GEOLOGIST EXAMINATION-2015
GENERAL ENGLISH

Time Allowed : Three Hours **M.M. : 100**

INSTRUCTIONS

- **Please reach each of the following instruction carefully before attempting questions:**
- There are seven 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.
- Precis question must be attempted only on the special precis sheet(s) provided. These precis sheets must be attached securely to the answer book.
- All parts and sub-parts of a question are to be attempted together in the answer book.
- You must not disclose your identify in any of your answers.

1. Write an essay on any ***one*** of the following topics in not less than 800 words : **[30]**
   (a) Leadership is not a position but a responsibility.
   (b) Does the rise of materialism lead to erosion of values?
   (c) Understanding is the best form of hospitality.
   (d) Individual freedom versus Social responsibility.
   (e) The scientific temper of the modern world.

2. Make a precis of the following passage in about one-third of the original length, using your own words. (**Note:** The precis must be written only on the special sheets provided for this purpose, writing one word in each/block. The sheet should be fastened securely inside the answer book.) **[20]**

   There are two ways in which science affects human affairs. The first is familiar to everyone; Directly, and to an even greater extent indirectly, science produces aids that have completely transformed human existence. The second way in educational in character — it works on the mind. Although it may appearl less obvious to cursory examination, it it no less incisive than the first.

   The most conspicuous practical effect of science is that it makes possible the contriving of things that enrich life, though they complicate it at the same time — inventions such as the steam engine, the railway, electric power and light, the telegraph, radio, automobile, airplane, dynamite, etc. To these must be added the life-preserving achievements of biology and medicine, especially the production of pain relievers and preservative methods of storing food. The greatest practical benefit which all these inventions confer on man I see in the fact that they liberate him from the excessive muscular drudgerg that was once indispensable for the preservation of bare existence. Insofar as we may at all claim that slavery has been abolished today, we owe its abolition to the practical consequences of science.

On the other hand, technology — or applied science — has confronted mankind with problems of profound gravity. The very survival of mankind depends on a satisfactory solution of these problems. It is a matter of creating the kind of social institutents and traditions without which the new tools must inevitably bring disaster of the worst kind.

Technology has shortened distance and created new and extraordinary effective means of destruction which, in the hands of nations claiming unrestricted freedom of action, become threats to the security and very survival of mankind. This situation requires a single judicial and executive power for the entire planet, and the creation of such a central authority is desperately opposed by national traditions. Here too we are in the midst of a struggle whose issue will decide the fate of all of us.

Means of communication, finally — reproduction processes for the printed word, and the ratio — when combined with modern weapons, have made it possible to place body and soul under bondage to a central authority — and here is a third source of danger to mankind. Modern tyrannies and their destructive effects show plainly how far we are from exploiting these achievements organizationally for the benefit of mankind. Here too circumstances require an international solution, with the psychological foundation for such a solution not yet laid.

Let us now turn to the intellectual effects that proceed from science. In prescientific times it was not possible by means of thought alone to attain results that all mankind could have accepted as certain and necessary. Still less was there a conviction that all that happens in nature is subject to inexorable laws. The fragmentary character of natural law, as seen by the primitive observer, was such as to foster a belief in ghosts and spirits. Hence, even today primitive man lives in constant fear that supernatural and arbitrary forces will intervence in his destiny.

It stands to the everlasting credit of science that by acting on the human mind it has overcome man's insecurity before himself and before nature. In creating elementary mathematics the Greeks for the first time wrought a system of thought whose conclusions no one could escape. The scientists of the Renaissance then devised the combination of systematic experiment with mathematical method. This union made possible such precision in the formulation of natural laws and such certainty in checking them by experience that as a result there was no longer room for basic differences of opinion in natural science. Since, that time each generation has built up the heritage of knowledge and understanding, without the slightest danger of a crisis that might jeopardize the whole structure.

The general public may be able to follow the details of scientific research to only a modest degree; but it can register at least one great and important gain: confidence that human thought is dependable and natural law universal. (670 words).

3. Write a paragraph in about 200 words on any ***one*** of the following expression/statements: **[10]**

(a) All that glitters is not gold.
(b) Time and tide wait for none.
(c) A bird in hand is worth two in the bush.
(d) Brevity is the soul of wit.
(e) To err is human; to forgive is divine.

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. **[5×2=10]**

(a) Loquacious
(b) Topsy-turvy
(c) Mentor
(d) Enigmatic
(e) Nefarious

5. Use the following homonyms in sentences so as to bring out the difference in meaning clearly without changing the form. **[5×2=10]**

(a)	(b)	(c)	(d)	(e)
Compliment	Canvas	Device	Ghostly	Cite
Complement	Canvass	Devise	Ghastly	Site

6. Make the directed changes in the following sentences without changing their meaning. **[5×2=10]**

(a) I know him.
(Change into passive voice)

(b) The stranger said, "Could you tell me where the post office is" ?
(Change into indirect speech)

(c) I did not spend as much money as you.
(Change into comparative degree)

(d) You are allowed into the club only if you are a member.
(Rewrite the sentence using 'unless')

(e) Join the two simple sentences to make one complex sentence.
We enjoyed our holiday. It rained a lot.

7. Correct the following sentences without changing their meaning. Do not make unnecessary changes in the original sentence. **[1×10=10]**

(a) Despite of repeated reminders, the company has not responded.

(b) All the students will attend the function, wouldn't they ?

(c) This is one of the best books that has been recently purchased for the library.

(d) Flying on the northern part of India we could see the peak of the Everest.

(e) Your friend is waiting for you since morning.

(f) People expect a lot from an university scholar.

(g) The sun is rising in the East everyday.

(h) When we arrived at the station, the train already left.

(i) Neither the officer nor his PS were in the office.

(j) The minister along with his wife are leaving for London.

Geo-Scientist Paper 2015

Paper-I

SECTION-A

1. Answer all of the following: **5×10=50**

(a) Carbon tetrachloride is inert towards water but boron trichloride hydrolyses in moist air. Suggest a reason. **[5]**

(b) Francium has a smaller atomic radius than cesium and radium is smaller than barium. Explain, why. **[5]**

(c) Consider the complex ions dibromourate (I) and tetrabromourate (III). Which is more stable in aqueous solution and why? **[5]**

(d) Although 18 valence electrons are found in $\left[Fe\left(H_2O\right)_6\right]^{2+}$, the effective atomic number rule is violated. Explain. **[5]**

(e) Substitution reactions of polynuclear metal carbonyls with tertiary phosphines often induce the formation of bridging carbonyls. Provide an explanation. **[5]**

(f) Draw the radial part of the wave functions for hydrogen atom with $n = 3, \ell = 2$; $n = 3, \ell = 0$; $n = 2, \ell = 1$ **[5]**

(g) Draw the molecular orbital diagrams of O_2 and CO, and give the number of unpaired electrons and bond order in each case. **[5]**

(h) Describe the structures of F_3ClO and XeF_6. What is the difference between the lone pairs present in the two compounds? **[5]**

(i) Distinghish between nuclear fission and nuclear fusion reactions. **[5]**

(j) Why is AgI_2^- complex stable but AgI_3^- complex is not? **[5]**

SECTION-B

2. (a) What is meant by 'isoelectronic ions'? How does the size vary in the following series? Explain :

$$N^{3-}, O^{2-}, F^-$$ **[10]**

(b) Calculate the size of tetrahedral site in closed-packed structure. **[10]**

(c) The second ionization energy of sodium is very high as compared to its first ionization energy. Give reason. **[10]**

3. (a) Explain on the basis of MO theory as to why.
(i) oxygen molecule is paramagnetic while nitrogen molecule is diamagnetic.
(ii) hydrogen forms diatomic molecule while helium remains monatomic. **[10]**

(b) What is the lattice energy? Discuss Born-Haber cycle for experimental determination of lattice energy. **[10]**

(c) What is polarization of molecules and ions? Discuss Fajan's rules regarding polarization. What are their effects? **[10]**

SECTION-C

4. (a) What are meant by the terms labile and inert complexes? Explain, on the basis of crystal field theory, the cause of lability and inertness of octahedral complexes. **[15]**

(b) Mention theories of trans-effect. Discuss any one of them in detail. Which theory explains better trans-effect of CO compared to pyridine? **[15]**

5. (a) "All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases". Comment on the statement. **[10]**

(b) Discuss briefly the solvent system concept of acids and bases. What are the limitations of this concept? **[10]**

(c) What is a conjugate acid-base pair? Show that a strong acid has a weak conjugate base and a weak acid has strong conjugate base. **[10]**

SECTION-D

6. (a) Balance the following ionic reaction by ion-electron method in acid medium. **[10]**

$$MnO_4^- \rightarrow Mn^{2+}$$

(b) Balance the above reaction by ion-electron method in basic medium. **[10]**

(c) What is electrode potential? Explain why copper roofs get covered by a green layer of a mixture of $CuSO_4$ and $CuCO_3$ in damp environments. **[10]**

7. (a) Define crystal field stabilization energy. Calculate its value for the following systems. **[10]**
(i) d^5 low-spin complexes.
(ii) d^6 tetrahedral complexes

(b) How does the valence bond theory account for the following facts? **[10]**

(i) $\left[Ni(CN)_4\right]^{2-}$ is diamagnetic and square planar

(ii) $\left[NiCl_4\right]^{2-}$ is paramagnetic and tetrahedral.

(iii) $Ni(CO)_4$ is paramagnetic and tetrahedral.

(c) Account on the basis of valence bond theory that the complex ion $\left[Co(NH_3)_6\right]^{3-}$ is octahedral and diamagnetic while the complex ion $\left[CoF_6\right]^{3-}$ is also octahedral but paramagnetic. **[10]**

SECTION-E

8. (a) Explain why boron trichloride is monomeric while aluminium trichloride is dimeric. **[10]**

(b) Discuss the structure of $(SiO_4)^{4-}$ ion **[10]**

(c) Discuss the variation of bond angles in hydrides of group 15 elements : **[10]**

$$NH_3(107.3^o),\ PH_3(93.6^o),\ AsH_3(91.8^o),\ SbH_3(91.3^o)$$

9. (a) Discuss the preparation and structure of ferrocene. **[10]**

(b) Show how CO molecule functions as sigma-donor and π-acceptor ligand both. **[10]**

(c) A living plant acquires a definite fraction of $^{14}_{6}C$ nuclei in its carbon content. If a freshly cut piece of wood gives 16.1 counts per minute per gram and an old wooden bowl gives 9.6 counts per minute per gram of carbon, calculate the age of the wooden bowl. The half-life of $^{14}_{6}C$ is 5770 years. **[10]**

SECTION-F

10. (a) Compare the alkali metals with alkaline earth metals with respect to their (i) electronic configuration, (ii) size of atoms and ions, and (iii) ionization potential **[10]**

(b) "There occurs a progressive increase in metallic character in moving down a family of representative elements.". Justify the above statement with reference to group 17. **[10]**

(c) An electronegative element A has the electronic configuration $(n-2)s^2(n-1)s^2(n-1)p^6ns^2np^5$ and an electropositive element B has the electronic configuration $(n-2)s^2(n-1)s^2(n-1)p^6ns^1$.

(i) Name the two elements if n = 3.

(ii) To which block of elements in the periodic table, A and B belong to?

(iii) what would be the nature of the two elements - metallic or non-metallic?
(iv) what type of bond will be formed if the two elements combine together to form the compound AB and what properties are expected to be associated with the compound? **[10]**

11. Comment on the following statements:
(a) Actinides have a greater tendency to form complexes than lanthanides **[10]**
(b) Lanthanides have little tendency to form complexes but their compounds are generally brilliantly coloured. **[10]**
(c) Chemically actinides show a somewhat wider range of oxidation states. **[10]**

Paper - II

SECTION-A

1. Answer all of the following: **5×16 = 80**

(a) Derive the relationship $TV^{\gamma-1}$ = constant for a reversible adiabatic expansion.
(b) Show that, for a van der Waals gas, the Boyle temperature $T_b = a/Rb$.
(c) The half-life period of a first order reaction is 3 min. Calculate the time taken to complete 75% of the reaction.
(d) For the cell, $Mg \mid Mg^{2+} \parallel Ag^{+} \mid Ag$, calculate the equilibrium consant at 25ºC and also the maximum work that can be obtained by operating the cell. Given that

$E^0_{Mg^{2+}|Mg} = -2.37V$ and $E^0_{Ag^{+}|Ag} = +0.80V$

(e) 0.001 kg of a water-insoluble substance of density 0.8 kg dm^{-3} is dispersed in a 1 dm^3 of water, forming a colloidal solution having 10^{19} particles of spherical shape per dm^3. Calculate the radius of the particles.
(f) Which of the three vibrations of an AB_2 molecule are infrared or Raman active if it is
(i) linear and (ii) angular
(g) The pH of a 0.10 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid?
(h) "While the viscosity of a gas increases with increase in temperature, that of a liquid decreases with increase in temperature". How do you account for this?
(i) State and explain the term 'quantum yield'. How do you explain the fact that the quantum yield of the photochemical reaction.

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ is low (~0.01), while that of the reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is very high (~10^5)?

(j) Calculate the thermal de-Broglie wavelength of a hydrogen atom at 3000K confined to move in a box of volume 0.25 m^3.
(k) Discuss the ^1H NMR of pure ethanol and acidified ethanol.
(l) Justify the following statments:
(i) Fluorescence is favoured at very low pressures
(ii) Phosphorescence, unlike fluorescence, cannot be studied in the liqud phase.
(m) Derive an expression for the variation of fugacity with temperature
(n) why is a bathochromic shift observed with increasing conjugation in electronic spectra?
(o) Calculate the interplanar spacing (d_{hkl}) between the following set of planes : (i) 110, (ii) 111 (iii) 222 for cubic systems
(p) Calculate the root mean square velocity of helium gas at 25ºC.

SECTION-B

Attempt any SIX question: Each question carries 10 marks.

2. (a) Can the activation energy of a reaction be zero or negative? Explain **[3]**
(b) The activation energy of a non-catalyzed reaction at 37ºC is 83.68 kJ mol^{-1} and that of the same reaction catalyzed by an enzyme is 25.10 kJ mol^{-1}. Calculate the ratio of rate constants of the enzyme-catalyzed and non-catalyzed reaction. **[4]**
(c) For a reaction of the type **[3]**

$$P \xrightarrow{k_1} Q \xrightarrow{k_2} R$$

Given that $[P]_0 = 1\,M$, $k_1 = 1\times10^{-3}s^{-1}$ and $k_2 = 1\times10^{-4}s^{-1}$, find the time at which the concentrations of Q and R become 0.5966 and 0.03555 M, respectively.

3. (a) For a certain reaction, $\Delta G^0 = +45$ kJ mol^{-1} and $\Delta H^0 = +90$ kJ mol^{-1} at 0ºC. At what temperature (K) is $\Delta G^0 = 0$, assuming that ΔH^0 and ΔS^0 are independent of temperature. **[5]**

(b) Given the data below, calculate the equilibrium constant at 25ºC for the reaction : **[5]**

$$2NO_2(g) = N_2O_4(g)$$

Compound	ΔG (kJ mol)
NO_2	51.29
N_2O_4	97.82

4. (a) At 460 nm, a blue filter transmits 72.7% of light and a yellow filter 40.7% of light. What is the transmittance at the same wavelength if the two filters are in combination. **[5]**

(b) In a cell of a certain length and a pressure of 100 mm Hg, gaseous acetone transmits 25.1% of incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98% of the incident radiation will be absorbed. **[5]**

5. (a) One mole of an ideal gas, initially at 25ºC, is compressed isothermally to half its initial value. Calculate W, ΔU and ΔS for the process. **[4]**

(b) A carnot cycle operates at a temperature difference of 200K, one-third of the heat absorbed from the source is discharged as waste heat to the sink at T_1. The cycle does 400 J of work. Calculate the values of q_1, q_2, T_1 and T_2. **[3]**

(c) Determine the mean ionic mobility of a 0.5 molal solution of ferric chloride. **[3]**

6. Show that eigenfunctions corresponding to different eigenvalues are orthogonal. **[10]**

7. What is sacrificial protection of iron from corrosion?
Explain the following :
(i) Passivation of kinetic protection
(ii) Impressed current cathodic protection **[10]**

8. (a) To 0.5 dm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of the acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg mol^{-1} and 0.997 kg dm^{-3}, respectively. **[6]**

(b) Which colligative property is preferred for the molar mass determination of macromolecules and why? **[2]**

(c) Explain why doctors advise persons suffering from high blood pressusre to take less quantity of common salt. **[2]**

9. (a) The g value for the proton is 5.5854. Calculate the energy difference between the two levels of protons in a field of 1 Tesla. In what range of electromagnetic radiation does the above difference lie? **[5]**

(b) Why does the magnetic moment vector execute Larmor precession instead of alignment with the magnetic field? **[5]**

SECTION-C

Attempt any THREE question: Each question carries 20 marks.

10. (a) Outline the assumptions made for the derivation of the Langmuir adsorption equation and derive it. **[10]**

(b) Show that at low surface coverage, the Langmuir isotherm corresponds to the Freundlich expression with n = 1, and at high surface coverage, it corresponds to the Freundlich expression with n equal to infinity. **[5]**

(c) Calculate the surface area of a catalyst that adsorbs 1000 dm^3 of nitrogen at STP per kg in order to form a monolayer. The effective area occupied by a nitrogen molecule on the surface is 0.162 nm^2. **[5]**

11. (a) Giving reasons, classify the following molecules into different categories exhibiting pure rotational, pure vibrational, rotational Raman and vibrational Raman spectra. **[10]**

$H_2, HCl, CH_4, H_2O, CO_2, N_2, NO_2, N_2O$

(b) Show that the rotational level whose quantum number is given by the expression **[10]**

$$J = \sqrt{\frac{kT}{2\tilde{B}hc}} - \frac{1}{2}$$

has the maximum population.

12. Derive hte limiting equation of Debye and Huckel activity coefficients of strong electrolytes. **[20]**

13. (a) Set up the Schrodinger equation for a particle in a one-dimensional box. Show that the solution of the Schrodinger equation leads to quantization of the translational motion and hence derive the expression

$$E = \frac{n^2h^2}{8mL^2}$$ **[10]**

(b) What are the permitted values of the quantum number n? Explain why a zero value of n is not permitted. **[5]**

(c) Show that, for a free particle moving in an unbounded region of space, the translational energy is virtually unquantized. **[5]**

Paper - III

SECTION-A

Answer **ALL** of the following: **5×8 = 40**

1. (a) Suggest an analytical method for the quantitative estimation of Fe_2O_3, Al_2O_3 and TiO_2 in naturally occuring bauxite. **[5]**

(b) 500 mg of $ZnSO_4.7H_2O$ was placed in a 250 ml standard volumetric flask and was dissolved in water, the volume of the solution was made up to 250 ml. Express the concentration of zinc (Zn) in terms of
(i) Normality (ii) Molarity (iii) Molality (iv) Formality (v) ppm. **[5]**

(c) What will be the concentration of Pb^{+2} in saturated solution of $PbBr_2$ in water satured solution of $PbBr_2$ in which $[Br^-]$ is somehow fixed at 0.10 M? **[2.5×2]**

(d) What are primary standards? Can an accurately weighed $KMnO_4$ dissolved in an exact volume of water be treated as a standard solution? Justify your answer. **[5]**

(e) Define the following:
(i) Accuracy (ii) Precision (iii) Standard Deviation
(iv) Determinant erro (v) Indeterminant error **[5]**

(f) What is the difference between combustion and pyrolysis? **[2.5×2]**

Write a balanced equation for the combustion of $C_8H_7NO_2SBrCl$ in a C, H, N, S element analyser.

(g) How does the column temperature affect the performance of the separation in chromatography? Describe a method for the determination of number of plates in a chromatographic column. **[2.5×2]**

(h) How can you estimate the water content of a petroleum sample? **[5]**

2. **[7+8 = 15]**

(a) Cubic crystals are formed by copper. When they were shined with X-rays from a copper target (wave length 1.5405 Å), reflections were found at 45.30, 50.42, 74.12, 89.92, 95.16º and other higher angles.
(i) Determine the type of lattice formed by copper
(ii) What is the unit cell length at room temperature. **[3.5×2]**

(b) What is the equivalence volume, Ve, in the titration of 100.0 mL of 0.100 M cocaine ($K_b = 2.6\times10^{-6}$) with 0.20 M HNO_3?
Calculate the pH of the solution after the addition of following volumes of acid, Va:
Va = 0.0, 10, 20, 25, 30, 40, 49, 49.9, 50, 50.1, 51.0 and 60 mL.
Draw a graph of pH versus volume of the acid added, Va **[8]**

3. **[10+5=15]**

(a) What do you understand by plate height in a chromatogprahic column?
What would be the effect of the following on the plate height of a column?
(i) Increasing the flow rate
(ii) Decreasing the rate of sample injection
(iii) Reducing the particle size of the packing
(iv) Increasing the injection port temperature
(v) Increasing the weight of the stationary phase **[5+5]**

(b) Write a balanced equation for the redox reaction involving ferrous ammonium sulphate and potassiu permanganate solution in acidic medium. **[5]**

4. **[7+8=15]**

(a) What is skin effect?
Discuss the advantages of ICP over flame AES arising due to the skin effect. **[7]**

(b) 700 mg of a sample containing Fe(III) was dissolved in 20 ml of 0.0500 M EDTA solution. The unreacted EDTA was titrated with 0.0420 M (Cu) solution, total volume of Cu(II) solution consumed was equal to 5.08 ml.
Calculate the amount of Fe(III) in the sample, report your result as % of Fe_2O_3 in the sample. **[8]**

5. **[5+10=15]**

(a) Why is atomic emission more sensitive to flame instability than atomic absorption? **[5]**
(b) What is the function of flame in flame photometry and in atomic absorption sepctrometry? **[3+3]**
What is the purpose of using an internal standard in flame emission method of analysis? **[4]**

6. **[10+5=15]**

(a) Solid residue weighing 8.4448 g from an aluminium refining process was dissolved in an acid to give Al^{+3} in solution. **[10]**
The solution was treated with 8-hydroxy quinoline to precipitate Al (8-hydroxy quinoline) which was ignited to give Al_2O_3 weighing 0.8554 g.
Calculate the weight percentage of Al in the original mixture.

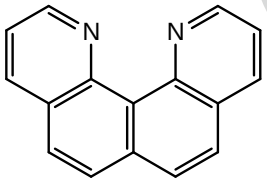
(b) What is the importance of Lambert-Beer's law in quantitative analysis? What are its limitations? **[10]**

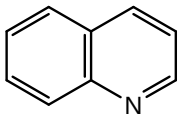
SECTION-B

Attempt any FIVE question: (Q.7 which is compulsory).

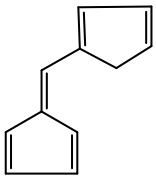
7. Answer **ALL** of the following: **[4×10=40]**

(a) Explain why quino [7, 8-h] quinoline is a stronger base than quinoline, whereas quinoline is a stronger nuclephilie between the two **[4]**

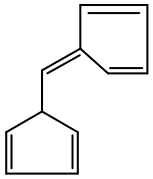




(b) Which of the following molecules would you expect to absorb at a longer wavelength in the UV region? Explain your answer **[4]**

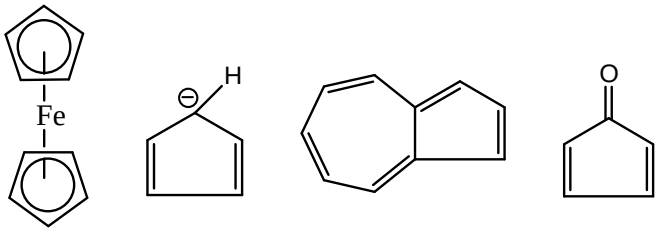


(A)



(B)

(c) Explain Huckel's rule for aromaticity. Identify the compound which is not aromatic among the following and explain why. **[4]**

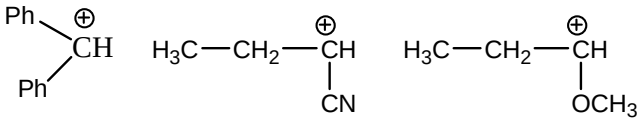


(d) Explain why cyanide ion is a specific catalyst in benzoin condensation and the reaction falls when attempted with p-nitrobenzaldehyde. **[4]**

(e) Tell precisely how you would use the proton NMR spectra to distinguish between the following pairs of compounds (i) Ethyl acetate and methyl propionate, (ii) Propanal and propanone. **[4]**

(f) Illustrate the application of Gabriel's phthalimide synthesis in the preparation of 1, 2-diaminoethane from corresponding dihalide. **[4]**

(g) Predict the stability order of the following carbocations. Briefly explain your reasoning.

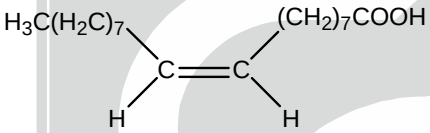


[4]

(A) **(B)** **(C)**

(h) Propose appropriate reagents/catalysts for the following reactions: **[4]**

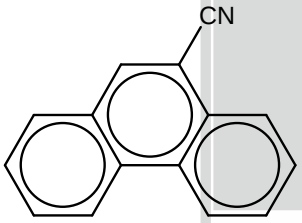
(A) $CH_3(CH_2)_7C \equiv C(CH_2)_7COOH \xrightarrow{?}$



(B) $C_6H_5CH = CHNO_2 \xrightarrow{?} C_6H_5CH_2CH_2NO_2$

(i) Predict the products in the following : **[4]**

(A)

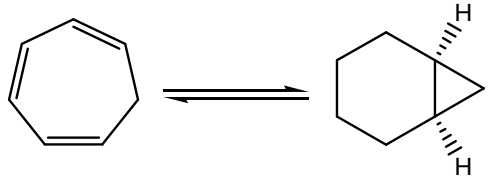


$+ CH_3Mg \xrightarrow{H_3O^+} ?$

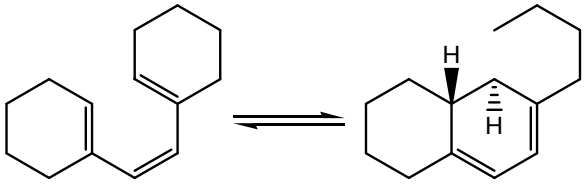
(B) $PhC \equiv CMgBr + (CH_3CC)_2O \xrightarrow{H_3O^+} ?$

(j) Identify the mode of cyclization and the pathway, thermal or photochemical, involved in each of the following electrocyclic reactions **[4]**

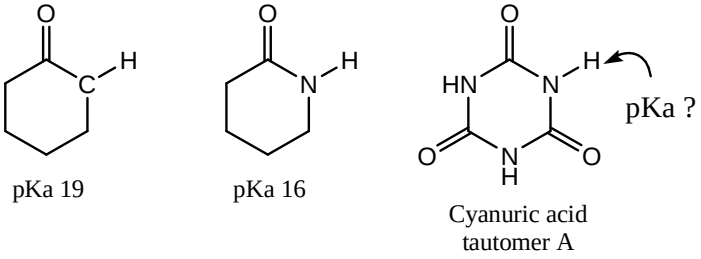
(A)



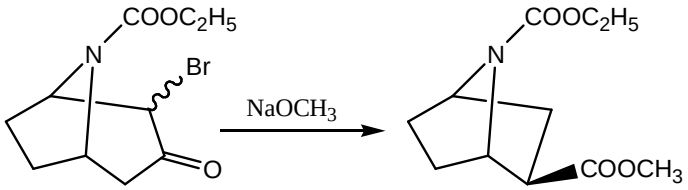
(B)



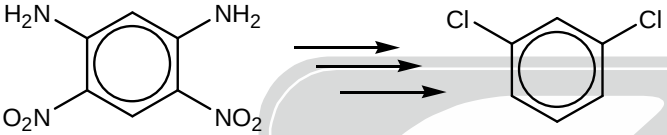
8. (a) Using the given pKa values as a guide, estimate the approximate pKa for N-H bond of cyanuric acid tautomer A. Briefly justify your answer **[5]**



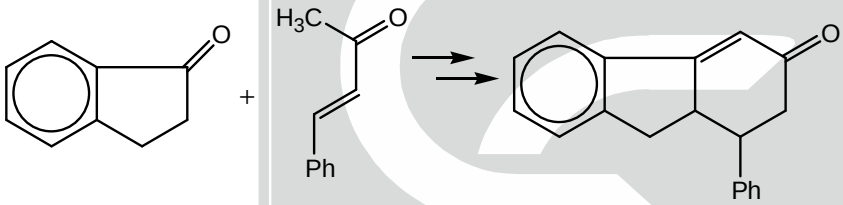
(b) Identify the name reaction and propose mechanism for the following reaction: **[5]**



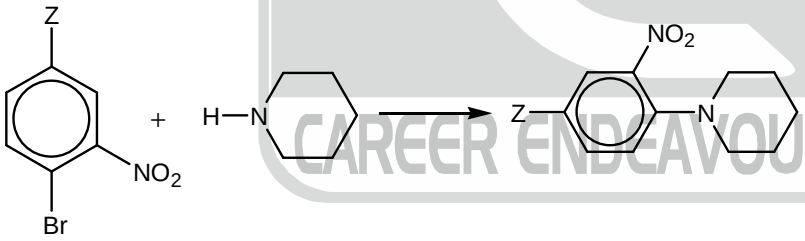
(c) Suggest a reaction sequence that would permit synthesis of the aromatic compound shown below : **[5]**



9. (a) Give sequence of reactions, with mechanism, for the following conversion : **[5]**



(b) Predict the effect of substituent Z on the relative rates in the following reaction. Also give the mechanism involved. **[5]**



A : Z = NO_2 and B : Z = OCH_3

(c) Give the advantages of stork enamine alkylation over direct base catalysed alkylation of aldehydes and ketones. Predict the major product of methylation with CH_3I of 2-methylcyclohexanone via pyrrolidine enanmine. **[5]**

10. (a) Given below are the relative reactivities of various hydrogen atoms of n-butylchloride towards further photochlorination. Account for the striking difference in the reactivity of hydrogens towards photochlorination.

$H_3C—CH_2—CH_2—CH_2—Cl$

8 17 5.5 1 **[5]**

(b) What are the stereoelectronic requirements of E-2 elimination reactions? Which of the following two isomers would be expected to undergo base-catalysed dehydrohalogenation at a faster rate? Explain your answer **[5]**

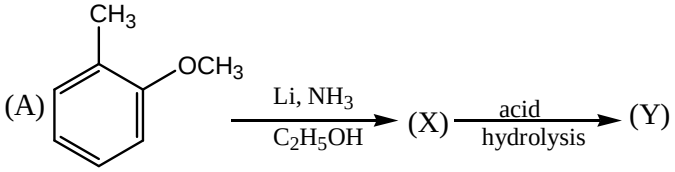
(A) **(B)**

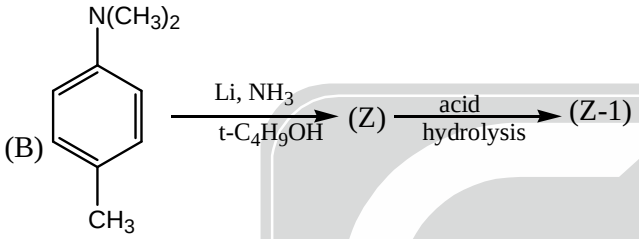
(c) Give HOMO and LUMO orbitals of 1, 3-butadiene, 1, 3, 5-hexatriene, allyl cation and allyl anion in ground state. **[5]**

11. (a) Discuss important similarities and differences between conjugation and aromaticity. **[5]**

(b) Show by construction of orbital symmetry correlation diagram whether CON or DIS rotatory mode of cyclization is symmetry allowed for 1, 3-butadiene via photochemica pathway. **[5]**

(c) Complete the following equations: **[5]**





12. (a) Determine the structure of an organic compound with molecular formula $C_{11}H_{12}O_2$ which shows the following spectra data : **[5]**

$\text{IR}\left(\text{cm}^{-1}\right): 1720, 1600, 1580, 770, 710$

$\text{PMR}\left(\delta \text{ ppm}\right): 1.3\left(\text{t}, 3\text{H}\right)\left(\text{J} = 7.00 \text{ Hz}\right),$

$4.2\left(\text{q}, 2\text{H}\right)\left(\text{J} = 7.00 \text{ Hz}\right), 6.3\left(\text{d}, 1\text{H}\right)\left(\text{J} = 16\text{Hz}\right)$

$7.3\left(\text{m}, 5\text{H}\right), 8.5\left(\text{d}, 1\text{H}\right)\left(\text{J} = 16\text{Hz}\right)$

(b) What is he McLafferty rearrangement in mass spectrometry? Mass spectrum of 1-phenylbutanone exhibits m/e (mass by charge) 105 as base peak and m/e 120 as one of the major peaks. Account for the same **[5]**

(c) Give mechanism involved in Witting reaction, Phosphorane, $\left(C_6H_5\right)_3P = CHCOOC_2H_5$, reacts rapidly with aldehydes but with ketone the reaction is sluggish. Explain why. **[5]**