2025

(May–June)

FYUP : 4th Semester Examination

CHEMISTRY

(Physical Chemistry—I)

(CHE–252)

(Theory)

Marks : 75

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. *(a)* Describe *P-V* isotherm of CO_2 with the help of a diagram at varying temperatures. 6

(b) Write the expression for—

(i) most probable velocity;

(ii) root mean square velocity.

Also mention the differences between them. 2+2+2=6

(c) Write notes on the following : 2×2=4

(i) Collision diameter

(ii) Collision number

(d) Calculate the average velocity of SO_2 at 427 °C. [Given : $R = 8 \cdot 314$ J-K^{-1} mol^{-1}] 3

OR

2. (a) Derive mathematical equation to represent Maxwell's distribution of energies. 6

(b) Discuss the principle of equipartition of energy. 4

(c) Discuss the effect of temperature and pressure on the following : 3+3=6

(i) Collision frequency

(ii) Mean free path

(d) Calculate the temperature at which the hydrogen molecules will have an average velocity of 176400 cm s^{-1}. [Given : $R = 8 \cdot 314$ J-K^{-1} mol^{-1}] 3

3. (a) State and explain Carnot theorem. How can the efficiency of a heat engine be increased? 3+1=4

(b) Calculate the amount of heat supplied to Carnot's cycle working between 368 K and 288 K if the maximum work obtained is 895 joules. 3

(c) Differentiate between the following : 2×2=4

(i) Helmholtz free energy

(ii) Gibbs free energy

(d) Derive Gibbs-Helmholtz equation. 5

(e) State the first law of thermodynamics mentioning its limitations. 1+2=3

OR

4. (a) Prove that in a reversible process net entropy change for the system and surroundings is zero. 3

(b) Calculate the maximum efficiency of a steam engine operating between 110 °C and 25 °C. 3

(c) How does Gibbs' free energy vary with temperature and pressure? 5

(d) Derive Clausius-Clapeyron equation. 5

(e) State and explain Trouton's rule. 3

5. *(a)* Write three points of differences between metallic and electrolytic conductors. 3

(b) If molar conductivities at infinite dilution of NaCl, HCl and CH_3COONa are—

$126{\cdot}4$, $426{\cdot}1$ and $91{\cdot}0\ \Omega^{-1}cm^2mol^{-1}$

respectively, what will be that of CH_3COOH? 3

(c) What are specific conductance and equivalent conductance? Explain how they vary with dilution for strong and weak electrolyte. 3+4=7

(d) Derive Ostwald's dilution law. What are its uses and limitations? 3+2=5

OR

6. *(a)* Describe the moving boundary method for the determination of transport numbers. 4

(b) Discuss the curves obtained by conductometric titration of—

(i) a strong acid with a weak base;

(ii) a weak acid with a strong base. 3×2=6

(Continued)

(c) The equivalent conductance of a very dilute solution of $NaNO_3$ at 18 °C is $105{\cdot}2\ \Omega^{-1}\ cm^2$. If the ionic conductance of NO_3^- ion in the solution is $61{\cdot}7\ \Omega^{-1}\ cm^2$, calculate the transport number of Na^+ ions in the solution. 2

(d) Explain the following : 3×2=6

(i) Asymmetric effect

(ii) Electrophoretic effect

7. *(a)* What is meant by electrochemical series? Explain why zinc (Zn) reacts with H_2SO_4 to give H_2 but silver does not. 2+2=4

(b) Briefly explain the different types of reversible electrodes. 4

(c) Write the cell reaction and calculate E° for the cell

$$Zn\left|Zn^{2+}\ (1\ M)\right|\left|Fe^{3+}\ (1\ M)\right|Fe^{2+},\ Pt$$

Given,

$$E^\circ_{Fe^{3+}/Fe^{2+}} = +0{\cdot}77\ V$$

$$E^\circ_{Zn^{2+}/Zn} = -0{\cdot}76\ V$$

2+3=5

(Turn Over)

(d) Derive the relation between e.m.f. of a cell with the following thermodynamic parameters of a cell reaction : 2+2+2=6

(i) Free energy

(ii) Enthalpy

(iii) Entropy

OR

8. (a) Derive Nernst equation for measuring the e.m.f. of the cell. 3

(b) What is an electrochemical cell? Write a representation of an electrochemical cell, using important sign conventions, taking the example of Zn-Cu cell. 2+3=5

(c) Represent schematically the cell made up of the following half-cell reactions :

$$Mg \rightarrow Mg^{2+}(0 \cdot 01\,M) + 2e^{-}$$

$$E^{\circ} = +2 \cdot 34\,V$$

$$Sn^{2+}(0 \cdot 1\,M) + 2e^{-} \rightarrow Sn$$

$$E^{\circ} = -0 \cdot 136\,V$$

Calculate the e.m.f. of the above cell at 25 °C. 2+3=5

(Continued)

(d) What is liquid junction potential? How can it be minimized? 2+1=3

(e) What are concentration cells? Mention different types of concentration cells. 1+2=3

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