[This question paper contains 7 printed pages.]

919 *Your Roll No.* .....

B.Sc. (Hons.) / III **C**

CHEMISTRY - Paper XVII

(Physical Chemistry - III)

Time : 3 Hours *Maximum Marks : 38*

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt **six** *questions in all, including Question No.* **1** *which is compulsory.*
Attempt Atleast **One** *Question from each section.*
Use of scientific calculator as well as log tables is permitted.

1. Explain briefly any **four** of the following :

   (a) Photosynthesis is a photosensitized reaction.

   (b) A photochemical reaction with quantum efficiency of one shows no temperature dependence.

   (c) A first order reaction never completes.

P.T.O.

(d) Why we cannot use a voltmeter for determining the electromotive force of a galvanic cell.

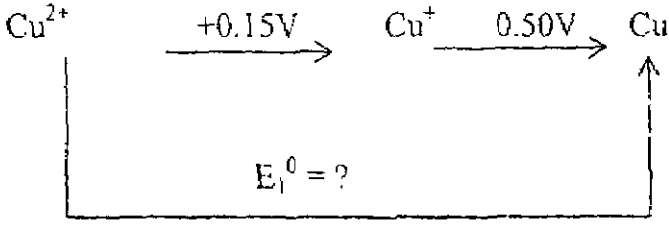
(e) Absorption of gases on the surface of adsorbent is no more monolayer at high pressure and low temperature. (4×2)

SECTION – A

2. (a) How pH of a solution is determined with the help of a glass electrode.

If the solution pH is greater than 9, the experimentally obtained pH value is usually lower than the true value why ?

(b) The reduction potential diagram for Cu in acid solution is



Calculate E_1^0. (2×3)

3. (a) The emf of the cell

$$Ag|AgCl\ (s)|KCl\ (aq)|Hg_2Cl_2(s)|H_g$$

is 0.0455 V at 298K and the temperature coefficient is $3.38 \times 10^{-4} VK^{-1}$. Write the cell reaction and calculate ΔG, ΔH and ΔS of the cell.

(b) Why potential measurement is used to get equivalence point of acid-base, redox and precipitation titrations.

If V ml. of 0.1 N solution of $Cr_2O_7^{2-}$ be titrated against V mL of 0.1 M solution of Fe^{2+} with half-cell reduction reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

Deduce the expression for potential at the equivalence point of the titration. (2×3)

SECTION – B

4. (a) Describe the activated complex theory and find out its rate expression. Compare this rate constant to Arrhenius equation and show that

$$E_a = RT + \Delta^{\neq}U^0$$

(b) Derive an expression for the rate constant on the basis of collision theory for bimolecular reaction. (2×3)

5. (a) For a homogeneous gaseous phase first order reaction $2A \longrightarrow 3B + C$ the initial pressure of reactant was P^0 while pressure at time t was P. Find the pressure after time 2t.

(b) An acid HA catalyses the substrate S to products by the reaction

$$S + HA \underset{k_-}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

Deduce the rate law for the reaction. State

the condition under which it becomes general acid catalysis and specific hydrogen ion catalysis. (2×3)

6. (a) Derive the differential rate law for the stationary chain reaction.

$$H_2 + Br_2 \longrightarrow 2HBr$$

Using steady state approximation. The proposed elementary steps are

$$Br_2 \xrightarrow{k_1} 2Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

(b) A first order reaction completes 50% in 10 second. How much time will it take for the completion of 90% of the reaction? (2×3)

P.T.O.

SECTION – C

7. (a) Define quantum efficiency. What are the reasons of low and high quantum efficiency of a photochemical reaction ?

(b) In the photochemical combination reaction of $H_2(g)$ and $Cl_2(g)$ a quantum efficiency of about 1×10^6 is obtained with a wavelength of 480 nm. What amount of HCl(g) would be produced under these conditions per calories of radiant energy absorbed ? (2×3)

8. (a) A protein with a molar mass of 60,000 g mol^{-1} forms an ideal gaseous film on water. What area of film per milligram of protein will produce a pressure of 0.005 Nm^{-1} at 298 K ?

(b) Discuss the effect of temperature on physisorption and chemisorption.

(c) The Brunauer, Emmett and Teller (BET) equation for multilayer adsorption of gases is given by

$$P/[V_{total}\ (P_0 - P)] = 1/(V_{mono}C) + (C-1)\ P/[(V_{mono}C)\ P_0]$$

What is the physical significance of the term C in the BET equation. (3·2)

9. Write short notes on any **three** of the following :

(a) Chemiluminiscence

(b) Laws of photochemistry

(c) Calomel electrode

(d) Enzyme Catalysis (3·2)