M.Sc. CHEMISTRY
FOURTH SEMESTER
PHYSICAL CHEMISTRY-IV
(CHEMICAL DYNAMICS & ELECTROCHEMISTRY)
MSC-402 C

(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. Symmetry number for CH_4 molecule is:
   a. 2 b. 4 c. 6 d. 12

2. Hammett equation is applicable for:
   a. Aliphatic substances
   b. Aromatic substances
   c. Both aliphatic and aromatic substances
   d. None of the above

3. In cage effect, the number of collision per encounter is:
   a. Smaller than the viscosity of solvent
   b. Similar to the viscosity of solvent
   c. Greater than the viscosity of solvent
   d. None of the above

4. A positive value of reaction constant in Hemmett equation shows that the reaction is accelerated by:
   a. Electron withdrawing substituent
   b. Electron donating substituent
   c. Temperature only
   d. None of these

5. MEC is a:
   a. Pharmacokinetic parameter.
   b. Pharmacodynamic parameter.
   c. Both pharmacokinetic and pharmacodynamic parameter.
   d. None of these.

6. Relative bio-availability of 1 implies:
   a. Complete absorption of drug.
   b. 50% absorption of drug.
   c. Bio-availability from both dosage form is same but does not indicate complete absorption.
   d. None of these.

7. The ratio of rate constant k_H/k_D is:
   a. Less than k_H/k_T
   b. More than k_H/k_T
   c. Equal to k_H/k_T
   d. Equal to 1

8. Two most important sites for drug elimination are:
   a. Pulmonary and liver
   b. Kidney and liver
   c. Kidney and pulmonary
   d. Skin and liver

9. The highest point along the reaction coordinate in potential energy surface is known as:
   a. Activation point
   b. Transition Point
   c. Saddle point
   d. None of these

10. Which of the following is true for activation energy of potential energy profile in case of exothermic reaction?
    a. Ea = 48.1 + 0.75Q
    b. Ea = 48.1 - 0.75Q
    c. Ea = 48.1 + 0.25Q
    d. Ea = 48.1 + 0.25Q

11. Polarography maxima can be suppressed by addition of:
    a. Picric acid
    b. β-napthol
    c. Phenol
    d. Gelatin

12. If m and t are respectively the flow rate and drop time of Hg of the DME, the limiting diffusion current I_d is proportional to:
    a. $m^{2/3}t^{1/6}$
    b. $m^{1/6}t^{2/3}$
    c. $m^{2/3}t^{1/6}$
    d. $m^{1/6}t^{1/6}$

13. The potential at the point on the polarographic wave where the current is equal to one-half of the diffusion current is:
    a. Half wave current
    b. Full wave current
    c. Half-wave potential
    d. Full wave potential

14. Hanging mercury drop electrode is a working electrode in:
    a. Cyclic voltammetry
    b. Cathodic stripping voltammetry
    c. DC polarography
    d. Both b & c

15. The low detection limit obtained in stripping analysis are a result of:
    a. Faster measurements, which increase flux of the analyte to the electrode surface.
    b. Preconcentration of the analyte at the hanging Hg drop electrode.
    c. Lower double layer charging currents than in pulse methods or cyclic voltammetry.
    d. The chemical interactions between the reduced analyte ion on the Hg drop.

16. Which statement is true about polarography?
    a. The diffusion current is caused by solution stirring.
    b. The addition of supporting electrolytes is necessary for a migration current.
    c. The diffusion current is proportional to the square root of the concentration of the electroactive species.
    d. The magnitude of the diffusion current is proportional to concentration of electroactive species.

17. Which of the following is not an example of fuel cell?
    a. Hydrogen-oxygen cell
    b. Methyl-oxygen-alcohol cell
    c. Propane-oxygen cell
    d. Hexanone-oxygen cell

18. Advantage of fuel cell over petrol is its only product:
    a. Oxygen
    b. Nitrogen
    c. Water
    d. All of these

19. Which one is not a reference electrode?
    a. Ag-AgCl
    b. Hg-Calomel
    c. Dropping Hg
    d. Hydrogen

20. The excitation waveform used in a cyclic voltammetry:
    a. Linear scan
    b. Differential pulse
    c. Square wave
    d. Triangular

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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. i. Explain in brief the principle of anodic stripping voltammetry. A solution believed to contain trace amounts of Ca^{2+} and Cd^{2+} is analyzed using ASV. Sketch a representative plot of current versus voltage. 5+5=10
   ii. How can you determine Linear Free Energy Relationship (LFER) from Hammett equation?

2. What is Activated Complex Theory? Derive an expression for Eyring equation using this theory. How can you determine the standard entropy value for first order gaseous molecule? 2+5+3=10

3. i. What do you mean by Taft equation? How does it differ from Hammett equation? 5+5=10
   ii. What is isokinetic temperature? Determine isokinetic temperature from isokinetic relationship.

4. i. Draw a set-up of a dropping mercury electrode and different components in a polarographic experiment. Indicate the advantages of dropping mercury electrode. 5+5=10
   ii. Draw a typical current vs applied voltage polarogram and indicate the various components.

5. i. Stretch plasma-drug concentration-time profile diagram. Explain different pharmacokinetic and pharmacodynamic parameters involved in it. 6+4=10
   ii. What are the factors affecting protein-drug binding.

6. Using appropriate diagram discuss the role of potential energy surface for $H + H_2$ reaction. Calculate activation energy for any potential energy surface. 5+5=10

7. i. Explain the basic principle involved in cyclic voltammetry. How do we obtain diffusion coefficient from a cyclic voltammogram? 5+5=10
   ii. Explain the excitation signals used in voltammetry.

8. What is fuel cell? Describe the reactions involved in an alkaline and phosphoric acid fuel cell. Give the applications of each type. 2+6+2=10

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