2022/07

M.Sc. CHEMISTRY
SECOND SEMESTER
PHYSICAL CHEMISTRY II
MSC - 203

(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. In an unimolecular reaction at low pressure the order of the reaction is
   a. First order
   b. Third order
   c. Zero order
   d. Second order

2. Which of the following is a unimolecular reaction
   a. $CH_3COOCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr$
   b. $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$
   c. $SO_2Cl_2 \rightarrow SO_2 + Cl_2$
   d. None of these

3. Energized molecule A* produced in RRK theory are
   a. Zero lifetime
   b. Limited lifetime
   c. Random lifetime
   d. None of these

4. Conversion of cyclopropane into propylene is a
   a. Unimolecular reaction
   b. Bimolecular reaction
   c. Pseudounimolecular reaction
   d. None of these

5. Which of the following is the correct Line weaver-Burk equation?
   a. $\frac{1}{V_0} = \frac{K_M}{V_{max}[S]} + \frac{1}{V_{max}}$
   b. $\frac{1}{V_{max}} = \frac{K_M}{V_0[S]} + \frac{1}{V_0}$
   c. $V_0 = \frac{V_{max}[S]}{K_M + [S]}$
   d. $V_{max} - \frac{V_0[S]}{K_M + [S]}$

6. The rate determining step of Michaelis-Menten kinetics is _____
   a. The complex dissociation step to produce products
   b. The complex formation step
   c. The product formation step
   d. None of the mentioned

7. The catalytic efficiency of two distinct enzymes can be compared based on which of the following factor?
   a. K_m
   b Product formation
   c. Size of the enzymes
   d pH of optimum value

8. Miller indices are same for
   a. Crystal planes
   b Parallel planes
   c. Perpendicular planes
   d Three crystallographic planes

9. The miller indices of the plane, whose intercepts along the axes are (a, 2b, 3c) is
   a. (1 2 3) b. (3 2 1) c. (2 3 6) d. (6 3 2)

10. A disturbance in a region between two ideal parts of a crystal is known as _____
   a. Boundary defect b Point defect
   c. Line defect d Volume defect

11. Increase in _____ of the adsorbent increases the total amount of the gas adsorbed
   a. Density b Volume
   c. Surface area d Surface tension

12. Which of the following is not an equation for Freundlich Adsorption Isotherm?
   a. $x/m = KP^{1/n}$ b. $x/m = KC^{1/n}$
   c. $\log (x/m) = \log K + 1/n \log P$ d. None of the above

13. The adsorption isotherm is defined as dependence of
   a. Surface coverage on the temperature at fixed pressure
   b. Surface coverage on the pressure at fixed temperature
   c. Rate of surface reaction on the pressure at fixed temperature
   d. None of the above

14. The adsorption of gas is described by Langmuir isotherm with the equilibrium constant $K = 0.9\ kPa^{-1}$ at 25 □C. The pressure in (KPa) at which fractional surface coverage 0.95 is
   a. 1/ 11.1 b. 21.1
   c. 11.1 d. 42.2

15. A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as _____.
   a. Solid sol b. Gel
   c. Emulsion d. Sol

16. The symmetry number for CH_4 molecule is
   a. 3 b. 4 c. 8 d. 12

17. Which one is right for canonical partition function, Q and molecular partition function, q?
   a. Distinguishable particles $Q = q^N/N!$ b. Indistinguishable particle $Q = q^N$
   c. Both a & b d. None of them

18. Sterling approximation is
   a. $\ln x! = x \ln x - x$ b. $\ln x! = x \ln x - \ln x$
   c. $\ln x! = \ln x - x$ d. $\ln x! = x - x \ln x$

19. Which pair is correct?
   a. Canonical ensemble: N, V, E common
   b. Microcanonical ensemble: μ, V, T common
   c. Grandcanonical ensemble: N, V, T common
   d. None of them

20. If V_i and V_f are change in volume of a monoatomic ags then according to Sackur-Tatrode equation the change in entropy is proportional to
   a. V_f/V_i b. V_i/V_f
   c. $\ln V_f/V_i$ d. $\ln V_i/V_f$

PART-B : Descriptive

Time : 2 hrs. 40 min. Marks : [illegible]

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

1. a. Explain the differences between octahedral and tetrahedral voids. Write two differences between Schottky defect and Frenkel defect. **5+3+2 =10**

   b. Explain the importance and mechanism of surfactant.

   c. What is residual entropy? What is its value for CO?

2. What are the fast reactions? Give some characteristics of fast reactions. Using suitable diagram describe the continuous and stopped flow method for studying kinetics of fast reactions. What are the disadvantages of continuous flow method? **2+6+2 =10**

3. a. What is Marcus theory of electron transfer reaction? Give the mechanism of electron transfer reaction between donor (D) and acceptor (A). **5+5=10**

   b. What are the limitations of Lindermann theory of unimolecular reactions? Explain the RRKM theory of unimolecular reactions.

4. a. Calculate the maximum radius ratio for a trigonal site. **3+3+4 =10**

   b. Estimate the mole fraction of Schottky and Frenkel defects in a NaCl crystal at 1000K. The energies of formation of these defects are 2 eV and 3 eV respectively. (Given that 1 eV=1.602×10^{-19} J, k = 1.38×10^{-23} JK^{-1}).

   c. Discuss using diagram the structure of calcium fluoride.

5. a. What are semiconductors? Explain what is meant by *n*-type and *p*-type semiconduction. **5+3+2 =10**

   b. Derive rotational contribution to molecular partition function for linear rotors.

   c. What is symmetry number? What is its value for symmetric linear molecule like H_2.

6. a. What is Sorption and Desorption? Write two applications of adsorption. **3+4+3 =10**

   b. Discuss the effect of pressure in Langmuir adsorption isotherm and how it is related to order of a reaction.

   c. The nondissociative adsorption of oxygen on tungsten is described by the Langmuir isotherm with K = 0.35 $K.Pa^{-1}$. Calculate the fractional surface coverage at a pressure of 1KPa.

a

7. a. Why the shape of liquid drop is spherical. Explain. 2+1+4+3=10
   b. Write the Gibbs adsorption equation.
   c. What is micelle, critical micelle concentration and Kraft temperature? Explain the difference between micelle and reverse micelle?
   d. Derive $\beta = 1/k$.

8. a. Differentiate between MB (Maxwell-Boltzmann), BE (Bose-Einstein) and FD (Fermi-Dirac) Statistics. 4+3+3=10
   b. Derive relationship of Gibb's free energy with molar partition function.
   c. Derive relationship between equilibrium constant and partition function.

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