Total No. of Printed Pages—12

5 SEM TDC CHM M 1 (N/O)

2017

(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 : 1×5=5

(a) The equation for rate constant, is

$$k = Ae^{-E_a/RT}$$

The chemical reaction will proceed more rapidly, if there is a decrease in

(i) k

(ii) A

(iii) T

(iv) E_a

(b) The vapour pressure of a dilute aqueous solution of glucose is 740 mm of mercury at 373 K. The mole fraction of the solute is

(i) $\frac{1}{20}$

(ii) $\frac{1}{38}$

(iii) $\frac{1}{76}$

(iv) $\frac{1}{740}$

(c) The function of alum used for the purification of water is to

(i) coagulate the sol particles

(ii) disperse the sol particles

(iii) emulsify the sol particles

(iv) absorb the sol particles

(d) In gas masks, the poisonous gases are adsorbed by activated charcoal. The activated charcoal acts as

(i) adsorbate

(ii) adsorbent

(iii) catalyst

(iv) All of the above

(e) 0·01 *M* solution each of urea, common salt and sodium sulphate are taken, the ratio of depressions in freezing point of these solutions is

(i) 1 : 1 : 1

(ii) 1 : 2 : 1

(iii) 1 : 2 : 3

(iv) 2 : 2 : 3

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

(a) Describe one method for determining the order of a reaction.

(b) When a gas is adsorbed by a solid sample, then both the enthalpy and entropy of the system decrease. Explain.

(c) State and explain Nernst distribution law.

(d) The rate constant for a reaction of zero order with respect to reactant *A* is 0·0030 mol l^{-1} s^{-1}. How long will it take for the initial concentration of *A* to fall from 0·10 *M* to 0·075 *M*?

(e) Explain what is observed when an electrolyte NaCl is added to hydrated ferric oxide sol.

(f) Describe the cleansing action of soaps on the basis of micelle formation.

(g) What is chemical potential? Mention its significance.

UNIT—I

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

(a) Deduce the integrated rate expression of the following second-order reaction :

$$A + B \longrightarrow \text{products}$$

Prove that when either A or B is taken in excess, then this second-order reaction shows first-order kinetics. 4+2=6

(b) (i) Describe Lindemann's theory of unimolecular gas phase reaction. 5

(ii) Give one example of zero-order reaction. 1

(c) (i) What is steady-state approximation? 1

(ii) For the reaction $2NO + Cl_2 = 2NOCl$, following mechanism has been proposed

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2$$

$$NO + NOCl_2 \xrightarrow{k_2} 2NOCl$$

(Continued)

Show that the overall rate of the reaction is given by $k[NO]^2[Cl_2]$ assuming $k_2[NO] << k_{-1}$. 5

UNIT—II

4. Answer any *one* question : 5

(a) What is solvent extraction? Show that multistep extraction is more economical than single-step extraction. 1+4=5

(b) (i) Discuss how the elevation of boiling point of a solution of non-volatile, non-electrolyte solute is related to the molecular mass of the solute. 3

(ii) Determine the number of mol of $CaCl_2$ ($i = 2 \cdot 47$) dissolved in $2 \cdot 5$ litre of water such that its osmotic pressure is $0 \cdot 75$ atm at 27 °C. 2

UNIT—III

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

(a) State and explain Le Chatelier's principle. 3½

(b) Derive Duhem-Margules equation. 3½

(c) (i) What is fugacity? Write its physical significance. 1+1½=2½

(Turn Over)

(ii) Write the effect of pressure on the following equilibrium : 1

$$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$$

UNIT—IV

6. Answer any *one* question : 4

(a) Write the postulates of Langmuir adsorption isotherm. Also write four important applications of adsorption. 2+2=4

(b) Derive Gibbs' adsorption equation for the adsorption of a solute on the surface of a liquid. 4

UNIT—V

7. Answer any *one* question : 5

(a) (i) What is peptization? Explain with example. 2

(ii) Write the differences between lyophilic sol and lyophobic sol. 3

(b) (i) Describe any one method for preparing a colloidal solution. 2

(ii) What is critical micelle concentration? Mention two properties of the ionic surfactant solution which undergo abrupt change at CMC. 1+1+1=3

(Continued)

(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 : 1×5=5

(a) The equation for rate constant, is

$$k = Ae^{-E_a/RT}$$

The chemical reaction will proceed more rapidly, if there is a decrease in

(i) k

(ii) A

(iii) T

(iv) E_a

(b) An aqueous soltuion of Na_2CO_3 is

(i) basic

(ii) acidic

(iii) neutral

(iv) unpredictable

(c) The function of alum used for the purification of water is to

(i) coagulate the sol particles

(ii) disperse the sol particles

(iii) emulsify the sol particles

(iv) absorb the sol particles

(d) In gas masks, the poisonous gases are adsorbed by activated charcoal. The activated charcoal acts as

(i) adsorbate

(ii) adsorbent

(iii) catalyst

(iv) All of the above

(e) 0·01 *M* solution each of urea, common salt and sodium sulphate are taken, the ratio of depressions in freezing point of these solutions is

(i) 1 : 1 : 1

(ii) 1 : 2 : 1

(iii) 1 : 2 : 3

(iv) 2 : 2 : 3

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

(a) Describe one method for determining the order of a reaction.

(b) When a gas is adsorbed by a solid sample, then both the enthalpy and entropy of the system decrease. Explain.

(c) State and explain Nernst distribution law.

(d) The rate constant for a reaction of zero order with respect to reactant A is 0·0030 mol l^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0·10 M to 0·075 M?

(e) Explain what is observed when an electrolyte NaCl is added to hydrated ferric oxide sol.

(f) Describe the cleansing action of soaps on the basis of micelle formation.

(g) Deduce the relatiohsip between solubility and solubility product of a sparingly soluble salt.

UNIT—I

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

(a) Deduce the integrated rate expression of the following second-order reaction :

$$A + B \longrightarrow \text{products}$$

Prove that when either A or B is taken in excess, then this second-order reaction shows first-order kinetics. 4+2=6

(b) (i) Describe Lindemann's theory of unimolecular gas phase reaction. 5

(ii) Give one example of zero-order reaction. 1

(c) (i) Define order and molecularity of a reaction. Write one difference between these two. 2+1=3

(ii) Describe the effect of temperature on the rate of a reaction. 3

UNIT—II

4. Answer any *one* question : 5

(a) What is solvent extraction? Show that multistep extraction is more economical than single-step extraction. 1+4=5

(b) (i) Discuss how the elevation of boiling point of a solution of non-volatile, non-electrolyte solute is related to the molecular mass of the solute. 3

(ii) Determine the no. of mol of $CaCl_2$ ($i = 2 \cdot 47$) dissolved in $2 \cdot 5$ litre of water such that its osmotic pressure is $0 \cdot 75$ atm at 27 °C. 2

UNIT—III

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

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

(b) *(i)* Distinguish solubility product from ionic product. 1

(ii) 50 ml of $6 \cdot 0 \times 10^{-3}$ *M* $CaCl_2$ is mixed with 30 ml of 0·04 *M* NaF. Will precipitation of CaF_2 occur? K_{sp} for CaF_2 is $4 \cdot 0 \times 10^{-11}$. 2½

(c) *(i)* What are buffer solutions? Classify them giving examples. 1+1=2

(ii) Explain why NH_4Cl should be added to the solution before adding NH_4OH solution for Gr-IIIA precipitation. 1½

UNIT—IV

6. Answer any *one* question : 4

(a) Write the postulates of Langmuir adsorption isotherm. Also write four important applications of adsorption. 2+2=4

(b) Derive Gibbs' adsorption equation for the adsorption of a solute on the surface of a liquid. 4

UNIT—V

7. Answer any *one* question : 5

(a) (i) What is peptization? Explain with example. 2

(ii) Write the differences between lyophilic sol and lyophobic sol. 3

(b) (i) Describe any one method for preparing a colloidal solution. 2

(ii) What is critical micelle concentration? Mention two properties of the ionic surfactant solution which undergo abrupt change at CMC. 1+1+1=3

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5 SEM TDC CHM M 3 (N/O)

2017

(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) $Ni(CO)_2$ is isolobal with

(i) CH_2^+

(ii) CH_2^-

(iii) CH^+

(iv) CH^-

(b) Rhodamine 6G is an example of

(i) acid-base indicator

(ii) metal-ion indicator

(iii) adsorption indicator

(iv) redox indicator

(c) EAN of $[Fe(CO)_2(NO)_2]$ is

(i) 35 (ii) 34

(iii) 38 (iv) 36

(d) The number 0·003040 has ____ significant figures.

(i) three (ii) four

(iii) five (iv) six

(e) Total electron count for the compound $[Fe_4C(CO)_{12}]^{2-}$ is

(i) 62

(ii) 72

(iii) 74

(iv) 86

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

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

(b) What is meant by reductive elimination reaction? Give example.

(c) Explain why two nitrosyl groups can substitute three carbonyl groups from metal carbonyl compounds.

(Continued)

(d) Assuming 18-electron rule is valid, find the number of metal-metal bonds in $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$.

(e) Define standard deviation in quantitative analysis.

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

(a) What is 18-electron rule? How is 18-electron rule helpful in determining the number of metal-metal bonds in metal carbonyl complexes?

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

(c) Explain with example, the procedure for predicting the skeletal structures of low nuclearity carbonyl clusters.

(d) Complete the following reactions :

(i) $Fe(CO)_5 + NO \xrightarrow{95\,^\circ C} ?$

(ii) $[Mn(CO)_5I] + NO \longrightarrow ?$

(iii) $Na_4[Fe(CN)_6] + NO \longrightarrow ?$

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

4. Answer the following questions (any *three*) : 3×3=9

(a) Explain how nitric oxide can form metal complexes as (i) 3-electron donor, (ii) 2-electron donor and (iii) 1-electron donor. Give one example of each.

(b) Give the chemical reactions involved in the preparation of sodium nitroprusside and explain its structure.

(c) Explain the term metal cluster compounds. How are they classified?

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

(i) $Rh_6(CO)_{16}$

(ii) $[Fe_5C(CO)_{15}]$

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

5. Answer the following questions (any *three*) : 3×3=9

(a) Explain the action of diphenyl amine indicator in titrating ferrous ion with potassium dichromate in acidic medium.

(b) Analysis of a sample of ferric oxide gave the following percentage values for the iron content :

7·08, 7·12, 7·21, 7·16, 7·09
7·14, 7·18, 7·11, 7·14, 7·07

Calculate the standard deviation.

(c) Mention the types of errors encountered in quantitative analysis. How can errors be minimized?

(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) 8-hydroxyquinoline

(b) Diphenyl carbazide

(c) Thiourea

(d) Salicylaldoxime

(e) 1-nitroso-2-naphthol

(Old Course)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

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

(a) $[Fe(CO)_3]^-$ is isoelectronic with

(i) $Mn(CO)_5$

(ii) $Cr(CO)_3$

(iii) $Co(CO)_3$

(iv) $Co(CO)_2$

(b) The number 0·007050 has _____ significant figures.

(i) three

(ii) four

(iii) five

(iv) six

(c) Sodium nitroprusside contains which species?

(i) NO (ii) NO^+

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

(d) Patton and Reeder's indicator is an example of

(i) adsorption indicator

(ii) acid-base indicator

(iii) metal-ion indicator

(iv) redox indicator

(e) Vaska's compound is

(i) $[IrCl_3CO(PPh_3)_2]$

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

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

(iv) $[Ir(CO)_4(PPh_3)_2]$

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

(a) Assuming 18-electron rule is valid, find the number of metal-metal bonds in $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$.

(Continued)

(b) What do you mean by oxidative addition reaction? Give an example.

(c) Give a method of preparation of sodium nitroprusside.

(d) Define standard deviation in quantitative analysis.

(e) What are metal clusters? How are they generally classified?

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

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

(b) What is synergic effect? Discuss how this effect is observed in metal carbonyls.

(c) Discuss the structure of ferrocene.

(d) Explain the route of hydroformylation reaction catalysed by $HCo(CO)_4$.

4. Answer the following questions (any *three*) : 3×3=9

(a) Outline the rules for polyhedral skeletal electron pair theory.

(b) In what ways NO can form bond with a metal? Discuss.

(c) Give the preparation and structure of a metal cluster containing three metal atoms.

(d) Complete the following reactions :

(i) $Co_2(CO)_8 + H_2 \xrightarrow[200\,°C]{200\ atm} ?$

(ii) $Na_4[Fe(CN)_6] + NO \longrightarrow ?$

(iii) $Fe_2(CO)_9 \xrightarrow{50\,°C} ?$

5. Answer the following questions (any *three*) : 3×3=9

(a) What are determinate errors? Explain additive and proportional errors.

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

(c) What type of indicator is used in the titration of Fe^{2+} with potassium dichromate in acidic medium?

(d) Write a note on minimisation of errors.

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

(a) 1-nitroso-2-naphthol

(b) Salicylaldoxime

(c) Diphenyl carbazide

(d) Oxine

(e) Thiourea

★★★

Total No. of Printed Pages—15

5 SEM TDC CHM M 5 (N/O)

2017

(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 : 1×5=5

(a) In the ground state, HOMO of 1,3-butadiene is symmetric with respect to

(i) mirror plane (*m*)

(ii) C_2-axis

(iii) both mirror plane and C_2-axis

(iv) None of the above

(b) Epimeric carbohydrates differ through their

(i) functional group

(ii) ring size

(iii) configuration at α-C atom

(iv) None of the above

(c) In the double helix of DNA, guanine of one coil involves pairing with cytosine of the other through

(i) one H bond

(ii) two H bonds

(iii) three H bonds

(iv) Not through H-bond

(d) Chloramphenicol is an example of

(i) broad spectrum antibiotic

(ii) narrow spectrum antibiotic

(iii) polypeptide

(iv) lincomycin

(e) The nature of the —OH group in the α-terpineol is

(i) primary alcohol

(ii) secondary alcohol

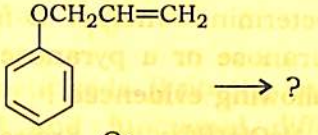
(iii) tertiary alcohol

(iv) aryl alcohol

UNIT—I

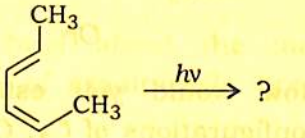
2. *(a)* Draw the molecular orbitals of 1,3-butadiene and indicate which is HOMO and LUMO in the ground state. 2

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



Or

In the following reaction, predict whether conrotatory or disrotatory motion will take place under the mentioned condition against the compound :



(c) With the help of FMO approach, show that [4 + 2] cycloaddition is thermally allowed but photochemically forbidden.

1½+1½=3

UNIT—II

3. *(a)* Draw the conformational structure of β-D-glucopyranose. 1

(b) Convert D-glucose into D-fructose. 2

Or

Write in brief about the mutarotation of D-glucose.

(c) Establish the cyclic structure of D-(+)-glucose. 3

(d) Determine whether D-fructose is in a furanose or a pyranose form from the following evidences : 3

$$\text{D-fructose } C_6H_{12}O_6 \xrightleftharpoons{\text{MeOH/HCl}} A \xrightarrow[\text{NaOH}]{\text{Excess } Me_2SO_4} B \longrightarrow$$

$$\xrightarrow{\text{dil. HCl}} C \xrightarrow{\text{dil. } HNO_3} D \xrightarrow[H_2SO_4]{KMnO_4} \delta\text{-lactose}$$

$$\xrightarrow[HNO_3]{\text{Oxidation}} \text{Arabinotrimethoxy glutaric acid}$$

Or

How would you establish that the configurations of C_3, C_4 and C_5 atoms of D-glucose and D-mannose are the same?

(e) D-glucose reacts with HCN but not with $NaHSO_3$. Explain. 2

UNIT—III

4. *(a)* Distinguish between nucleotide and nucleoside. 2

(b) Synthesize uracil from urea. 2

(Continued)

Or

Discuss briefly the mechanism of enzymatic action.

(c) Explain the stereospecificity of enzyme with the help of a suitable example. Define coenzyme. 2+1=3

Or

Define genetic code. Write the important structural and functional differences between DNA and RNA. 1+2=3

(d) Discuss briefly about the replication of DNA. 2

UNIT—IV

5. *(a)* Write in brief about the medicinal importance of azadirachtin present in neem. 2

(b) Draw the structure of vitamin C and write about its medicinal importance. 2

Or

Synthesize paracetamol from *p*-nitrophenol.

(c) Draw the structure of chloramphenicol and write in brief about its clinical properties. 1+2=3

Or

Write down the synthesis of anti-malarial drug chloroquine. 3

(d) Starting from acetanilide, write down the synthesis of sulphanilamide. 2

Or

Write down the green synthesis of ibuprofen.

UNIT—V

6. *(a)* Explain about special isoprene rule. 2

(b) In citral, one of the double bonds is at α, β-position with respect to aldehydic group. Explain. 2

(c) How will you synthesize citral from 6-methyl-hept-5-en-2-one? 2

Or

How can you synthesize α-terpineol starting from *p*-toluic acid?

(d) Write down the structure of *cis*- and *trans*-isomer of citral. 1

Total No. of Printed Pages—12

5 SEM TDC CHM M 7 (N/O)

2017

(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 : 1×5=5

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

(b) A particle is moving in a 1-D box, N_n is the number of nodes in a state with quantum number n. The ratio of $N_{n=2} : N_{n=1}$ has a value

(i) 1

(ii) 2

(iii) 3

(iv) ∞

(c) The energy required to excite (to first excited state) a particle of mass m confined in a length l is

(i) $\frac{3h^2}{8ml^2}$

(ii) $\frac{h^2}{8ml^2}$

(iii) 0

(iv) h^2

(d) The eigenvalue of the function $\psi = 8e^{4x}$ for the operator $\frac{d^2}{dx^2}$ is

(i) 16

(ii) 32

(iii) 8

(iv) 4

(Continued)

(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 is the matrix representation of rotation-reflection axis (S_n) in symmetry?

(b) Briefly describe Compton effect.

(c) Distinguish bonding molecular orbitals from antibonding molecular orbitals.

(d) Show that the functions $\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2}$ and $\psi_2 = \left(\frac{1}{\pi}\right)^{1/2} \cos x$, in the interval $x = 0$ to $x = 2\pi$, are orthogonal to each other.

(e) Hermitian operators have real eigenvalues. Explain.

(f) Show that the energy levels in a simple harmonic oscillator are equally spaced.

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) $CHCl_3$

(ii) NH_3

(iii) PCl_5

(b) Construct the character table for C_{2v} point group. 3

(c) What are dihedral planes of symmetry? Explain with example. 2+1=3

(d) Distinguish Abelian groups from non-Abelian groups by taking a suitable example. 3

UNIT—II

Answer any *two* questions : 9×2=18

4. *(a)* A wave function is described by $\psi(\theta) = \sin\theta$, where θ can change continuously from 0 to 2π. Show whether it is normalized or not. If it is not, then find the normalizing factor. 2+2=4

(b) Show that $\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$ is an eigenfunction of ∇^2. What is the eigenvalue? 2+1=3

(c) Verify that the operator ∇^2 is linear. 2

5. (a) Solve Schrödinger's wave equation for a particle moving freely in a one-dimensional box. Find the eigenfunction and energy also. 5

(b) 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 $0 \leq x \leq \frac{a}{4}$. What is the limiting probability when $n \to \infty$? 3+1=4

6. (a) Define rigid rotator. Write the Schrödinger's wave equation for this system and separate the variables. 1+4=5

(b) Sketch the variation of radial probability density against the distance from the nucleus for 2s state for hydrogen atom. 2

(c) Determine the degree of degeneracy of the energy level $\frac{6h^2}{8ma^2}$ of a particle in a cubical box. 2

UNIT—III

7. (a) Explain the valence bond treatment for H_2 molecule. 4

Or

Compare the MO and VB treatment of hydrogen molecule in the ground state.

(b) Write the MO configuration of CN^- ion and predict its magnetic character. 2