

Bachelor of Science (B.Sc.) Semester II (C.B.S.) Examination
CHEMISTRY (Physical Chemistry)
Compulsory Paper—2

Time : Three Hours]

[Maximum Marks : 50

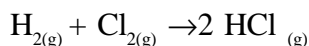
N.B. :— (1) All **FIVE** questions are compulsory and carry equal marks.
(2) Draw diagrams and give chemical equations whenever necessary.

1. (A) Derive an expression for w , q , ΔE and ΔH for expansion of gases under isothermal reversible process. 5

(B) Explain :

- (i) Average bond energy, and
- (ii) Bond dissociation energy.

Calculate the enthalpy change of the following reaction :



Given that the bond dissociation energies of $\text{H} - \text{H}$, $\text{Cl} - \text{Cl}$ and $\text{H} - \text{Cl}$ are $437.0 \text{ KJ mol}^{-1}$, $244.0 \text{ KJ mol}^{-1}$ and $433.0 \text{ KJ mol}^{-1}$ respectively. 5

OR

- (C) Distinguish between reversible and irreversible processes. $2\frac{1}{2}$
- (D) Explain with examples : $2\frac{1}{2}$
- (i) Intensive, and
 - (ii) Extensive properties.
- (E) Show that in Joule-Thomson experiment the enthalpy remains constant under adiabatic expansion of a real gases. $2\frac{1}{2}$
- (F) Calculate the enthalpy of combustion of ethylene (g) to form $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$ at 298 K and 1 atmospheric pressure. The enthalpies of formation of CO_2 , H_2O and C_2H_4 are -393.7 , -241.8 and $+52.3 \text{ KJ mol}^{-1}$ respectively. $2\frac{1}{2}$

2. (A) Draw and discuss the phase diagram of Lead-Silver system. 5
 (B) What is critical solution temperature ? Discuss Phenol-water and Triethylamine - water systems. 5

OR

- (C) Explain why $\text{KCl} - \text{NaCl} - \text{H}_2\text{O}$ system should be regarded as a 3-component system whereas $\text{KCl} - \text{NaBr} - \text{H}_2\text{O}$ system should be regarded as a 4-component system. $2\frac{1}{2}$
 (D) Draw well-labelled diagram of water system. $2\frac{1}{2}$
 (E) State and explain the Raoult's law of ideal solutions. $2\frac{1}{2}$
 (F) In the distribution of benzoic acid between water and benzene, the following results were obtained :

C_1 (in water)	1.50	1.95	2.97
C_2 (in benzene)	24.20	41.20	97.00

Assuming that benzoic acid exists as single molecule in water, show that it exists as double molecule in benzene. $2\frac{1}{2}$

3. (A) Explain the terms :

- (i) Specific conductance
 (ii) Equivalent conductance
 (iii) Molar conductance

The resistance of 0.01N NaCl solution at 25°C is 200 ohms. Cell constant of the conductivity cell is 1 cm^{-1} , calculate the equivalent conductance of the solution. 5

- (B) State and explain Kohlrausch's law of independence migration of ions. How can it be used to determine equivalent conductance at infinite dilution for weak electrolytes ? 5

OR

- (C) What are the postulates of Arrhenius theory of Electrolytic Dissociation ? $2\frac{1}{2}$
 (D) Write a note on Relaxation effect. $2\frac{1}{2}$
 (E) The equivalent conductance of a very dilute solution NaNO_3 at 18°C is $105.2\text{ mhos cm}^2\text{ g eq}^{-1}$. If the ionic conductance of NO_3 ion in the solution is $61.7\text{ mhos cm}^2\text{ g eq}^{-1}$, calculate the transport number of Na^+ ion in the solution. $2\frac{1}{2}$
 (F) Discuss conductometric titration of weak acid with strong base. $2\frac{1}{2}$

4. (A) Describe half-life period for the determination of order of reaction. The half-life of a chemical reaction at a particular concentration is 50 minutes. When the concentration is doubled, the half-life becomes 100 minutes. Find out the order of reaction. 5
 (B) Discuss Transition State theory. Derive an expression for the rate constant based on equilibrium constant. 5

OR

- (C) Describe the various factors affecting the rate of reaction. $2\frac{1}{2}$
- (D) Derive an expression for rate constant for the reactions of first order. $2\frac{1}{2}$
- (E) For a reaction $A \rightarrow B$, the rate constant doubled when temperature was raised from 25°C to 35°C .
Calculate the activation energy of the reaction. $2\frac{1}{2}$
- (F) Discuss the Lindemann's theory as applied to the unimolecular reaction. $2\frac{1}{2}$
5. Attempt any **TEN** questions out of the following :
- (i) Define isolated system.
 - (ii) Give two statements of first law of thermodynamics.
 - (iii) Define inversion temperature.
 - (iv) Write Gibbs phase rule equation.
 - (v) State Henry's law.
 - (vi) Give any two Limitations of Nernst distribution law.
 - (vii) Write Debye-Huckel Onsagar equation.
 - (viii) What do you mean by transport number ?
 - (ix) Write an equation for solubility product of AB_2 type electrolyte.
 - (x) Define order of reaction.
 - (xi) What is Pseudo unimolecular reaction ?
 - (xii) Define activation energy of a reaction. $1 \times 10 = 10$