

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

Time : Three Hours]

[Maximum Marks : 50

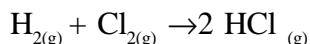
**N.B. :—** (1) All **FIVE** questions are compulsory and carry equal marks.  
(2) Draw diagrams and give chemical equations whenever necessary.

1. (A) Derive an expression for  $w$ ,  $q$ ,  $\Delta E$  and  $\Delta H$  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  $H - H$ ,  $Cl - Cl$  and  $H - Cl$  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 :  
(i) Intensive, and  
(ii) Extensive properties.  $2\frac{1}{2}$

(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  $CO_{2(g)}$  and  $H_2O_{(g)}$  at  $298 \text{ K}$  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  $\text{NaCl}$  solution at  $25^\circ\text{C}$  is 200 ohms. Cell constant of the conductivity cell is  $1 \text{ cm}^{-1}$ , 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  $\text{NaNO}_3$  at  $18^\circ\text{C}$  is 105.2 mhos  $\text{cm}^2 \text{ g eq}^{-1}$ . If the ionic conductance of  $\text{NO}_3^-$  ion in the solution is 61.7 mhos  $\text{cm}^2 \text{ g eq}^{-1}$ , calculate the transport number of  $\text{Na}^+$  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  $25^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ . 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  $\text{AB}_2$  type electrolyte.
- (x) Define order of reaction.
- (xi) What is Pseudo unimolecular reaction ?
- (xii) Define activation energy of a reaction.  $1 \times 10 = 10$