M.Sc. CHEMISTRY
CHEMICAL DYNAMICS & ELECTROCHEMISTRY
FOURTH SEMESTER
MSC – 401C

(Use Separate Answer Scripts for Objective & Descriptive)

Duration : 3 hrs. Full Marks : 70

[PART-A: Objective]

Time : 20 min. Marks : 20

Choose the correct answer from the following: ***1X20=20***

1. The relation between the rate constant and viscosity for diffusion controlled reaction is
   a. Rate constant is directly proportional to viscosity
   b. Rate constant is inversely proportional to viscosity
   c. Rate constant is half of the viscosity
   d. No relation

2. Taft equation is
   a. $\log (K_X/K_H)=\rho\sigma$
   b. $\log (K/K_0) = \sigma^*\rho^* + E_s$
   c. $\log (K_X/K_H)=\rho[\sigma+r (\sigma^+- \sigma)]$
   d. $\log (K_{Nucx}/K_{H2O})=\alpha.En+\beta.H$

3. The Grunwald-Winstein equation is
   a. $\log (K_X/K_H)=\rho\sigma$
   b. $\log (K_{\text{t-BuCl, sol}})/K_{\text{t-BuCl, 80\% EtOH, 20\% H2O}})= mY$
   c. $\log (K_X/K_H)=\rho[\sigma+r(\sigma^+- \sigma)]$
   d. $\log (K_{Nucx}/K_{H2O})=\alpha.En+\beta.H$

4. Chemical energy is converted to _____ energy by a fuel cell.
   a. solar
   b. potential
   c. electrical
   d. mechanical

5. In a fuel cell, the electrons flow from : (CO –
   a. Anode to cathode through the electrolyte
   b. Cathode to anode through the solution
   c. Anode to cathode through the external circuit
   d. Cathode to anode through the external circuit

6. "Cage effect" appears for the
   a. Gaseous phase reactions
   b. Solution phase reactions
   c. Occurs in both gaseous and solution phase reaction
   d. None of the above

7. The factors which depend on diffusion of reactant are
   a. Movement of the reactant
   b. Size of the reactant
   c. Solubility
   d. All of the above

8. The kinetics of gaseous phase reactions are studied using the following mechanism
   a. Steady state approximation
   b. Lindemann–Hinshelwood mechanism
   c. Both (a) and (b)
   d. None of the above

reaction" - The statement is

a. True
b. False
c. Partially True
d. Partially False

10. The Hammett substituent constant, σ is based on

a. The dissociation of Benzoic acid
b. The dissociation of Phenol
c. The hydrolysis of ethyl benzoate
d. In Ester hydrolysis

11. In voltammetry, what are the common parameter involves?

a. Potential and current
b. Potential and resistance
c. Current and resistance
d. Current and electrodes

12. Which of the following electrodes are often used as counter or auxiliary electrode in voltammetry?

a. Calomel electrode
b. Carbon paste
c. Platinum wire
d. Mercury thin film

13. Which of the following items is not the electrode in voltammetry?

a. Auxiliary electrode
b. Working electrode
c. Reference electrode
d. Conducting electrode

14. Which of the following voltammetric techniques enhances the sensitivity through improving the faradaic current?

a. Differential pulse voltammetry
b. Square wave voltammetry
c. Cyclic voltammetry
d. Stripping voltammetry

15. In polarography, DME is stands for.....

a. Double Mercury Electrode
b. Dropping Mercury Electrode
c. Double Metal Electrode
d. Dropping Methyl Electrode

16. Flow system in which there is no stiring in the reactor is called

a. Plug flow
b. Continuous flow
c. Stopped flow
d. Quenched flow

17. Which of the following calculation is odd one?

a. LEP
b. Modified LEP
c. Varriational
d. BEBO

18. For comparison purpose a hypothetical reaction of $\Delta + H2$ was studied where mass of "Δ" hydrogen was

a. 12
b. 13
c. 14
d. 15

19. If vibrational frequencies of typical bonds are ~ 10^{13} Hz what is vibrational frequency of the loosely bound cluster in activated complexes?

a. 10^{13} Hz
b. $10^{14} - 10^{15}$ Hz
c. $10^{11} - 10^{12}$ Hz
d. None of them

20. Which of the following rate/equilibrium constants are needed for calculation of electron transfer rate constant?

a. Equilibrium constant for association of reactants to form complex
b. Equilibrium constant for electron transfer between reactants
c. Rate constant for dissociation of complex
d. All of them

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PART-B : Descriptive

Time : 2 hrs. 40 min. Marks : 50

[Answer question no.1 & any four (4) from the rest]

1. a. What is cage effect? 3+3+4 =10

   b. Write a note on cathodic stripping voltammetry.

   c. Describe and differentiate between stopped and quenched flow techniques.

2. a. Write the differences between gaseous phase reactions and solution phase reactions? 2+4+4 =10

   b. Derive Debye-Smoluchowski equation for diffusion controlled reactions?

   c. What is double sphere model? Derive the equation for double sphere model?

3. a. Write a short note on Solid oxide fuel cell. 4+3+3 =10

   b. What are LFERs? Write the Hammett equation? Illustrate it graphically.

   c. Estimate the diffusion controlled rate constant for the combination of molecules A and B in water at 50 □C. The coefficient of viscosity of water at this temperature is 2 cP.

4. a. What is solid polymer fuel cell? Write the half reactions of solid polymer fuel cell? Explain the drawbacks of the solid polymer fuel cell. 4+3+3 =10

   b. Illustrate the Primary kinetic isotope effects and secondary kinetic isotope effects?

   c. Write chemical composition of the electrolyte used in molten carbonate fuel cell. Write the half reaction for this fuel cell. What are the advantages of the MCFC over the other fuel cells?

5. a. What is a supercapacitor? Explain the basic design of a supercapacitor. **4+3+3 =10**

   b. Among different energy storage devices why supercapacitor have been recognized as more important? Explain the applications of supercapacitors.

   c. What do you mean by DC and pulse polarography?

6. a. What are the Tafel equation and Tafel plot. **3+7=10**

   b. What is cyclic voltammetry? Give the principle, electrode system and experiment details of cyclic voltammetry.

7. a. What are the electrodes used in polarography method of analysis? What is the principle of polarography? **4+2+4 =10**

   b. Using appropriate diagram discuss the role of potential energy surface for $H + H_2$ reaction.

   c. What are semi-emperical methods. Discuss two such methods for creation of potential energy surface.

8. a. Describe with help of graphs three indicators that tunneling has occurred in a reaction. **6+4=10**

   b. Derive rate equation using either vibrational partition function of loose vibration or translational partion function of motion of a particle.

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