# M.SC. (CHEMISTRY) - 1ST SEMESTER EXAMINATIONS; DEC.-2017
## (SUBJECT: INORGANIC CHEMISTRY-I; PAPER CODE - 09040101)

**Time: 03:00 Hrs.**            **Max Mark: 60**

**Instructions:**
1. Write your Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with the correct question paper. Complaints in this regards, If any, should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Each Part is Compulsory. Marks are indicated against each question.
4. Draw the diagram wherever required.

## PART-A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

**ATTEMPT ALL QUESTIONS:-**

**Q. 1.** Which of the following is the term used to denote kinetic stability:-    (1)
  a) Unstable      b) Stable      c) Labile      d) Inert

**Q. 2.** Chelate effect is driven by:-    (1)
  a) Gibb's Free Energy    b) Enthalpy      c) Entropy      d) Internal energy

**Q. 3.** In the Irving William series of stability constants, $Cu^{2+}$ is more stable than $Ni^{2+}$ because of:-    (1)
  a) Crystal Field Stabilization Energy      b) Jahn-Teller effect
  c) Electronegativity      d) Charge to size ratio

**Q. 4.** For class 'a' metals, which is the correct order of bonding of ligands:-    (1)
  a) Se>Te>S>O      b) S>Se>Te>S      c) O>>S>Se>Te      d) O<<S<Se<Te

**Q. 5.** Macrocyclic effect is shown by the following ligands:-    (1)
  a) Crown ethers      b) Flouride      c) Carbonyl      d) Ammonia

**Q. 6.** Match the hybridization scheme to the Carbon atom in each molecule. Which pair is incorrect:-    (1)
  a) $sp^3$; $CH_4$      b) $sp^3$; $CH_2Cl_2$      c) $sp^2$; $CO_2$      d) $sp^2$; $H_2CO$

**Q. 7.** Apply the VSEPR model to predict a structure of $OF_2$, and then suggest a suitable hybridization scheme for the O atom. Which pair below is the correct combination:-    (1)
  a) Non-linear; $sp3$      b) Linear; $sp$      c) Non-linear; $sp^2$      d) Linear; $sp^2$

**Q. 8.** For $OH^-$ catalysed $S_N1$ conjugate base mechanism of $[Co(NH_3)_5Cl]^{2+}$, the species obtained in the first step of the reaction is/are:-    (1)
  a) $[Co(NH_3)_5(OH)]^{2+} + Cl^-$      b) $[Co(NH_3)_4(NH_2)Cl]^+ + H_2O$
  c) $[Co(NH_3)_4(NH_2)]^{2+} + Cl^-$      d) $[Co(NH_3)_5Cl(OH)]^+$ only

**Q. 9.** Anation is:-    (1)
  a) the substitution of an uncharged ligand by an anionic ligand
  b) the substitution of an uncharged ligand by a cationic ligand
  c) the substitution of an uncharged ligand by another uncharged ligand
  d) the substitution of an anionic ligand by an uncharged ligand

**Q. 10.** Pathway by which octahedral complexes racemize via an intermediate of $D_{3h}$ point group symmetry:-    (1)
  a) a dissociative pathway

b) a pathway involving a 5-coordinate species in which one $ox^?$ ligand is monodentate

c) the Ray-Dutt twist mechanism
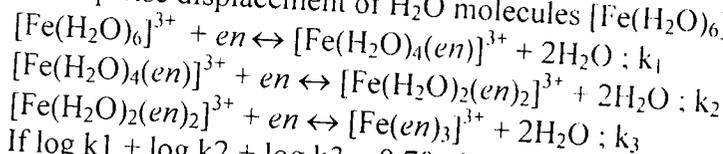
d) the Bailar twist mechanism

**Q. 11.** Among the divalent ions of first row transition metals (Mn, Cu, Ni, Fe), the tendency to form stable complexes (as per Irving-William order) increases as:-

a) $Mn^{II} < Fe^{II} < Ni^{II} < Cu^{II}$

c) $Cu^{II} > Mn^{II} > Fe^{II} > Ni^{II}$

b) $Mn^{II} < Cu^{II} < Ni^{II} < Fe^{II}$    (1)

d) $Ni^{II} < Mn^{II} < Cu^{II} > Fe^{II}$

**Q. 12.** The reactions of $[PtCl_4]^{2-}$ with $NH_3$ (reaction I) and of $[PtCl_4]^2$ with $[NO_2]$ followed by $NH_3$ (reaction II) are ways of preparing:-

a) I: trans-$[PtCl_2(NH_3)_2]$; II: trans-$[PtCl_2(NH_3)(NO_2)]$

b) I: cis-$[PtCl_2(NH_3)_2]$; II: trans-$[PtCl_2(NH_3)(NO_2)]^-$    (1)

c) I: cis-$[PtCl_2(NH_3)_2]$; II: cis-$[PtCl_2(NH_3)(NO_2)]^-$

d) I: trans-$[PtCl_2(NH_3)_2]$; II: cis-$[PtCl_2(NH_3)(NO_2)]^-$

**Q. 13.** The stepwise displacement of $H_2O$ molecules $[Fe(H_2O)_6]^{3+}$ by en is represented as:-

$[Fe(H_2O)_6]^{3+} + en \leftrightarrow [Fe(H_2O)_4(en)]^{3+} + 2H_2O$ ; $k_1$    (1)

$[Fe(H_2O)_4(en)]^{3+} + en \leftrightarrow [Fe(H_2O)_2(en)_2]^{3+} + 2H_2O$ ; $k_2$

$[Fe(H_2O)_2(en)_2]^{3+} + en \leftrightarrow [Fe(en)_3]^{3+} + 2H_2O$ ; $k_3$

If $\log k1 + \log k2 + \log k3 = 9.70$, then overall formation constant of complex entity is:-

a) log 9.70

b) antilog 9.70

c) 9.70

d) Ln 9.70

**Q. 14.** ABABA. represents an arrangement of layers called:-

a) hexagonal closed packing

c) body centred cubic packing

b) cubic closed packing    (1)

d) fluorite close packing

**Q. 15.** Resonance structures for $PF_5$ can be drawn so that each atom obeys the octet rule. Only three resonance structures for $PF_5$ can be drawn in which the P atom obeys the octet rule:-

a) True

b) False    (1)

**Q. 16.** A dissociative mechanism is a 2-step mechanism with the leaving group departing in the second step:-

a) True

b) False    (1)

**Q. 17.** The trans-influence is kinetic in origin, whereas the trans-effect has a thermodynamic origin:-

a) True

b) False    (1)

**Q. 18. Assertion:** The basicity of the following amines increases in the order:-

$NF_3 < NCl_3 < NBr_3 < NI_3$
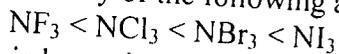
**Reason;** Iodine is larger in size than Flourine    (1)

a) Both A and R are true and R is the correct explanation for A

b) Both A and R are true but R is not the correct explanation for A

c) A is true but R is false

d) A is false but R is true

**Q. 19. Assertion:** In the Irving-William series, $Cu^{II}$ is more stable than $Ni^{II}$:-

**Reason:** $Cu^{II}$ has more Crystal Field Stabilization Energy than $Ni^{II}$    (1)

a) Both A and R are true and R is the correct explanation for A

b) Both A and R are true but R is not the correct explanation for A

c) A is true but R is false
d) A is false but R is true

**Q. 20. Assertion:** Five and six-membered chelate rings give the least stable complexes:-
**Reasoning:** This is because larger rings are less rigid and less entropy is lost in forming them

a) Both A and R are true and R is the correct explanation for A
b) Both A and R are true but R is not the correct explanation for A
c) A is true but R is false
d) A is false but R is true

**Q. 21. Assertion:** In Associative $S_N2$ mechanism for octahedral complexes, a seven-coordinate intermediate is formed in the rate determining step:-
**Reason:** Reaction is bimolecular and the entering group adds to the complex

a) Both A and R are true and R is the correct explanation for A
b) Both A and R are true but R is not the correct explanation for A
c) A is true but R is false
d) A is false but R is true

**Q. 22.** Examples of macrocyclic ligands are as follows:-
I) Crown ethers
II) Ethylene Diamine
III) Porphyrins
IV) Ethylene Diamine Tetraacetic Acid
V) Phthalocyanines

a) I and II      b) I, III and V      c) III and IV      d) I, IV and V

**Q. 23.** Factors which determine $S_N1$ or $S_N2$ in the rate of acid hydrolysis are:-
I) Charge on the complex
II) Number of rings of the chelate
III) Inductive effect of the inert group
IV) Steric effects
V) Number of donor atoms

a) I and V      b) II and IV      c) I, III and IV      d) II and V

**Q. 24.** $K_{diss}$ for $][Cu(NH_3]^{2+}$ is $1.0 * 10^{-12}$. $K_{for}$ is:-
a) $1.0 * 10^3$      b) $2.5 * 10^{41}$      c) $1.0 * 10^{12}$      d) $1.6 * 10^{-35}$

**Q. 25.** Between $[Ni(H_2O)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[Ni(EDTA)]^{2-}$ and $[Ni(NH_3)_6]^{2+}$, which has the largest $K_f$?:-
a) $[Ni(H_2O)_6]^{2+}$      b) $[Ni(en)_3]^{2+}$      c) $[Ni(EDTA)]^{2-}$      d) $[Ni(NH_3)_6]^{2+}$

**Q. 26.** Calculate the ionic radius of a $Cs^+$ ion assuming the cell edge length for CsCl is 0.4123 nm and that the ionic radius of a $Cl^-$ ion is 0.181 nm:-
a) 0.176 nm      b) 0.231 nm      c) 0.358 nm      d) 0.116 nm

**Q. 27.** $K^+$ has the most affinity for the following crown ether:-
a) 12-crown-4      b) dibenzo-18-crown-6
c) diaza-18-crown-6      d) diaza-18-crown-6

**Q. 28.** Above is the graph for a:-



Energy

Reactants

Products

Reaction Progress

(1)

a) Bimolecular reaction
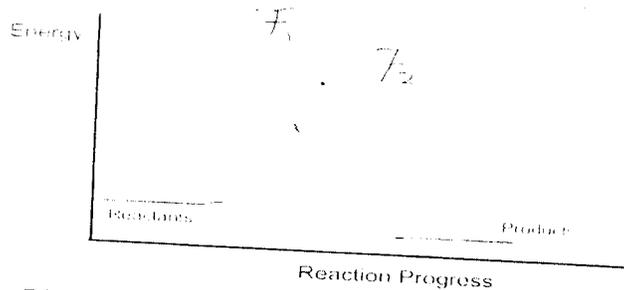
c) Zero order reaction

b) Unimolecular reaction

d) Enzyme catalysis

**Q. 29.**

(1)

| | Column A | | Column B |
|---|---|---|---|
| A | Cumulative constant | 1 | Hard |
| B | Potentiometric method | 2 | Chelate |
| C | Class 'a' metals | 3 | Overall stability constants |
| D | Ethylene Diamine Tetraacetic Acid | 4 | pH |

a) A-1; B-2; C-3; D-4

c) A-2; B-4; C-1; D-3

b) A-3; B-4; C-1; D-2

d) A-4; B-3; C-2; D-1

**Q. 30.**

(1)

| | Column A | | Column B |
|---|---|---|---|
| A | Unimolecular | 1 | Inner sphere |
| B | Tunneling | 2 | Associative |
| C | Bimolecular | 3 | Outer sphere |
| D | Bridge | 4 | Dissociative |

a) A-4; B-3; C-2; D-1

c) A-2; B-3; C-4; D-1

b) A-1; B-2; C-3; D-4

d) A-3; B-4; C-1; D-2

# PART-B (DESCRIPTIVE TYPE)

**SHORT ANSWER TYPE QUESTIONS:-**

**Q.1.** Attempt any **FOUR** of the following:-

(4X3=12)

a) Discuss Job's method for determnation of stability constant of complexes.

b) Define stepwise formation of complexes, stepwise formation constant, overall formation constant and relation between them.

c) Discuss the mechanism of aquation of *cis* and *trans* $[Co(en)_2Cl(OH)]^+$.

d) Give the inner sphere and outer sphere mechanism for electron transfer reaction.

e) Draw and discuss the structure of Corundum.

f) What are heteropoly acids? Compare the heteropoly molybdate with heteropoly tungstate and their physical characteristics

**Q.2.** Attempt any **FIVE** of the following:-

(5X2=10)

a) Why is the bond angle of $PH_3$ less than that of $PF_3$?

b) What are tris chelate complexes? Give two examples.

c) Explain the structure of anti flourite.

d) Explain base hydrolysis

e) Define isopoly acids.

f) Define heteropoly blue.

g) Differentiate between inert and labile complexes.

h) Differentiate between $S_N1$ and $S_N2$ reaction for octahedral complexes.

**Q.3. Attempt any ONE of the following:-** (1×8-8)

a) How does *trans* effect and solvent effect affect the rates of substitution reaction in square planar complexes?

b) What is Base hydrolysis? Discuss three mechanisms by which Base hydrolysis reactions proceed.

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## M.Sc.(CHEMISTRY) – 1$^{ST}$ SEMESTER EXAMINATIONS; DECEMBER - 2017
### (SUB:- INORGANIC CHEMISTRY; PAPER CODE:-09040101)

**TIME: 03:00 Hrs.**                                      **Max Marks:80**

**Instructions:-**
1. Write your Roll No. on the Question Paper.
2. Candidates should ensure that they have been provided with correct question paper. Complaints in this regard, if any should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Attempt **five (05)** questions in all and **Q.1** is compulsory. Students are required to attempt four (04) questions selecting one question form each unit in addition to **Q.1**. Marks are indicated against each question.
4. Draw the diagram wherever required.

**Q.1.** Answer all the following questions:-                                      (8x2=16)
- a) Define bent rule.
- b) Give Irving William order of stability.
- c) What do you mean by labile complexes?
- d) Define acid hydrolysis.
- e) Define trans effect.
- f) Explain two electron transfer reaction.
- g) Explain the structure of β-Crystobalite.
- h) Define isopoly and heteropoly acids.

## UNIT-I

**Q.2.** a) What is chelate effect? Why it is considered as an entropy effect? Predict which of the following pair would give higher order of stability and why?                                      (8)
- I) $[Cu(en)_2]^{+2}$ and $[Cu(NH_3)_4]^{+2}$
- II) $[Cu(acac)_2]^{+2}$ and $[Cu(en)_2]^{+2}$
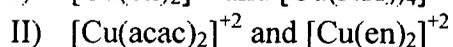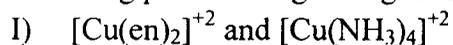
b) Discuss the Bjerrum method for determination of stability constant.                                      (4)

c) Explain how the nature of metal ion affects the stability of complexes.                                      (4)

**Q.3.** a) Define stepwise formation of complexes, stepwise formation constant, overall formation constant and relation between them.                                      (4)

b) Explain:                                      (4x3=12)
- I) dπ-pπ bonding in $SO_2$ and $XeO_2F_2$.
- II) Shapes of $ClO_3^-$ and $SO_4^-$ using VSEPR theory.
- III) Effect of bent rule on bond angle and bond length.
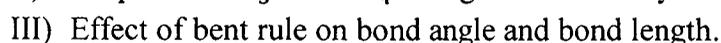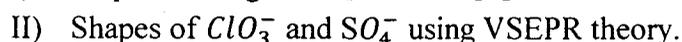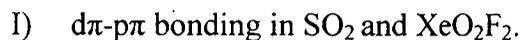
## UNIT-II

**Q.4.** a) How the substitution reaction takes place in octahedral complexes without the rupture of metal-ligand bond? Explain with example.                                      (6)

b) What type of mechanism for acid hydrolysis of octahedral complexes is suggested by the following factors?                                      (10)
- a) Charge on substrate
- b) Strength of metal-leaving group bond
- c) Inductive effect of ligand
- d) Solvation effect

P.T.O.

**Q.5.** a) Discuss acid hydrolysis reaction in six coordinate $[Co(en)_2Cl(NO_2)]^+$ complexes. (6)

b) Explain briefly the $S_N^1$ CB mechanism for base hydrolysis. (10)

## UNIT-III

**Q.6.** a) Discuss electrostatic polarization and $\pi$ bonding theories of trans effect. (8)

b) Explain the mechanism for ligand displacement reaction in square planner complexes. (8)

**Q.7.** a) Discuss inner sphere mechanism of electron exchange reaction. (8)

b) The trans effect has proved many useful in rationalizing known synthetic procedure and in devising new ones. Explain. (4)

c) Explain the factors effecting rate of electron transfer reaction. (4)

## UNIT-IV

**Q.8.** a) How 1:12 (tetrahedral heteroatom) heteropoly anion is prepared? Describe the structure of this acid. (12)

b) Describe heteropoly blue.

**Q.9.** Draw and discuss the crystal structure of: (8x2=16)

a) $ReO_3$

b) $Mn_2O_3$

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# M.SC. (CHEMISTRY) - 1ˢᵀ SEMESTER EXAMINATIONS; DEC.-2017
## (SUBJECT: PHYSICAL CHEMISTRY-I; PAPER CODE – 09040102)

Time: 03:00 Hrs.                                        Max Mark: 60

**Instructions:**
1. Write your Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with the correct question paper. Complaints in this regards, If any, should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Each Part is Compulsory. Marks are indicated against each question.
4. Draw the diagram wherever required.

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## PART-A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

**ATTEMPT ALL QUESTIONS:-**

**Q. 1.** Find all correct statements:-                                           **(1)**
- a) QM describes the state of any particle by a "Wave Function", $\Psi(x, y, z, t)$
- b) Wave function need not be governed by any rule
- c) The Probability density function of a quantum mechanical particle is $\Psi^*(x, y, z, t)\Psi(x, y, z, t)$ where $\Psi(x, y, z, t)$ is the wave function
- d) The probability of finding a particle in the volume between v and v+dv is $\Psi^*(x, y, z, t)\Psi(x, y, z, t)dv$

**Q. 2.** For 1D wave function $\psi(x,t)$ in x-direction, find all correct statements. :-        **(1)**
- a) $\int \psi^*(x,t)\psi(x,t)dx = 1$
- b) $\int \psi^*(x,t)\psi(x,t)dx = 0$
- c) $\int \psi^*(x,t)\psi(x,t)dx = \infty$
- d) $\int \psi^*(x,t)\psi(x,t)dx$ can take any arbitrary value

**Q. 3.** Identifly all correct statements about momentum:-                          **(1)**
- a) Momentum in classical mechanics is used as-is in quantum mechanics
- b) Momentum in quantum mechanics, for one dimention, is treated as an operator $-i\hbar \dfrac{\partial}{\partial x}$
- c) Momentum in quantum mechanics, for one dimention, is treated as an operator $+i\hbar \dfrac{\partial}{\partial x}$
- d) Momentum operator communtes with position operator in quantum mechanics

**Q. 4.** Q4: For each dynamical variable, $\xi$, the way to calculate the expectation value, $<\xi>$, is given by, for one-dimentional motion, is               **(1)**

(A) take wave function $\psi$ and the corresponding operator, $\xi_r$, for that dynamical variable, $\xi$, and calculate
- a) $\int \psi^*(x,t)\xi_r\psi(x,t)dx$
- b) $\int \psi^*(x,t)\psi(x,t)dx$
- c) $\int \psi^*(x,t)\, x\, \psi(x,t)dx$
- d) $\int \psi^*(x,t)x\xi_r\psi(x,t)dx$

**Q. 5.** Identify correct statements:-
  a) If two operators commute, then their physical observables can be known simultaneously
  b) If two operators do not commute, there exists an uncertainty relationship between them that defines the relative simultaneous knowledge of their observables.
  c) For any two operators, physical observables can always be known simultaneously
  d) Uncertainly principle applies even if the operators commute          *(1)

**Q. 6.** Identify all correct answers:-
  a) Time is considered to be an operator in standard quantum mechanics          (1)
  b) Because time is an operator, there exists energy-time uncertainty relationship
  c) Time is not considered to be an operator in standard quantum mechanics
  d) Energy time uncertainty relation reads as $(\Delta T)\,(\Delta E) < \hbar/2$

**Q. 7.** For a particle under an infinite potential well at the boundary in 1D, with a finite boundary of width L and zero potential inside the walls, identify all correct wave functions:-          (1)



Position
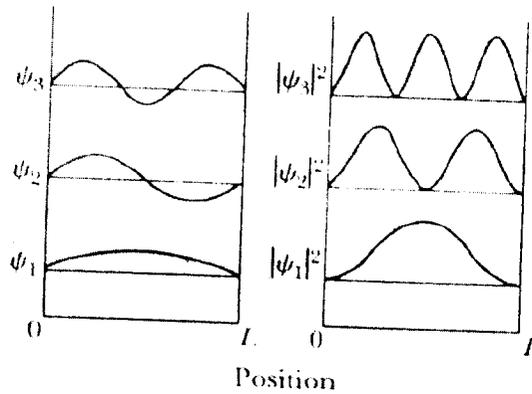
  a) $\Psi_1$, $\Psi_2$ and $\Psi_3$ are all valid wave functions
  b) Only $\Psi_1$ is a valid wave functions
  c) Only $\Psi_2$ is a valid wave functions
  d) Only $\Psi_3$ is a valid wave functions

**Q. 8.** Characteristic of wave is existence of interference and interference. Identify the correct statement:-
  a) Electron beam would show interference/diffraction in Young's double-slit experiment as does light          (1)
  b) Electron is a matter and hence is not expected to have wave property at all
  c) Electron is a matter and its position and momentum can be determined with infinite accuracy as predicted by Newton's laws of motion
  d) In electron diffraction experiment, if we try to determine the position with infinite accuracy, the momentum too would be determined with infinite accuracy and this would violate uncertainty principle

**Q. 9.** Identify the correct statement regarding usage of electron confined in Quantum Well (QW):-          (1)
  a) it may be used for single-electron constructing laser
  b) QM cannot be used in laser
  c) QW is more suitable for infrared laser than UV laser
  d) QW cannot describe motion of electron

**Q. 10.** According to second law of thermodynamics, the entropy of an isolated system:-
  a) remain constant          (1)
  c) Increases          b) decreases
  d) either remain constant or increases

**Q. 11.** The partial molar quantities are:- **(1)**
   a) extensive properties and depend on the size of the system
   b) intensive properties and depends on the size of the system
   c) intensive properties and does not depends on the size of the system
   d) extensive properties and does not depends on the size of the system

**Q. 12.** Efficiency of a reversible engine working between given source and sink is:- **(1)**
   a) 100%
   b) maximum
   c) Minimum
   d) depends on the nature of working substance

**Q. 13.** The quantity k in a rate law expression:- **(1)**
   a) Is independent of concentration
   b) Is called the Arrhenius constant
   c) Is dimensionless
   d) Is independent of the temperature

**Q. 14.** Which concentration plot is linear for a first-order equation? (A is one of the reactants):- **(1)**
   a) [A] versus time
   b) Square root of [A] versus time
   c) ln [A] versus time
   d) $[A]^2$ versus time

**Q. 15.** In a lab, each of the following factors will vary to affect reaction rate except:- **(1)**
   a) Catalyst used
   b) Concentration of reactants
   c) Identity of reactants
   d) Oxygen availability

**Q. 16.** The Deybe-Hueckel equation provides a means to estimate the activity coefficients of single ions in solution, but requires knowledge of:- **(1)**
   a) The ionic strength of the solution and the hydrated radius of the ion of interest
   b) Sizes of the hydrated ionic species
   c) Which ions most influence the total ionic strength and charges on these ions
   d) Ionic strength of the solution, size of the hydrated ion for which the activity coefficient is being calculated and its charge

**Q. 17.** Which of the followings are state functions:- **(1)**
   a) Work done
   b) Heat absorbed
   c) Internal energy
   d) Entropy

**Q. 18.** The effect that tends to retard the mobilities of ions in solution is:- **(1)**
   a) Asymmetry effect
   b) Relaxation effect
   c) Electrophoretic effect
   d) All of these

**Q. 19.** Spontaneous change in a process is reversible:- **(1)**
   a) True
   b) False

**Q. 20.** When equilibrium state is reached, the internal energy of a thermo dynamical system become minimum:- **(1)**
   a) True
   b) False

**Q. 21.** An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to increase in ionic mobility of ions:- **(1)**
   a) True
   b) False

**Q. 22.** A+B+C → Product, is a bimolecular reaction:- **(1)**
   a) True
   b) False

**Q. 23.** **Assertion:** First law of thermodynamics states that all forms of energy change in to one another and also extent of convertibility of one form of energy into other. **(1)**

Reason: because this law predicts that whether a particular reaction can occur, and if it occurs, then to what extent

a) Both A and R are true and R is the correct explanation for A
b) Both A and R are true but R is not the correct explanation for A
c) A is true but R is false
d) A is false but R is true

Q. 24. **Assertion:** Equivalent conductance of weak electrolyte increases on dilution. (1)
**Reason:** On dilution degree of ionization increases.

a) Both A and R are true and R is the correct explanation for A
b) Both A and R are true but R is not the correct explanation for A
c) A is true but R is false
d) A is false but R is true

Q. 25. **Assertion:** Corrosion of Iron is known as rusting. (1)
**Reason:** Corrosion of Iron occurs in the presence of air and water.

a) Both A and R are true and R is the correct explanation for A
b) Both A and R are true but R is not the correct explanation for A
c) A is true but R is false
d) A is false but R is true

Q. 26. The degree of dissociation of an electrolyte depends upon:- (1)
a) Nature of solute
b) Nature of solvent
c) Concentration of solute
d) All of these

Q. 27. The first-order rate constant for the decomposition of $N_2O_5$ to $NO_2$ at 70°C is $6.82 \times 10^{-3} s^{-1}$. Suppose we start with 0.300 mol of $N_2O_5(g)$ in a 0.500 L container. How many moles of $N_2O_5$ will remain after 1.5 min:- (1)
a) 0.081 mol
b) 0.555 mole
c) 0.162 mol
d) 0.340 mol

Q. 28. Match the following:- (1)
i) First Order
ii) Second Order
iii) Third Order

(A) rate = k [A] [B]$^2$
(B) rate = k [A]
(C) rate = k [A]$^2$

a) (i)-B, (ii)-C , (iii)-A
b) (i)-C, (ii)-B , (iii)-A
c) (i)-A, (ii)-C , (iii)-B
d) (i)-B, (ii)-A, (iii) C

Q. 29. Which of the following expression holds good for a weak electrolyte ($\alpha$ is the degree of dissociation):- (1)
a) $K_c = \alpha/V$
b) $K_c = \alpha^2/V$
c) $K_c = \alpha/V^2$
d) $K_c = \alpha^2/V^2$

Q. 30. Which of the following statements is true:- (1)
a) Ostwald's dilution law holds good only for strong electrolytes and fails completely when applied to weak electrolytes
b) Ostwald's dilution law holds good only for weak electrolytes and fails completely when applied to strong electrolytes
c) Ostwald's dilution law holds good for both weak and strong electrolytes
d) Ostwald's dilution law does not hold good for both weak and strong electrolytes

# PART-B (DESCRIPTIVE TYPE)

**Q.1. Attempt any FOUR of the following:-** (4X3=12)

a) According to Quantum Mechanics, the position and momentum of atomic-scale particle cannot be determined with infinite accuracy. Elaborate the restriction.

b) If electron can be described as a wave, mention one experiment with explanation that would unequivocally establish that nature.

c) What are the limitations of first law of thermodynamics? How second law overcome these?

d) Discuss kinetic salt effects.

e) What are pseudo and true unimolecular reactions. Explain with examples.

f) Briefly discuss Deybe-Hückel theory of activity coefficients of strong electrolytes

**Q.2. Attempt any FIVE of the following:-** (5X2=10)

a) Uncertainty principle is relevant irrespective of whether two operators commute or not. i.e., order of operation matters or not. Validate this statement with example.

b) Why do we insist on Hermitian operators in Quantum Mechanics? Please explain.

c) How is entropy related to (1) thermo dynamical probability (ii) unavailable energy.

d) Write the conditions of spontaneity and equilibrium in terms of Gibbs free energy change

e) A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion?

f) Give the difference between order and molecularity of a reaction.

g) Explain relaxation effect.

h) Differentiate between Deybe length and Bjerrum length.

**Q.3. Attempt any ONE of the following:-** (1X8=8)

a) Write down Schroedinger equation for a particle in dimensional box (potential well) and derive the energy eigenvalues and the eigenfunctions.

b) Develop the concept of entropy. How the entropy changes with temperature.
   i) at constant pressure
   ii) at constant volume

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## M.Sc.(CHEMISTRY) – 1ST SEMESTER EXAMINATIONS; DECEMBER - 2017
## (SUB:- PHYSICAL CHEMISTRY-I; PAPER CODE:-09040102)

**TIME: 03:00 Hrs.**                                 **Max Marks:80**

**Instructions:-**
1. Write your Roll No. on the Question Paper.
2. Candidates should ensure that they have been provided with correct question paper. Complaints in this regard, if any should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Attempt **five (05)** questions in all and **Q.1** is compulsory. Students are required to attempt four (04) questions selecting one question form each unit in addition to **Q.1**. Marks are indicated against each question.
4. Draw the diagram wherever required.

**Q.1.** Answer all the following questions:-                               (8x2=16)

     a)    Write Schrodinger wave equation for a practical of mass m moving in a potential field $V(x)$.

     b)    Draw a figure representing spherical coordinate system and specify a point in r, $\theta$ and $\Phi$.

     c)    Write first law & second of thermodynamics.

     d)    One mole of an ideal gas expand against a constant external pressure of 1 atm from a value of $10dm^3$ to $30dm^3$. Calculate the work done by the gas.

     e)    Half life time of first order reaction is 30 min. How long it will take to complete 75% of the reaction?

     f)    Give unit of half-life for first and second order reaction.

     g)    What is unit of Debye Huckel reciprocal length in SI unit?

     h)    Write expression for Debye Huckel reciprocal length.

## UNIT-I

**Q.2.** Set up and solve the Schrodinger wave equation for (a) one dimensional box and (b) hydrogen atom.                               (16)

**Q.3.** Show that for a particle in a one dimensional box the wave functions $\psi_1$ and $\psi_2$ are orthogonal, given that $\psi_1 = \sqrt{(2/a)} \, Sin(\pi x/a)$ and $\psi_2 = \sqrt{(2/a)} Sin(2\pi x/a)$, where $a$ is the width of the box and $0 < x < a$.             (16)

## UNIT-II

**Q.4.** Derive the expressions for entropy changes in reversible and irreversible processes. Also give the effect of temperature, pressure and volume on entropy change.          (16)

**Q.5.** The free energy change ($\Delta G$) involving a process at 298.15K and 308.15K are -33. 1 and -28.0 kj/mol, respectively. Calculate the heat of reaction ($\Delta H$) at 303.15K.          (16)

**P.T.O.**

## UNIT-III

**Q.6.** Explain the salient feature of the collision theory and discuss the significance of the steric factor.

(16)

**Q.7.** For the first order reversible reaction $A \underset{K_{-1}}{\overset{k1}{\rightleftharpoons}} B$, prove that

$$k_1 + k_{-1} = \frac{1}{t} \ln\left(\frac{x_e}{x_e - x}\right)$$

(16)

## UNIT-IV

**Q.8.** Derive Debye-Huckel-Onsager equation for strong electrolytes.

(16)

**Q.9.** Write Debye-Huckel-Onsager conductance equation and discuss it for aqueous electrolytes.

(16)

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## M.Sc. (CHEMISTRY) - 1ˢᵀ SEMESTER EXAMINATIONS; DECEMBER-2017
## (SUBJECT: ORGANIC CHEMISTRY-I; PAPER CODE – 9040103)

Time: 03:00 Hrs.                                                     Max Mark: 60

**Instructions:**

1. Write your Roll No. on the Question Paper.
2. Candidate should ensure that they have been provided with the correct question paper. Complaints in this regards. If any, should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Each Part is Compulsory. Marks are indicated against each question.
4. Draw the diagram wherever required.

### PART-A (OBJECTIVE TYPE QUESTIONS OMR SHEETS)

**ATTEMPT ALL QUESTIONS:-**

**Single Response Questions:-**

**Q. 1.** Which of the following pairs of compounds are tautomers:-                              (1)
a) Propanol and propanone
b) 1-Propanol and 2-propanol
c) Ethanol and vinyl alcohol
d) Vinyl alcohol and ethanal

**Q. 2.** Larger the number of hyper conjugation structures, the stability of free radicals will:-   (1)
a) Increase
b) Decrease
c) Remain same
d) None of the mentioned.

**Q. 3.** Identify the incorrect statement regarding aromaticity:-                                (1)
a) It is the extra stability possessed by a molecule
b) p-orbitals must be planar and overlap
c) Cyclic delocalization takes place
d) It does not follow Huckel's rule

**Q. 4.** Which of the following is not aromatic?:-                                              (1)
a) Napthalene
b) Cyclooctatetraene
c) Cyclopenta dienylanion
d) Tropylium cation

**Q. 5.** Stability of $CH_2=CH_2-CH_2^+$ explained by:-                                         (1)
a) Inductive effect
b) electromeric effect
c) resonance
d) polar effect

**Q. 6.** Which of the following compound is not chiral:-                                        (1)
a) 1-chloro pentane
b) 2- chloro pentane
c) lactic acid
d) glyceraldehyde

**Q. 7.** Which of the following will show geometrical isomerism?:-                               (1)
a) 1-Butene
b) 2- Butene
c) ethane
d) propane

**Q. 8.** The number of optically active isomers of tartaric acid is:-                            (1)
a) 2
b) 3
c) 4
d) 5

**Q. 9.** Hexane and 3-methylpentane are examples of:-                                           (1)
a) Enantiomers
b) stereoisomers
c) diastereomers
d) constitutional isomers

**Q. 10.** Meso tartaric acid is optically inactive due to the presence of:-                      (1)
a) molecular symmetry
b) molecular asymmetry
c) external compensation
d) two asymmetric carbon atoms

**Q. 11.** Meso tartaric acid and d- tartaric acid are:                                          (1)
a) Position isomers
b) racemic mixture
c) enantiomers
d) diastereomers

**Q. 12.** Among the following compounds one which exhibits optical activity is:-                  (1)
a) 1-propanol
b) 2- propanol
c) 1- butanol
d) 2- butanol

**Q. 13.** Which is a meso compound?:-                                                           (1)
a) (2R,3R)-2,3-Dibromobutane
b) (2R,3S)-2,3-Dibromopentane
c) (2R,4R)-2,4-Dibromopentane
d) (2R,4S)-2,4-Dibromopentane

P.T.O.

**Q. 14.** Which one of the following can exist in optically active forms?:
  a) cis-1,3-Dichlorocyclohexane    b) trans-1,3-Dichlorocyclohexane
  b) cis-1,4-Dichlorocyclohexane    d) trans-1,4-Dichlorocyclohexane                                                          (1)

**Q. 15.** Which of the following is an example of optically active compound without chiral center?:                           (1)
  a) Tartaric acid        b) lactic acid        c) glyceraldehyde        d) substituted Allene

**Q. 16.** How many optically active stereo isomers are possible for butane 2,3-diol?:-                                        (1)
  a) 1                    b) 2                  c) 3                     d) 4

**Q. 17.** Mutarotation is shown by?:-                                                                                         (1)
  a) sucrose              b) starch             c) cellulose             d) fructose

**Q. 18.** Benzyne can give which of the following reactions?:-                                                                (1)
  a) Diels alder addition                       b) Ene reaction
  c) 1,3 dipolar cyclo addition                 d) All of these

**Q. 19.** In which reaction reaction intermediate is carnanion?:-                                                            (1)
  a) Reformatshy reaction                       b) Aldol condensation
  c) Pinacol – pinacolone rearrangement         d) All of these

**Q. 20.** Elimination reaction generally occurs with the formation of:-                                                      (1)
  a) One sigma bond                             b) one pi bond
  c) one sigma and one pi bond                  d) none of these

**Q. 21.** Dehydration of alcohols involves:-                                                                                 (1)
  a) Free radical         b) carbocation        c) carbanion             d) carbene

**Q. 22.** The stability of given carbocation in decreasing order is:-                                                         (1)
  1. $CH_2=CH_2-CH_2^+$              2. $C_6H_5-CH_2^+$
  3. $C_6H_5-CH^+-C_6H_5$           4. $CH_3^+$
  a) 3>4>1>2              b) 1>2>3>4            c) 3>2>4>1               d) 3>2>1>4

**Q. 23.** Arrange the following species in decreasing stability:-                                                            (1)
  1. Benzene                         2.Cyclopropyl anion
  3. Cyclopenta dienyl anion         4.cyclopropane
  a) 1>3>2>4             b) 2>3>4>1            c) 3>2>4>1               d) 3>2>1>4

**Q. 24.** Disaccharides ($C_{12}H_{22}O_{11}$) are also called as:-                                                          (1)
  a) simple sugars        b) polymer sugar      c) complex sugar         d) compound sugar

**Q. 25.** Milk sugar is made from:-                                                                                          (1)
  a) maltose and fructose                       b) sucrose and fructose
  c) glucose and fructose                       d) glucose and galactose

**Q. 26.** Lactose on hydrolysis gives:-                                                                                      (1)
  a) 2 moles of glucose                         b) 2 moles of galactose
  c) Glucose + galactose                        d) Glucose+Fructose

**Q. 27.** Which of the following is an example of azo dye?:-                                                                  (1)
  a) Congo red            b) malachite green    c) martius yellow        d) indigo

**Q. 28.** The basic dye among the following is:-                                                                             (1)
  a) Alizarin             b) aniline yellow     c) congored              d) indigo
**Q. 29.** Which one is an example of vat dye:-                                                                               (1)
  a) Congo red            b) alizarin           c) malachite green       d) indigo

**Q. 30.** Diazocoupling is useful to prepare some:-                                                                          (1)
  a) Vitamins             b) Proteins           c) Pesticides            d) dyes

Q.1.    Attempt any <u>one of</u> the following:-                                    (1x8 8)

    a)    Briefly explain the following

        (i)    perturbation molecular orbital theory

        (ii)    Catenanes

    b)    (i)    Explain with suitable examples, R-S system of configuration of optical isomers?

        (ii)    Explain the structural elucidation of alizarin?

Q.2.    Attempt any <u>four of</u> the following :-                                    (4x3 12)

    a)    Distinguish between absolute and relative configuration?

    b)    Write explanatory notes on stereochemistry of biphenyls?

    c)    Write a note on substitution reactions?

    d)    How carbenes are generated? Comment on the stability of singlet and triplet carbenes?

    e)    Explain the synthesis of sucrose?

    f)    Explain the structural elucidation of Indigo Blue?

Q.3.    Attempt any <u>five of</u> the following :-                                    (5x2=10)

    a)    What is the difference between anomer and tautomer?

    b)    Write the structure of $\beta$–Cyclo dextrin? Give one of its applications?

    c)    What are the conditions of a molecule to be optically active?

    d)    Write the two examples of optically active compounds without chiral centers?

    e)    What is Curtin-Hammett principle?

    f)    How carbenes are generated?

    g)    Give any two examples of indigo dyes?

    h)    Give any two examples of deoxy sugars?

**\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\***

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Sr. No: --------------------          Roll No_____

## M. Sc. (Chemistry) – 1<sup>ST</sup> SEMESTER EXAMINATION; DECEMBER - 2017
### [SUB: - ORGANIC CHEMISTRY-I; PAPER CODE: 09040103]

**Time: 3 Hrs.**                                                    **Max. Marks: 80**

**Instructions:-**
1. Write your Roll No. on the Question paper.
2. Candidates should ensure that they have been provided correct question paper. Complaints in this regard, if any, should be made within 15 minutes of the commencement of the exam. No complaint(s) will be entertained thereafter.
3. Attempt Five (5) Questions in all, Question No. 1 is compulsory. Attempt other 4 questions selecting one question from each unit. Marks are indicated against each question paper
4. Draw diagram wherever required.

**Q1.** Answer all the following questions :-                      (2X8=16)

1. What are alternate and non-alternate hydrocarbons?
2. What are anti-aromatic compounds? Give two examples.
3. Define prochirality with two examples.
4. Define epimer and anomer.
5. Draw potential energy diagram for a three step exothermic reaction with third step as rate determining.
6. What is Hammond's postulate?
7. Sketch the structure of starch.
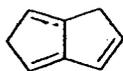8. What are the structure two heterocyclic dyes?

### UNIT-I

**Q2.** (a) Identify the following compound as aromatic, antiaromatic, non aromatic and why? Explain with proper definition.                      (8)
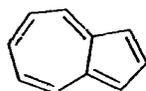


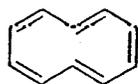I         II         III      IV      V

(b) Write a short note on crown ether.                      (8)
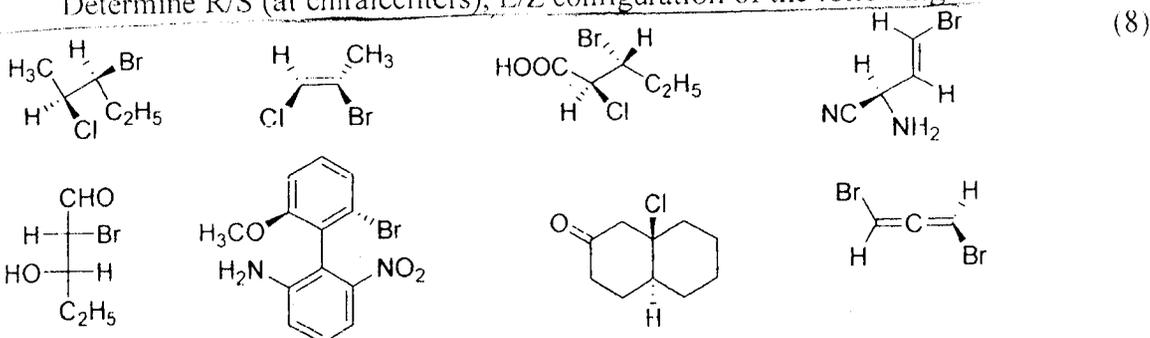
**Q3.** (a) Define the following term with examples.                      (8)
1. Tautomerism.
2. Resonance.
3. Hyperconjugation.

(b) Write a short note on PMO approach.                      (8)

## UNIT-II

**Q4.** (a) Identify which of the following compounds will show optical activity? Determine R/S (at chiralcenters), E/Z configuration of the following **(8)**



(b) What do you understand by Axial and planar chirality? Give examples of each. **(8)**

**Q5.** (a) Define the following term with examples: **(8)**
1. Optical purity
2. Enantiotopic atoms
3. Diastereotopic atoms.

(b) Write a short note on asymmetric synthesis. **(8)**

## UNIT-III

**Q6.** (a) Giving suitable examples, describe the role of stereochemical evidences and Isotopic labeling in determining the mechanism of a reaction. **(8)**

(b) Discuss the carbene their type and difference? Explain the difference on the basis of structure reactivity and reaction specificity if any. **(8)**

**Q7.** (a) What is Hammett equation? Derive it and show that it represents a linear free energy relationship. **(8)**

(b) By giving suitable examples describe the thermodynamic and kinetic control of the reaction. **(5)**

(c) Discuss the factors affecting the stability of $t$-butyl, benzyl and allyl carbocation. **(3)**

## UNIT-IV

**Q8.** (a) Explain the anomeric effect by taking the example of glucose. **(5)**

(b) How will you determine the structure of lactose and Sucrose? **(8)**

(c) What are amino sugars? Give three examples. **(3)**

**Q9.** (a) Write a brief note on the interaction between dyes and fibers. **(6)**

(b) How will you elucidate the structure of indigo? **(10)**

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