**M.Sc. (WEEK END) DEGREE EXAMINATION
NOVEMBER 2010**

Chemistry

ORGANIC CHEMISTRY—I

(NCBCS—1995-2001 Batch)

Time : 3 Hours   Maximum : 100 Marks

Answer **all** the questions.

$(5 \times 20 = 100)$

1.   (a)   What are nitrenes ? Give two examples.

(3)

(*Or*)

(b)   Explain homoaromaticity with an example.   (3)

(c)   Account for the following :

(i)   Aniline is less basic than methylamine.

(ii) H_2O exists as a liquid but H_2S is a gas.

(iii)   Cyclopenta dienyl anion is aromatic while its cation is antiaromatic.

$(2 + 2 + 3)$

(*Or*)

(d) (i) Discuss the kinetic and thermodynamic control of a reaction with a suitable example.

(ii) Account for the aromaticity of tropolone.

(4 + 3)

(e) (i) State and explain hyperconjugation with an example.

(ii) State and explain Hammond postulate.

(6 + 4)

(*Or*)

(f) (i) What are alternant and non-alternant hydrocarbons ? Give examples.

(ii) Discuss any two non-kinetic methods of determination of reaction mechanism.

(4 + 6)

2. (a) Explain Von-Richter reaction with an example.

(3)

Or

(b) Explain coupling reaction with an example.

(3)

(c) (i) Discuss the mechanism and the stereo chemical aspects of SN^2 reaction.

(ii) How is acetophenone prepared from benzene ? What is the name of the reaction ?

$(4 + 3)$

Or

(d) Discuss the mechanism of

(i) SE_2 reaction.

(ii) Nitration of benzene.

$(4 + 3)$

(e) (i) How are carboxylic acids esterified ? Discuss its mechanism

(ii) Discuss the mechanism of chlorination of toluene.

$(5 + 5)$

(*Or*)

(f) (i) Discuss the effects of substrate structure nature of nucleophile and leaving group in aliphatic nucleophilic substitution reactions.

(ii) What is Vilsmier-Haack reaction ?

$(8 + 2)$

3. (a) What is Wittig reaction ? Explain with an example.

(3)

(*Or*)

(b) Explain Diels-Alder reaction with two examples.

(3)

(c) (i) Discuss the mechanism of E1 reaction ? What is its stereoschemical evidence ?

(ii) Discuss the mechanism of 1,2 –and 1,4– addition of HBr to 1,3 butadiene.

(4 + 3)

Or

(d) (i) Discuss the mechanism of Mannich reaction.

(ii) Explain the term regioselectivity of a reaction.

(5 + 2)

(e) Discuss the mechanism of

(i) Dieckmann condensation.

(ii) Cannizaro reaction.

(5 + 5)

(*Or*)

RW-6214

(f) (i) Explain EICB mechanism with an example.

(ii) Distinguish between Saytzetf and Hofmann rules with examples.

(5 + 5)

4. (a) Draw the chemical structures of morphine, codeine and the baine.

(3)

Or

(b) How is 1-bromo codeinone converted to morphine ?

(3)

(c) How are the following synthesised ?

(i) Uracil.

(ii) Carbazole.

(iii) Uric acid ?

(2 + 2 + 3)

Or

(d) Write a brief note on the bio synthesis of alkaloids.

(7)

(e) (i) How would you synthesise the following :

(1) Quercetin ;

(2) Coumarin ;

(3) Cyanidin chloride ?

$(2 + 2 + 2)$

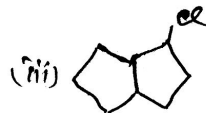(ii) How is morphine converted into apomorphine ?

(4)

Or

(f) (i) Give the synthesis of norcotine. (7)

(ii) How is tropic acid synthesised ? (3)

5. (a) State and explain isoprene rule. (3)

Or

(b)   Name the following compounds.

(i)   (ii)   (iii)

(3)

(c)   Elucidate the structure of cellulose.   (7)

Or

(d)   Establish the structure of zingiberene.   (7)

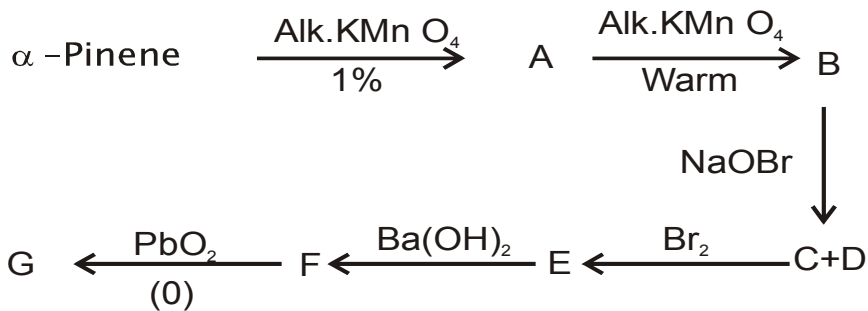(e)   (i)   Establish the structure of camphoronic acid ?

(ii) How is camphoronic acid synthesised ?

(6 + 4)

Or

RW-6214

(f) (i) How is dehydroascorbic acid synthesised ?

(ii) Formulate the structures of products of the following sequence of reactions :

$$\alpha\text{-Pinene} \xrightarrow[1\%]{\text{Alk.KMn O}_4} A \xrightarrow[\text{Warm}]{\text{Alk.KMn O}_4} B$$

$$B \xrightarrow{\text{NaOBr}}$$

$$G \xleftarrow[(0)]{\text{PbO}_2} F \xleftarrow{\text{Ba(OH)}_2} E \xleftarrow{\text{Br}_2} C+D$$

(7+3)

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M.Sc., (WEEK END) DEGREE EXAMINATION NOVEMBER 2010

Chemistry

INORGANIC CHEMISTRY—I

(NCBCS—1995–2001 Batch)

Time : 3 Hours   Maximum : 100 Marks

Answer **all** questions.   (5 × 20 = 100)

1. (a) Give the molecular structure of the following complexes.

   (i) Trimethyl borane

   (ii) Potassium hexaflurosilicate.

   (iii) Tetrammine dichloro cobalt III chloride.

(3)

(*Or*)

(b) Explain the term Stereoisomerisms with examples.

(3)

(c) Describe the spectroscopic method of determining the stability constant of a complex.

(7)

(*Or*)

(d) (i) What are the applications of crystal field theory ?

(4)

(ii) How does MO theory differs from VB theory ?

(3)

(e) (i) Illustrate with examples the John Teller theorem.

(5)

(ii) Describe the geometrical isomerism in square planar complexes with suitable examples.

(5)

(*Or*)

(f) Describe the bonding of $[Ni(NH_3)_6]^{2+}$ with each of the following :

(i) VB theory

(ii) Crystal field theory

(iii) MO theory.

(10)

2. (a) Distinguish between crystalline solids and amorphous solids.

(3)

(*Or*)

(b) Write short notes on Inter metallic compounds.

(3)

(c) Define Bragg's law and explain the term crystal lattice.

(4 + 3)

(*Or*)

(d) Explain the crystal structure of Rutile.

(7)

(e) (i) Draw unit cell for BCC and FCC structures.

(ii) Calculate the number of atoms in each.

(5 + 5)

(*Or*)

(f) Write short notes on :

(i) Structure of diamond and graphite

(ii) Crystal defects.

(5 + 5)

3. (a) Explain the following terms :

(i) Isotopes

(ii) Isotones and

(iii) Isobars.

(3)

(*Or*)

(b) What are the merits and demerits of GM counter ?

(3)

(c) Write short notes on :

(i) Binding energy

(ii) Packing fraction.

(4 + 3)

(*Or*)

(d) What are the uses of neutron activation and isotopic dilution techniques.

(4 + 3)

(e) (i) What is radioisotope ? Give examples and applications

(ii) The Half life time of Kr – 85 is 10.6 years. How much time it would reach its 80% disintegration ?

(5 + 5)

(*Or*)

(f)   Write short notes on :

(i)   Artificial radioactivity

(ii)   Hydrogen bombs.

(5 + 5)

4. (a) What are metal alklyl and aryls ? Give examples ?

(3)

(*Or*)

(b) What are fluxional molecules and give some examples.

(3)

(c) Discuss the Dewar–Chart approach to bonding in olefin complexes.

(7)

(*Or*)

RW-6215

(d) Write short notes on :

    (i) Oxidative addition

    (ii) Reductive elimination reaction.

$(4 + 3)$

(e) Write short notes on :

    (i) Hydroformylation.

    (ii) Heterogeneous catalysis.

$(5 + 5)$

(*Or*)

(f) Explain the Zeigler Natta process for the polymerisation of olefin.

(10)

5. (a) What is the difference between mineral and an ore ?

(3)

(*Or*)

(b) Explain why copper utensils turn green when exposed in air.

(3)

(c) (i) What is the difference between pig iron and wrought iron ?

(ii) What is bessimeriasation ?

(4 + 3)

(*Or*)

(d) Discuss the metallurgy of nickel.

(7)

(e) Mention the ores of Tungsten ? How is it extracted from its ore ?

(5 + 5)

(*Or*)

RW-6215

(f) (i) How iron is extracted from hematite ? How is it converted in to Wrought iron and

(ii) Steel ?

(5 + 5)

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**M.Sc., (WEEK END) DEGREE EXAMINATION
NOVEMBER 2010**

Chemistry

PHYSICAL CHEMISTRY—I

(NCBCS—1995 – 2001 Batch)

Time : 3 Hours   Maximum : 100 Marks

Answer **all** the questions.   (5 × 20 =100)

1. (a) Derive any two Maxwells relations.

(*Or*)

(b) Explain the term activity and activity coefficients.

(6)

(c) State and explain the Nernst heat theorem.

(*Or*)

(d) Derive Duhem-Margules equation and mention its significance.

(7)

(e) Define the term fugacity and explain its determination by graphical method.

(*Or*)

(f) Define chemical potential. How does chemical potential vary with temperature and pressure ?

(7)

2. (a) Explain Wein and Falken Hagen effects.

(*Or*)

(b) Explain the Born model of ion-solvent interactions.

(6)

(c) Derive the Nernst equation and mention its application.

(*Or*)

(d) Discuss the application of conductivity measurements.

(7)

(e) Derive the Butler-Volmer equation.

(7)

(*Or*)

RW-6216

(f) Discuss in detail about the different types of over voltages.

(7)

3. (a) An electron is confined in a one-dimensional box of length 1Å. Calculate its ground state energy in electron volts.

(*Or*)

(b) What are the basic postulates of quantum mechanics ?

(6)

(c) Explain the following :

(i) Eigenvalues and Eigenfunctions.

(ii) Uncertainty principle.

(*Or*)

RW-6216

(d) Derive an expression for the energy of a particle in a one dimensional box.

(7)

(e) Discuss the properties of Hermitian operator.

(*Or*)

(f) Discuss the solution of Schrödinger wave equation for a particle in a three-dimensional box.

(7)

4. (a) Write notes on Fluorescence and phosphorescence.

(6)

(*Or*)

5

(b)   Write a note on Energy transfer in Photochemical reactions.

(c)   Discuss about Solar energy conversion.

(7)

(*Or*)

(d)   Discuss about the hydrogen-halogen photochemical reactions.

(7)

(e)   Explain the following :

  (i) Hydrated electron.

  (ii) Photosensitization.

(*Or*)

(f) Discuss the determination of quantum yield.

(7)

5. (a) Write notes on explosion reactions.

(6)

(*Or*)

(b) Write a note on collision theory.

(6)

(c) Discuss briefly ARRT in thermodynamic terms.

(*Or*)

RW-6216

(d) Discuss the Hinshelwood treatment for unimolecular reactions.

(7)

(e) Discuss in detail about kinetic isotopic effect.

(*Or*)

(f) Describe the theory of unimolecular reactions based on Lindemann's concept.

(7)

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M.Sc., (WEEK END) DEGREE EXAMINATION NOVEMBER 2010

Chemistry

INSTRUMENTAL METHODS OF ANALYSIS

(NCBCS—1995–2001 Batch)

Time : 3 Hours　　　　　　　　Maximum : 100 Marks
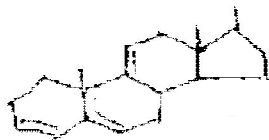
Answer **all** questions.　　(5 × 20 = 100)

All questions carry equal marks.

1. (a) Calculate λ_{max} for the following compounds :

(i) 　　(ii)

$(2 \times 1\frac{1}{2} = 3)$

(*Or*)

(b) What are overtones and combination bands ?

(3)

(c) How will you distinguish the following pairs using spectral data (UV and IR) ?

    (i)   *Cis*-stilbene and *trans*-stilbene.   (2)

    (ii)   Salicyclic acid and p-hydroxy benzoic acid.

(2)

    (iii) Anisole and benzyl alcohol.

(3)

(*Or*)

(d) (i) What type of transitions are observed in α, β-unsaturated carbonyl compounds ? How absorption maximum and intensity are shifted when carbonyl group is not conjugated ? What is the effect of solvent polarity in R-band ?

(5)

(ii) Write a note on Finger print region.

(2)

(e) (i) Define the terms chromophore, auxochrome, bathochromic shift and hypsochromic shift.

(8)

RW-6217

(ii)   What happens on absorption of UV- radiation by a molecule ?

(2)

(*Or*)

(f)   (i) The IR of amino acids in the solid state display absorptions near 1,400 and 1,600 cm^{-1}. In solutions of low pH, amino acids show an absorption near 1720 cm^{-1}. Interpret the above data.

(5)

(ii)   Write briefly on IR spectroscopy of organic molecules with respect to inter and intra molecular hydrogen bonding.

(5)

2. (a) Describe how does inductive effect shift the normal position of a proton.

(3)

(*Or*)

(b) What is meant by zero field splitting ? Explain.

(3)

(c) Explain double resonance technique in NMR with examples.

(7)

(*Or*)

(d) (i) Which technique is sensitive to the slowest process, NMR or ESR ? Explain.

(4)

(ii) For a paramagnetic compound of a d- metal compound having one unpaired electron, outline the mass difference between an ESR spectrum measured in aqueous solution at RT and that recorded for a frozen solution.

(3)

(e) Write briefly on :

(i) Deuterium exchange reactions. (4)

(ii) Principle of FT-techniques. (3)

(iii) Coupling constant. (3)

(*Or*)

(f) Explain briefly the application of ESR in the study of organic compounds.

(10)

3. (a) State and explain the nitrogen rule.

(3)

(*Or*)

(b) What is paper chromatography ? Mention its principle.

(3)

(c) Explain the basic principle of mass spectroscopy briefly.

(7)

(*Or*)

(d) State and explain the principle and applications of thin layer chromatography.

(7)

(e) (i) What is HPLC ? Give its principle and important applications.

(7)

(ii) Ethyl butanoate in the mass spectrum shows two characteristic peaks because of odd electron ions at m/e = 88 and 60 and an abundant ion at m/e = 71. Explain the fragmentation.

(3)

(*Or*)

(f) Explain briefly the principle and applications of ORD and CD.

(10)

RW-6217

4. (a) State and explain the principle of turbidimetry.

(3)

(*Or*)

(b) Explain the thermogram of calcium oxalate monohydrate.

(3)

(c) State and explain the principle and applications of flame photometry.

(7)

(*Or*)

RW-6217

(d) Explain the principle and instrumentation of DSC.

(7)

(e) What are thermometric titrations ? Explain the various types of thermometric titrations with suitable examples.

(10)

(*Or*)

(f) (i) Explain briefly the principle and applications of fluorimetry.

(5)

(ii) What is the principle of colorimetry ? How is Ni^{2+} estimated by this technique ?

(5)

5. (a) What is the principle of electrogravimetry ? Explain.

(3)

(*Or*)

(b) What is student's *t*-test ? Explain.

(3)

(c)   What is chronopotentiometry ? Explain its
      principle. Mention its merits and demerits.

(7)

(*Or*)

(d) (i) Distinguish between precision and
         accuracy.

(3)

(ii) Explain null hypothesis in error analysis.

(4)

RW-6217

(e) What is meant by error ? What are its different types ? Explain them briefly.

(10)

(*Or*)

(f) Explain briefly the principle and applications of cyclic voltammetry.

(10)

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M.Sc., (WEEK END) DEGREE EXAMINATION NOVEMBER 2010

Chemistry

ORGANIC CHEMISTRY—II

(NCBCS—1995–2001 Batch)

Time : 3 Hours　　　　　　　　Maximum : 100 Marks

Answer **all** the questions.　　(5 × 20 = 100)

1. (a) Discuss the mechanism of the following reaction :

   Camphene to Isobornyl chloride.

   (3)

   (*Or*)

   (b) Illustrate the use of Lead Tetra Acetate as an oxidising agent.

   (3)

   (c) (i) What is WOLF-KISHNER reduction ? Illustrate it with any two examples.

   (4)

(ii) Discuss the significance of Curtius rearrangement.

(3)

(*Or*)

(d) (i) Explain the mechanism of the following reaction

Hydrazobenzene $\rightarrow$ Benzidine.

(3)

(ii) How does Periodic Acid oxidise (1) 1,2-diols and (2) Dicorbornyl compunds.

(4)

(e) Discuss the mechanism of (i) Fries rearrangement (ii) Meerwein–Ponndorf–Verley reduction.
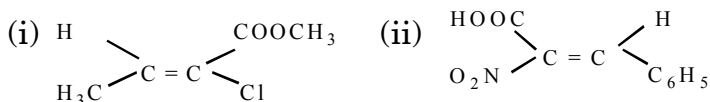
(5 + 5)

(*Or*)

(f) (i) Compare the salient features of chromic acid and Selenium dioxide used as oxidising agents.

(5)

(ii) Describe the different steps involved in the preparation of Benzilic Acid from Benzil.

(5)

2. (a) Assign the Entgegen on Zusammen Nomenclature to the following compounds.

(i)

$$\underset{H_3C}{\overset{H}{>}} C = C \overset{COOCH_3}{\underset{Cl}{<}}$$

(ii)

$$\underset{O_2N}{\overset{HOOC}{>}} C = C \overset{H}{\underset{C_6H_5}{<}}$$

(iii)

$$\underset{Br}{\overset{HO}{>}} C = C \overset{H}{\underset{H}{<}}$$

(3)

(Or)

(b) Write the Fischer projection formulae for

(i) (2R, 3S) – Tartaric acid.

(ii) (2S, 3R) 2,3 dibromopentane and

(iii) Erythro-3-chloro-2-butanol.

(3)

(c) (i) Discuss the preferential crystallization by Inoculation method of resolution of racemic modification.

(4)

(ii) Explain the method of cyclization of determination of the configuration of geometrical isomers.

(3)

(*Or*)

(d) (i) How will you determine the configuration of geometrical isomers by the method of dipole moments ?

(3)

(ii) Discuss the optical activity of an organic compound having two similar asymmetric carbon atoms.

(4)

RW-6218

(e) (i) Define : Racemic Modification. Explain the methods for determining the nature of a racemic modification.

(5)

(ii) Discuss the optical isomerism of Nitrogen and Sulphur compounds.

(5)

(*Or*)

(f) (i) Distinguish between Partial asymmetric synthesis and Absolute asymmetric synthesis.

(5)

(ii) What are Allenes ? Discuss their stereochemistry by giving examples.

(5)

3. (a) Discuss the mechanism of Hunsdiecker reaction.

(3)

(*Or*)

(b) Write a note on the conformation of 1,2-dimethyl cyclohexane, and comment on their stability.

(3)

(c) What are Decalins ? Write the conformations for *cis*- and *trans*-decalins. How will you calculate the difference in energy content between these two forms ?

(2 + 1 + 4)

(*Or*)

(d) How are free-radicals formed ? Give a comparative account of short-lived radicals and long-lived radicals.

(2 + 5)

(e) (i) Discuss the mechanism of Pschorr synthesis.

(5)

(ii) Explain the participation of (1) acetoxyl group and (b) bromine atom as neighbouring groups in nucleophilic substitution.

(5)

(*Or*)

(f) (i) Write any three methods by which free radicals can be detected ?

(5)

(ii) Illustrate the following : (a) Auwers - Skita rule (2) 3-alkyl ketone effect.
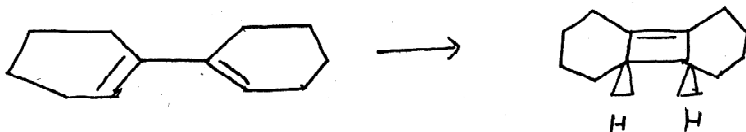
(5)

4. (a) Discuss the mechanism of Paterno-Buchi Reaction.

(3)

(*Or*)

(b) How does the following reaction proceed ? Distinguish between CON rotatory manner and DIS rotatory manner :

(3)

(c) Distinguish between Norrish type I reaction and Norrish type II reaction.

(7)

(*Or*)

(d) What are electrocyclic reactions ? Give two examples.

(7)

(e) Define and illustrate :

(i) Photoreduction

(ii) Photo addition

(iii) Photo oxidation

(iv) Photo substitution reactions.

$(4 \times 2\frac{1}{2})$

(*Or*)

(f) (i) Draw the molecular orbital correlation diagram to explain the conrotatory ring closure of 1,3,5-hexatriene by photochemical process.

(5)

(ii) What is sigmatropic rearrangement ? Why is it so called ? Explain it with an example.

(5)

5. (a) Write equations for the following reactions of Vitamin K with

(i) Acidified potassium permanganate

(ii) Hydrogen in presence of platinum catalyst.

(3)

(*Or*)

(b) How will you establish the position of the double bond in cholesterol ?

(3)

(*Or*)

RW-6218

(c) Write the structure of Stigmasterol. Explain its (i) ozonolysis (ii) Bromination (iii) hydrogenation (iv) Hydroxylation reactions.

(2 + 2 + 3)

(*Or*)

(d) Write the source chemical name and any one use for Vitamin D. Explain its reactions, establish its structure and hence its synthesis.

(1 + 1 + 1 + 4)

(e) (i) Starting from cyano acetamide and Ethoxyacetylacetone, how is pyridoxine synthesized ?

(5)

(ii) How does Equilenin react with (a) zinc
` dust (b) sodium and ethyl alcohol (c) diazonium chloride in sodium Hydroxide ?How is it synthesized ?

(5)

(*Or*)

RW-6218

(f) (i) Discuss the synthesis of Progesterone from Ergosterol.

(5)

(ii) Write equations for the reactions of L (+) ascorbic acid with (1) hot hydrochloric acid (2) Phenyl Hydrazine, and (3) Ferric chloride.

(5)

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RW-6218

**M.Sc., (WEEK END) DEGREE EXAMINATION
NOVEMBER 2010**

Chemistry

INORGANIC CHEMISTRY—II

(NCBCS-1995–2001 Batch)

Time : 3 Hours   Maximum : 100 Marks

Answer **all** questions.   (5 × 20 = 100)

All questions carry equal marks.

1. (a) What are actinides ? Explain the oxidation
   states of actinides.

   (4)

   (*Or*)

   (b) Explain why the 4*f* electrons in lanthanide
   elements do not affect their chemistry and
   crystal field stabilization.

(c) How will you extract thorium from its ores ? What are their importances, properties and uses ?

(6)

(*Or*)

(d) What do you mean by Lanthanide contraction ? Discuss its effect on the relative properties of elements before and after the lanthanide series.

(6)

(e) Discuss the electronic structure, Magnetic properties and oxidation states lanthanides.

(7)

(*Or*)

(f) What are transuranic elements ? How is neptunium synthesis ?

(7)

(g) Explain why Ce^{2+} and Tb^{3+} are colourless but show strong absorption in UV region.

(3)

(*Or*)

(h) Actinides form oxocations but Lanthanides don't. Explain.

(3)

2. (a) Discuss the π -bonding theory of trans effect. How is trans effect used in the synthesis of inorganic compound ?

(7)

(b) What are the factors affecting the stability constant ?

(7)

(c) Explain aquation reaction with suitable example.

(3)

(*Or*)

(d) Illustrate the process of isomerisation in complexes.

(3)

(e) Square planar complexes are more prone to undergo substitution by SN^2 mechanism. Substantiate.

(5)

<center>(*Or*)</center>

(f) Distinguish trans effct and trans influence. Give two applications of trans effect.

<div align="right">(5)</div>

(g) Compare the acid and base hydrolysis of octahedral complexes with respect to (i) Mechanis (ii) Factors affecting the rate of the reactions.

<div align="right">(5)</div>

<center>(*Or*)</center>

(h) Explain the terms stability, instability, lability and inertness as applied to complexes with examples.

<div align="right">(5)</div>

RW-6219

3. (a) Explain using suitable example the outer sphere mechanism in electron transfer reactions.

(4)

(*Or*)

(b) What are electron transfer reaction ? How they are divided ? Give one example for each type.

(4)

(c) What are adiabatic and non-adiabatic electron transfer reactions? Illustrate with suitable examples.

(6)

(*Or*)

(d) Discuss the role of bridging role of electron transfer reactions.

(6)

(e) The electron transfer from $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ is extremely slow, what is the reason ?

(5)

(*Or*)

(f) The electron transfer from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ is very rapid. Explain.

(5)

(g) What are Macrocylic complexes ? Give one method of synthesis of Macrocylic ligand.

(5)

(*Or*)

7

(h) What are the factors which favour innersphere electron transfer reaction ?

(5)

4. (a) How are $Fe(CO)_5$, $Cr(CO)_6$ and $Co_2(CO)_8$ prepared ? Discuss its structures.

(6)

(*Or*)

(b) CO is a very weak ligand yet it forms stable carbonyls with metals.

(6)

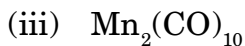(c) How is $Fe_2(Co)_9$ prepared ? Write its structure.

(4)

(*Or*)

(d) Distinguish between mononuclear and polynuclear carbonyls.

(4)

(e) Calculate the EAN for the central metal in each of the following metal carbonyls :–

(i) $Mo(CO)_6$ (ii) $Co_2(CO)_8$

(iii) $Mn_2(CO)_{10}$

(4)

(Or)

(f) What is Wilkinson's catalyst ? Give its uses.

(4)

(g) Write the advantages of homogeneous catalysis over heterogeneous catalysis.

(6)

(*Or*)

(h) State and explain the Zeigler-Natta catalyst.

(6)

5. (a) Write a note on structural feature of diborane.

(6)

(*Or*)

(b) State Wade's rule ? How does the boranes and carboranes classified based on these rules ?

(6)

(c) What are pyreoxine and amphiboles ? Give one example for each type.

(4)

(*Or*)

(d) What are closo and nido carboranes ? Give one example for each type.

(4)

(e) Give an account of phosphonitrilic compounds with their structural aspects.

(6)

(*Or*)

(f) How is B_4H_{10} prepared ? Discuss the structure and bonding type.

(6)

(g) What are metal clusters ? How is $Re_2 Cl_8^{2-}$ prepared ?

(4)

(*Or*)

(h) What are Isopoly and heteropoly anions ? Give one example for each type.

(4)

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M.Sc., (WEEK END) DEGREE EXAMINATION NOVEMBER 2010

Chemistry

PHYSICAL CHEMISTRY—II

(NCBCS—1995–2001 Batch)

Time : 3 Hours Maximum : 100 Marks

Answer **all** questions. (5 × 20 = 100)

1. (a) Define System, Assembly and Ensemble.

(*Or*)

(b) State the conditions of statistical equilibrium and express mathematically.

(3)

(c) Derive the Bolzman Distribution Law.

(*Or*)

(d) Derive the relationship between partition function and thermodynamic functions.

(7)

(e) Derive Fermi-Dirac statistics and discuss the calculation of Fermi energy of Gas in the metal.

(*Or*)

(f) Explain Deby theory of specific heat, derive the expression and discuss its limiting cases.

(10)

2. (a) State the variation principle and give two secular equation.

(*Or*)

(b) Explain Pauli's exclusion principle.

(3)

(c) Discuss how to evaluate $\langle x^2 \rangle$ for the harmonic oscillator and how to get the value $\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2 \right]^{\frac{1}{2}}$.

(*Or*)

(d) Set up Schrö dinger wave equation for rigid rotator and how to solve to get eigenvalue and eigen energy.

(7)

(e) Discuss the steps involved in construction of sp^3, sp^2 and sp hybrid orbitals.

(*Or*)

(f) Write short note on :

(i) Born Oppenheimer approximation. (5)

(ii) SCF method. (5)

3. (a) Explain reducible and irreducible representation.

(*Or*)

(b) Construct the multiplication table for the group C_{2V}.

(3)

(c) For ozone molecule, using the valence shell orbitals on each of the three oxygen atoms, construct molecular orbitals of the proper symmetry.

(*Or*)

(d) If the valence shell orbitals on the nitrogen and the three fluorine atoms of NF_3, the character of the representation is $E = 16$, $2C_3 = 1$, $3\sigma_v = 4$, how is this representation composed of the irreducible representation.

(7)

(e) Discuss vibrational mode of analysis to arrive at the symmetries of fundamental mode of vibrations of water molecule.

(*Or*)

(f) Discuss the application of group theory to electronic spectroscopy.

(10)

4. (a) With suitable example explain the theory of heterogeneous catalysis.

(*Or*)

(b) Sketch and explain the variation of logarithm of the rate constant with pH for specific acid hydrolysis of an ester.

(3)

(c) Derive Bronsted-Bjerrum equation and give its significance.

(*Or*)

(d) Discuss enzyme catalysed reaction and derive Michaelis-Menten equation.

(7)

(e) Discuss in detail the effects of ion-ion and ion-dipole to solution kinetics.

(*Or*)

(f) Write explanatory notes on Hammelt and Taft equations.

(10)

5. (a) Suggest a Gibbs energy argument for why a liquid drop is spherical.

(*Or*)

(b) Two bubbles of different radii are connected to hollow tube. What happens ?

(3)

(c) Colloidal particles of the same charge immersed in an electrolyte solution attract each other by van der Waa'ls a forces and repel each other by Debye screened interactions. Why does the ease of coagulation increase rapidly with increasing solution ionic strength.

(*Or*)

RW-6220

(d) Derive Langmuir adsorption isotherm and the physical significance of the adsorption constants :

(7)

(e) Write notes on :

    (i)   Kelvin equation.   (5)

    (ii)   Micelles and detergent   (5)

(*Or*)

(f) Discuss how to compute specific surface of a catalyst using BET adsorption isotherm.

(10)

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M.Sc., (WEEK END) DEGREE EXAMINATION NOVEMBER 2010

Chemistry

PHYSICAL CHEMISTRY—II

(NCBCS—2006 Batch)

Time : 3 Hours   Maximum : 80 Marks

Answer **all** questions. $(5 \times 16 = 80)$

1. (a) Write the expression for rotational partition function and explain the terms in it.

(3)

(*Or*)

(b) Give the statistical interpretation of Third Law of Thermodynamics.

(3)

(c) Explain the Maxwell's Law for distribution of Molecular velocities. Represent the distribution graphically, at the temperatures T_2 and T_1 so that $T_1 < T_2$.

(5)

(*Or*)

(d) Describe the salient features of Einstein's model for the heat capacity of solids.

(5)

(e) Discuss the principles and important applications of Fermi-Dirac statistics.

(8)

(*Or*)

(f) Distinguish between Thermal Entropy and Vibrational Entropy.

(8)

2. (a) What is the significance of Born-Oppen-heimer approximation ?

(3)

(*Or*)

(b) Derive the normalised wave function for a particle in one-dimensional box.

(3)

RW-6221

(c) What do you mean by a Simple Harmonic Oscillator ? Deduce an expression for the fundamental frequency of a harmonic oscillator ?

(5)

(*Or*)

(d) Describe the application of Wave Mechanics to rigid rotor.

(5)

(e) Discuss the Hortnee-Fock self consistent Field Method. Illustrate it with an example.

(8)

(*Or*)

RW-6221

(f) Explain the perturbation method and obtain the first order connection for energy and wave function.

(8)

3. (a) Predict the point groups for the following molecules : (i) Water (ii) Ammonia and (iii) Benzene.

(3)

(*Or*)

(b) Show that the operations inversion and rotation commute.

(3)

(c) Obtain the electronic transitions systematically for formaldehyde using Group Theory.

(5)

(*Or*)

(d) Construct the character table for $C_{\infty V}$ point group.

(5)

(e) State and explain the Great Orthogonality theorem.

(8)

(*Or*)

RW-6221

(f) Define and illustrate : (i) cyclic group (ii) Abelian group (iii) Symmetry element and (iv) symmetry operation.

(8)

4. (a) What is Hammett Equation ? What is its significance ?

(3)

(*Or*)

(b) Discuss the effect of temperature on enzyme catalyzed reactions.

(3)

(c)   State and explain the importance of Linewaven–Burke equation.

(5)

(*Or*)

(d)   Explain how the Theory of Absolute reaction rates is applicable to reactions in ideal solution.

(5)

(e)   Discuss the significance of Michaelis-Mention equation.

(8)

(*Or*)

RW-6221

(f) Compare the salient features of primary salt effect and secondary salt effect.

(8)

5. (a) What are surfactants ? Illustrate with two examples.

(3)

(*Or*)

(b) Write the Freundlich's equation and explain the terms involved in it. State and explain any two of its limitations.

(3)

(c) Derive GIbb's adsorption isotherm. State and explain its significance

(5)

(*Or*)

(d) Explain Langmuir-Hinshelwood Mechanism of bimolecular surface reactions.

(5)

(e) How is surface area of the solid determined by (i) Harkins and Jura method (ii) Radioactive tracer method and (iii) point B method ?

(8)

(*Or*)

(f) Distinguish between Physi-sorption and chemi-sorption. Illustrate your answer with examples.

(8)

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