M.Sc. CHEMISTRY
THIRD SEMESTER (SPECIAL REPEAT)
PHYSICAL CHEMISTRY-III
MSC-303
(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. Among $^1S_0$, $^3P_2$, $^3P_0$ and $^1D_2$, which one is the ground energy state for an orbital which follow normal multiplicity?
   a. $^1S_0$ b. $^3P_2$
   c. $^3P_0$ d. $^1D_2$

2. Which of the following multiplicity is observed in f^6 orbital?
   a. Normal multiplicity   b. Inverted multiplicity
   c. Both normal and inverted multiplicity   d. None of the above

3. If spin-spin coupling is more than that of spin-orbital coupling, then the molecule show
   a. Fluorescence   b. Phosphorescence
   c. Chemiluminiscience   d. Inter system crossing

4. The ground state for Co^{+3} ion is
   a. $^5F_4$ b. $^5F_0$
   c. $^5D_4$ d. $^5D_0$

5. Among the following, in which region, maximum spontaneous emission occur?
   a. Microwave region   b. Radio frequency region
   c. Visible region   d. X-ray region

6. If separation between a donor and an acceptor (R) is half than that of critical energy transfer distance (R_0), the rate of transfer is proportional to
   a. $(1/2)^6$ b. $(2)^6$
   c. $(1/2)^3$ d. $(2)^3$

7. Which of the following is true for Photodynamic therapy?
   a. It is a chemiluminiscience process   b. It is a photosensitization process
   c. It is a thermal process   d. None of the above

8. Excited stable state of a dimer is known as
   a. Excimer   b. Exciplex
   c. Photo-dimer   d. None of the above

9. Which of them is correct?
   a. True electrolyte is strong electrolyte   b. True electrolyte is weak electrolyte
   c. Potential electrolyte is strong electrolyte   d. None of them

10. If W_d is work of discharging, W_{tr} is work of transfer and W_c is work of charging with respect to Born model, which of the following is wrong?
    a. $W_{tr} = 0$ b. $W_d = W_c$
    c. $W_d + W_c$ =salvation free energy   d. All of them

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11. Which of the following is true for Bontha-Pintauro model?
    a. It includes a solvent dipole rearrangement term
    b. It contains no adjustable parameter
    c. Both A & B
    d. None of the above

12. According to assumtions of Debye-Huckel theory
    a. $q_j\Psi_j < kBT$
    b. $q_j\Psi_j > kBT$
    c. $q_j\Psi_j = kBT$
    d. None of the above

13. Which of the following is true regarding interaction energy and local counterions number?
    a. $U_{ij}(r) > 0 \; n_j(r) < n_j^\infty$
    b. $U_{ij}(r) < 0 \; n_j(r) > n_j^\infty$
    c. $U_{ij}(r) = 0 \; n_j(r) = n_j^\infty$
    d. All of the above

14. What is the valence factor Fv for MgSO4?
    a. 2
    b. 3
    c. 4
    d. 6

15. The electrocapillary maximum is defined as
    a. Potential of zero charge
    b. Potential at which surface tension is maximum
    c. Summit of the vs V curve (parabola)
    d. All the above

16. The constant capacity with change of potential is a postulate of
    a. Parallel-plate model
    b. Gouy-Chapman model
    c. Stern model
    d. Debye-Huckel model

17. Which of the following is not naturally occurring zeolites?
    a. Na+
    b. Al3+
    c. Si4+
    d. Ca2+

18. Which of the following is an example of homogeneous catalysis?
    a. Enzyme catalysis
    b. Hardening of animal and vegetable oils
    c. Haber process
    d. Cracking of heavy oil for synthesis of gasoline

19. Why is standard hydrogen electrode called as the reference/nonpolarizable electrode?
    a. It has a known output potential
    b. It has a constant output potential
    c. It has a zero potential
    d. None of these

20. The correct expression for the surface excess is (are the no. of moles of species i after and had there been no double layer; other symbols have their usual meanings)
    a.
    $$\Gamma_i = \frac{n_i}{A} - \frac{n_i^0}{A}$$
    b.
    $$\Gamma_i = \frac{n_i^0}{A} - \frac{n_i}{A}$$
    c. $\Gamma = \gamma A$
    d. None of these

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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. Explain Einstein treatment for absorption of electromagnetic radiation.   6+4=10
   Discuss the favorable conditions for both spontaneous and stimulated
   emission.

2. Explain with suitable examples about the photosensitizer and   10
   photosensitization process. Discuss one of the applications of
   photosensitization process.

3. a. Show that the graphical representation of the ratio of quantum yields,   5
      in absence of fluorescence to in presence of fluorescence with
      concentration of the quencher follow a straight line.
   b. Calculate the interaction energy between an ion of charge $z_i e_0$ and a 5
      dipole.

4. a. What do you mean by normal multiplicity and inverted multiplicity?   5
      Determine the term symbols for f^5 and f^8 orbitals. What are their
      ground states and how?
   b. Why does activity coefficient of a single species cannot be measured?   5
      For a 1:1 electrolyte define and derive the expression of the mean
      activity coefficient.

5. a. What is meant by fluorescence and phosphorescence? Write some of   5
      the differences between them.
   b. Explain the principle of half-wave potential in polarography.   5

6. a. Write down the main assumptions of Debye-Huckel theory.   5
   b. Show that the total charge on the surrounding ion cloud is equal and   2
      opposite to that on the central reference ion.
   c. Derive Einstein Smoluchowski equation.   3

7. Derive the fundamental electrocapillary equation for polarizable   7+3=10
   interfaces. Hence determine the charge density on the electrode.

8. a. What is electrical double layer? How is it formed at the   6
      electrode/electrolyte interface? Define Helmholtz-Perrin model for
      electrical double layer. Apply this model to relate the surface tension
      change with potential of an electrolyte solution.
   b. Explain what are polarizable and non-polarizable interfaces.   4

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