

**M.Sc., CHEMISTRY**

**SUBJECT= REACTION KINETICS, ELECTRODE  
KINETICS AND PHOTOCHEMISTRY**

**SUB CODE= PCH1015T,**

**SEMESTER=IV**

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### **UNIT-I**

#### **One and Two Marks**

1. Write the rate constant equation, as per collision theory of reaction.
2. What is Bronsted catalysis law for acid and base catalysis.
3. Write Eyring equation relating enthalpy and entropy of activation.
4. What is collision frequency?
5. What is meant by elastic and inelastic collisions?
6. The experimentally determined energy of activation for the decomposition of hydrogen iodide is  $184 \text{ kJ mol}^{-1}$ . Calculate the energy of activation at  $400^\circ \text{C}$  according to the collision theory.
7. Find out the statistical correction factors  $p$  and  $q$  of Bronsted relationship for the bases  $\text{RCOO}^-$  and  $\text{HPO}_4^{2-}$ .
8. The pre-exponential terms for two bimolecular gas reactions occurring at  $300^\circ \text{C}$  are  $7.4 \times 10^{10}$  and  $8.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the entropy of activation in each case. How do the results depend on the standard state used?
9. The rate of the thermal decomposition of acetone is found to be given by the expression.  
$$-\frac{d[\text{CH}_3\text{COCH}_3]}{dt} = k_i k_p k_{p2} k_t [\text{CH}_3\text{COCH}_3]$$

the energies of activation  $(E_a)_i$ ,  $(E_a)_p$ ,  $(E_a)_{p2}$ , and  $(E_a)_t$  are  $351.5$ ,  $62.8$ ,  $200.0$  and  $20.9 \text{ kJ mol}^{-1}$  respectively.

Calculate the overall energy of activation.

10. If the rate constant at high pressures (first order) for the isomerization of cyclopropane is  $1.2 \times 10^{-4} \text{ s}^{-1}$  and that at low pressures (second order) is  $5.14 \times 10^{-6} \text{ torr}^{-1} \text{ s}^{-1}$ , below what pressure will the isomerization be, for all practical purposes, a second order reaction?
11. How does dielectric constant affect the rate of reaction in solution.
12. Write down the effect of temperature on reaction rate.
13. How does temperature influence rate of a reaction.
14. Write the mechanism for a specific base catalysed reaction.
15. Write Eyring equation relating enthalpy and entropy of activation.

**(QUESTIONS ABOVE 2 MARKS)**

1. For a first order reaction, if the  $E_a$  is  $109.4 \text{ kJ/mol}$  and rate constant is  $9.12 \times 10^{-1} \text{ s}^{-1}$  at  $130^\circ \text{C}$  calculate the standard entropy of activation.
2. Calculate the translational partition function for carbon monoxide in standard state of  $10^3 \text{ mol m}^{-3}$  at  $27^\circ \text{C}$ . What will be the molar free energy associated with translation?
3. Calculate the translational partition function for ethyl alcohol at  $27^\circ \text{C}$  the density of ethyl alcohol is  $785 \text{ kg m}^{-3}$ . What will be its molar free energy?
4. Calculate the rate constant for the decomposition of hydrogen iodide at  $556 \text{ K}$ , using the collision theory formula, given the energy of activation to be  $184.2 \text{ kJ/mol}$ . Compare this value with the experimental value of  $3.5 \times 10^{-7} \text{ l/mol/s}$ . The collision diameter of hydrogen iodide may be taken to be  $3.5 \times 10^{-8} \text{ cm}$ .
5. If the rate constant at high pressures (first order) for the isomerization of cyclopropane is  $1.2 \times 10^{-4} \text{ s}^{-1}$  and that at low pressures (second order) is  $5.14 \times 10^{-6} \text{ torr}^{-1} \text{ s}^{-1}$ , below what pressure will the isomerization be, for all practical purposes a second order reaction?
6. The platinum catalysed decomposition of hydrogen iodide obeys the rate law  $-dp_{\text{HI}}/dt = k$  at high pressure with  $k = 500 \text{ torr s}^{-1}$  at the same temperature. Calculate the pressure of HI at which the rate would be  $250 \text{ torr s}^{-1}$  at the same temperature.
7. Derive rate expression for the reaction of first order kinetics opposed by first order.

8. In the acid hydrolysis reaction  $A + H_2O + H^+ \longrightarrow$   $p[H^+] = 0.1 \text{ mol dm}^{-3}$  and  $[H_2O]$  is present in large excess, the apparent rate constant is  $1.5 \times 10^{-5} \text{ s}^{-1}$ . Calculate the true rate constant.
9. Explain the mechanism of acid catalysed reaction.
10. For a reaction, if the  $E_a$  is  $205.8 \text{ kJ/mol}$  and rate constant is  $1.33 \times 10^{-4} \text{ s}^{-1}$  at  $127^\circ\text{C}$ . Calculate the standard entropy of activation.

## UNIT-II

### One and Two Marks

1. Draw Langmuir's plot for the kinetics of a gaseous reaction on solid surface.
2. Write about flash photolysis.
3. Write BET equation explaining the terms.
4. Kinetics of consecutive reaction.
5. Show that the slope of Lineweaver-Burk plot is not altered by the presence of an uncompetitive inhibitor?
6. What is meant by the term relaxation time in fast reaction?
7. What are reversible reaction? Give an example.
8. What is meant by the term flux in irreversible thermodynamics?
9. The relaxation time for the fast reaction  $A \rightleftharpoons B$  is  $10 \text{ micro s}$  and the equilibrium constant is  $1.0 \times 10^{-3}$  calculate the constant for the forward reaction.
10. What are catalysis? How are they classified?
11. Write a short note on catalysis by enzymes.
12. Write the limitation of BET isotherm.
13. Draw BET plot for adsorption.

### QUESTIONS ABOVE 2 MARKS

1. Derive Langmuir adsorption isotherm.
2. How to study fast reaction using temperature jump method.
3. The following Rice-Herfeld mechanism has been proposed for the gas phase pyrolysis of methane,  $\text{CH}_4$

'M' IS molecule ( $\text{CH}_4$  OR  $\text{C}_2\text{H}_6$ ) which can away the energy of recombination of  $\text{CH}_3$  and H. assuming the steady state approximation for  $[\text{H}]$  AND  $[\text{CH}_3]$  derive the rate law for the formation of  $\text{C}_2\text{H}_6$ .

4. Derive an expression for langmuir's adsorption isotherm.
5. Using appropriate diagram discuss the role of potential energy surfaces in reaction kinetics.
6. Write a note on types of complex reactions.

### **UNIT-III**

#### **One and Two Marks**

1. State debye-huckel limiting law
2. Guoy-chapman and Stern model of electrical double layer.
3. What are Onsager's phenomenological relations.
4. Calculate the ionic strength of 0.15g molal KCl solution.
5. Calculate the mean ionic activity co-efficient of 0.001 molal sodium sulphate.

6. Calculate the ionic strength of 0.25 molal  $K_2SO_4$  solution.
7. What is meant by the term flux in irreversible thermodynamics.
8. State Lipmann equation.
9. Show schematic graphical representation for Stern model.
10. Write a short note on Onsager's theorem.

### 5 and 8 Marks

1. Outline the mathematical steps in the Debye-Huckel theory of determining the activity coefficients of strong electrolytes in solution.
2. Write a brief note on electrokinetic phenomena.
3. Write about Gouy-Chapman and Stern model of electrical double layers.
4. Explain about activity, activity coefficient.

### UNIT-IV

#### One and Two Marks

1. Explain Franck-Condon principle.
2. Differentiate internal conversion and intersystem crossing.
3. Differentiate radioactive and non-radiation process.
4. Write quantum yield and any two examples for fluorescence.
5. Explain the term fluorescence and phosphorescence.
6. Distinguish fluorescence and phosphorescence.
7. What is meant by spin multiplicity.
8. What is IC and ISC?
9. What is spin forbidden radiative transition?
10. Give the types in decay of electronically excited states.
- 11.1. A photochemical reaction takes place by the absorption of (a) visible and ultraviolet radiations (b) Infrared radiations (c) heat energy (d) none of these  
Answer. (a)
12. Photochemistry deals with the study of (a) photons (b) photos (c) reactions which proceed with absorptions of UV light (d) reactions which proceed with absorption of IR light  
Answer. (c)
13. The wavelength of ultraviolet and visible regions of electromagnetic spectrum is (a) less than  $2000 \text{ \AA}$  (b) more than  $8000 \text{ \AA}$  (c)  $2000^\circ$  to  $8000 \text{ \AA}$  (d) none of these  
Answer. (c)
14. Which of the following statements about the photochemical reactions is true?  
(a) the presence of light is the primary requirement for reactions to take place (b) temperature has a very little effect on the rate of photochemical

- reactions (c)  $\Delta G$  for photochemical spontaneous reactions may +ve or -ve  
(d) all of the above Answer. (d)
15. Photochemical activation is highly selective. This statement is (a) true (b) false (c) sometimes true (d) none of these Answer. (a)
16. The number of photons that pass through a unit area in a unit time is called (a) amplitude of light (b) frequency of light (c) intensity of light (d) wavelength of light Answer. (c)
17. "It is only the absorbed light radiations that are effective in producing a chemical reaction." This is the statement of (a) Lambert law (b) Lambert-Beer law (c) Grothus-Draper law (d) Stark-Einstein law Answer. (c)
18. "In a photochemical reaction each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products." This is the statement of (a) Lambert-Beer's law (b) Grothus-Draper law (c) Stark-Einstein law (d) Lambert's law Answer. (c)
19. Which of the following statements is true? (a) it is the secondary reaction in which absorption of radiation takes place (b) it is the primary reaction in which absorption of radiation takes place (c) the absorption of radiation takes place in both – the primary and secondary reactions (d) none of the above Answer. (b)
20. The number of molecules reacted or formed per photon of light absorbed is called (a) yield of the reaction (b) quantum efficiency (c) quantum yield (d) quantum productivity Answer. (c)
21. A species which can both absorb and transfer radiant energy for activation of the reactant molecule is called (a) radioactive substance (b) an ioniser (c) a photochemical substance (d) a photosensitizer Answer. (d)
22. The substances that when exposed to light radiations of short wavelength emit light of longer wavelength are called (a) photosensitized substances (b) phosphorescent substances (c) fluorescent substances (d) none of these Answer. (c)
23. \_\_\_\_\_ stops as soon as the incident radiation is cut off (a) fluorescence (b) phosphorescence (d) chemiluminescence (d) none of these Answer. (a)
24. Sulphates of calcium, barium and strontium exhibit (a) chemiluminescence (b) fluorescence (c) phosphorescence (d) none of these Answer. (c)
25. The emission of light as a result of chemical action is called \_\_\_\_\_ (a) phosphorescence (b) fluorescence (c) chemiluminescence (d) none of these Answer. (c)

26. The light emitted in a chemiluminescent reaction is also called (a) cold light (b) hot light (c) bright light (d) none of these Answer. (a)
27. The glow of fireflies is due to the aerial oxidation of luciferin. It is an example of (a) fluorescence (b) phosphorescence (c) chemiluminescence (d) none of these Answer. (c)
28. A solution of quinine sulphate on exposure to visible light exhibits (a) fluorescence (b) phosphorescence (c) chemiluminescence (d) none of these Answer. (a)
29. The reactions which are caused by heat and in absence of light are called (a) photochemical reactions (b) catalytic reactions (c) exothermic reactions (d) thermal or dark reactions Answer. (d)
30. A glass of certain thickness is found to have a transmission of 70% of light. If the thickness of glass is reduced, the transmission of light would (a) decrease (b) increase (c) remain the same (d) reduce to zero Answer. (a)
31. A substance in a cell length (l) absorbs 20% of incident light. If the cell length is changed to 5l, the fraction of incident light that will be absorbed is (a) also increased (b) decreased (c) unchanged (d) none of these Answer. (a)
32. "Only the fraction of incident light that is absorbed by the substance can bring about a chemical change". is (a) First law of photochemistry (b) Second law of photochemistry (c) Third law of photochemistry (d) none of these Answer. (a)
33. The energy of an einstein of radiation of wavelength 400 nm is \_\_\_\_\_ than that of radiation of 300 nm (a) lesser (b) greater (c) equal to (d) none of these Answer. (a)
34. Photochemical decomposition of a substance is called (a) thermal dissociation (b) thermolysis (c) photolysis (d) none of the above Answer. (c)
35. Out of the photons corresponding to light of wavelengths 200 nm, 400 nm, 600 nm and 800 nm, the one with highest energy will be (a) photon of light with 200 nm wavelength (b) photon of light with 400 nm wavelength (c) photon of light with 600 nm wavelength (d) photon of light with 800 nm wavelength Answer. (a)
36. The substances which initiate a photochemical reaction but itself does not undergo any chemical change is called (a) catalysis (b) fluorescent (c) sensitizer (d) none of these Answer. (c)
37. Organic dyes like eosin, chlorophyll, ultrarine etc. show \_\_\_\_\_ in the visible or UV region (a) fluorescence (b) phosphorescence (c) chemiluminescence (d) none of these Answer. (a)

38. In photochemical reactions, the absorption of light takes place in (a) primary processes only (b) secondary processes only (c) either primary or secondary process (d) both primary and secondary processes Answer. (a)

### 5 and 8 Marks

1. Explain Stern-Volmer analysis.
2. Draw and discuss the Jablonski diagram with its process.
3. What are excimers and exciplexes.
4. Explain static and dynamic quenching.
5. Explain kinetics of bimolecular photophysical process.
6. Write a note on energy transfer process.

### UNIT-V

#### One and Two Marks

1. What are quantum yields in photochemistry?
2. Define G-value.
3. Write a short note on chemical actinometry in photochemistry.
4. What are primary and secondary processes in radiation chemistry?
5. Write a note on solar energy conversion.
6. Explain steady state principle.
7. What are photo voltaic and photo galvanic.
8. Explain photo redox reaction.
9. Explain photo substitution reaction.
10. Write a note on photo isomerization and photosensitized reactions.
11. What is meant by radiolysis of water?
12. Write about photo-assisted electrolysis of water.
13. ----- is the wavelength range for photochemical changes.
14. Write about electron spins and multiplicities.
15. ----- is the relationship between energy gap and ISC efficiency.
16. ----- solvents are suitable for photochemistry.
17. ----- type of intermediates are formed in photochemical reactions.
18. Time taken for electronic transitions is -----.
19. Time taken for vibration of a bond is -----.
20. Electronic transitions with retention of spin of electrons is -----.
21. One einstein of energy is (a)  $E = 51.2859 \times 10^3 \text{ cal mol}^{-1} \times \lambda$  (b)  $E = 51.2859 \times 10^3 \text{ kcal mol}^{-1} \times \lambda$  (c)  $E = 51.2859 \times 10^3 \text{ J mol}^{-1} \times \lambda$  (d)  $E = 51.2859 \times 10^3 \text{ kJ mol}^{-1} \times \lambda$  Answer. (b)



22. For a reaction that obeys Einstein law, (a)  $\phi = 1$  (b)  $\phi > 1$  (c)  $\phi < 1$  (d)  $\phi = \alpha$   
 Answer. (a)
23. In some photochemical reactions low quantum yield is obtained. It is due to  
 (a) deactivation of reacting molecules (b) occurrence of reverse primary reaction (c) recombination of dissociated fragments (d) all of these Answer. (d)
24. The quantum yield,  $\phi$ , of a photochemical reaction is expressed as (a) no. of molecules decomposed or formed / no. of photons of radiation energy absorbed (b) no. of molecules activated / no. of photons of radiation energy absorbed (c) no. of molecules of reactants = no. of photons of radiation energy absorbed (d) none of the above Answer. (a)
25. The energy associated with a photon is given by the equation (a)  $E = h \times \lambda$  (b)  $E = h \times \nu$  (c)  $E = h \times c$  (d)  $E = h \times c^2$  Answer. (b)
26. One einstein is the energy associated with (a) one molecule (b) one photon (c) Avogadro number of photons (d) Faraday number of photons  
 Answer. (c)
27. The energy per einstein depends upon the wavelength of photon. The higher the wavelength, the \_\_\_\_\_ will be the energy per einstein. (a) higher (b) smaller (c) zero (d) infinity Answer. (b)
28. The ratio of energy per einstein and that of a photon is (a) equivalent number (b) Einstein number (c) Lambert's number (d) Avogadro's number Answer. (d)

### 3,5 and 8 Marks

- Write a note on
  - Photo redox reactions.
  - Photo substitution reactions.
- Write a short note on
  - Photo isomerization reactions.
  - Photo sensitized.
  - Photo voltaic cell.
  - Photo galvanic cell.
- Explain the photo assisted electrolysis of water.
- A certain system absorbs  $3 \times 10^8$  quanta of light per second. On irradiation for 400 s, 0.001 mole of the reactant was found to have reacted. Calculate

- the quantum yield for the process. (Avogadro's number =  $6.023 \times 10^{23} \text{ mol}^{-1}$ ) Answer.  $50.19 \times 10^8$
5. A certain system absorbs  $2 \times 10^{16}$  quanta of light per second. On irradiation for 10 minutes, 0.001 mole of the reactant was found to have reacted. Calculate the quantum yield for the process. (Avogadro's number =  $6.024 \times 10^{23}$ ) Answer. 50.2
  6. State and explain the law of photochemical equivalence and calculate the value of 1 einstein for light having  $\lambda = 2000 \text{ \AA}$ . Answer. 142.9 kcal
  7. Calculate the energy of a photon corresponding to wave length 360 nm. Given : velocity of light =  $3 \times 10^8 \text{ m sec}^{-1}$ ;  $h = 6.62 \times 10^{-34} \text{ J sec}^{-1}$ . Answer.  $5.525 \times 10^{-19} \text{ J}$
  8. Calculate percentage of light transmitted through 5 mm length of a liquid of absorption coefficient 2.5. Answer. 28.65%
  9. What percentage of light will be transmitted through two cells put together in the path of light, if their individual transmissions are 60% and 30%. Answer. 18%
  10. A 2 mm thick plate of a material transmits 70% of the incident light. Calculate the percentage of light transmitted if the thickness of the plate is 0.5 mm. Answer. 91.47
  11. Explain radiolysis of water.
  12. Write about hydrated electron.
  13. Explain the aspects of solar energy conversion.
  14. Explain photoassisted electrolysis of water.
  15. Explain Chemical actinometry.
  16. Explain the kinetics of hydrogen-halogen reaction.