(16)

PARLIAMENT OF INDIA
(JOINT RECRUITMENT CELL)
MAIN EXAMINATION FOR POSTS OF EXECUTIVE/LEGISLATIVE/COMMITTEE/PROTOCOL
OFFICER AND RESEARCH/REFERENCE OFFICER IN LOK SABHA SECRETARIAT
26th AUGUST, 2008
CHEMISTRY - Paper-I

INSTRUCTIONS : Answers must be written in English only. Candidates should attempt at least 2
questions from each section and total 5 questions. Assume suitable data if considered necessary
and indicate the same clearly. The number of marks carried by each question is indicated against
the same.

Time: 3 hours | Marks: 300

Section 'A'

			Marks
Q.1.	(a)	Explain the formation of σ and π bond on the basis of MO theory.	12
	(b)	How does MO theory explain the paramagnetic character of oxygen?	13
	(c)	Predict the bond order and nature of different bonds in N_2 molecule on the basis of MO theory.	10
	(d)	Calculate the de Broglie wave length of an electron in a hydrogen atom. It has a mass of 9.1×10^{-31} kg and moves with a velocity of 2.188×10^6 m s^{-1}.	15
	(e)	Briefly explain the nature of intermolecular forces acting between molecules of gases.	10

Q.2.	(a)	What is meant by "coordination number"? State its relation with radius ratio.	10
	(b)	What are different types of structures of 1:1 ionic compounds? Give their main features and differences.	15
	(c)	What will be the coordination numbers of A^{n+} and B^{n-} ions if the compound AB is isomorphus with (a) NaCl. (b) CsCl and (c) ZnS.	15
	(d)	Discuss (a) Schottky and (b) Frenkel defects.	10
	(e)	In fluorite. each unit cell contains four Ca^{2+} ions and eight F$^-$ ions. The edge of a CaF_2 cubic cell has a length of 5.4×10^{-8} cm. What is the density of CaF_2 in g cm^{-3}?	10

Q.3.	(a)	Differentiate between
		    (i) isolated and closed systems
		    (ii) isothermal and adiabatic changes
		    (iii) internal energy and enthalpy
			15

	(b)	What is the physical significance of entropy? State and explain the third law of thermodynamics on this basis.	12
	(c)	What is the relation between free energy change and equilibrium constant?	8
	(d)	Calculate the enthalpy of formation of benzene. given that: $C_6H_6(l) + 15/2\ O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)\ \Delta H^{\circ} = -3303$ kJ and $\Delta H^{\circ}_f(CO_2,\ g) = -393.5$ kJ and $\Delta H^{\circ}_f(H_2O,\ l) = -285.8$ kJ	15
	(e)	Show that R. the gas constant has dimensions of energy per mole per	10

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Q.4. (a) Conductivity of any electrolyte decreases on dilution of its solution whereas its equivalent conductivity increases. Explain.

(b) What is a Voltaic Cell? Explain its construction and functioning with a suitable example and draw its sketch.

(c) Corresponding to each cell denoted below, write down the half-reactions and overall reactions. Correct the cell notation if its has been wrongly written 16

(i) $Mg(s) | Mg^{2+}(aq) || Co^{2+}(aq) | Co(s)$ $E^\circ = +2.09$ V

(ii) $Pt | Fe^{2+}(aq), Fe^{3+}(aq) | Ni^{2+}(aq) | Ni(s)$ $E^\circ = -1.02$ V

(iii) $Pt | Cl_2(g) | Cl^-(aq) || Au^{3+}(aq) | Au(s)$ $E^\circ = +0.14$ V

(iv) $Pb(s) | Pb^{2+}(aq) || Zn^{2+}(aq) | Zn(s)$ $E^\circ = -0.63$ V

(d) An electric current was passed through solutions of copper sulphate and silver nitrate in separate electrolytic cells connected in series when 0.106 g copper was deposited from the former. How much silver was deposited in the latter? (Atomic masses of Cu = 63.55, Ag = 107.9). 14

(e) Two samples of gas are at the same temperature. The molecules of sample A are traveling at three times the speed of molecules of sample B. What is the ratio of masses of A and B. 10

Q.5. (a) Explain the basic principle of polarography. Write Ilkovic equation explaining all the terms and show that diffusion current is directly proportional to concentration. 10

(b) What do you understand by the terms "liquefaction of gases"? Explain critical temperature and critical pressure. 12

(c) Draw the shapes of d-orbitals. How do these split up in the presence of octahedral and tetrahedral fields? Calculate the magnetic moments of $FeSO_4.6H_2O$ and $[Ni(NH_3)_6]SO_4$ and predict their geometries. 16

(d) Electronic spectra of coordination compounds cannot be explained by valence bond theory and it is essential to consider splitting in d-orbitals. Justify. 12

(e) Compare the solvent behaviour of liquid ammonia with that of water especially with regard to solvolysis, redox and complexometric reactions. 10

Section 'B'

Q.6. (a) Briefly explain the different methods used for determining the order of a reaction. 10

(b) Explain why rates of most reactions increase with rise in temperature? 8

(c) What are main difficulties in study of fast reactions? Which techniques are used to study them? 12

(d) The reaction between mercuric chloride and potassium oxalate can be represented as: 18

$2HgCl_2(aq) + K_2C_2O_4(aq) \longrightarrow Hg_2Cl_2(s)\downarrow + 2KCl + 2CO_2$

The reaction was started with different initial concentrations of the reactant and amount of Hg_2Cl_2 precipitated in short intervals of time was measured. The results of the experiments are:

S. No.	Initial Concentrations (mol dm^{-3})		Time (/s)	Amount of Hg_2Cl_2 Precipitated (/mol)
	$HgCl_2$	$K_2C_2O_4$		
1.	0.16	0.8	135	0.0136
2.	0.08	0.8	132	0.0064
3.	0.16	0.4	250	0.0062

Find out the rate law for the reaction and the order of the reaction.

(e) The rate constant of a reaction was found to be $3.46 \times 10^{-5} s^{-1}$ at 25 °C and $1.35 \times 10^{-4} s^{-1}$ at 35 °C. calculate the activation energy of the reaction.   12

Q.7. (a) What distinguishes the transition elements. and the lanthanides & actinides?   8

(b) Write notes on: 12
(i) magnetic behaviour of the first row transition metal ions.
(ii) lanthanide contraction

(c) Write the general outer shell electronic configuration for atoms of f-block transition elements. Which electrons are primarily involved in chemical bonding?   12

(d) What is the most common oxidation state for the lanthanides? Why are cerium (IV) and terbium (V) oxidation states extra stable?   12

(e) A container is filled with a mixture of oxygen and nitrogen both of which have same partial pressure. If a hole is made in the container and the gas is allowed to escape. will the escaping gas be richer in nitrogen or oxygen? What is relative rate of escape of nitrogen as compared to that of oxygen?   16

Q.8. (a) What are outer and inner orbital complexes?   8

(b) Using valence bond theory. discuss the paramagnetic nature of $[NiCl_4]^{2-}$ complex ion (due to two unpaired electrons). and diamagnetic nature of $[Ni(CN)_4]^{2-}$ complex ion.   15

(c) Name the following complexes: 10
(a) $K_3[Mn(CN)_6]$ (b) $[Pd(NH_3)_4 (OH)_2]$
(c) $K_2[Fe(C_2O_4)_2].2H_2O$ (d) $Na[AgI_2]$
(e) $[Ni(NH_3)_4 (H_2O)_2] (NO_3)_2$ (f) $[Co(H_2O)_6]^{3+}$
(g) $K[Cr(NH_3)_2 (H_2O)_2 Cl_2]$ (h) $Na[Al(H_2O)_2 (OH)_4]$

(d) A student prepared one sample of $CoCl_3.4NH_3$ which was violet coloured and another sample of $CoCl_3.4NH_3$ which was green. Explain. using structural diagrams. how this could be possible?   12

(e) Draw the structures of cis and $trans$ isomers of   15
(i) $[Pt(Py)_2Cl_2]$. a square planer structure where Py represents the monodentate ligand pyridine.
(ii) $[Cr(H_2O)_4 (NO_2)_2]^+$. an octahedral complex.

Q.9. (a) Distinguish between physical and chemical adsorption.

(b) What is an adsorption iosthem? Briefly discuss Freundlich's isotherm. Is applicable to adsorption from solutions as well?

(c) How do the solid catalysts function?

(d) What are the differences in the characteristics of homogeneous and heterogeneous catalysts? 8

(e) Give five examples of important industrial processes in which heterogeneous catalysts are used. 20

Q.10. (a) Giving suitable examples. explain Aufbau principle. Hund's rule of maximum multiplicity and Pauli's exclusion principle. What is their significance in writing electronic configuration? 15

(b) How liquid crystals are different from solid crystals? Compare their characteristic features. 8

(c) What do you understand by imperfection in crystals? Explain various types of defects and resulting change in properties. 12

(d) Explain ionization. coordination. linkage and optical isomerism in coordination compounds with a suitable example for each. 10

(e) How metal carbonyls are synthesized? What are the characteristic features of metal-carbon bonding in carbonyls? Draw the structures of $Ni(CO)_4$. $Fe(CO)_5$ and $Cr(CO)_6$. 15

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26th AUGUST, 2008

CHEMISTRY - Paper-II

INSTRUCTIONS : Answers must be written in English only. Candidates should attempt at least 2 questions from each section and total 5 questions. Assume suitable data if considered necessary and indicate the same clearly. The number of marks carried by each question is indicated against the same.

Time: 3 hours   Marks: 300

SECTION - A

Q.1 (a) Classify the following compounds as aromatic or non-aromatic.   (5×4 = 20 marks)
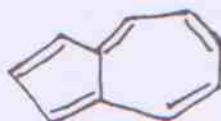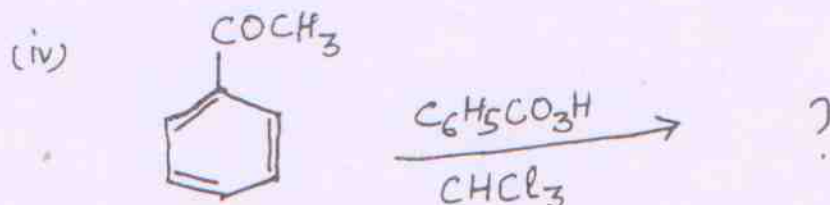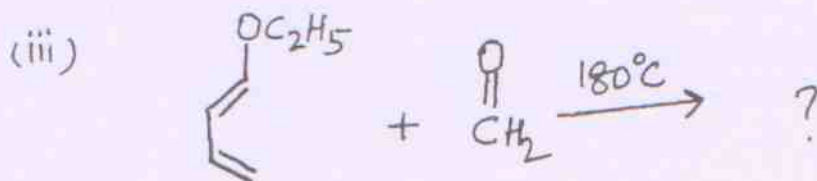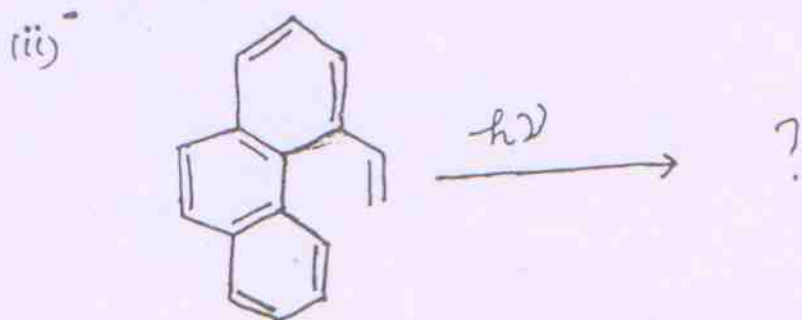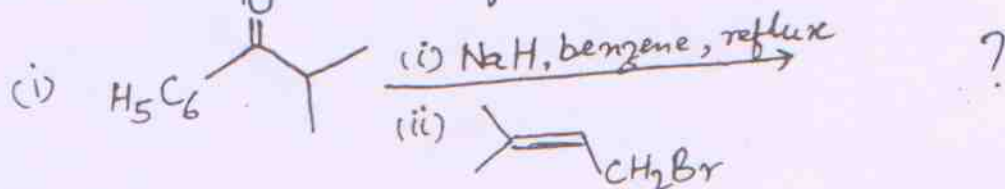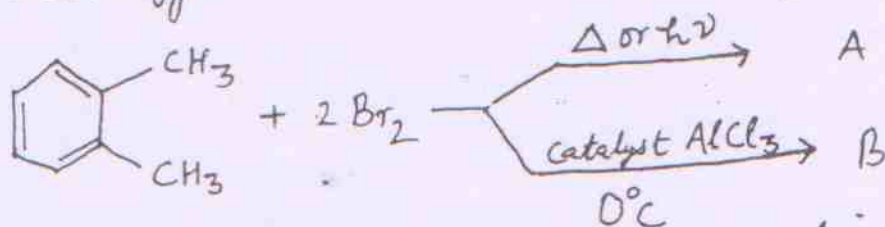
(i)

(ii)

(iii)

(iv)

(b) Discuss the hydrolysis reaction of 3-chloro-1-butene. Explain why the products obtained are optically inactive

irrespective of whether the starting material
enantiomer.

(c) Give the products of the following reactions:

(i) H_5C_6 —C(=O)—CH(CH$_3$) $\xrightarrow[\text{(ii)} \searrow\!\!\text{CH}_2\text{Br}]{\text{(i) NaH, benzene, reflux}}$?

(ii) [structure] $\xrightarrow{h\nu}$?

(iii) [structure with OC_2H_5] + $\overset{O}{\underset{CH_2}{\|}}$ $\xrightarrow{180°C}$?

(iv) [structure with $COCH_3$] $\xrightarrow[\text{CHCl}_3]{C_6H_5CO_3H}$?

Q.2. (a) Identify A and B in the following reaction: (20 marks)

[o-xylene with CH$_3$, CH$_3$] + 2 Br$_2$ $\xrightarrow{\Delta \text{ or } h\nu}$ A
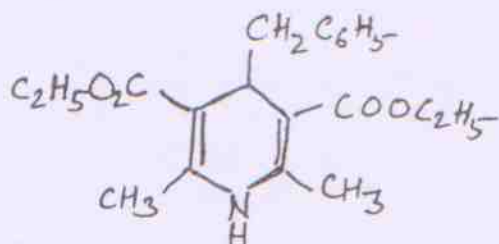
$\xrightarrow[0°C]{\text{catalyst AlCl}_3}$ B

Also give reasons for their formation.

(b) How will you prepare the following
...ting ...ch pyridine

(3

Synthesis ? Give the mechanism of the reaction. $\left(\begin{array}{c}20 \\ \text{marks}\end{array}\right)$

(c) Discuss the catalytic hydrogenation of $\underline{E}$ and $\underline{Z}$ stilbenes giving the structure and the stereochemistry of products. $\left(\begin{array}{c}20 \\ \text{marks}\end{array}\right)$

Q.3. (a) complete the following sequence of reactions: $\left(\begin{array}{c}15 \\ \text{marks}\end{array}\right)$

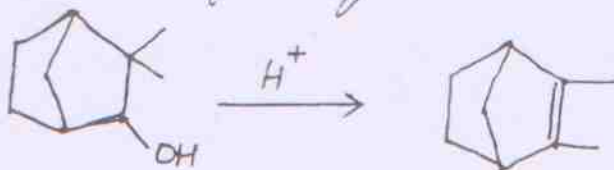$$\xrightarrow[\text{CHCl}_3]{m-ClC_6H_4CO_3H} \quad A \xrightarrow[\text{ether}]{LiAlH_4} \quad B$$
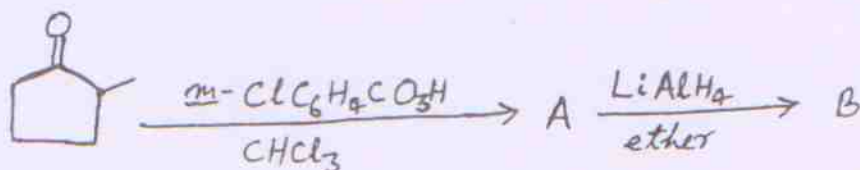
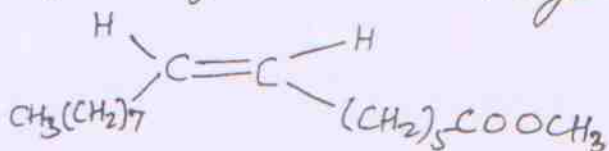(b) Arrange the following free radicals in the increasing order of their stabilities and give reasons in support of your answer: $\left(\begin{array}{c}15 \\ \text{marks}\end{array}\right)$

$$\cdot CH_3 \quad , \quad (CH_3)_2\overset{\cdot}{C}H \quad , \quad (CH_3)_3\overset{\cdot}{C} \quad , \quad \overset{\cdot}{C}HCH_3$$

(c) Explain giving mechanism, the pinacol rearrangement of the following: $\left(\begin{array}{c}20 \\ \text{marks}\end{array}\right)$

(d) Explain the following reaction: $\left(\begin{array}{c}10 \\ \text{marks}\end{array}\right)$

following as the starting compound: (10 marks)

$$CH_3(CH_2)_7 \diagdown C = C \diagup H \atop \diagdown (CH_2)_5 COOCH_3$$

(b) (i) Give the structure of the expected Saytzeff product when 2-chloro-2,4,4-trimethylpentane undergoes elimination reaction in the presence of a base. (20 marks)
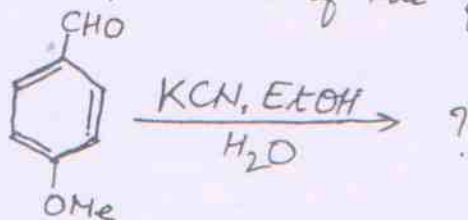
(ii) The actual product in the above reaction is a terminal alkene. Explain giving reasons.

(C) (i) Draw and explain the molecular orbitals of butadiene and identify HOMO and LUMO. (20 marks)

(ii) Using the orbitals in (i) above and the frontier orbital description, explain the following reaction: (10 marks)
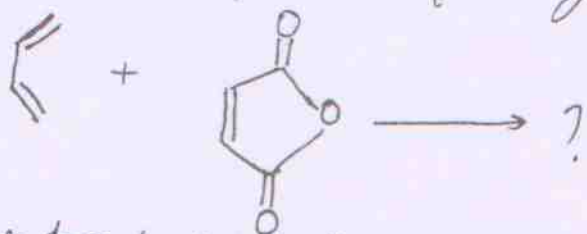
5 (a). Give the product of the following reaction: (20 marks)

Discuss the mechanism and give the name of the reaction.

(b) Discuss Wittig reaction with the help of a suitable example. Also give the mechanism of the reaction. (20 marks)

(C) Mustard gas hydrolyses much more rapidly than its sulphur free analog i.e., 1,5-dichloropentane. Explain. (10 marks)

(d) Identify A, B and C in the following sequence of reactions: (10 marks)

$\xrightarrow{OH^-} A \xrightarrow{Br_2/KOH/H_2O} B \xrightarrow{H^+} C$
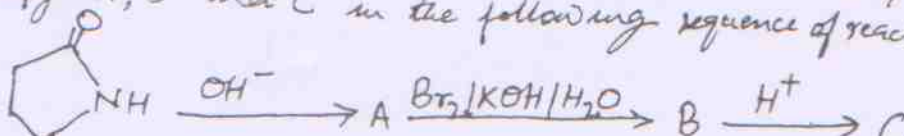
SECTION B

Q.6. (a) Calculate the number average and mass average (15 marks) molecular weights for a polymer sample which has the following composition:

Number of Chains	Molecular weight
3	1000
2	1200
5	1400

What is the ratio $\dfrac{M_W}{M_n}$ called?

(b) How are the following polymers obtained? (15 marks) Give the structure of the monomers and the polymers.
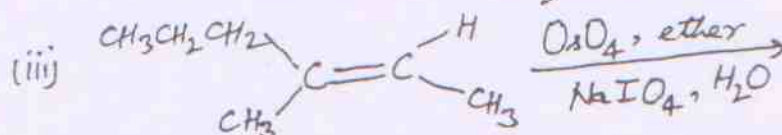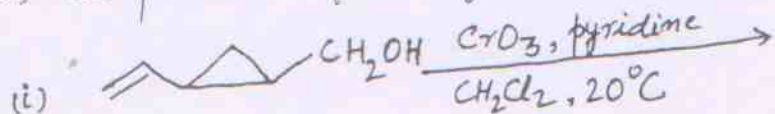
(i) Nylon 66

(ii) Nylon 6

(iii) PET

(C) What is meant by the primary, secondary and (15 Marks) tertiary structures of proteins? Explain.

(d) Complete the following reactions: (15 marks)

(i) $\overset{CH_2OH}{\wedge\wedge\wedge}$ $\xrightarrow[CH_2Cl_2, 20°C]{CrO_3, pyridine}$

(ii) $\wedge\wedge\wedge$ $\xrightarrow[benzene]{m-CPBA}$

(iii) $\underset{CH_3}{\overset{CH_3CH_2CH_2}{>}}C=C\underset{CH_3}{\overset{H}{<}}$ $\xrightarrow[NaIO_4, H_2O]{OsO_4, ether}$

Q.7. (a) Explain the photochemical reaction of isobutene (10 Marks) with cyclohexenone in hexane. Also give the stereochemistry of the product formed.

(b) Complete the following sequence of reactions giving (20 Marks) the stereochemistry involved:

$\wedge\wedge$ $\xrightarrow{B_2H_6}$ $\xrightarrow{H_2O_2}$

(C) Give the major products of the following reactions along with the correct stereochemistry: (20 marks)

(i) $\xrightarrow{\text{LiAlH}_4}$

(ii) $\xrightarrow{\text{LiAlH(OC}_4\text{H}_9\text{-t)}_3}$
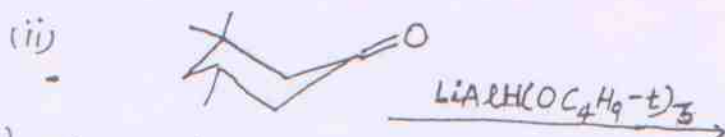
(d) A compound having molecular formula $C_6H_{12}O_2$ showed the following spectral data: (10 marks)
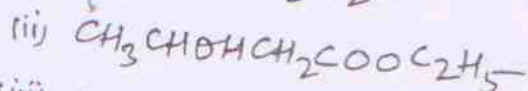
IR : 1740 and ~ 1200 cm^{-1}

NMR : (δ. CDCl$_3$) : 4.12 (q, 2H), 2.31 (septet, 1H), 1.34 (3H, triplet), 1.15 (6H, doublet)

Predict the structure of the compound and assign the observed signals to the structural units responsible for them.
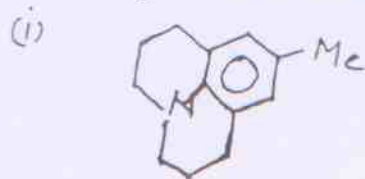
Q. 8. (a) How will you reduce ethyl acetoacetate to the following compounds? (20 marks)

(i) $CH_3CHOHCH_2CH_2OH$

(ii) $CH_3CHOHCH_2COOC_2H_5$

(iii) $CH_3COCH_2CH_2OH$

(b) Give the products when the following compounds undergo the reactions given in the parenthesis: (20 marks)

(i) (Birch reduction)

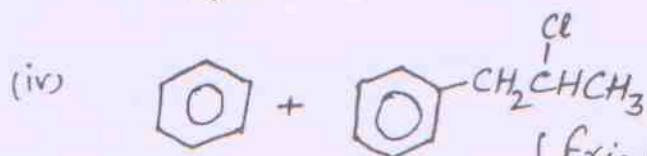(ii) (Baeyer-Villiger reaction)

(7)
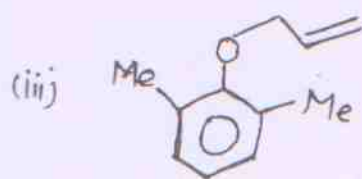
(iii)   Me $\overset{O}{\underset{}{\bigcirc}}$ Me   (Claisen rearrangement)

(iv) $\bigcirc$ + $\bigcirc - CH_2\overset{Cl}{C}HCH_3$ (Friedel-Crafts alkylation)

(c) Discuss McLafferty rearrangement with the help of a suitable example.   (20 marks)

Q. 9. (a) Match the following compounds with their λ_{max} values. Also give reasons for your answer.   (20 marks)

Column I Compound	Column II λ_{max} (nm)
(i) Ethene	280
(ii) trans-2-Hexene	216
(iii) 1,3-Butadiene	256
(iv) trans-1,3,5-Hexatriene	184
(v) Cis-Stilbene	177

(b) How many vibrational degrees of freedom does CO_2 molecule have? Draw the possible vibrational modes and classify them as IR active or IR. inactive.   (20 marks)

(c) Discuss Norrish Type I and Norrish Type II reactions with the help of suitable examples.   (20 marks)

Q. 10. (a) Explain the signals observed and their

(8)

(b) For HCl molecule, the transition from $J = 0$ to $J' = 1$ takes place at $\bar{\nu} = 21.18 \text{ cm}^{-1}$. What is the bond length of $^1H^{35}Cl$ bond? (20 marks)

(c) The ESR spectrum of hydrogen atom shows two equally intense lines which are 506.8 G apart. Explain their origin. (20 marks)

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26th AUGUST, 2008

SOCIOLOGY - Paper-I (General Sociology/Foundations of Sociology/Fundamentals of Sociology)

INSTRUCTIONS : Answers must be written in English only. Candidates should attempt at least 2 questions from each section and total 5 questions. All questions carry equal marks.

Time: 3 hours

Marks: 300

SECTION – A

1. Write short notes on <u>any three</u> of the following (each note should not exceed 200 words):

    a) Relationship of Sociology with Social Anthropology
    b) Measurement in social research
    c) Alienation
    d) Latent and manifest functions

2. Discuss Parsons' thesis on the family and industrial society.

3. What is historical materialism? How does it help in understanding the social change? Discuss with reference to the work of Karl Marx.

4. Elaborate Emile Durkheim's analysis on the role of religion in primitive society, how does he explain the existence of religion in industrial societies?

5. What is an ideal type? How did Weber analyse bureaucracy as the ideal type?

SECTION - B

6. Write short notes on <u>any three</u> of the following (each note should not exceed 200 words):

    (a) Socialization and the family
    (b) Industrialisation and post industrial society
    (c) Pressure groups and political parties
    (d) Features of social movement

7. Define social stratification. Describe how social mobility occurs in closed and open systems of stratification?

8. Discuss the thesis of division of labour in pre-industrial and industrial society with reference to Durkheim.

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SOCIOLOGY - Paper-II (Study of Indian society)

INSTRUCTIONS :   Answers must be written in English only. Candidates should attempt at least 2 questions from each section and total 5 questions. All questions carry equal marks.

Time: 3 hours   Marks: 300

SECTION – A

1. Analyse the impacts of land reforms on agrarian class structure in India.

2. Explain the various factors contributing towards the emergence of Dalit consciousness in India. What are their social ramifications?

3. Examine the relationships between education and social mobility with suitable illustrations.

4. What do you understand by globalisation?   Discuss various dimensions of globalisation.

5. Write short notes on <u>any three</u> of the following in about 200 words each:

      a)   Sanskritisation and Westernisation
      b)   Trade Union Movement
      c)   Classes among the tribes
      d)   Impacts of regionalism on Indian politics
      e)   Elite Formation in India

SECTION - B

6. Illustrate the various problems encountered by the religious minorities in India. Suggest a few measures for the eradication of these problems.

7. Critically analyse the major features of tribal policy in India.

8. What do you mean by inclusive growth? How can this growth pattern be achieved?

9. Define peasant movements and discuss the major features of peasant movements in India.

10. Write short notes on <u>any three</u> of the following topics in about 200 words each:

      (a)   Secularism and fundamentalism.
      (b)   Roles of mass media in social change