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2 SEM TDC CHMH (CBCS) C 4

2023

(May/June)

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) Which of the following is an intensive property?

(i) Internal energy

(ii) Enthalpy

(iii) Entropy

(iv) Temperature

(b) One mole of methane gas is formed from its constituents at temperature T. The difference between the heats of reaction at constant pressure and at constant volume is

(i) $-RT$

(ii) RT

(iii) $2RT$

(iv) 0

(c) One molal solution of a non-electrolyte boils at 100·51 °C, while pure water boils at 100 °C. Ebullioscopic constant K_b is

(i) 100·51 K kg mol^{-1}

(ii) 0·51 K kg mol^{-1}

(iii) 1·02 K kg mol^{-1}

(iv) 0·51 K mol kg^{-1}

(d) Chemical potential is

(i) partial molar enthalpy

(ii) partial molar volume

(iii) partial molar free energy

(iv) partial molar internal energy

(Continued)

(e) For a hypothetical gaseous reaction

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

(i) $K_p = K_c RT$

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

(iii) $K_p = K_c$

(iv) $K_c = 1/K_p$

(f) At constant temperature, the decrease in Helmholtz free energy is equal to the

(i) reversible work done by the system

(ii) irreversible work done by the system

(iii) total work done minus pressure-volume work in a reversible manner

(iv) decrease in entropy

2. Answer any *six* questions from the following : 2×6=12

(a) Explain why equimolar solutions of NaCl and glucose are not isotonic.

(b) Deduce a relation between k_1 and k_2 for the following equilibrium :

$$A_2 + B_2 \underset{}{\overset{k_1}{\rightleftharpoons}} 2AB$$

$$AB \xrightarrow{k_2} \frac{1}{2}A_2 + \frac{1}{2}B_2$$

(Turn Over)

(c) Explain the physical significance of chemical potential.

(d) Prove that Joule-Thomson effect is isoenthalpic in nature.

(e) State and explain Hess's law of constant heat summation.

(f) Calculate the entropy change for the melting of 1 mole of ice at 0 °C. Given that $\Delta H_{fus\ (ice)} = 334 \cdot 72\ J\ g^{-1}$.

(g) State and explain the third law of thermodynamics.

UNIT—I

Answer any *two* questions from the following : 8×2=16

3. (a) Define heat capacity of a substance. Explain why heat capacities are different at constant volume and at constant pressure. Show that for one mole of an ideal gas $C_P - C_V = R$. 1+1½+3½=6

(b) For reactions involving condensed phases, show that $\Delta H = \Delta E$. 2

4. (a) How are the pressure and volume related to each other during the adiabatic expansion of an ideal gas? Deduce the relation. 2½

(b) Deduce an expression for the entropy changes associated with the changes in temperature and volume of an ideal gas. 3½

(c) One mole of an ideal gas at 300 K expands reversibly and isothermally from $4 \times 10^{-2}\ m^3$ to $8 \times 10^{-2}\ m^3$. Calculate the entropy change for the gas. 2

5. (a) Write the physical significance of Helmholtz free energy and Gibbs free energy. 2

(b) Deduce an expression showing the variation of Helmholtz free energy with volume at constant temperature for an ideal gas. 2½

(c) Deduce the following relation : 2

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

(d) For a reaction, ΔH and ΔS values are $4 \cdot 4\ kJ\ mol^{-1}$ and $400\ J\ mol^{-1}$, respectively. Calculate the temperature at which the reaction will be in equilibrium. 1½

UNIT—II

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

(a) For a system of ideal gases, prove the relation

$$\mu_i = \mu_i^0 + RT \ln p_i$$ 3

(b) Define partial molar quantity. Deduce the expression for variation of chemical potential with temperature. 1+2=3

UNIT—III

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

(a) Discuss any one characteristic of chemical equilibrium. Deduce the relationship between standard Gibbs free energy change and the equilibrium constant of a reaction. 1+3=4

(b) Find the value of Gibbs free energy change for mixing of ideal gases and prove that it is a spontaneous process. 4

(c) *(i)* Find the relation between K_p and K_c for the following equilibrium : 2½

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

(ii) Calculate K_c for the reaction—

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

for which $K_p = 3{\cdot}5 \times 10^{-25}$ at 27 °C. 1½

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UNIT—IV

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

(a) What is depression in freezing point? Derive a relation between depression in freezing point and molecular weight of the solute. 1+3=4

(b) What is osmotic pressure? Derive the relation between osmotic pressure and concentration of a solution having non-volatile solute. 1+3=4

(c) Define molal elevation constant. What is van't Hoff factor? The boiling point of 5% (w/w) of non-volatile solute in water is 100·45 °C. Calculate the molecular mass of the solute. 1+1+2=4

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