5 SEM TDC CHM M 1 (N/O)

2018

(November)

CHEMISTRY

(Major)

Course : 501

(Physical Chemistry—II)

(New Course)

Full Marks : 48
Pass Marks : 14

Time : 2 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer of the following : 1×5=5

(a) For the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\frac{d[NH_3]}{dt} = 4\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$. The rate of decomposition of N_2 is

(i) $6\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

(ii) $8\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

(iii) $2\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

(iv) $10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

(b) Which of the following 0·01 m aqueous solutions will have the lowest freezing point?

(i) KNO_3

(ii) $Al(NO_3)_3$

(iii) $C_6H_{12}O_6$

(iv) $Ba(NO_3)_2$

(c) The exothermic formation of ClF_3 is represented by the reaction

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \quad \Delta_r H = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?

(i) Increasing the temperature

(ii) Removing Cl_2

(iii) Increasing volume of the container

(iv) Adding F_2

(d) Adsorption is accompanied by

(i) decrease in enthalpy and increase in entropy

(ii) increase in enthalpy and increase in entropy

(iii) decrease in enthalpy and decrease in entropy

(iv) increase in enthalpy and decrease in entropy

(e) The gold numbers of A, B, C and D are 0·04, 0·002, 10 and 25 respectively. The protecting powers of A, B, C and D are in the order

(i) $A > B > C > D$

(ii) $B > A > C > D$

(iii) $D > C > B > A$

(iv) $C > A > B > D$

2. Answer any *five* questions of the following : 2×5=10

(a) Show that a first-order reaction can be studied even when the initial concentration of the reactant is unknown.

(b) A solution contains 6 g urea and 18 g glucose in 1000 cc of water at 27 °C. Calculate the osmotic pressure of the solution.

(c) Show that

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\, n_1,\, n_2, \cdots} = \overline{V}_i$$

(d) Heat of adsorption is greater for chemisorption than physisorption. Why?

(e) State and explain Hardy-Schulze rule.

(f) Describe how the activation energy of a reaction may be determined.

(g) What is fugacity? Write its physical significance.

UNIT—I

3. Answer any *two* questions of the following : 6×2=12

(a) Using a suitable mechanism for the reaction $H_2 + Br_2 \rightarrow 2HBr$; and assuming steady-state approximation for H and Br, derive the following rate expression for the formation of HBr

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k' \frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}$$

where k and k' are constants. 6

(b) (i) Show that for a first-order reaction, the time required for 99·9% completion of the reaction is 10 times that required for 50% completion. 2

(ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction. 2

(iii) Give one example of pseudo-unimolecular reaction. 1

(iv) What is steady-state approximation? 1

(c) The following mechanism has been suggested for the decomposition of O_3 :

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the overall reaction is

$$-\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$$

What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation? 5+1=6

UNIT—II

4. Answer any *one* question of the following : 5

(a) (i) State Nernst distribution law. How is the law modified when the solute undergoes association in one of the solvents? 1+3=4

(ii) State Henry's law. 1

(b) Explain the term 'molal elevation constant'. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression utilized for determining molar mass of non-volatile solute? 1+3+1=5

UNIT—III

5. Answer any *two* questions of the following : 3½×2=7

(a) With the help of Le Chatelier's principle, work out the condition which would favour the formation of $SO_3(g)$ in the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad \Delta_r H = -189{\cdot}4 \text{ kJ}$$ 3½

(b) Explain the term 'chemical potential'. Derive Gibbs-Duhem equation for two-component system. 1+2½=3½

(c) Deduce the relationship between $\Delta G°$ and K_c of a reversible reaction. 3½

UNIT—IV

6. Answer any *one* question of the following : 4

(a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. 3+1=4

(b) (i) Write four differences between physical adsorption and chemical adsorption. 2

(ii) Give reason why a finely divided substance is more effective as an adsorbent. 2

UNIT—V

7. Answer any *one* question of the following : 5

(a) *(i)* Distinguish between peptization and coagulation of colloids. 2

(ii) Explain why lyophilic sols are more stable than lyophobic sols. 2

(iii) Define zeta potential. 1

(b) Write short notes on the following : $2\frac{1}{2} \times 2 = 5$

(i) Protective action of lyophilic colloid

(ii) Donnan membrane equilibria

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer of the following : 1×5=5

(a) For the reaction, $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$; $\frac{d[NH_3]}{dt} = 4\times10^{-4}\ mol\,dm^{-3}\,s^{-1}$. The rate of decomposition of N_2 is

(i) 6×10^{-4} mol dm^{-3} s^{-1}

(ii) 8×10^{-4} mol dm^{-3} s^{-1}

(iii) 2×10^{-4} mol dm^{-3} s^{-1}

(iv) 10^{-4} mol dm^{-3} s^{-1}

(b) Which of the following 0·01 m aqueous solutions will have the lowest freezing point?

(i) KNO_3

(ii) $Al(NO_3)_3$

(iii) $C_6H_{12}O_6$

(iv) $Ba(NO_3)_2$

(c) A buffer solution is prepared by mixing equal concentration of acid (ionization constant K_a) and a salt. The pH of buffer is

(i) $pK_a + 7$

(ii) $14 - pK_a$

(iii) pK_a

(iv) $pK_a + 1$

(d) Adsorption is accompanied by

(i) decrease in enthalpy and increase in entropy

(ii) increase in enthalpy and increase in entropy

(iii) decrease in enthalpy and decrease in entropy

(iv) increase in enthalpy and decrease in entropy

(e) The gold numbers of *A*, *B*, *C* and *D* are 0·04, 0·002, 10 and 25 respectively. The protecting powers of *A*, *B*, *C* and *D* are in the order

(i) $A > B > C > D$

(ii) $B > A > C > D$

(iii) $D > C > B > A$

(iv) $C > A > B > D$

(Turn Over)

2. Answer any *five* questions of the following : $2 \times 5 = 10$

(a) Show that half-life period ($t_{1/2}$) of a first-order reaction is independent of the initial concentration of the reactant.

(b) A solution contains 6 g urea and 18 g glucose in 1000 cc of water at 27 °C. Calculate the osmotic pressure.

(c) An aqueous solution of CH_3COONa is basic. Why?

(d) Heat of adsorption is greater for chemisorption than physisorption. Why?

(e) State and explain Hardy-Schulze rule.

(f) Describe how the activation energy of a reaction may be determined.

(g) Distinguish between solubility product and ionic product.

UNIT—I

3. Answer any *two* questions of the following : 6×2=12

(a) Using a suitable mechanism for the reaction $H_2 + Br_2 \rightarrow 2HBr$; and assuming steady-state approximation for H and Br, derive the following rate expression for the formation of HBr :

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k' \frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}$$

where k and k' are constants. 6

(b) (i) Show that for a first-order reaction, the time required for 99·9% completion of the reaction is 10 times that required for 50% completion. 2

(ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction. 2

(iii) Give one example of pseudo-unimolecular reaction. 1

(iv) What is steady-state approximation? 1

(c) The following mechanism has been suggested for the decomposition of O_3 :

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the overall reaction is

$$-\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$$

What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation? 5+1=6

UNIT—II

4. Answer any *one* question of the following : 5

(a) (i) State Nernst distribution law. How is the law modified when the solute undergoes association in one of the solvents? 1+3=4

(ii) State Henry's law. 1

(b) Explain the term 'molal elevation constant'. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression utilized for determining molar mass of non-volatile solute? 1+3+1=5

UNIT—III

5. Answer any *two* questions of the following : 3½×2=7

(a) Derive an expression for the pH of an aqueous solution of a salt of strong acid and weak base. 3½

(b) Define ionic product of water. Explain the effect of temperature on ionic product of water. Show that

$$pK_w = pH + pOH$$ 1+1+1½=3½

(c) (i) Define buffer capacity. 1

(ii) Derive Henderson equation for a basic buffer solution. 2½

UNIT—IV

6. Answer any *one* question of the following : 4

(a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm. 3+1=4

(b) *(i)* Write four differences between physical adsorption and chemical adsorption. 2

(ii) Give reason why a finely divided substance is more effective as an adsorbent. 2

UNIT—V

7. Answer any *one* question of the following : 5

(a) *(i)* Distinguish between peptization and coagulation of colloids. 2

(ii) Explain why lyophilic sols are more stable than lyophobic sols. 2

(iii) Define zeta-potential. 1

(b) Write short notes on the following : $2\frac{1}{2}\times 2=5$

(i) Protective action of lyophilic colloid

(ii) Donnan membrane equilibria

★★★

5 SEM TDC CHM M 3 (N/O)

2018

(November)

CHEMISTRY

(Major)

Course : 503

(Inorganic Chemistry—II)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answer from the following : 1×5=5

(a) The oxidation states of metal atoms in halide and oxide clusters have

(i) low formal oxidation states +1, 0, −1

(ii) high formal oxidation states +2 to +3

(iii) low formal oxidation states +3 to +5

(iv) None of the above

(b) Bromocresol is an example of

(i) redox indicator

(ii) neutralization indicator

(iii) metal ion indicator

(iv) adsorption indicator

(c) $Co(CO)_3$ is isolobal with

(i) CH_2^+

(ii) CH_2

(iii) CH

(iv) CH_3

(d) $C_{54}H_{45}ClP_3Rh$ is

(i) Vaska's compound

(ii) Wilkinson's catalyst

(iii) Cupferron

(iv) Zeise's salt

(e) 4-(4-nitrophenylazo) resorcinol is mainly used for determining the presence of

(i) Ca in solution

(ii) Mg in solution

(iii) Na in solution

(iv) Li in solution

2. Answer the following questions : $2\times4=8$

(*a*) Outline the conditions necessary for isolobality of two molecular fragments.

(*b*) Give an example of reaction in which $HCo(CO)_4$ is used as catalyst.

(*c*) Give the classification of metal cluster compounds.

(*d*) Write the preparation of a cobalt nitrosyl compound.

3. Answer any *three* questions : $3\times3=9$

(*a*) Define oxidative addition and reductive elimination reactions with examples. $1\frac{1}{2}+1\frac{1}{2}=3$

(*b*) Draw the reaction path for hydrogenation of olefin with the help of Wilkinson's catalyst.

(*c*) What is 18-electron rule? Examine the 18-electron rule in the following compounds : $1+\frac{1}{2}\times4=3$

(*i*) $Co_2(CO)_8$

(*ii*) $Mn(CO)_6$

(*iii*) $Fe_2(CO)_9$

(*iv*) $Fe(CO)_2\ (\alpha\text{-}C_5H_5)\ (\pi\text{-}C_5H_5)$

(*d*) Discuss the structure and bonding of anion of Zeise's salt.

(*Turn Over*)

4. Answer the following questions : 4×2=8

(a) Explain the structure and bonding of ferrocene. (Give emphasis on orbital diagram, orbital symmetry and energy.) 4

(b) (i) Outline the PSEP theory. 2

(ii) Predict the structures of the following clusters in the light of PSEP theory : 2

(1) $[Fe_4(CO)_{13}]^{2-}$

(2) $[Os_5(CO)_{16}]$

5. Answer any *two* questions : 3×2=6

(a) Outline the synthesis of a low-nuclearity carbonyl cluster. Discuss the structure of the cluster. 1+2=3

(b) What are nitrosyl complexes? Give the preparation of nitrosoferrous sulphate.

(c) Give a common discussion for structure and bonding of metal nitrosyl compound.

6. Answer any *two* questions : 3×2=6

(a) Discuss about the nature and type of indicator used in the titration of—

(i) strong acid and weak base;

(ii) strong acid with strong base.

(b) Define accuracy, precision and mean deviation.

(c) Analysis of a sample of $CaCl_2$ gave the following percentage values for Ca content :

10·08, 10·12, 10·21, 10·16, 10·09

10·14, 10·18, 10·11, 10·14, 10·07

Calculate the standard deviation.

(d) Write a note on adsorption indicator.

7. Discuss the uses of the following reagents in inorganic analysis (any *three*) : 2×3=6

(a) Magneson

(b) 1,10-phenanthroline

(c) 8-hydoxyquinoline

(d) Salicylaldoxime

(e) Dithizone

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Select the correct answer from the following : 1×5=5

(a) The total electron count of a cluster is $12n + 2(n + 1)$. The structure will be

(i) hypo (ii) arachno

(iii) nido (iv) closo

(b) Sodium nitroprusside contains which of the following species?

(i) NO (ii) NO^+

(iii) NO^- (iv) NO^{2-}

(c) Methylene blue is an example of

(i) adsorption indicator

(ii) redox indicator

(iii) acid-base indicator

(iv) metal-ion indicator

(d) Wilkinson's catalyst is

(i) $[HCo(CO)_4]$

(ii) $[RhCl(PPh_3)_3]$

(iii) $[Rh(PPh_3)_3H_2O]Br$

(iv) $[IrCl(CO)(PPh_3)_2]$

(e) $Co(CO)_3$ is isolobal with

(i) CH_2^+ (ii) CH_2

(iii) CH (iv) CH_3

2. Answer the following questions : 2×5=10

(a) Explain oxidative addition reaction with the help of Vaska's compound.

(b) Give a method of preparation of nitroso-ferrous sulphate.

(c) Mention the conditions necessary for isolobality of two molecular fragments.

(*d*) $Fe_2(CO)_9$ contains both bridging and terminal CO. Justify the statement.

(*e*) Define standard deviation and mean deviation.

3. Answer any *three* questions : 3×3=9

(*a*) Discuss the bonding in Zeise's salt in the light of DCD model.

(*b*) Give the reaction path of hydrogenation of olefin with the help of Wilkinson's catalyst.

(*c*) Discuss about the bonding in mono-nuclear metal carbonyls.

(*d*) Give the preparations of ferrocene and Zeise's salt.

4. Answer any *three* questions : 3×3=9

(*a*) Discuss the bonding between NO and the metal atom showing NO as (*i*) 3-electron donor, (*ii*) 2-electron donor and (*iii*) 1-electron donor.

(*b*) What is metal cluster? Discuss about their classification. 1+2=3

(*c*) Outline the PSEP theory.

(*d*) Give one preparation of sodium nitro-prusside. Discuss briefly about its structure.

5. Answer any *three* questions : 3×3=9

(a) What do you mean by an error? How are they classified? 1+2=3

(b) Discuss the choice of indicator in acid-base titrations.

(c) Discuss the structural change in diphenylamine indicator which is used in the titration of Fe^{2+} with potassium dichromate in acidic medium.

(d) Write a short note on adsorption indicator.

6. Discuss the uses of the following reagents in inorganic analysis (any *three*) : 2×3=6

(a) 1-nitroso-2-naphthol

(b) Cupferron

(c) Oxine

(d) Dithizone

(e) Magneson

★★★

Total No. of Printed Pages—16

5 SEM TDC CHM M 5 (N/O)

2 0 1 8

(November)

CHEMISTRY

(Major)

Course : 505

(Organic Chemistry)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answer from the following : $1\times5=5$

(a) Thermal (conrotatory) ring opening of *trans*-3,4-dimethyl cyclobutene gives

(i) *Z,Z*-hexa-2,4-diene

(ii) *E,E*-hexa-2,4-diene

(iii) *E,Z*-hexa-2,4-diene

(iv) *Z,E*-hexa-2,4-diene

(b) The product of the reaction

$$C_6H_{12}O_6\ (\text{glucose}) \xrightarrow[\text{2) } H_3O^+]{\text{1) HCN}} \xrightarrow{P/HI} ?$$

is

(i) D-glucitol

(ii) D-gluconic acid

(iii) *n*-heptanoic acid

(iv) 2-methyl heptanoic acid

(c) α-Terpineol is a

(i) diterpenoid

(ii) monoterpenoid

(iii) sesquiterpenoid

(iv) terpenoid

(d) Artimisinin is

(i) an antimalarial drug

(ii) an antibacterial drug

(iii) a sulpha drug

(iv) an antiseptic

(e) 2-Acetoxy benzoic acid is

(i) antiseptic

(ii) aspirin

(iii) paracetamol

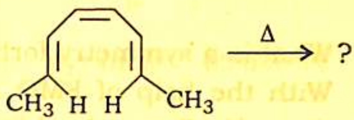
(iv) disinfectant

UNIT—I

Answer *any* **one** question

2. (a) Draw the MO of 1,3-butadiene indicating HOMO in the ground and excited states. 2

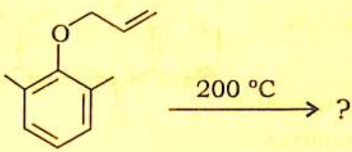
(b) Predict the stereochemical outcome from the following electrocyclic reaction : 1



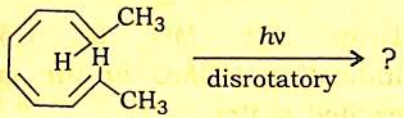
2*E*, 4*Z*, 6*E* octatriene

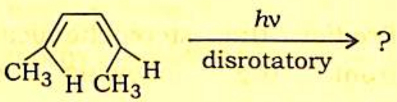
(c) The Diels-Alder reaction is a concerted [4 + 2] process. It proceeds with retention of configuration of both the diene and the dienophile. Explain with suitable examples. 1+1=2

(d) Complete the following reaction and suggest the mechanism : 2



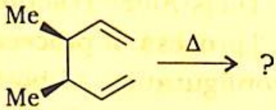
3. *(a)* Predict the stereochemical products obtained in the following electrocyclic reactions : $1 \times 2 = 2$

(i) 

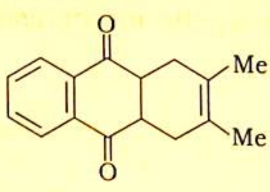
(ii) 

(b) What is a symmetry forbidden reaction? With the help of FMO approach, show that [4+2] cycloaddition is photochemically forbidden. $1+2=3$

(c) Complete the following reaction : 1



(d) What diene and dienophile would you employ to synthesize the following compound? 1



UNIT—II

Answer *any* **one** question

4. (a) Sketch the stable conformational structure of α-D-mannopyranose. 1

(b) How would you methylate the —OH groups of α-D-glucopyranose other than enomeric —OH group? 2

(c) How is the configuration of D-glucose determined? Explain. 3

Or

Discuss the pyranose structure of D-glucose.

(d) Define epimerization. Explain it considering the conversion of D-mannose to D-glucose. 1+2=3

(e) What happens when D-erythrose is subjected to Ruff degradation? 2

5. (a) Convert D-fructose to D-glucose and D-mannose. 2

(b) Complete the following reactions : 3

$$\text{D-Erythrulose} \xrightarrow{\text{HCN}} \text{Epimeric cyanohydrin}$$

$$\xrightarrow[\text{2) } H_2SO_4]{\text{1) } Ba(OH)_2} \begin{array}{c}\text{Epimeric polyhydroxy}\\ \text{carboxylic acids}\end{array} \xrightarrow{\text{HI/red P}} \begin{array}{c}\text{2-Methyl substituted}\\ \text{carboxylic acid}\end{array}$$

(c) How would you establish the ring structure of D-glucose? 4

(d) Glucose and fructose give same osazone. Explain giving reactions. 2

UNIT—III

Answer *any* **one** question

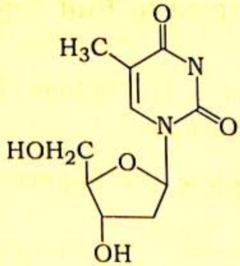
6. (a) Draw the structure of the following (any *one*) : 1

(i) dADP

(ii) ATP

(b) Synthesize one important purine present in both DNA and RNA. 2

(c) Identify the base and monosaccharide used to form the following nucleoside and then name it : 2



(d) What is stop codon? Give example. 2

(e) Write, how the DNA molecule is replicated during cell division. 2

7. *(a)* What are coenzymes? Discuss their functions. 1+1=2

(b) Write in brief about the Watson and Crick double-helix model of DNA. 3

(c) What do you mean by the terms 'transcription' and 'translation'? 2

(d) How are the following compounds related? 2

Adenosine and AMP

UNIT—IV

8. *(a)* Write in brief about the medicinal importance of curcumin. 2

(b) Synthesize chloroquine using the following sequential steps : 1+1+1=3

Step I : AAE to 5-diethyl amino 2-aminopentane

Step II : *m*-Chloroaniline + Oxalyl acetic ester $\rightarrow$ 4,7-dichloroquinoline

Step III : 4,7-dichloroquinoline + 5-diethyl amino, 2-amino pentane $\rightarrow$ Chloroquine

Or

Give the preparation of the following : $1\frac{1}{2}\times2=3$

(i) Sulphaguanidine from acetanilide

(ii) Ibuprofen by using green method

(c) What are antipyretics? Synthesize a drug which is used to bring down body temperature during fever. 2

(d) Write down the laboratory synthesis of chloramphenicol. 2

UNIT—V

9. (a) Synthesize citral starting from acetylene and acetone. 3

Or

Complete the following oxidative degradation reactions of α-terpeniol :

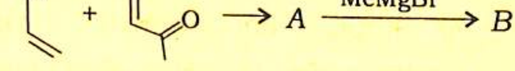
$$\underset{C_{10}}{\alpha\text{-Terpineol}} \xrightarrow[KMnO_4]{1\%\text{ alk.}} \underset{C_{10}}{\text{A trihydroxy compound}} \xrightarrow{CrO_3}$$

$$\underset{C_{10}}{\text{Ketohydroxy acid}} \longrightarrow \underset{C_{10}}{\text{Ketolactone}} \xrightarrow{\text{warm, alk. } KMnO_4}$$

$$\underset{C_8}{\text{Terpenylic acid}} \xrightarrow{KMnO_4} \underset{C_7}{\text{Terebic acid}} + CH_3COOH$$

(b) What are geraniol and nerol? 2

(c) Find out A and B in the following reaction : 2



(Old Course)

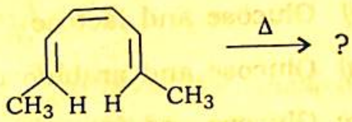
Full Marks : 48

Pass Marks : 19

Time : 3 hours

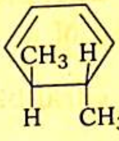
1. Select the correct answer/Answer the following : 1×5=5

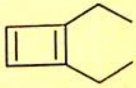
(a) The product obtained during the thermal reaction

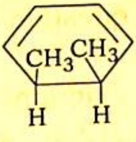


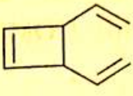
2*E*, 4*Z*, 6*E* octatriene

is

(i) 

(ii) 

(iii) 

(iv) 

(Turn Over)

(b) The pyrimidine bases present in DNA are

(i) cytosine and guanine

(ii) cytosine and thymine

(iii) cytosine and uracil

(iv) cytosine and adenine

(c) Sugars are characterized by the preparation of osazone derivative. Which sugars have identical osazones?

(i) Glucose and lactose

(ii) Glucose and arabinose

(iii) Glucose and fructose

(iv) Glucose and maltose

(d) Draw the structure of chloramphenicol. Give one important use of it. 1

(e) What are citral-a and citral-b? 1

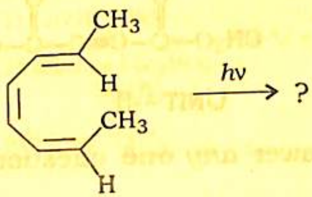
UNIT—I

Answer *any* **one** question

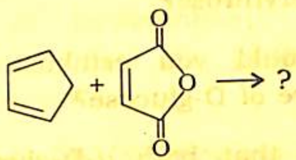
2. *(a)* Draw the π-orbital diagrams for the ground and the excited states of 1,3-butadiene indicating HOMO in each case. 2

(b) What are pericyclic reactions? With the help of FMO approach, show that Diels-Alder reaction is a concerted stereospecific reaction. 1+2=3

(c) Predict the stereochemical products obtained in the following reactions : 1×2=2

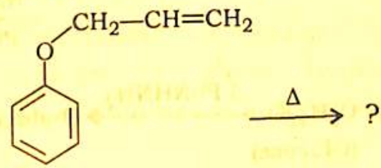
(i) 

2E, 4Z, 6Z octatriene

(ii) 

3. (a) Explain with the help of FMO theory that [1, 5] sigmatropic shift of hydrogen is thermally allowed and occurs in a suprafacial process. 3

(b) Complete the following reaction and suggest the mechanism : 2



(c) Write the products with stereochemistry in the following Diels-Alder reaction : 1×2=2

(i)  + Dimethylmaleate $\longrightarrow$?

(ii) *trans*-, *trans*-2,4-hexadene +

$$CH_3O-\overset{\overset{\displaystyle O}{\|}}{C}-C\equiv C-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \longrightarrow ?$$

UNIT—II

Answer *any* **one** question

4. (a) What are the structures of D-threose and D-erythrose? 1

(b) How would you establish the ring structure of D-glucose? 4

(c) Explain that both α-D-glucopyranose and α-D-allopyranose give the same strontium salt having same specific rotation, by using periodic oxidation. 3

(d) Complete the following reactions : 1½×2=3

(i) $\underset{\text{(Open str)}}{\text{D-fructose}} \xrightarrow{H_2/Ni} ? \xrightarrow[\text{[O]}]{\substack{\text{controlled}\\ HNO_3}} ? \xrightarrow{\Delta} ?$

$\xrightarrow[PH_{3-5}]{\text{Na-Hg}}$ a pair of epimers

(ii) $\underset{\text{(Glucose)}}{C_6H_{12}O_6} \xrightarrow{3\ PhNHNH_2} \text{D-glucosazone} \xrightarrow{CuSO_4}$ Glucosotriazole

5. (a) Convert D-ribose to a pair of epimeric D-aldohexoses by using Fischer-Kiliani synthesis. 2

(b) Determine whether D-fructose is a furanose or a pyranose structure from the following sequential steps : 4

$$C_6H_{12}O_6 \text{ (fructose)} \xrightarrow[\text{2) Excess } Me_2SO_4 \text{ NaOH}]{\text{1) MeOH/HCl}} (A) \xrightarrow{\text{dil HCl}} (B)$$

$$\xrightarrow{\text{dil } HNO_3} (C) \xrightarrow{KMnO_4/H_2SO_4} \delta\text{-lactone} \xrightarrow[HNO_3]{\text{Oxidation}}$$

D-Arabinotrimethyl glutaric acid

(c) What is mutarotation? Why does D-glucose show the phenomenon of mutarotation? 1+2=3

(d) Complete the following reaction : 2

$$\text{An aldohexose} \xrightarrow{Br_2/H_2O} (A) \xrightarrow{CaCO_3} \text{Cal. salt}$$

$$\xrightarrow{H_2O_2/Fe_2(SO_4)_3} (B)$$

UNIT—III

Answer *any* **one** question

6. (a) Synthesize guanine from uric acid. 2

(b) What are complementary bases? Draw the structures to show hydrogen bonding between guanine and cytosine. 1+2=3

(c) Write a short note on coenzyme. 2

(d) Draw the structure of the following nucleotide (any *one*) : 2

(i) Uridine 5′ phosphate (UMP)

(ii) Deoxy guanosine 5′ phosphate (dGMP)

7. (a) Explain the stereospecificity of enzyme with the help of a suitable example. 2

(b) How thymine be synthesized from urea? 2

(c) What do you understand by the term genetic code? Discuss briefly the chemical basis of heredity. 1+2=3

(d) Write the structures and names of purines and pyrimidines present in DNA. 2

UNIT—IV

Answer *any* **one** question

8. (a) Synthesize an antibiotic which is active against certain gram-positive bacteria and gram-negative bacteria. 3

(b) What is tincture of iodine? What is its use? 1

(c) Write the structure of vitamin C. Name the food sources and the deficiency disease caused due to the lack of vitamin C. 1+1+1=3

(d) Synthesize paracetamol from p-nitrophenol. 2

9. (a) Draw the structure with the name of an antimalarial which is active against vivax and falciparum malaria. 2

(b) Give the preparation of the following (any *one*) : 2

(i) Ibuprofen from isobutyl benzene

(ii) Sulphaguanidine

(c) How does sulpha drugs prevent the growth and multiplication of bacteria when administered into host body? 3

(d) Draw the structure of curcumin and write in brief about its medicinal importance. 1+1=2

UNIT—V

Answer *any* **one** question

10. (a) What is isoprene rule? Indicate the isoprene units in the structure of citral. 1+1=2

(b) Complete the following reactions : 1½×2=3

(i) $\text{Geranial} \xrightarrow{\text{alk. } KMnO_4} (A) \xrightarrow{CrO_3} \text{Acetone} + \text{Oxalic acid} + \text{Laevulic acid}$

(*Turn Over*)

(ii) $\text{Isoprene} + \text{MVK} \longrightarrow (A) \xrightarrow[\text{2) } H_3O^+]{\text{1) MeMgBr}}$

An optically active monterpenoid

(c) How will you establish the position of double bonds (α,β and isolated) in citral? 2

11. (a) How would you synthesize citral by using the following sequence of reactions? 2

$$\text{6-Methylhept-5-en-2-one} \xrightarrow[\text{2) } H_3O^+]{\text{1) } I\text{—}CH_2\text{—}COOC_2H_5/Zn} (A)$$

$$\xrightarrow{Ac_2O} \text{Geranic ester} \xrightarrow[(HCO_2)_2Ca]{\text{cal. salt +}} \text{Citral}$$

(b) What happens when—

(i) citral is treated with aqueous Na_2CO_3;

(ii) geraniol is oxidized with $Na_2Cr_2O_7/H_2SO_4$? 1+1=2

(c) Synthesize α-terpineol from *p*-toluic acid. 3

★★★

Total No. of Printed Pages—11

5 SEM TDC CHM M 7 (N/O)

2018

(November)

CHEMISTRY

(Major)

Course : 507

(Symmetry and Quantum Chemistry)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answer from the following : $1 \times 5 = 5$

(a) The wave function which is acceptable in quantum mechanics is

(i) $\psi = x$ (ii) $\psi = x^2$

(iii) $\psi = \sin x$ (iv) $\psi = e^x$

(b) The de Broglie wavelength of an electron moving with $\frac{1}{10}$th of the velocity of light is

(i) $2 \cdot 42 \times 10^{-11}$ m

(ii) $2 \cdot 42 \times 10^{-11}$ cm

(iii) $2 \cdot 42 \times 10^{-10}$ m

(iv) None of the above

(c) Quantum mechanical operator for momentum is

(i) $\frac{h}{2\pi i}\nabla$

(ii) $-\frac{h^2}{8\pi^2 m}\nabla^2$

(iii) $\frac{h}{2\pi i}$

(iv) $\frac{\hbar}{2i}\nabla$

(d) Quantum mechanical operator must be

(i) linear

(ii) Hermitian

(iii) Neither (i) nor (ii)

(iv) Both (i) and (ii)

(e) The point group of $[PtCl_4]^{2-}$ is

(i) D_{4h}

(ii) D_{3h}

(iii) D_{5h}

(iv) C_{4v}

2. Answer any *five* questions from the following : 2×5=10

(a) Taking NH_3 as an example of trigonal pyramid molecule, discuss symmetry operations in C_{3v} point group molecules.

(b) What are the main differences between VBT and MOT?

(c) Show that the function $\psi = \cos ax \cos by \cos cz$ is an eigenfunction of the Laplacian operator. Find the corresponding eigenvalue.

(d) Show that the length of a one-dimensional box is an integral multiple of $\lambda/2$, where λ is the wavelength associated with the particle wave.

(e) Calculate the expectation value of p_x (linear momentum along x direction) for a particle in a one-dimensional box of length a.

(f) What do you understand by the terms 'eigenfunction' and 'eigenvalue'?

UNIT—I

3. Answer any *three* questions from the following : $3\times3=9$

(a) Set up the group multiplication table for C_{2v} point group.

(b) Write down the symmetry elements and point groups of the following : $1\times3=3$

(i) CO_2

(ii) BF_3

(iii) BrF_5

(c) State, without any derivation, the five rules about irreducible representation of a group and their characters by making use of 'great orthogonality theorem'.

(d) Write down the matrix representation for σ operation taking x, y, z as bases.

UNIT—II

Answer any *two* questions : $9\times2=18$

4. (a) (i) The functions given below are defined in the interval $x=-a$ and $x=+a$ as follows :

$$F_1(x) = N_1(a^2 - x^2)$$

$$F_2(x) = N_2 x(a^2 - x^2)$$

Assuming the value of the function to be zero for $x < -a$ and $x > +a$, calculate the values of normalization constants N_1 and N_2. 3+3=6

(ii) Show that the functions $F_1(x)$ and $F_2(x)$ in the above problem are orthogonal. 3

(b) *(i)* Solve Schrödinger's wave equation for a particle moving freely in a three-dimensional cubic box. Find the eigenfunction and energy. 4+1+1=6

(ii) Determine the energy required for a transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ state for an electron in a cubic hole of a crystal with 10^{-8} cm edge-length. 3

(c) *(i)* The distance between the atoms of a diagonal molecule is r and its reduced mass is μ. If its angular momentum is L and moment of inertia is I, then prove that

$$\text{kinetic energy, } T = \frac{L^2}{2\mu I^2}$$ 3

(ii) Calculate the probability density for a 1s-electron at the nucleus of H-atom. Given

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3} \right)^{1/2} e^{-zr/a_0}$$

$$a_0 = 0 \cdot 529 \text{ Å}$$ 3

(iii) Set up Schrödinger's wave equation for a simple harmonic oscillator. "The zero-point energy of a simple harmonic oscillator cannot be zero." Explain. 2+1=3

UNIT—III

5. (a) Taking suitable trial wave function for hydrogen molecule ion, obtain the expressions for the possible energies and the corresponding eigenfunctions. 4

(b) Explain with a diagram, the formation of bonding and anti-bonding molecular orbitals on the basis of LCAO approximation. 2

Or

Draw the MO configuration of NO molecule and predict its magnetic character. 2

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Select the correct answer from the following : 1×5=5

(a) Eigenvalues of a Hermitian operator are

(i) real

(ii) complex

(iii) imaginary

(iv) both real and imaginary

(b) The quantum mechanical operator for kinetic energy is

(i) $-\frac{h^2}{8\pi^2 m}\nabla^2$ *(ii)* $\frac{h}{2\pi i}\nabla$

(iii) $\frac{h}{2\pi i}\cdot\frac{d}{dx}$ *(iv)* V

(c) The wave function ψ satisfies the equation

$$\int_{-\infty}^{+\infty}\psi^{*}\,\psi\,dx = 0$$

The function is said to be

(i) normalized

(ii) diagonal

(iii) orthogonal

(iv) All of the above

(*Turn Over*)

(d) The number of nodes in the radial probability distribution curve of s-orbital of any energy level is equal to

(i) $\frac{n}{2}$ (ii) $n-1$

(iii) $n-2$ (iv) $n-l-1$

(e) The point group of NH_3 is

(i) T_d (ii) D_{2h}

(iii) C_{2v} (iv) C_{3v}

2. Answer any *five* questions from the following : 2×5=10

(a) What do you understand by eigenfunctions and eigenvalues?

(b) Differentiate between linear and non-linear operators with examples.

(c) What are the main differences between VBT and MOT?

(d) Show that e^{-ax^2} (a is a constant) is an eigenfunction of operator $\frac{1}{x} \cdot \frac{d}{dx}$. Find the eigenvalue.

(e) Write a short note on crystallographic point group.

(f) Determine the degree of degeneracy of the energy levels $\frac{14h^2}{8ma^2}$ of a particle in a three-dimensional box.

UNIT—I

3. Answer any *three* questions from the following : 3×3=9

(a) Write the symmetry elements and point groups of the following : 1×3=3

(i) H_2O

(ii) BCl_3

(iii) CO_2

(b) State, without any derivation, the five rules about irreducible representation of a group and their characters by making use of 'great orthogonality theorem'.

(c) Give the reducible representation of character table for C_{2v} point group.

(d) Write down the matrix representation for σ operation taking x, y, z as bases.

UNIT—II

Answer any *two* questions : 9×2=18

4. *(a)* *(i)* Deduce Schrödinger's wave equation on the basis of classical wave concept. 4

(ii) What is photoelectric effect? State two significant experimental observations concerning photoelectric effect. Explain the observations with the help of classical theory or any other theory of light. 1+2+2=5

(b) *(i)* Solve Schrödinger's wave equation for a particle in a one-dimensional box and find its energy. Why is the value $n = 0$ of the quantum number not permitted? 4+1=5

(ii) A particle of mass m is confined in a one-dimensional box of length a. Calculate the probability of finding the particle in the region $0 \le x \le \frac{a}{3}$. What is the limiting probability when $n \to \infty$? 3+1=4

(c) *(i)* Write a short note on radial and angular part of wave function. 3

(ii) Calculate the probability density for a 1s-electron at the nucleus of H-atom. Given

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0}$$

$$a_0 = 0 \cdot 529 \text{ Å}$$ 3

(iii) Set up Schrödinger's wave equation for a simple harmonic oscillator. "The zero point energy of a simple harmonic oscillator cannot be zero." Explain. 2+1=3

UNIT—III

5. (a) Taking suitable trial wave function for hydrogen molecule ion, obtain the expressions for the possible energies and the corresponding eigenfunctions. 4

(b) Draw the MO configuration of NO molecule and predict its magnetic character. 2

Or

Explain why H_2 molecule is more stable than H_2^+ ion. 2

★★★