GEOLOGIST EXAMINATION-2016
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.

- 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.

- 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) India suffers from paucity of role models.
   (b) The progress of a nation depends on the way its universities function.
   (c) "The more comprehensive and diversified the social order, the greater the responsibility and the freedom of the individual".
   (d) Should betting in sports be legalized?
   (e) The benefits of organic foods are greatly overrated.

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 sheets should be fastened securely inside the answer book.) **[30]**

   Why is it so important to close the educational gaps, and to remove the enormous disparities in educational access, inclusion and achievement? One reason, among others, is the importance of this for making the world more secure as well as more fair. H. G. Wells was not exaggerating when he said, in his *Outline of History* : "human history becomes more and more a race between education and catastrophe". If we continue to leave vast sections of the people of the world outside the orbit of education, we make the world not only less just, but also less secure.

   The precariousness of the world is now greater than it already was in H. G. Wells's time in the early twentieth century. Indeed, since the terrible events of September 11, 2001—and what followed after that—the world has been very aware of problems of physical insecurity. But human insecurity comes in many different ways—not just through terrorism and violence. Indeed, even on the very day of September 11, 2001, more people

died from AIDS than from physical violence including the atrocity in New York. Human insecurity can develop in many different ways, and physical violence is only one of them. While it is important to fight terrorism and genocide, we must also recognize the plural nature of human insecurity and its diverse manifestations.

As it happens, widening the coverage and effectiveness of basic education can have a powerfully preventive role in reducing human insecurity of nearly every kind. It is useful to consider briefly the different ways in which removing discrepancies and neglects in education can contribute to reducing human insecurity across the world.

The most basic issue relates to the elementary fact that illiteracy and innumeracy are forms of insecurity in themselves. Not to be able to read or write or count or communicate is a tremendous deprivation. The extreme case of insecurity is the certainty of deprivation and the absence of any chance of avoiding that fate. The first and the most immediate contribution of successful school education is a direct reduction of this basic deprivation—this extreme insecurity. The difference that basic education can make to human life is easy to see. It is also readily appreciated even by the poorest of families. The parents of even the most depressed families long to give basic education to their children, to make them grow up without the terrible handicaps from which they—the parents—had themselves suffered.

Of course, there are many obstacles in giving shape to the dreams of parents. The economic circumstances of the families often make it very hard for them, particularly when there are fees to be paid. This obstacle of unaffordability must be firmly removed.

There are other obstacles too like schools being thinly staffed and parents often worried about the safety of children, especially girl children. Then there are other barriers as well. Very poor families often rely on labour contributions from everyone, even the children, and this can compete with the demands of schooling. This unfortunate practice, though generated out of hardship, must also be removed, through regulation as well as by making the economic benefits of schooling clearer to all. This brings us to the second issue in understanding the contribution of schooling in removing human insecurity. Basic education can be very important in helping people to get jobs and gainful employment. This economic connection, while always present, is particularly critical in a rapidly globalizing world in which quality control and production according to strict specification can be crucial.

Also, when people are illiterate, their ability to understand and invoke their legal rights can be very limited, and educational neglect can also lead to other kinds of deprivation. Indeed, this tends to be a persistent problem for people at the bottom of the ladder, whose rights are often effectively alienated because of their inability to read and see what they are entitled to demand and how. The educational gap clearly has a class connection. It also has a gender connection since it can be very important for women's security. Women are often deprived of their due, thanks to illiteracy. There are often legal rights that are not used because the aggrieved cannot read. This distances them from the ways and means of fighting against gender discrimination.

Empirical work in recent years has brought out veiy clearly how the relative respect and regard for women's well-being is strongly influenced by women's literacy and educated participation in decisions within and outside the family. Even the survival disadvantage of women compared with men seems to go down sharply—and may even get eliminated—with progress in women's empowerment, for which literacy is a basic ingredient.

3. Write a paragraph in about 200 words on any one of the following expressions/statements :
   (a) The hand that rocks the cradle rules the world.   **[10]**
   (b) Those who live in glasshouses shouldn't throw stones.
   (c) Two wrongs don't make a right.
   (d) No man is an island.
   (e) Actions speak louder than words.

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) venerate   (b) aberration   (c) callous
   (d) circumspect   (e) enunciate

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5. Use the following phrasal verbs in sentences so as to bring out their meaning clearly :

(a) abide by   (b) iron out   (c) wear down   **[1×5=5]**

(d) rule out   (e) scape through

6. Correct the following sentences without changing their meaning. Do not make unnecessary changes in the original sentence : **[1×15=15]**

(a) The latest copy of the book is more preferable to any that has been published so far.

(b) Scarcely had the doctor left after examining him than the patient died.

(c) I don't think I have met the girl whom you say has topped in the examination.

(d) Raids were carried in all over the city to unearth illegal ammunition.

(e) The teacher did not take the test today as all the students were not present.

(f) There is hardly no reason to suspect his story.

(g) One of my friends are going abroad this summer.

(h) Unless the entire nation does not cooperates, we cannot hope to maintain law and order.

(i) Everyone in the room were amazed at the ease with which he was evading the questions asked.

(j) It is unfortunate that she could not avail of the opportunity to better her prospects.

(k) The doctor has prescribed two spoonful of the medicine to be taken three times everyday.

(l) The teacher was saying that one must do his duty honestly.

(m) Had you played well you would win the match.

(n) He behaves as if he was the chief of the organization.

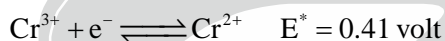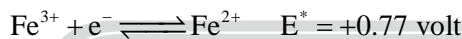(o) The teacher asked me if I was not ashamed of what I did.
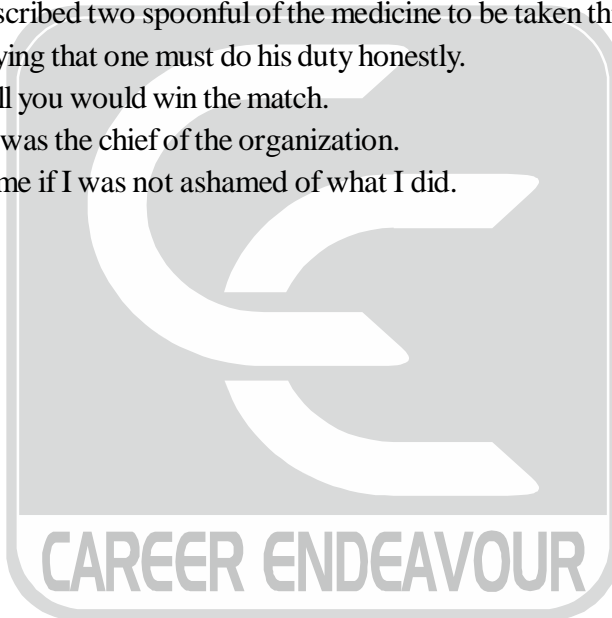
Geo-Scientist Paper 2016

Paper-I

SECTION-A

1. Answer all of the following: $5 \times 10 = 50$

(a) Lithium does not occur with sodium and potassium though all belong to group I. Explain **[5]**

(b) How does bond order change in the cases (i) O_2 to O_2^- and (ii) N_2 to N_2^+? Show with MO diagram.

[5]

(c) Why HF is a strong acid in liquid ammonia but is a weak acid in water? **[5]**

(d) Consider the following reaction:

$$3ClO^- \rightarrow 2Cl^- + ClO_3^-$$

Name the type of such reactions and give name and example of the reverse type. **[5]**

(e) Which of the two ions Fe(II) and Cr(III) would be easily oxidized?

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^* = +0.77 \text{ volt}$$

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \quad E^* = 0.41 \text{ volt}$$

E^* is standard reduction potential.

(f) Explain why H_2 molecule exists but He_2 does not. **[5]**

(g) Explain packing fraction. **[5]**

(h) Explain briefly geometrical isomerism. Draw the strcutures of various geometrical isomers of the following complexes:

(i) $\left[PtCl_2 (NH_3)_2 \right]$

(ii) $\left[Pt(NO_2)(C_5H_5N)(NH_3)(NH_2OH) \right]$ **[5]**

(i) Identify the ground term symbol of set of terms ^1G, ^3F, ^3P, ^1F. Specify the spin (S) and angular momenta (L) of ground state and also the possible total angular momentum (J) value.

(j) In which of the following the EAN rule is not followed? Explain: **[5]**

(i) $Co_2(CO)_8$

(ii) $V(CO)_6$
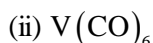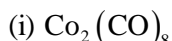
SECTION-B

Attempt any one question:

2. (a) Explain briefly the liquid-drop model of a nucleus. Show that usuall $^{238}_{92}U$ is an α-emitter and not a β-emitter. **[15]**

(b) Explain the concept of VSEPR theory and illustrate its efficacy in predicting gross geometrical structures of BeF_2, NH_3 and CCl_4. **[15]**

3. (a) Write down all term symbols for d^2-configuration. Identify the term symbol for ground state and show how it is split up by spin-orbit coupling. **[10]**

(b) Explain, 'mass defect' and 'binding energy'. How are they related? **[10]**

(c) Explain the structure of Cu(II) acetate dihydrate. **[10]**

SECTION-C

4. Attempt any one question:

(a) Show diagramatically the crystal field splitting of d-orbitals in octahedral and tetrahedral environment. Show that

$$\Delta_{td} = \frac{4}{9}\Delta_{oct}$$
[15]

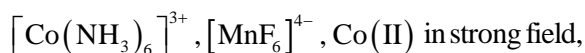(b) The log k value of Cr-EDTA complex is 23.0, still Cr(III) cannot be titrated with EDTA directly. Explain **[5]**

(c) Explain the structure and bonding in $Fe_3(CO)_9$. **[10]**

5. (a) What is diagonal relationship in the periodic table? Discuss with reference to lithium, magnesium, beryllium and aluminium. **[10]**

(b) Explain why the magnetic moment of Gd^{3+} (Z = 64) complexes can be obtained by spin-only formula but not of Tb^{3+} (Z = 65) complexes. **[10]**

(c) Discuss the bonding of CO in metal carbonyls. Find EAN of metal atoms in $Ni(CO)_4$ and $Fe(CO)_5$. Also give their structures. **[10]**

SECTION-D

Attempt any one question:

6. (a) Explain briefly tetragonal distortion of octahedral complexes. In which of the following complexes. In which of the following complexes, it is observed? **[10]**

$$\left[Co\left(NH_3 \right)_6 \right]^{3+}, \left[MnF_6 \right]^{4-}, Co\left(II \right) \text{ in strong field,}$$

$$\left[Ni\left(H_2O \right)_6 \right]^{2+} \text{ and Mn(III) in weak field.}$$

(b) Explain the Lewis concept of acids and bases. **[10]**

(c) What is pK_a value of a weak acid? How is it related to its pH? Explain **[10]**

7. (a) Differentiate between thermodynamic and stoichiometric stability constant. Under which condition the two will be identical? **[10]**

(b) Calculate the magnetic moment of $\left[Mn\left(CN \right)_6 \right]^{3-}$ and $\left[MnBr_4 \right]^{2-}$ **[10]**

(c) Write down a brief note on peroxy acids **[10]**

SECTION-E

Attempt any one question:

8. (a) What are fluorocarbons? Give their method of preparation, properties and commercial applications. **[15]**

(b) Explain which of the following has the shortest bond length:

$$NO, NO^-, NO^+, NO^{++}$$ **[10]**

(c) Write the structure of diborane **[5]**

9. (a) Explain the structures of different types of silicates **[15]**

(b) Balance the following ionic reaction by 'ion electron' method in acidic medium:

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$ **[7]**

(c) Write down the ionic oxidation reaction for the liberation of iodine from potassium iodide in acidic medium by potassium dichromate. **[8]**

SECTION-F

Attempt any one question:

10. (a) Name all the elements belonging to group 14 and commet on the group trend in properties in respect of
   (i) metallic character;
   (ii) chemical reactivity
   (iii) stability of tetrahalides
   (iv) basicity of oxides. **[10]**

(b) Explain the configuration and oxidation states of 'lanthanides'. **[10]**

(c) How is Cu^{2+} estimated iodometrically? Explain the reactions involved **[10]**

11. (a) Comment on the following:

(i) $SnCl_2$ dissolves in HCl but not in ammonia.

(ii) CO_2 is a molecular gas but SiO_2 is a solid.

(iii) $SnCl_2$ shows reducing behaviour, $PbCl_2$ does not.

(b) How are nuclear radiations detected and measured ? Discuss one method.

Paper-II

SECTION-A

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

(a) What is virial equation of state for real gases? Express van der Waals equation in the form of virial equation. Discuss the physical significance of virial coefficients. **[5]**

(b) A cipillary tube of radius 0.001 cm is inclined at an angle of 45° to the surface of the liquid. The liquid wets the wall of the tube. Calculate the distance along the capillary to the miniscus of the liquid if the density of the liquid is 0.85 g cm^{-3} and the surface tension is 36 dynes cm^{-1}.

(c) Justify the following statements: **[5]**

(i) The net entropy of the universe increases.

(ii) X rays are used for diffraction by crystals.

(d) Applying the law of equipartition of energy, estimate the energy of H_2 molecule assuming that all the degrees of freedom are excited and contribute towards the energy of the molecule. Give the statement of the law. **[5]**

(e) Calculate the fall in temperature of He gas initially at temperature 15°C when it is suddenly expanded to eight (8) times its volume. (Given : $\gamma = \dfrac{5}{3}$) **[5]**

(f) Deduce the equation to show the variation of K_P with temperature and show that K_P is independent of pressure **[5]**

(g) Calculate the pH of 0.01 M NH_4Cl in water at 25°C. pK_b for NH_4OH is 4.74. Ion product of water is 10^{14}. **[5]**

(h) Explain the term reverse-osmosis. **[5]**

2. (i) The following data were obtained for the reaction $A + B \rightarrow$ products . Derive the rate law.

[A] mole dm^{-3}	[B] mole dm^{-3}	[C] mole dm^{-3}s^{-1}
6.0×10^{-3}	1.0×10^{-3}	0.012
6.0×10^{-3}	2.0×10^{-3}	0.024
2.0×10^{-3}	1.5×10^{-3}	0.002
4.0×10^{-3}	1.5×10^{-3}	0.008

(j) 130 ml of N_2 (corrected to 0°C and 1 bar pressure) was required to form a monolayer on a solid. Calculate the surface area of the solid. Cross sectional area of N_2 is 16.2 Å^2. **[5]**

(k) A current of 800 mA was passed through a dilute solution of $CuSO_4$ for 20 minutes. What are the products liberated at anode and cathode? Find the amount. **[5]**

(l) If sufficient energy is absorbed by an atom, an electron can be lost by the atom and a positive ion formed. The amount of energy required is called the ionization energy. In the hydrogen atom, the ionization energy is that required to change the electron from n = 1 to n = ∞ . Calculate the ionization energy (in kJ mol^{-1}) for He^+ ions. Is the ionization energy of the He^+ ion more or less than that of hydrogen? **[5]**

(m) Using a radiation source of 250 W at 250 nm, a compound was irradiated for 90 mins. 40% of the light was reflected off and the rest was absorbed by the compound. After irradiation, 0.02 moles of the compound was found to have decomposed. Calculate the quantum yield for the decomposition. **[5]**

(n) Show that hte function $A \sin \dfrac{n\pi x}{L}$ for a particle in a one-dimensional box of length L is not an eigenfunction of the momentum operator, $\hat{p}_x = \dfrac{\hbar}{i} \dfrac{d}{dx}$, but it is so of $\hat{p}^2$. Discuss the significance of the result. **[5]**

(o) Discuss the molecular orbitals and the various electronic transitions possible in formaldehyde, CH_2O. Draw an appropriate energy level diagram displaying these transitions. **[5]**

(p) By predicting the appearance of its proton NMR spectrum, show how each member of the following pair of isomers may be distinguished :

1, 1-dimethoxyethane, and 1, 2-dimethoxyethane.

SECTION-B

Attempt any **SIX** questions.

2. A space capsule is filled with neon gas at 1.0 atm and 290 K. The gas effuses through a pinhole into outer space at such a rate that the pressure drops by 0.30 torr/s.
   (i) If the capsule were filled with NH_3 at the same temperature and pressure, what would be the pressure drop? **[5]**

   (ii) When the capsule was filled with 30.0 mol % helium, 20 mol% oxygen and 50 mol % nitrogen at the total pressure of 1.0 atm and at the temperature of 290 K, what would be the rate of pressure drop? **[5]**

3. Define chemical potential. Deduce the Gibbs-Duhem equation and show that the variation of chemical potential affects the value of other component **[10]**

4. What do you mean by an orthorhombic crystal? Show that for an orthorhombic lattice, the distance $\left(d_{hkl}\right)$ between two crystal planes defined by $\left(hkl\right)$ is given by

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

a, b and c are the length of the edges. **[10]**

5. For two parallel reactions, $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$ find equations for the concentration of A, B and C as a function of time. Represent graphically. **[10]**

6. For the dissociative chemisorption of gases A_2 at pressure P $A_{2(g)} \rightleftharpoons 2A_{(ads)}$, derive equation for the fractional surface coverage $\left(\theta\right)$ using Langmuir theory. **[10]**

7. A series of photophysical measurements are carried out on an aqueous solution of compound X. The fluorescence quantum yield is found to be 0.6, the fluorescence lifetime is 20 ns and the intersystem crossing (S_1 to T_1) quantum yield is 0.4. The phosphorescence quantum yield is 0.1 and the phosphorescence lifetime is 1s. No photochemical decomposition occurs. Draw a Jablonskii energy level diagram showing the groud (S_0) and first excited (S_1) singlet elecrtronic states and the lowest triplet (T_1) electronic state for molecule X. Using the photophysical information provided above, indicate in your digram all the radiative and non-radiative processes operating between these states following absorption of light. **[10]**

8. The harmonic oscillator model provides a means of interpreting the vibrations of small molecules. When applied to a homonuclear diatomic molecule made up of atoms with mass m, the model yields vibrational energy levels given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

where n = 0, 1, 2, ... is the vibrational quantum number, $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, k is the force constant of the

chemical bond, and $\mu = \frac{1}{2}m$ is the reduced mass.

(i) Sketch an energy level diagram for the harmonic oscillator, showing the first four energy levels in units of hν.
(ii) The ground state wavefunction for the harmonic oscillator is given by

$$\psi_0 \propto \exp\left(-\beta x^2\right)$$

where x is the deviation from the equilibrium bond separation and $B = \sqrt{\mu k}/\hbar$. Sketch the wavefunction and then determine the most probable value of x and the average value of x.

(iii) The vibrational wavenumber of diatomic chlorine, $^{35}Cl_2$, is 559.71 cm^{-1}. Calculate the force constant for the Cl-Cl bond. Assume that the atomic weight of Cl is exactly 35. **[3, 3, 4]**

9. (a) Explain concisely what is meant by nuclear spin-spin coupling using the ^{1}H NMR spectrum of $CHBr_2CHO$ as an example. Explain how spin-spin coupling arises in this example **[8]**
(b) What is meant by the term coupling constant (J)? **[2]**

SECTION-C

Attempt any **THREE** questions.

10. (a) Calculate the energy in Joule to disperse one spherical drop of radius 3.0 mm into spherical drops of radius 3.0×10^{-3} mm if the surface tension of the drop is 72.8 dynes cm^{-1}. **[10]**

(b) Deduce the expression for the work done W, change of internal energy ΔU and change of enthalpy ΔH for the reversible expansion from volume V_1 to volume V_2 for a van der Waals gas **[10]**

11. Define zeta potential. Explain its significance. Discuss one method of determining zeta potential. **[20]**

12. (a) (i) HI molecules absorb radiation of wavelength 2309.5 cm^{-1}. Calculate the accompanying change in internal energy of an HI molecule in Joule.
(ii) Determine the number of normal vibrational modes of each of the following molecules : hydrogen chloride; hydrogen cyanide, ethene, benzene.
(iii) Deduce which of the following molecules will show a microwave (rotational) spectrum and explain your answer :

$$Br_2, NO, O_2 \qquad \textbf{[3, 4, 3]}$$

(b) (i) What are Rayleigh, Stokes and Anti-Stokes lines? Is the intensity of Stokes lines different from that of the anti-Stokes lines? Explain.
(ii) Sketch the normal modes of vibration of CO_2 and explain which of these are Raman and which are IR active. **[5, 5]**

13. (a) In the rotational spectrum of a diatomic molecule, the first three transitions are observed at 17.68 cm^{-1}, 35.36 cm^{-1} and 53.04 cm^{-1}

(i) Calculate the rotational constant, $\tilde{B}$, of the molecule.
(ii) Predict the wavenumber of the transition from J = 4 to J = 5
(iii) What other information would you need to be able to calculate the bond length of the molecule? Explain your answer. **[2, 2, 2]**

(b) Calculate the wavelength of light that an electron in a 1×10^{-9} m box must absorb to change its quantum number from 1 to 2. In what region of the spectrum would this be found? **[7]**

(c) A sample of a diene in methanol in a 1.00 cm cell shows an absorbance of 0.65 at 242.5 nm. What is the concentration of the diene? The molar absorptivity at this wavelength is 13, 100.   **[7]**

Paper-III
SECTION-A

1.   Answer all of the following questions: **4×10 = 40**

(a) pH of an aqueous solution at 400ºC is 6.76. What is the nature of the solution? (acidic/basic/neutral) {Given K_W at 400ºC is 2.92×10^{-14}}. Justify your answer.

(b) What are the alkaline error and the acid error of a glass membrane pH electrode?

(c) What is solid phase extraction? Write down the main principle involved in it.

(d) Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9^u).

(e) State the purpose of an auxiliary complexing agent and taking an example, illustrate its use.

(f) 20 ml of an aqueous solution of 0.10 M butyric acid was shaken with 10 ml ether. After the layers were separated, it wad determined by titration that 0.5 mol of butyric acid remained in the aqueous layer. What is the distribution ratio and the per cent extracted?

(g) 3% Ni in steel to be analyzed from 1.0 g of steel sample. What volume 1% wt of DMG (dimethyl glycoxime) in alcohol to be used to provide a 50% excess of DMG for the analysis. The density of alcohol (0.79 g/ml). FM : Ni(58.69), DMG (116.12).

(h) Write down the principles of high performance Liquid Chromatography (HPLC) and Gas Liquid Chromatography (GLC).

(i) In atomic absorption spectroscopy (AAS) what is the significance of background absorption and background correction.

(j) Given,

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^- ; \qquad E^0_+ = 0.071V$$

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad ; \qquad E^0_- = 0.799V$$

Compute the solubility product expressed as $AgBr(s) \rightleftharpoons Ag^+ + Br^-$

2.   (a) 25.00 ml liquid bleach was diluted to 1000 ml in a volumetric flask. An aliquot of 25 ml of this diluted sample was transferred to an Erlenmeyer flask and treated with excess KI. This gets oxidized to KI_3 and the bleach OCl^- to Cl^-. The liberated I_2 in the form of KI_3 required 8.96 ml of 0.09892 M $Na_2S_2O_3$ to titrate using starch as indicator. Find out the % W/V NaOCl in the bleach sample   **[5]**

(b) Lay down the procedure to separate and then estimate the constituents Cu, Zn, Sn, Pb and Fe of the Brass alloy.   **[5]**

(c) Consider a mixture of the two solids $BaCl_2.2H_2O$ (FM : 244.26) and KCl (FM : 74.55). When the crystallization is driven off. A sample originally weighing 1.783 g weighed 1.5623 g after heating. Calculate the weight % of Ba, K and Cl in the original sample.   **[5]**

3.   (a) The amount of Fe in a 0.4891 g sample of an ore was determined by a redox titration with $K_2Cr_2O_7$. The sample was dissolved in HCl and the iron brought in to +2 oxidation state using Jones reductor. Titration using diphenylamine sulfonic acid as indicator, the end point required 36.92 ml of 0.02153 M of $K_2Cr_2O_7$. Report the iron content of the ore as % W/W Fe_2O_3.   **[5]**

(b) Fill in the blanks:
(i) When you double the frequency of electromagnetic radiation, you _____ the energy
(ii) When you double the wavelength, you _____ the energy.
(iii) When you double the wave number, you _____ the energy.
(iv) 10% transmittance equals _____ absorbance.
(v) When you double the path length, you _____ absorbance.   **[5]**

(c) Write down the equations in terms of the acid dissociation constants and $[H^+]$ for the highest alpha value for each of the following: **[5]**

    (i) Titrate   (ii) Acetate   (iii) Phosphate   (iv) Nitrilo acetic acid   (v) EDTA

4. (a) Calculate the H_3O^+ (hydronium ion) concentration for a buffer solution of 2 M phosphonic acid and 1.5 M potassium hydrogen phosphate $[Ka_1 = 7.1\times10^{-3}; Ka_2 = 6.32\times10^{-8}]$. **[5]**

    (b) How many milligrams of CO_2 and H_2O will be produced from the combustion of 4.635 mg of benzoic acid? **[5]**

    (c) Define acid-base indicator. Suggest the transition pH-range with colour changes in methyl orange and phenolphthalein indicators. **[5]**

5. (a) A solution of carbon in face centered cubic iron has a density of 8.105 g cm^{-3} and a unit cell edge of 3.589 Å. Are the carbon atoms interstitial or do they substitute for iron atoms in the lattice? Calculate the weight % of carbon. **[5]**

    (b) A brown ore confuged as red hematite or pyrolusite requires different tarif rates for transport. As analyst, you performed a fusion test of the ore using Na_2CO_3-Na_2O_2. You leached colour would either be brown-violet or green in colour. On acidification with cold dilute H_2SO_4, the colour vanishes quickly or acquired a violet colour. Based on the observations, can you identify the brown ore. Explain the expected changes in colour if the ore was for an iron or for a manganese. **[5]**

    (c) Sketch photometric titration curves for the following conditions:

        (i) $\in_S = \in_P = 0$ S-Substrate

           $\in_T > 0$ P-Product

        (ii) $\in_T > \in_P > 0$ T-Titrant   **[5]**

           $\in_S = 0$

6. (a) In a UV-visible spectrum, if you observe a negative absorbance, suggest the reasons that can be responsible for this and possible remedies. **[5]**

    (b) Plot a meaured value of pipet against the percentage of measurements in an experiment to plot a histogram showing the distribution of say 50 results. Correlate this histogram with Gaussian Curve bearing same mean and standard deviation.

      [% in range : 6, 2, 14, 18, 26, 14, 10, 8, 2]

      [No. in range : 3, 1, 7, 9, 13, 7, 5, 4, 1]   **[5]**

    (c) 1.022 g of KIO_3 (FM : 214) was dissolved and made up to 500 mol in a standard measuring flask. When 50 ml of this solution was treated with excess KI (2g) and a mineral acid (10 ml of 0.5 M), I_3^- are produced. Find out the moles of I_3^-.
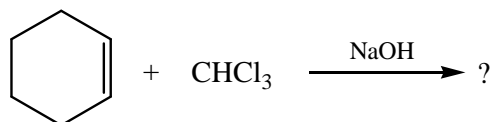
SECTION-B

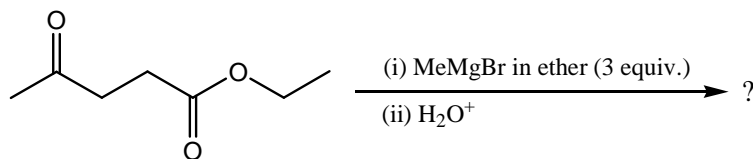7. Answer all of the following questions: $4\times10 = 40$

    (a) Arrange the following compounds in the order of decreasing acidity. Explain you answer

$$CH_3 - CH_2 - \overset{+}{N}H_3; \quad CH_3 - CH = \overset{+}{N}H_2; \quad CH_3 - C \equiv \overset{+}{N}H$$
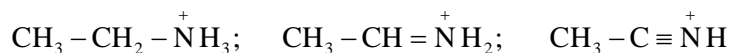
    (b) Predict the product of the following reaction and write the mechanism involved

$$\text{[cyclohexene]} + CHCl_3 \xrightarrow{\text{NaOH}} ?$$

    (c) Complete the following reaction and propose a suitable mechanism for it

$$\xrightarrow[\text{(ii) } H_2O^+]{\text{(i) MeMgBr in ether (3 equiv.)}} ?$$

(d) Which of the following compounds A and B has the greater dipole moment? Explain

and

(A)   (B)

(e) Complete the following reaction and propose a suitable mechanism

(f) Sketch the following π - molecular orbitals showing nodes:
    (i) HOMO for 1, 3-butadiene
    (ii) LUMO for allyl cation

(g) Explain why the compound A exists exclusively in the enol form and the compound B exists exclusively in the keto form

(h) Write the major product(s) of the following reaction sequence

(i) Arrange the compounds, A, B and C in the order decreasing stretching frequency of ⟩=O in the IR spectrum. Justify your arrangements

    (A)   (B)   (C)

(j) The mass spectrum of an unknown compound has a molecular ion peak with a relative intensity of 43.27% and an M + 1 peak with a relative intensity of 3.81%. How many carbon atoms are present in the compound?

8. (a) Classify the following compounds into aromatic, antiaromatic and non-aromatic. Explain your answer

(A) [structure with B-H] (B) [structure with S,S] (C) [structure] (D) [structure] **[5]**
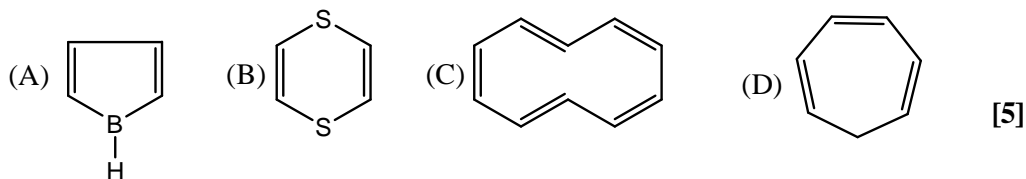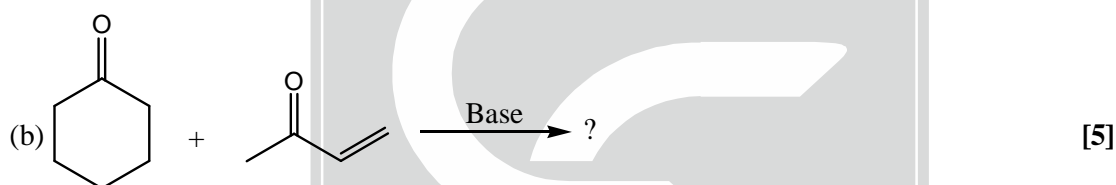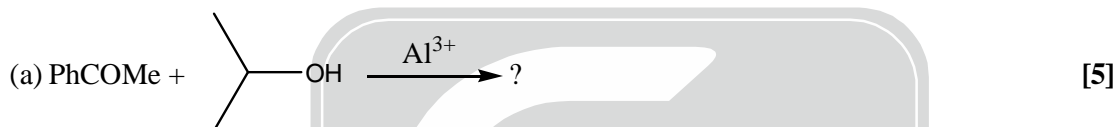
(b) Arrange the following carbanions in their decreasing order of stability. Give reasons for the order given by you. **[5]**
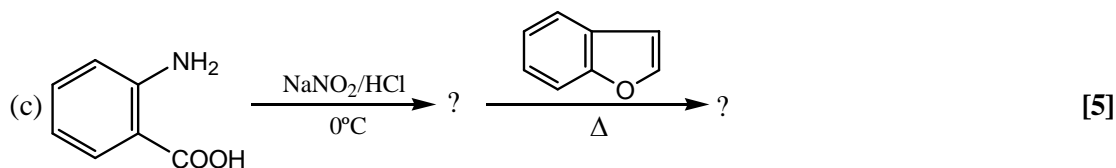
(A) (B) (C) (D)
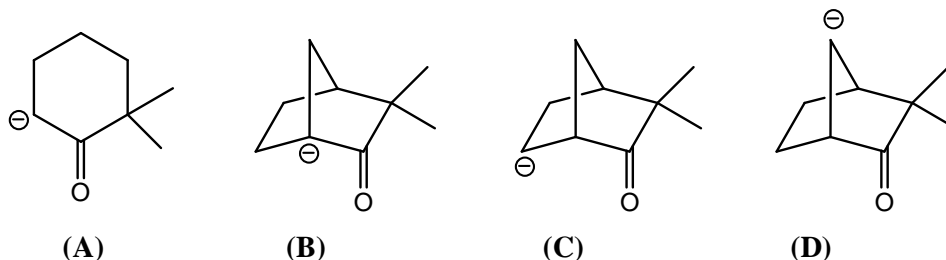
(c) Describe Heinsberg's method of separation of amines. **[5]**

9. Give the main product of the following reactions and give the plausible mechanisms involved for its formation.

(a) PhCOMe + [isopropanol] $\xrightarrow{Al^{3+}}$? **[5]**

(b) [cyclohexanone] + [methyl vinyl ketone] $\xrightarrow{Base}$? **[5]**

(c) [Ph-CH(Me)-CONH_2] $\xrightarrow[Br_2]{NaOH}$? **[5]**

10. Predict the major product(s) in the following reactions. Suggest a suitable mechanism involved in each case.

(a) ? $\xleftarrow{\Delta}$ [diene with CH_3 groups] $\xrightarrow{hv}$? **[5]**

(b) [structure with $\oplus NR_3$] $\xrightarrow{\ominus OH}$? **[5]**

(c) [anthranilic acid] $\xrightarrow[0°C]{NaNO_2/HCl}$? $\xrightarrow{\Delta}$? **[5]**
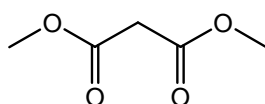
11. (a) The cyclic compound A exhibits enhanced acidity when compound to acyclic compound B. Rationalize the observation. **[5]**

(A)   (B)
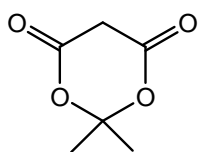
$pK_a = 7.42$ $pK_a = 15.87$

(b) What are ylides? How the stabilized and unstabilized phosphorus ylides yield different products in the Witting reaction with a cyclic ketone. **[5]**