

(PG70)

Roll No.

S.C.No.—M/20/18043/17038/16014

M. Sc. EXAMINATION, May 2020

(Second Semester)

(Re-appear 2018/2017/2016)

CHEMISTRY

CHE202

Physical Chemistry : Concepts and Applications

Time : 2 Hours

Maximum Marks : 80

Note : Attempt *Four* questions in all. All questions carry equal marks.

1. (a) What is Eutectic point in phase diagram ?
(b) State Nernst heat theorem. Justify if it is valid for gases or not.
(c) Define Turn over number and Turn over frequency.

(2-07/14) H-M/20/18043/17038/16014(PG70)

P.T.O.

- (d) What are Ladder operators ? Give their significance.
- (e) What do you mean by the term degeneracy ?
- (f) What is the canonical ensemble ? What properties are held constant in this ensemble ?
- (g) Write down Boltzmann formula and how can it predict the residual entropy ?
- (h) What is Residual entropy of the system ?
- (i) Define degree of freedom. Calculate the number of rotational degrees of freedom for linear and non-linear molecules.
- (j) What do you mean by triple point ?
- (k) Calculate the zero-point energy of a rigid diatomic molecule vibrating with frequency $1.66 \times 10^{13} \text{ sec}^{-1}$. (Plank's constant ' h ' = $6.6261 \times 10^{-34} \text{ J sec.}$)
- (l) Calculate the degree of freedom, number of components and number of phases in an aqueous solution of NaCl.

2. (a) Give details on phase diagram of sulphur system.
- (b) Derive Gibbs phase rule from thermodynamic consideration.
3. (a) Derive Clausius-Clapeyron equation for phase equilibrium.
- (b) At 373.15 K and 1 bar, the specific volume of water vapour is $1696 \text{ cm}^3\text{g}^{-1}$ and the value of dp/dT is $0.0362 \text{ bar K}^{-1}$. Calculate $\Delta_{\text{vap}}H_m$.
4. (a) Define Enzyme-catalysis phenomenon and derive Michaelis-Menten equation.
- (b) Define ionic strength and calculate its value for solutions of 0.1 M in FeCl_3 and 0.2 M cuprous sulphate.
5. (a) Give detail description on Primary and Secondary Salt effects.
- (b) What are Competitive and Non-Competitive Inhibitors in catalysed reactions ?

6. (a) What do you mean by Partition function? Give its significance.

(b) Evaluate the translational partition function for H_2 molecule confined to a volume of 100 cm^3 at 298 K .

7. (a) Derive the final equation for Bose-Einstein statistics.

(b) Calculate the relative populations of a linear rotor in the levels with $J = 0$ and $J = 5$, given that $B = 2.71 \text{ cm}^{-1}$ and a temperature of 298 K .

M19(P-22)

Roll No.

S.C.No.—M/19/0701203/7119/
7012/6909

M.Sc. EXAMINATION, May 2019

(Main/Reappear)

(2018/2017/2016/2015)

(Second Semester)

CHEMISTRY

CHE203

Organic Chemistry-II

(Organic Reaction Mechanism)

Time : 3 Hours

Maximum Marks : 80

Note : The question paper comprises of nine questions. Q. No. 1 is shall be compulsory. Attempt *four* more questions selecting *one* from each Unit. Each question shall carry equal marks.

(3-04/22)H-0701203/7119/7012/6909(P-22)

P.T.O.

1. (a) Explain benzyne mechanism with examples.
- (b) Distinguish between the Hofmann's rule and the Saytzeff's rule.
- (c) Give mechanism of Reimer-Tiemann Reaction.
- (d) Explain regioselectivity with example.
- (e) Write Aldol condensation reactions with example.
- (f) Explain, why only hydrogen atoms of carbonyl compounds take part in the condensation reaction ?
- (g) How can you convert Benzile to benzilic acid ?
- (h) Write curtius reaction with example.

16

Unit I

2. Explain the following with suitable examples.
- (a) Vilsmeier reaction
- (b) Diazonium coupling
- (c) Smiles rearrangement
- (d) Ipso attack.

16

3. (a) Explain the directing nature of the following groups in electrophilic substitution on benzene :

(i) $-\text{CN}$

(ii) $-\text{NHCOH}_3$

(iii) $-\text{COR}$

(iv) $-\text{OCOR}$

6

(b) Explain the benzyne mechanism of aromatic nucleophilic substitution. Discuss the effect of substrate structure on aromatic nucleophilic substitution. 10

Unit II

4. (a) Explain E1, E2 and Ecb mechanism with examples. 8

(b) Explain the following in detail with mechanism via taking an example :

(i) Michael reaction

(ii) Hydroboration.

8

5. (a) Explain sharpless asymmetric epoxidation with mechanism. 6
- (b) Explain hydrogenation of double and triple bonds. 6
- (c) Discuss the mechanism and orientation in pyrolytic elimination. 4

Unit III

6. (a) Give mechanism for the following :
- (i) Wittig reaction
 - (ii) Perkin reaction
 - (iii) Reaction of carbonyl compounds with Grignard reagent
 - (iv) Stobbe reaction. 12
- (b) Describe the synthetic uses Reformatsky reaction. 4
7. (a) Explain hydrolysis of ester under acidic and basic conditions. 8
- (b) Give mechanism of reduction by Lithium Aluminium Hydride of saturate and unsaturated carbony compounds. 8

Unit IV

8. (a) Write the products with mechanism from the reaction of peracid with cyclohexanone, reaction of diazomethane with cyclohexanone and reaction cyclohexanone with $\text{HN}_3/\text{H}_2\text{SO}_4$. 9
- (b) Write short notes on the following :
- (i) Wolff Rearrangement
 - (ii) Neber rearrangement. 7
9. (a) How is methylene cyclohexane obtained from cyclohexanone ? 4
- (b) Write short notes on the following :
- (i) Stevens rearrangement
 - (ii) Benzidine rearrangement. 6
- (c) Discuss mechanism with one example for each of nucleophilic, free radical and electrophilic rearrangement. 6

- (c) What is 3rd law of thermodynamics ?
Write its significance. 2
- (d) Discuss the concept of partition function. 2
- (e) Define microstates and macrostates with example. 2
- (f) What are eigen functions and eigen values ? 2
- (g) Discuss Zero point energy. 2
- (h) Explain the influence of pressure on reaction rates. 2

Unit I

- 2. (a) What is Nernst Heat theorem? How does this lead to third law of thermodynamics ?
Explain. 12
- (b) Why absolute zero cannot be attained ? 4
- 3. (a) Discuss the phase diagram of one component system ? Discuss its applications. 12

- (b) Calculate boiling point of water at a space station where the atmospheric pressure is 528 mm. Latent Heat of vaporization is 545.5 cal/g and $R = 1.987 \text{ cal /K/mol}$. 4

Unit II

4. Explain the kinetics and mechanism of enzyme catalyzed reaction in detail. Also evaluates the Michaelis constants for enzyme-substrate binding by Lineweaver-Burk plot. 16

5. Discuss the following terms : 16

- (i) Heterogeneous catalysis
- (ii) Competitive and noncompetitive inhibition
- (iii) Salt effect
- (iv) Ionic strength.

Unit III

6. Derive expression for Fermi-Dirac statistics and explain its application to extreme gas degeneration ? 16

7. What is Bose-Einstein statistics ? Derive relation for Bose-Einstein statistics. Discuss its application for photon gas.

16