



## GEOLOGIST EXAMINATION-2017 GENERAL ENGLISH

Time Allowed : Three Hours

M.M. : 100

### INSTRUCTIONS

- Please reach each of the following instruction carefully before attempting questions:
- There are six questions and all are to be attempted.
- The number of marks carried by a question/part is indicated against it.
- Answers must be written in ENGLISH only.
- Candidates are required to write clear, legible and concise answer and to adhere to word limits wherever indicated. Failure to adhere to word limits may be penalized.
- Any page or portion of the page left blank in the question-cum-answer booklet must be clearly struck off.

1. Write an essay on any *one* of the following topics in not less than 800 words: [30]  
(a) Books vs e-Books (b) Sports bodies should be governed by Sportspersons  
(c) Rights of Persons with Disabilities in India (d) Uses and Abuses of Sting operations in India  
(e) Family and Globalization

2. Make a precis of the following passage in about one-third of the original length, using your own words : [30]  
[Note : The precis must be written only on the special sheets provided for this purpose, writing one word in each block].

Two principal forms of the constitution are known to history — one is called unitary and the other is federal. The two essential characteristics of a unitary constitution are : (1) the supremacy of the central polity, and (2) the absence of subsidiary sovereign polities. On the contrary, a federal constitution is marked : (1) by the existence of a central polity and subsidiary politics side by side, and (2) by each being sovereign in the field assigned to it. In other words, federation means the establishment of a dual polity. The draft constitution is a federal constitution in as much as it establishes what may be a dual polity. This dual polity under the proposed constitution will consist of the Union at the centre and the States at the periphery, each endowed with sovereign powers to be exercised in the field assigned to them respectively by the constitution. This dual polity resembles the American Constitution. The American polity is also a dual polity, one of it is known as the Federal government and the other government of the States which correspond respectively to the Union government and the State governments of the draft constitution. Under the American Constitution the Federal government is not a mere league of the States nor are the States administrative units or agencies of the Federal government. In the same way, the Indian Constitution proposed in the draft constitution is not a league of States nor are the States administrative units or agencies of the Union government. Here, however, the similarities between the Indian and American Constitutions come to an end. The differences that distinguish them are more fundamental and glaring than the similarities between the two.

The points of difference between the American federation and the Indian federation are mainly two. In the USA, this dual polity is followed by a dual citizenship. In the USA there is a citizenship of the USA. But there



is also a citizenship of the State. No doubt the rigours of this double citizenship are much assuaged by the Fourteenth Amendment to the Constitution of the United States which prohibits the States from taking away the rights, privileges and immunities of the citizen of the United States. At the same time, as pointed out by William Anderson, in certain political matters, including the right to vote and to hold public office, the States may and do discriminate in favour of their own citizens. This favouritism goes even further in many cases. Thus to obtain employment in the service of a State or Local government one is in most places required to be a local resident or citizen. Similarly, in the licensing of persons for the practice of such public professions as law and medicine, residence or citizenship in the State is frequently required and in business where regulation must necessarily be strict, as in the sale of liquor, and of stocks and bonds, similar requirements have been upheld.

Each State has also certain rights in its own domain that it holds for the special advantage of its own citizens. Thus wild game and fish in a sense belong to the State. It is customary for the States to charge higher hunting and fishing license fees to non-residents than to its own citizens. The States also charge non-residents higher tuition in the State colleges and universities, and permit only residents to be admitted to their hospitals and asylums except in emergencies.

In short, there are a number of rights that a State can grant to its own citizens or residents that it may and does legally deny to non-residents, or grant to non-residents only on more difficult terms than those imposed on residents. These advantages, given to the citizen in his own State, constitute the special rights of State citizenship. Taken all together, they amount to a considerable difference in rights between citizens and non-citizens of the State. The transient and the temporary sojourner is everywhere under some special handicaps.

The proposed Indian Constitution is a dual polity with a single citizenship. There is only one citizenship for the whole of India. It is Indian citizenship. There is no State citizenship. Every Indian has the same rights of citizenship, no matter in what State he resides.

The dual polity of the proposed Indian Constitution differs from the dual polity of the USA in another respect. In the USA, the Constitutions of the Federal and the State governments are loosely connected. In describing the relationship between the Federal and the State governments, Bryce has said, "The central or national governments may be compared to a large building and a set of smaller buildings standing on the same ground, yet distinct from each other".

3. Write a paragraph in about 200 words on any *one* of the following expressions/statements: [10]
- (a) 'Make hay while the sun shines'. (b) One swallow does not make a summer.  
 (c) Discretion is the better part of valour. (d) As you sow, so shall you reap.  
 (e) If winter comes, can spring be far behind'.
4. Use the following words in sentences so as to bring out their meaning clearly. Do not change the form of the word. No credit will be given for a vague or ambiguous sentence. [2×5=10]
- (a) Prefatory (b) Ostentatious (c) Nemesis  
 (d) Expatriate (e) Lascivious
5. Use the following idioms and phrasal verbs in sentences so as to bring out their meaning clearly. [2×5=10]
- (a) make away with (b) play fast and loose (c) set off the hook  
 (d) eating humble pie (e) square pegs in round holes
6. Correct the following sentences without changing their meaning. Do not make unnecessary changes in the original sentence : [1×10=10]
- (a) Shocked of finding an unknown person, the army officer briskly caught hold of him.  
 (b) High population growing rate is one of the major reasons of poverty in India.  
 (c) He decided to reveal the corruption in his department to the media.  
 (d) I would have waited for you at the station if I knew that you would come.  
 (e) Although my car is expensive, I had a lot of trouble with it.  
 (f) He would have lent me some money if he was knowing that I had lost everything.  
 (g) No sooner the news reached him than he fainted.

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- (h) According to the Census Bureau, India will have a more problem.
- (i) Mr. Mishra said that he is doing fine now.
- (j) Non-teaching staffs of the college are agitating for their demands.
- (k) The President of France has left India yesterday.
- (l) Rahul stays with his parents in the Railway quarter.
- (m) He went on committing crime after crime and in spite of my best efforts. I could not prevent him from doing so.
- (n) To transport goods by the sea is cheaper than land.
- (o) It is a penal offence bribing a public servant.



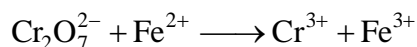
# GEOLOGIST EXAM-2017

## CHEMISTRY PAPER - I

### SECTION-A

1. Answer all of the following :

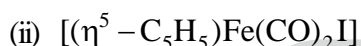
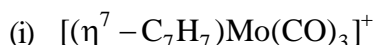
(a) Balance the following redox reaction in an acidic medium by the ion-electron method :



(b) When a few Si atoms are replaced by P atoms in pure crystal of Si, what is the consequence in the physical property ?

(c) The effective magnetic moment of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is  $\sim 3.20$  B.M. Is it higher or lower or equal to the  $\mu_{\text{spin-only}}$  value ? Provide an explanation.

(d) Identify the organometallic compound which obeys the 18 electron rule.



(e) Why are nuclei having 'Magic Number' of nucleons exceptionally stable ?

(f) Draw the structure of dimethyl beryllium and explain the bonding.

(g) Nowadays CFC (Chlorofluorocarbon)-free refrigerators are promoted in the market. Why and what is the consequence upon release of CFCs to the atmosphere ? [Write only relevant reactions]

(h) Compared to other actinides, why have the chemical properties of Th and U been extensively developed?

(i) Find the oxidation states of (i) Br in  $\text{Br}_3\text{O}_8$ , and (ii) C in  $\text{C}_3\text{O}_2$ .

(j) The radii of Mo ( $Z = 42$ ) and W ( $Z = 74$ ) are 140 and 141 pm, respectively, despite the latter having many more electrons. Provide an explanation.

### SECTION-B

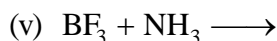
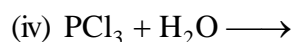
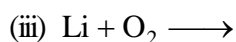
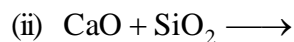
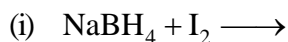
2. (a) Using a VSEPR model, arrive at and draw the shape of (i)  $\text{XeO}_2\text{F}_2$ , and (ii)  $\text{SO}_2\text{Cl}_2$ .

(b) In going from left to right of the 1<sup>st</sup> transition series for bivalent ions, the Lewis acidity steadily increases. Justify your answer.

(c) Iodine behaves differently in iodometric and iodimetric titrations. Provide an explanation.

3. (a) In the estimation of iron, copper and gold, three chemical methods are employed. Comment on these methods and explain with the chemical reactions involved in the extraction of these metals.

(b) Write the product(s) formed from the following reactions and balance the equation:



### SECTION-C

4. (a) Draw the structures of *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]$  and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]$ .  
(en = 1, 2-diaminoethane)

(b) Identify the presence or absence of Jahn-Teller distortion in  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . Justify your answer.

(c) Determine the spectroscopic ground-states of  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ .



5. (a) When an aqueous solution of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$  is reacted with sodium nitrite and sodium thiocyanate separately, four new complexes could be isolated. Draw the structure of the new complexes. What is the nature of the incoming ligands ?
- (b) Among the following complexes, which one assumes perfect octahedral geometry. Justify your answer.
- (i)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- (ii)  $[\text{VCl}_6]^{2-}$
- (iii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- (c) From the following two complexes, identify the complex which is kinetically labile or kinetically inert:  
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$

### SECTION-D

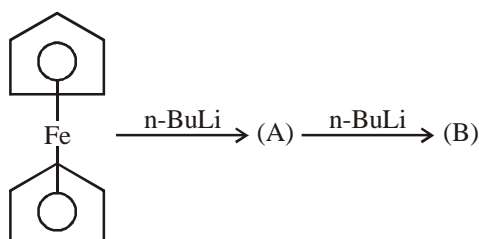
(Attempt any one question)

6. (a) Using MO diagrams, explain why  $\text{B}_2$  is paramagnetic and  $\text{C}_2$  is diamagnetic.
- (b) Write the balanced chemical reaction between (I)  $\text{Br}_2$ , and (II)  $\text{HCl}$  with (i) benzene, and (ii) borazine. Comment on the reactivity pattern.
- (c)  $\text{B}-\text{Br}$  bond of  $\text{BBr}_3$  is a single bond; however,  $\text{B}-\text{F}$  bond of  $\text{BF}_3$  is between a single and a double bond. Rationalize the observation.
7. (a)  $\text{B}_2\text{O}_3$  is acidic whereas  $\text{Al}_2\text{O}_3$  is amphoteric. Rationalize your answer.
- (b) Draw the structures of  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ .
- (c) (i) How is  $(\text{Me}_2\text{SiO})_n$  prepared starting from methyl chloride and silicon using copper as a catalyst ?  
 (ii) What are the applications of silicones ?

### SECTION-E

(Attempt any one question)

8. (a) Predict the number of metal-metal bonds present in the following organometallic compounds:  
 (i)  $\text{Ir}_4(\text{CO})_{12}$       (ii)  $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\mu-\text{CO})(\text{CO})]_2$
- (b) What is Zeise's salt ? Explain its metal-ligand bonding interactions.
9. (a) While chromium hexacarbonyl exists as a monomer, manganese carbonyl forms a dimer. Rationalize your answer.
- (b) The  $\text{C}-\text{C}$  distances in  $[(\text{L})\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$ ,  $\text{L} = \text{acetylacetonate}$ , are 201 – 202 pm ( $\text{H}_2\text{C} = \text{CH}_2$ ) and 217 – 219 pm ( $\text{F}_2\text{C} = \text{CF}_2$ ). Rationalize this observation.
- (c) Predict the product [(A) and (B)] of the following nucleophilic addition :



**SECTION-F****(Attempt any one question)**

10. (a) NaCl and NaOH cannot be used in place of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  for the precipitation of Group-III A metal ions in qualitative group analysis. Provide an explanation.
- (b) Nuclear stability is associated with packing fraction. Provide an explanation.
- (c) Lanthanides typically display weak but sharp absorption bands. Explain.
11. (a) In qualitative inorganic analysis,  $\text{H}_2\text{S}$  is passed in acidic medium for Group II metal ions while for Group III B metal ions the same is passed in basic medium. Provide an explanation.
- (b) Aqueous solutions of potassium permanganate exhibit very intense electronic transition at  $\sim 530$  nm. What is the nature of this transition? Justify your answer?
- (c) Write the ground state term symbols (L-S coupling) for  $d^1$  octahedral and  $d^9$  octahedral.



## SECTION-A

## 1. Answer all of the following :

- (a) Write down the equation of state for vander Waals gases with symbolic significances and And the dimension of van der Waals constants.
- (b) Helium gas at 500 K expands adiabatically and reversibly to double its volume. Find the final temperature of the gas in degree Celsius. (Assume that He gas behaves ideally).
- (c) Explain the Arrhenius theory of acids and bases with examples.
- (d) List the factors which influence the efficiency of Carnot engine. How?
- (e) The effect of temperature on the value of dimerization constant is negative. Justify with the help of van't Hoff equation isobar.
- (f) Derive the integrated rate equation for a zero-order reaction. Give one example of zero-order reaction.
- (g) What is van't Hoff factor (i) of a solution? Derive its relation with degree of ionization of solute in a solution.
- (h) Define 'molar extinction coefficient ( $\epsilon$ )'. What is its unit? What factor(s) can influence its value?
- (i) Show that the unit of magnetic dipole moment is  $\text{Am}^2$  which is also equivalent to  $\text{JT}^{-1}$ . Here T stands for tesla, the unit of magnetic field strength.
- (j) Why is surface tension of liquid ethanol greater than liquid dimethyl ether though both have same molecular mass?
- (k) Explain why  $\text{H}_2\text{O}$  is a liquid while  $\text{H}_2\text{S}$  is a gas at room temperature.
- (l) Show that  $y = e^{ikx}$  is an eigenfunction of the operator,  $\vec{A} = -i\hbar \frac{d}{dx}$ . What is the eigenvalue ?
- (m) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom? Give reason(s) :
- |                           |                          |
|---------------------------|--------------------------|
| (i) $2s \rightarrow 1s$   | (ii) $2p \rightarrow 1s$ |
| (iii) $3d \rightarrow 2p$ | (iv) $3d \rightarrow 4s$ |
| (v) $5p \rightarrow 3s$   |                          |

SECTION-B  
(Attempt any six questions)

2. Derive  $(C_p - C_v) = \left[ \left( \frac{\partial U}{\partial V} \right)_{T,n} + P \right] \left( \frac{\partial V}{\partial T} \right)_{P,n}$  (Symbols have their usual meanings).

Find the expression of  $(C_p - C_v)$  for a gas obeying equation of state,  $P(V - nb) = nRT$ .

3. 18.0 g of liquid water vaporizes at 1 bar and 373 K. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$  and  $\Delta G$  (in SI units) for this process. Given, latent heat of vaporization of liquid water at 1 bar and 373 K is  $540 \text{ cal g}^{-1}$ .
4. Derive Gibbs-Duhem equations for a mixture system at constant pressure and temperature.
5.  $0.1 \text{ kg mol}^{-1}$  aqueous solutions of two 1-1 electrolytes A and B freeze at  $-0.360^\circ\text{C}$  and  $-0.208^\circ\text{C}$ , respectively. Calculate (a) van't Hoff factor of each solution and (b) the degrees of ionization of A and B in their solution. Suggest the nature of electrolytes. Given,  $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$ .
6. (a) What will be the value of absorbance of transparent liquid water with respect to visible light? Give reason.  
(b) Write a note on 'photosensitized reaction' with example of photosynthesis.

7. (a) Define 'most probable speed' of a molecule in gaseous system, Derive its expression using the following speed distribution equation :

$$dN_c = 4\pi N \left( \frac{m}{2\pi k_B T} \right)^{3/2} c^2 e^{-\frac{mc^2}{2k_B T}} dc$$

(Symbols have their usual meanings).

- (b) Find the pH of  $10^{-4}$  (M) aqueous caustic soda solution.
8. (a) Show that for a first-order reaction, the time required for completion of 99.9% reaction is ten times of its half-life period.
- (b) The standard reduction potential value of  $Zn^{++}/Zn$  electrode is negative and of  $Cu^{++}/Cu$  electrode is positive. What will be the cell reaction, if we couple two electrodes to form a galvanic cell ? Give reason(s) in support of your answer.
9. A spherical water drop of radius 1.0 mm is sprayed into a million of droplets of same size. Find the work done in this process. Given that  $\gamma$  (surface tension) of water at the experimental temperature is  $72.0 \text{ dyne cm}^{-1}$ .
10. (a) Silver crystallizes in an f.c.c. structure with a unit cell length of 408.6 pm. Using Bragg equation, calculate the first-order diffraction angle for (111) plane using X-ray of wavelength 154.433 pm.
- (b) The force constant of a harmonic oscillator of reduced mass  $1.5 \times 10^{-27} \text{ kg}$  is  $10 \text{ Nm}^{-1}$ . Calculate its zero point energy.

### SECTION-C

(Attempt any three questions)

11. (a) Derive  $\Delta T_f = K_f m_2$  (symbols have their usual meanings) using thermodynamic concept of chemical potential. Mention all assumptions and approximations at proper places.
- (b) The temperature of a hot cup of tea decreases spontaneously in a closed system at constant pressure without losing its mass. So for this change  $\Delta H < 0$ ,  $\Delta S_{\text{univ}} > 0$  and  $\Delta G > 0$ . Justify with reasons.
12. (a) Discuss hypochromic effect in connection to UV spectra.
- (b) The quantum yield ( $\phi$ ) for the reaction,  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , at  $\lambda = 250 \text{ nm}$  is 2.0. If 3070 J of light is absorbed, find the number of moles of HI decomposed.
- (c) What is indicated by peak area in PMR spectrum ? How many peaks will be observed in PMR spectrum of pure ethanol ? What will be their peak area ratio ? Explain with diagram, if possible.
13. (a) Write down Debye-Hückel limiting equation with symbolic significances and units. Find the ionic strength of  $0.01 \text{ mol L}^{-1}$  aqueous solution of potassium ferrocyanide.
- (b) The average lifetime of phosphorescence is higher than fluorescence. Explain with Jablonsky diagram.
- (c) Hydrogen nucleus is NMR active but the nuclei of  $^{16}\text{O}$  and  $^{12}\text{C}$  are inactive.
14. (a) Derive Langmuir adsorption isotherm expression for the process  $\text{O}_3(\text{g}) \rightarrow 3\text{O}(\text{ads})$ . Calculate the equilibrium constant,  $K$  for this process when the coverage of  $\text{O}(\text{ads})$  is 0.50 at  $P_{\text{O}_3} = 1 \text{ atm}$ .
- (b) The wave number of  $J = 0$  to  $J = 1$  transition for pure rotational spectrum of  $^1\text{H}^{81}\text{Br}$  is  $16.93 \text{ cm}^{-1}$ . Assuming the molecule as a rigid rotor, calculate its moment of inertia in  $\text{kg m}^2$  and equilibrium bond length in m.
15. (a) Derive the expressions of critical constants ( $P_c$ ,  $V_c$  and  $T_c$ ) for van der Waals gases.
- (b) In an aqueous solution of HCl, the transport number of  $\text{H}^+$  ion is abnormally higher than  $\text{Cl}^-$  ion. Explain why.
- (c) Find the units of  $A$  and  $E_a$  (in SI units) using the equation,  $k = Ae^{-E_a/RT}$ .  $k$  is the zero-order rate constant.





## SECTION-A

Attempt any three questions including question no. 1 which is compulsory.

1. Answer all of the questions given below :

- (a) A mixture of CuO and  $\text{Cu}_2\text{O}$  with a mass of 10.50 g is reduced to give 8.66 g of pure Cu metal. What are the amounts of CuO and  $\text{Cu}_2\text{O}$  (in g) in the original mixture ?
- (b) To a mixture of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  solution,  $\text{Na}_2\text{SO}_4$  solution is added gradually. Which one of the two will be precipitated first ?

$$\text{Given: } S_{\text{SrSO}_4} = 2.8 \times 10^{-7}$$

$$S_{\text{BaSO}_4} = 4.2 \times 10^{-11}$$

- (c) Aniline is a weak organic base in aqueous solutions. Suggest a solvent in which aniline can become a strong base with proper scientific reason.
- (d) Explain the scientific basis of functioning of fluoride ion selective electrode.
- (e) Discuss the effect of organic solvents in AAS measurement.
- (f) How does flame ionization detector work? Name two compounds that cannot be measured by this detector.
- (g) Explain how proximity analysis of coal can be determined by thermogravimetric analyzer.
- (h) 0.1 g of dolomite ore was acid digested and a stock solution was prepared in a 25 mL volumetric flask using de-ionized water. An aliquot of 1 mL of the stock solution was pipetted into 100 mL volumetric flask and the volume was made up by de-ionized water. This solution was subjected to analysis of Fe content by ICP-MS. After suitable calibration, the output of ICP-MS analysis showed Fe concentration as 4  $\mu\text{g/L}$ . Find the concentration of Fe in the dolomite ore in  $\mu\text{g/g}$ .

2. (a) Arrange the following mixture of oxidant-fuel combination in the increasing order of flame temperature in AAS :

air-acetylene; air-natural gas; nitrous oxide-acetylene; oxygen-acetylene.

- (b) Explain the Doppler broadening effect in AAS.
- (c) Explain the principle of XRF technique and comment how this technique is useful for qualitative and quantitative analysis. Arrange the K, L and M X-ray of Au in energy dispersive XRF.
- (d) A mineral corresponding to orthorhombic system was studied by XRD using X-rays of wavelength  $\lambda = 1.54 \text{ \AA}$ . The X-ray reflection planes from (100), (010) and (001) were observed at  $2\theta = 22.5^\circ$ ,  $9.8^\circ$  and  $28.8^\circ$ , respectively. Find the dimension of the unit cell and the number of molecules of the mineral in the unit cell.

Given : Molecular weight of the mineral = 140 g/mol.

Density of the mineral = 4.2 g/cm<sup>3</sup>.

3. (a) Compare the features of different types of detectors used in HPLC system.
- (b) What is correlation index in petroleum analysis ? How is it useful for classification of petroleum ?
- (c) Match the combinations for cellulose powder and sephadex gel as sorbents with the chromatographic mechanisms and applications listed below in columns A and B, respectively :

Column A

Column B

(Chromatographic Mechanism)

(Applications)

- Exclusion principle
- Stereo-adsorptive interaction
- Modified partition

- Non-polar compound
- Amino acids
- Polymers



- Ion-exchange
- Partition
- Mixture of enantiomers
- Halides

(d) What is the principle involved in ICP-MS analysis ? Why should high salt content be avoided during sample preparation for ICP-MS analysis ?

4. (a) A mixture of  $\text{KMnO}_4$  and  $\text{K}_2\text{CrO}_4$  weighing 0.24 g on being treated with acidic KI solution is found to liberate iodine ( $\text{I}_2$ ) to react with 60 ml of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Find out the percentage of Cr and Mn in the mixture.

(b) Calculate the concentration of  $\text{Ni}^{2+}$  in a solution that was prepared by mixing 50.0 mL of 0.0300 M  $\text{Ni}^{2+}$  with 50.0 mL of 0.0500 M EDTA. The mixture was buffered to a pH of 3.0.

Given : Formation constant of

$\text{Ni}^{2+}$  -EDTA complex :  $4.2 \times 10^{18}$

$\alpha_4$  for  $\text{Ni}^{2+}$  -EDTA

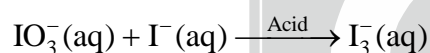
complex at pH = 3.0 :  $2.51 \times 10^{-11}$

(c) Explain the functions of

(i) Diphenylamine sulphonic acid

(ii) Methyl yellow  
as indicators.

5. (a) Write a balanced net ionic equation for the following reactions :



(b) A compound X contains only carbon, hydrogen, nitrogen and chlorine. When 1.00 g of X is dissolved in water and allowed to react with excess  $\text{AgNO}_3$ , 1.95 g of  $\text{AgCl}$  is collected. When 1.00 g of X is subjected to complete combustion, 0.900 g of  $\text{CO}_2$  and 0.735 g of  $\text{H}_2\text{O}$  are formed. What is the empirical formula of X ?

(c) Are the equivalence point and end point the same ? Justify your answer.

(d) Calculate the (i) molar concentration, and (ii) molality of a sulphuric acid solution of density 1.198  $\text{g}/\text{cm}^3$  containing 27%  $\text{H}_2\text{SO}_4$  by weight.

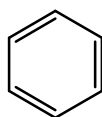
### SECTION-B

**Attempt any three questions including question no. 6 which is compulsory.**

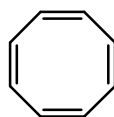
6. **Answer all the following :**

(a) Explain why p-nitrophenol is more acidic than m-nitrophenol.

(b) Draw *pi* molecular orbital diagram of the following species :



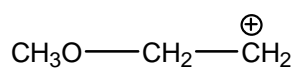
(I)



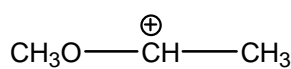
(II)

(c) Explain why acetaldehyde is more reactive than benzaldehyde for nucleophilic addition reaction.

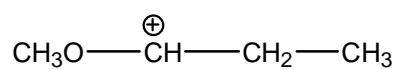
(d) Arrange the given carbocations in their decreasing order of stability and give reasons for your answer.



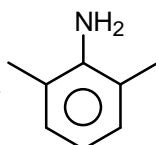
(I)



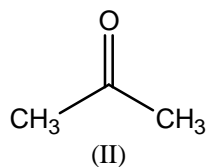
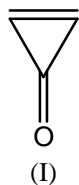
(II)



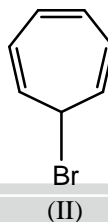
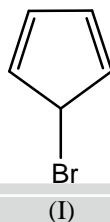
(III)

(e) Explain why  is more basic than aniline although both are aromatic primary amines.

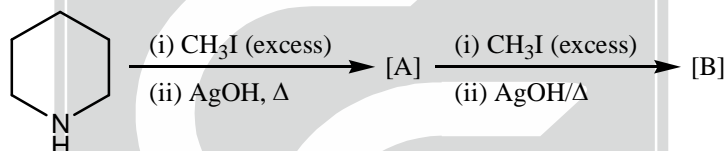
(f) Which one of the following compounds has higher dipole moment and why ?



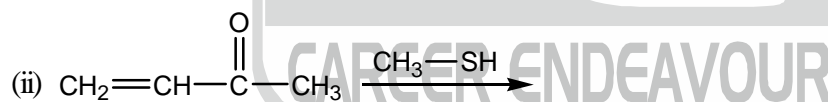
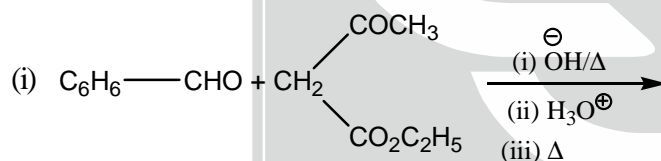
(g) Explain why one of the following compounds gives  $S_N1$  reaction :



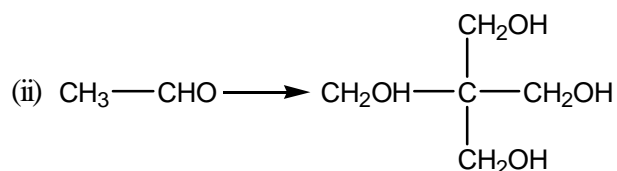
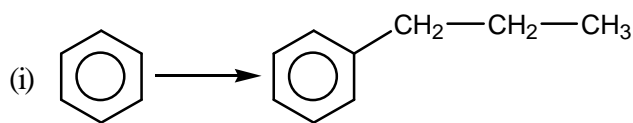
(h) Complete the following reaction and give the structure of the compounds [A] and [B] :



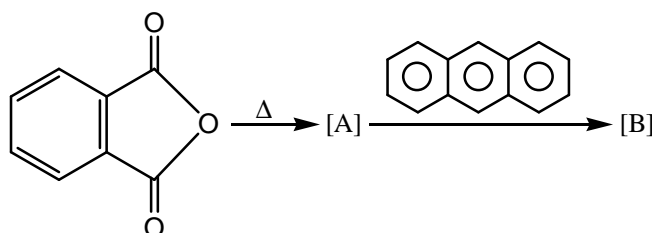
7. (a) Complete the following reactions and give their mechanisms :



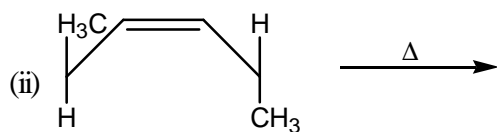
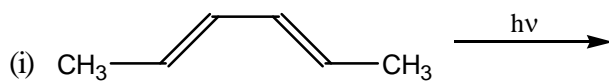
(b) How can the following conversions be achieved ? Provide suitable methods which give good yields.



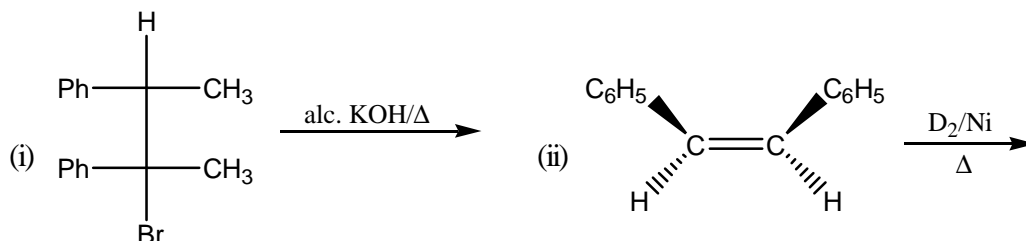
(c) Complete the following reaction and give the structure of [A] and [B] :



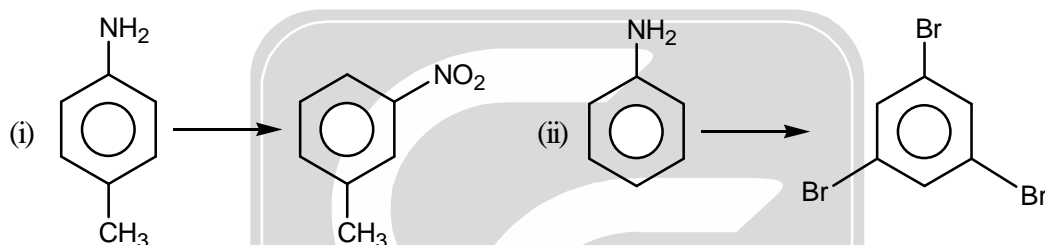
8. (a) Complete the following reactions and give the stereochemistry of the products(s) :



(b) Complete the following reactions and provide stereochemistry of the products :



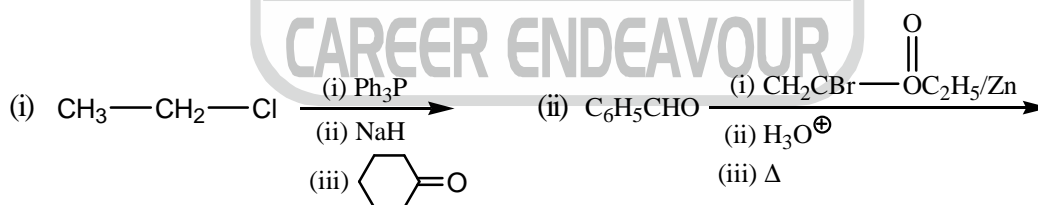
(c) How can the following conversions be achieved ?



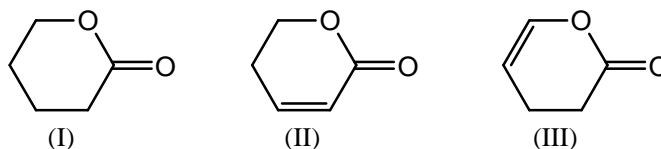
9. (a) What are the characteristics of pericyclic reactions ? Give  $\pi$  molecular orbital diagram of 1,3,5-hexatriene. Indicate

- Ground state HOMO and LUMO, and
- Excited state HOMO and LUMO of the system.

(b) Complete the following reactions :



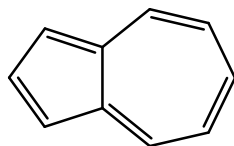
(c) Arrange  $\nu_{\text{max}}$  (C=O) of the following compounds in decreasing order. Give reasons in favour of your answer :



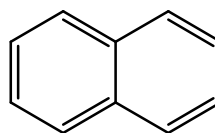
10. (a) Give relative intensities of the parent cations of the compound given below :



(b) Indicate the number of PMR and CMR signals of the given compounds :



(I)



(II)

(c) An organic compound  $C_6H_{12}O_2$  gave the following spectral data :

UV :  $\lambda_{max}$  283 nm,  $\epsilon_{max}$  27

IR : Significant absorption bands at 3450, 2900 and 1705  $cm^{-1}$ .

PMR :  $\delta$  1.3 (6H, S); 2.2 (3H, S) and 3.8 (1H, S : exchangeable with  $D_2O$ ); 2.5 (S, 2H).

CMR : (off-resonance decoupled) : Two singlets, one triplets and one quartet. One of the singlets is at 210 ppm and the other at 70 ppm.

Mass : Prominent peaks at  $m/z$  116, 58 and 43.

Deduce the structure of the compounds and explain the spectral data.

