892 | 1.0 |
|---|---|---|---|---|---|---|---|---|---|
| V × $10^6$, $m^3$/mol | 18.1 | 20.3 | 21.9 | 23.0 | 28.3 | 32.9 | 35.2 | 37.9 | 40.7 |

**4 + 8 = 12**

## Group - D

6. (a) What is excess thermodynamic property and how it is different from residual thermodynamic property? What is the condition when excess thermodynamic property and thermodynamic property change on mixing are equal? [(CO3)Understand/LOCQ]

(b) Determine an expression of excess entropy in terms of activity coefficient. Show that, logarithm of activity coefficient of a component in a solution is a partial molar property of the solution. [(CO3)Analyze/LOCQ]

**(2 + 2) + (4 + 4) = 12**

7. (a) What is maximum boiling and minimum boiling azeotrope? Draw a schematic P-x-y and T-x-y diagram of both type of azeotropic system with a single azeotropic composition. [(CO4)(Remember/LOCQ)]

(b) Construct a P-x-y diagram for the cyclohexane (1) –Benzene(2) system at 313 K. Given that at 313 K the vapour pressure are $P_1^{sat}$ = 24.62 kPa and $P_2^{sat}$ = 24.62 kPa. The liquid phase activity coefficients are given by $\ln \gamma_1 = 0.458x_2^2$ and $\ln \gamma_2 = 0.458x_1^2$. [(CO4)(Analyze/IOCQ)]

**6 + 6 = 12**

## Group - E

8. (a) How is equilibrium constant of chemical reaction defined? What are the factors on which equilibrium constant of chemical reaction depend? [( CO5)(Understand/LOCQ)]

(b) Derive an equation to evaluate the chemical reaction equilibrium constant at any temperature if the specific heat capacities of the species involved in the chemical reaction are quadratic function of temperature. [(CO5)(Analyze/LOCQ)]

**6 + 6 = 12**

9. (a) Estimate the maximum conversion of ethylene to ethanol by vapour phase hydration at $250^0$C and 35 bars for an initial steam to ethylene ratio of 5.

Data: The equilibrium constant (K) = $9.841 \times 10^{-3}$

| Material | Fugacity coefficient |
|---|---|
| Ethylene | 0.977 |
| Water vapour | 0.896 |
| Ethanol | 0.837 |

The reaction is:

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g).$$ [(CO5)(Evaluate/IOCQ)]

(b) Estimate the standard free energy change and equilibrium constant at 700 K for the reaction

$$A\ (g) + 3\ B\ (g) = 2\ R(g)$$

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)

$C_P = \alpha + \beta T$

| Component | A | B | R |
|---|---|---|---|
| α | 27.27 | 27.01 | 29.75 |
| β x $10^3$ | 4.93 | 3.51 | 25.11 |

[(CO5)(Evaluate/HOCQ)]

**7 + 5 = 12**

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| Cognition Level | LOCQ | IOCQ | HOCQ |
|---|---|---|---|
| Percentage distribution | 47.92 | 26.04 | 26.04 |

**Course Outcome (CO):**

After completion of the course students will be able to:

1. Ability to understand the basic knowledge that allows the students to solve problems relating fugacity of pure components as well as in mixture.
2. Ability to utilize the concept of chemical potential as criterion of phase equilibrium.
3. Ability to use concept of partial molar properties in solution thermodynamics.
4. Ability to understand the basic knowledge that allows the students to solve problems on equilibrium of different phases involving no chemical reaction.
5. Ability to understand the basic knowledge that allows the students to solve problems on chemical reaction equilibrium.

*LOCQ: Lower Order Cognitive Question; IOCQ: Intermediate Order Cognitive Question; HOCQ: Higher Order Cognitive Question.