Total No. of Printed Pages-7

2 SEM TDC CHMH (CBCS) C 4

2022

(June/July)

CHEMISTRY

(Core)

Paper: C-4

(Physical Chemistry—II)

Full Marks: 53
Pass Marks: 21

Time: 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer: 1×6=6

For a system to be at equilibrium, the value of ΔG at constant temperature and pressure must be

(i)
$$\Delta G_{T,P} > 0$$

(ii)
$$\Delta G_{T,P} < 0$$

(iii)
$$\Delta G_{T,P} = 0$$

(iv)
$$\Delta G_{T,P} \ge 0$$

(a)

- (b) The value of ΔS for an irreversible process is
 - (i) positive
 - (ii) negative
 - (iii) zero
 - (iv) None of the above
- (c) The chemical potential is
 - (i) partial molar enthalpy
 - (ii) partial molar volume
 - (iii) partial molar free energy
 - (iv) partial molar internal energy
- (d) For equilibrium in case of a hypothetical gaseous reaction

$$3A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

(i)
$$K_p = K_c RT$$

(ii)
$$K_p = K_c(RT)^2$$

(iii)
$$K_p = K_c$$

(iv)
$$K_c = \frac{1}{K_p}$$

- (e) Regardless of the atmospheric pressure, the boiling point of a dilute solution as compared to that of pure solvent is
 - (i) same
 - (ii) lower
 - (iii) higher
 - (iv) Any of the above
- (f) If z is a state function, then $\oint dz$ is equal to
 - (i) zero
 - (ii) positive
 - (iii) negative
 - (iv) infinity
- 2. Answer any six of the following questions:

2×6=12

- (a) Write any two differences between reversible and irreversible processes.
- (b) Six moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm³ to a volume of 10 dm³ at 27 °C. What is the maximum work done?

- (c) Establish the relationship between enthalpy change and internal energy change for a gaseous reaction.
- (d) What are partial molar properties? Define chemical potential.
- (e) Derive the relation between K_p and K_c for the following reaction:

$$aA + bB \rightleftharpoons cC + dD$$

- (f) How are osmotic pressure measurements utilized for determining molar mass of a non-volatile solute?
- (g) What are extensive and intensive properties? Explain with examples.

Unit--I

Answer any *two* questions from the following: $8 \times 2 = 16$

- 3. (a) Calculate the work done when a gas expands—
 - (i) isothermally and reversibly from volume V_1 to V_2 ;
 - (ii) isothermally and irreversibly from volume V_1 to V_2 .

From these, show that the work done in a reversible process is greater than that in an irreversible process. 2+2+2=6

(b)	What is Joule-Thomson coefficient? Derive a relation between Joule-Thomson coefficient and thermodynamic quantities.	2
(a)	Deduce a relation between temperature and volume for an adiabatic reversible expansion of an ideal gas.	2½
(b)	$(\overline{C}_V = 12.55 \text{ J K}^{-1} \text{ mol })$ at coordinate compressed adiabatically and reversibly to one-fourth of its original volume. What is the final temperature of the gas?	2½
(c)	Derive Kirchhoff's equation.	3
(a)	Deduce an expression for the entropy changes associated with the changes in temperature and pressure of an ideal gas.	4
(b)	and $\Delta S = 31 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K, decide whether the reaction is spontaneous or not at this temperature.	2
(c)	State and explain the third law of thermodynamics.	í 2

5.

UNIT-II

6. Answer either (a) or (b)) :
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- (a) Discuss the variation of chemical potential with temperature and pressure.
- (b) Derive Gibbs-Duhem equation.

UNIT-III

- 7. Answer any two questions from the following: 4×2=8
 - (a) State and explain Le Chatelier's principle. With the help of this principle, work out the conditions which would favour the formation of ammonia and nitric oxide in the following reactions:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta H = -99 \cdot 38 \text{ KJ}$$

 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g), \quad \Delta H = 180 \cdot 75 \text{ KJ}$
 $2+2=4$

- (b) (i) What are exergonic and endergonic reactions?
 - (ii) Calculate K_c and K_x for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ for which $K_p = 0.157$ atm at 27 °C and 1 atm pressure.

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(Continued)

(c) Derive the relation between Gibbs' free energy change and reaction quotient. From this, establish the relation between standard Gibbs' free energy change and equilibrium constant of a reaction.

I INIT-IV

- 8. Answer any two questions from the following:
 - (a) What is osmotic pressure? Derive a relation between osmotic pressure and relative lowering of vapour pressure.
 - (b) What are isotonic solutions? A solution containing 8.77 g per dm³ of urea (molar mass = 60 g mol⁻¹) was found to be isotonic with a 5-percent solution of an organic non-volatile solute. Calculate the molar mass of the latter.
 - (c) Derive the relation between the elevation of boiling point of a dilute solution and the molality of that solution. Define molal elevation constant.
