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

(a) 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) $\Delta G_{T,P} \geq 0$

(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 : $2 \times 6 = 12$

(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 dm^3 to a volume of 10 dm^3 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 : 8×2=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

4. (a) Deduce a relation between temperature and volume for an adiabatic reversible expansion of an ideal gas. 2½

(b) One mole of an ideal gas $(\overline{C}_V = 12 \cdot 55 \text{ J K}^{-1} \text{ mol}^{-1})$ at 300 K is 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

5. (a) Deduce an expression for the entropy changes associated with the changes in temperature and pressure of an ideal gas. 4

(b) For a reaction $\Delta H = 10 \cdot 5 \times 10^3$ J mol^{-1} and $\Delta S = 31$ J K^{-1} 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. 2

UNIT—II

6. Answer either *(a)* or *(b)* : 3

(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? 1

(ii) Calculate K_c and K_x for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ for which $K_p = 0 \cdot 157$ atm at 27 °C and 1 atm pressure. 3

(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. 3+1=4

UNIT—IV

8. Answer any *two* questions from the following : 4×2=8

(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 dm^3 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. 1+3=4

(c) Derive the relation between the elevation of boiling point of a dilute solution and the molality of that solution. Define molal elevation constant. 3+1=4

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