TDP (General) 1st Semester Exam., 2019

CHEMISTRY

(General)

FIRST PAPER

Full Marks : 40

Time : 2 hours

The figures in the margin indicate full marks for the questions

Answer **one** question from each Unit

Answer in separate answer-scripts for each Unit

UNIT—I

(General Chemistry)

1. (a) Write the statement of Heisenberg's uncertainty principle along with mathematical expression. What is its significance?

   (b) Discuss the physical significances of ψ and ψ^2.

   (c) What is $(n + l)$ rule? Explain with examples.   4+3+3=10

(2)

2. (a) Define atomic radii. Discuss the variations in atomic radii along the period and down the group.

(b) First ionization energy of Al is lower than that of Mg. Explain why.

(c) Calculate the amount of energy required to convert 1·5 g of potassium atoms in the gaseous state to form potassium ions. Ionization energy of potassium is 419 kJ mol^{-1} and atomic mass of potassium is 39 a.m.u.

(d) Which of the following orbitals are not possible? Give reason :

$$1p, \ 2s, \ 2p, \ 3f$$

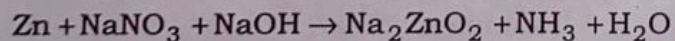(e) Write the set of quantum numbers for the last electron of chlorine.

$$3+2+2+2+1=10$$

UNIT—II

(Inorganic Chemistry)

3. (a) What is redox potential? Explain with an example.

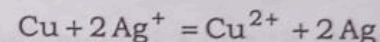(b) Balance the following chemical reaction by ion-electron method :

$$Zn + NaNO_3 + NaOH \rightarrow Na_2ZnO_2 + NH_3 + H_2O$$

20M/97a

(Continued)

(3)

(c) Calculate the standard potential of a cell in which the cell reaction is

$$Cu + 2Ag^+ = Cu^{2+} + 2Ag$$

Given, $E^{\circ}_{Cu/Cu^{+2}} = +0\cdot34 \text{ V};$

$$E^{\circ}_{Ag/Ag^{+2}} = +0\cdot80 \text{ V at } 25 \text{ °C}$$

(d) What indicator will you use in the titration of Fe^{+2} with $K_2Cr_2O_7$ solution in dilute H_2SO_4 medium?

(e) Write two basic features of a good indicator.　　$2+2+3+2+1=10$

4. (a) What is meant by artificial radioactivity? Give example.

(b) What is spallation? How does it differ from nuclear fission?

(c) Complete the following nuclear reactions :

(i) $_4Be^9 + _1H^1 \rightarrow \underline{\hspace{1cm}} + _2He^4$

(ii) $_6C^{12} + \underline{\hspace{1cm}} \rightarrow _5B^{10} + _2He^4$
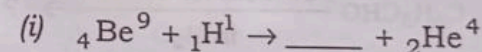
(d) The half-life of ^{65}Zn is 245 days. How much ^{65}Zn will remain if 1 mg amount is kept for 100 days?　　$2+3+2+3=10$

20M/97a

(Turn Over)

UNIT—III

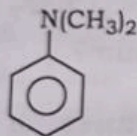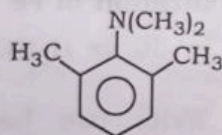### (Organic Chemistry)

5. (a) Explain $E1$ and $E2$ eliminations with an example of each.
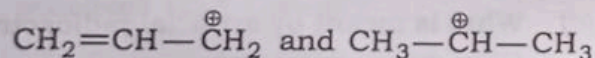
(b) Distinguish chemically between acetylene and ethylene.
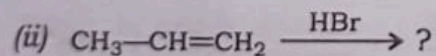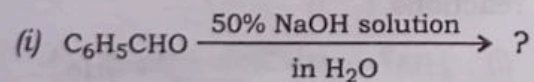
(c) Which one is more basic and why?

(d) Which one is more stable and why?

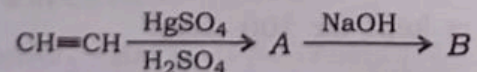$$CH_2=CH-\overset{\oplus}{C}H_2 \quad \text{and} \quad CH_3-\overset{\oplus}{C}H-CH_3$$

(e) Write a short note on hyperconjugation.

$$2+2+2+2+2=10$$

6. (a) Write the product(s) and suggest the mechanisms of the following reactions :

(i) $C_6H_5CHO \xrightarrow[\text{in } H_2O]{\text{50\% NaOH solution}} ?$

(ii) $CH_3-CH=CH_2 \xrightarrow{HBr} ?$

(b) Predict the products A and B in the following reaction :

$$CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A \xrightarrow{NaOH} B$$

(Continued)

(c) Predict D and E in the following reaction chain :
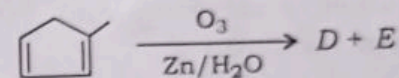
$$(3\times2)+2+2=10$$

UNIT—IV

(Physical Chemistry)

7. (a) Starting from the equation $PV = \frac{1}{3}mnc^2$, deduce the following :

(i) Graham's law of diffusion

(ii) Average kinetic energy per mole of a gas at a definite temperature

(b) What are the significances of van der Waals' constants a and b?

(c) Define collision diameter and collision frequency.

(d) Calculate average velocity of nitrogen molecule at 27 °C. $(2\times2)+2+2+2=10$

8. (a) What is the effect of temperature on surface tension? Define critical temperature.

(Turn Over)

(b) Give a statement of the first law of thermodynamics. Write down its mathematical form and explain each term involved.

(c) Indicate two criteria of spontaneity of a chemical reaction.

(d) Two moles of an ideal gas expanded isothermally and reversibly at 27 °C to twice the original volume. Calculate work done. (1+1)+(2+1)+2+3=10

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TDP (General) 1st Semester Exam., 2018

CHEMISTRY

(General)

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Answer each Unit in separate answer script

Answer **one** question from each Unit

UNIT—I

(General Chemistry)

1. (a) What is Hund's rule? Prove that an orbital cannot contain more than two electrons.

   (b) What is Compton effect? Explain with the help of a suitable diagram.

   (c) Derive de Broglie's equation for wavelength.

   (d) How many radial nodes are observed for 2s electron of H-atom? $(2+2)+3+2+1=10$

(Turn Over)

2. (a) Define electron affinity. How does it vary across the period and down the group in the periodic table? Explain why the 2nd EA of oxygen is positive.

(b) Write short notes on :

(i) Diagonal relationship between boron and silicon

(ii) Mulliken's scale of electronegativity

(c) Ionic radius of K^+ is less than atomic radius of K-atom. Why?

$$(1+2+1)+(2\frac{1}{2}\times 2)+1=10$$

UNIT—II

(Inorganic Chemistry)

3. (a) What do you mean by formal potential and standard potential?

(b) Balance the following chemical reaction by ion-electron method :

$$K_2Cr_2O_7 + HCl + KI \rightarrow CrCl_3 + KCl + I_2 + H_2O$$

(c) Calculate the equivalent weight of $K_2Cr_2O_7$ in acid medium. (Formula weight of $K_2Cr_2O_7 = 294$)

(d) What do you mean by redox indicator? Discuss the factors which effect the choice of indicator in redox titration. $3+2+2+3=10$

(Continued)

4. (a) State and explain Soddy's group displacement law.

(b) Show that the half-life period of a radioactive element is independent of its initial amount.

(c) $_{92}U^{238} \xrightarrow[6\beta \text{ particle}]{8\alpha \text{ particle}} {}_?X^?$
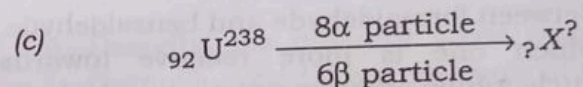
Find out the atomic number and atomic mass of daughter element.

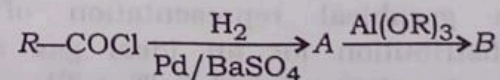(d) What is nuclear binding energy? How is it related to mass defect? $3+3+2+2=10$

UNIT—III

(Organic Chemistry)

5. (a) Between o-nitrophenol and p-nitrophenol, which one has higher boiling point and why?

(b) Distinguish between resonance and tautomerism.

(c) Predict the products A and B in the following reaction :

$$R—COCl \xrightarrow[Pd/BaSO_4]{H_2} A \xrightarrow{Al(OR)_3} B$$

(Turn Over)

(d) Write the value of bond angles a, b and c in the following compound :

$$R-CH_2-CH=C-C\equiv C-R$$

with labels c, a above and b, R below

$$2+3+2+3=10$$

6. (a) Between formaldehyde and benzaldehyde, which one is more reactive towards nucleophilic addition reaction and why?

(b) Convert acetylene to cis-2-butene.

(c) What happens when acetaldehyde is heated with hydrazine in presence of KOH? Give mechanism.

(d) Identify A, B and C in the following reaction sequence :

$$A \xrightarrow[443K]{\text{Conc. } H_2SO_4} CH_3-CH=CH_2 \xrightarrow{B_2H_6} B \xrightarrow[\underset{OH}{\ominus}]{H_2O_2} C$$

$$2+2+3+3=10$$

UNIT—IV

(Physical Chemistry)

7. (a) Write down the van der Waals equation for n moles of gas.

(b) State Maxwell's distribution law of molecular velocity of an ideal gas. Give a graphical representation of such distribution for an ideal gas at two temperatures T_1 and T_2 $(T_2 > T_1)$.

(c) What is meant by mean free path?

(d) Calculate r.m.s. velocity of He molecules at 27 °C.

$$2+(2+2)+2+2=10$$

8. (a) What do you mean by thermodynamically reversible process?

(b) Describe the different steps involved in Carnot's cycle taking one mole of an ideal gas and hence find the efficiency of an engine functioning in this principle.

(c) State the second law of thermodynamics.

(d) 1 mole of gas behaving as an ideal gas expand from 1 litre to 2 litres at 27 °C. Calculate the change in entropy.

$$2+4+2+2=10$$

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Answer each Unit in separate answer script.

Answer **one** question from each Unit

UNIT—I

(General Chemistry)

1. (a) Write the basic postulates of Bohr's theory. Deduce the equation for calculating the radius of Bohr orbit.

   (b) What do you mean by blackbody radiation? How did Planck explain the blackbody radiation?

   (c) Write down the mathematical representation of Heisenberg's uncertainty principle. $(2+3)+(1+3)+1=10$

(*Turn Over*)

(2)

2. (a) Define electronegativity. Is it an inherent property of the free atom? Write the equation for calculation of Pauling's scale of electronegativity.

(b) Arrange the following ions in increasing order of their ionic radii. Give explanation :

$$Na^+, Al^{3+}, N^{3-}, F^-$$
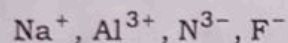
(c) Define ionization potential. How does it vary across the period and down the group in the periodic table? What are the factors controlling the magnitude of ionization potential? IP 2 of Li is greater than that of IP 1. Why?

$$(1+1+1)+2+(1+1+2+1)=10$$

UNIT—II

(Inorganic Chemistry)

3. (a) Balance the following reactions by ion-electron method :

(i) $Al + NO_3^- + H_2O + OH^- \rightarrow NH_3 + AlO_2^-$

(ii) $CuS + HNO_3 \rightarrow Cu(NO_3)_2 + NO + S + H_2O$
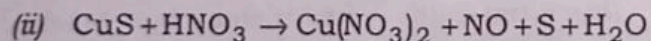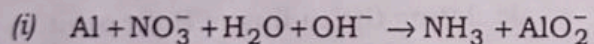
(b) What is formal potential? Explain how pH affects the standard potential with a suitable example.

(3)

(c) Calculate the standard potential of a cell in which the cell reaction is :

$$Cu + 2Ag^+ = Cu^{2+} + 2Ag$$
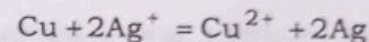
Given

$$E^\circ_{Cu/Cu^{2+}} = +0.34V;$$

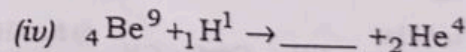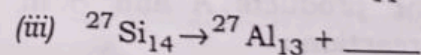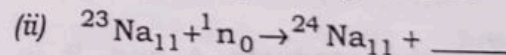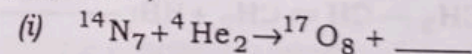$$E^\circ_{Ag/Ag^+} = +0.80V \text{ at } 25\ ^\circ C$$

$$(2+2)+(1+3)+2=10$$

4. (a) What are the differences between β-particle and electron?

(b) "Helium gas is found in all radioactive mines." Why?

(c) What do you mean by '1 curie', radioactivity of a sample?

(d) Half-life of ^{65}Zn is 245 days. How much ^{65}Zn will remain if 1 mg amount is kept for 100 days?

(e) Complete the following nuclear reactions (any three) :

(i) $^{14}N_7 + {}^4He_2 \rightarrow {}^{17}O_8 + \underline{\hspace{1cm}}$

(ii) $^{23}Na_{11} + {}^1n_0 \rightarrow {}^{24}Na_{11} + \underline{\hspace{1cm}}$

(iii) $^{27}Si_{14} \rightarrow {}^{27}Al_{13} + \underline{\hspace{1cm}}$

(iv) $_4Be^9 + {}_1H^1 \rightarrow \underline{\hspace{1cm}} + {}_2He^4$

(v) $_{13}Al^{27} + {}_0n^1 \rightarrow \underline{\hspace{1cm}} + {}_1H^1$
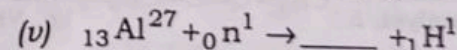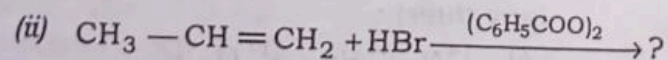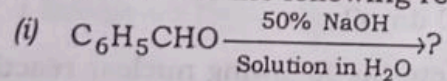
$$2+2+1+2+3=10$$

UNIT—III
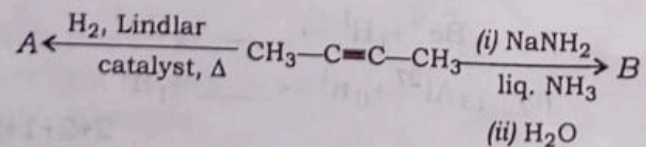
(Organic Chemistry)

5. (a) Between 1-butene and 2-butene, which one is more stable and why?

(b) Between CH_3F and CH_3Cl, which one has higher dipole moment and why?

(c) Distinguish chemically between 1-butyne and 2-butyne.

(d) Between 2-bromobutane and 2-bromo 2-methyl propane, which one is more reactive towards S_N1 reaction and why?

(e) Write a short note on hyperconjugation.

$$2+2+2+2+2=10$$

6. (a) Write the products and suggest the mechanisms of the following reactions :

(i) $C_6H_5CHO \xrightarrow[\text{Solution in } H_2O]{50\% \text{ NaOH}} ?$

(ii) $CH_3-CH=CH_2 + HBr \xrightarrow{(C_6H_5COO)_2} ?$

(b) Predict the products A and B in the following reaction :

$$A \xleftarrow[\text{catalyst, } \Delta]{H_2, \text{ Lindlar}} CH_3-C\equiv C-CH_3 \xrightarrow[\text{liq. } NH_3]{\text{(i) } NaNH_2} B$$

(ii) H_2O

(Continued)

(c) Predict D and E in the following reaction chain :

$$D \xrightarrow[Zn/H_2O]{O_3} CH_3CHO + CH_3COCH_3 \xrightarrow{E}$$

$$C_2H_6 + C_3H_8$$

$$(3+3)+2+2=10$$
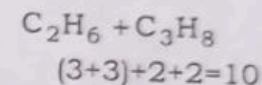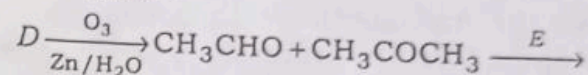
UNIT—IV

(Physical Chemistry)

7. (a) State the basic postulates of kinetic theory of gases.

(b) With the help of kinetic theory of gas equation, deduce Graham's law of diffusion.

(c) Prove that $C_P - C_V = R$ for 1 mole of an ideal gas.

(d) Calculate the kinetic energy of 32 gm of methane at 27 °C.

$$3+2+3+2=10$$

8. (a) Give a concise statement of the first law of thermodynamics. Write down its mathematical form and explain each term involved.

(b) Show that for an adiabatic process $PV^\gamma = $ constant (where the terms have their usual meanings).

(Turn Over)

(c) Two moles of an ideal gas expanded isothermally and reversibly at 27 °C to twice the original volume. Calculate q, w, ΔU and ΔH for the process.   (2+2)+3+3=10

★★★

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(General)

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UNIT—I

(General Chemistry)

1. (a) Deduce de Broglie's relation for matter waves and explain the terms involved in it.

   (b) Write three-dimensional Schrödinger wave equation for hydrogen atom and explain each term in it.

   (c) Draw the figure for radial distribution function for 1s-, 2s- and 3d-orbitals.

   (d) Write a brief note on screening effect of orbitals. $3+2+2+3=10$

(Turn Over)

2. (a) Arrange the following species in order of their increasing radii. Justify your answer :

$$Cl, \ Cl^+, \ Cl^-$$
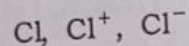
(b) Taking suitable example, define the term diagonal relationship.

(c) State and explain the F-test and t-test used in statistical calculation in analytical chemistry. $\qquad 3+3+4=10$

UNIT—II

(Inorganic Chemistry)

3. (a) Explain whether the following reaction is possible or not :

$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$$
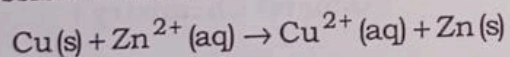
Given,

$$E^{\circ}_{Cu^{2+}/Cu} = +0.34 \text{ volt}$$
$$E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ volt}$$

(b) What are the basic features of a good indicator?

(c) Calculate the equivalent weight of $K_2Cr_2O_7$ in acid medium. (Formula weight of $K_2Cr_2O_7 = 294$)

(Continued)

(d) Complete and balance the following chemical reactions by ion-electron method :

(i) $Cr_2O_7^{2-} + H^+ + I^- \rightarrow$
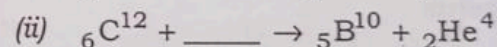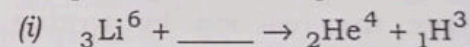
(ii) $MnO_4^- + H^+ + Fe^{2+} \rightarrow$
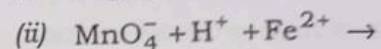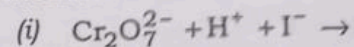
$$2+2+2+(2+2)=10$$

4. (a) State and explain Soddy's group displacement law.

(b) Show that the half-life period of a radioactive element is independent of its initial amount.

(c) Complete the following nuclear reactions :

(i) $_3Li^6 + \underline{\qquad} \rightarrow _2He^4 + _1H^3$

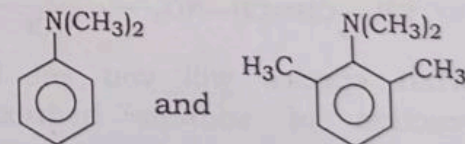(ii) $_6C^{12} + \underline{\qquad} \rightarrow _5B^{10} + _2He^4$

(d) A radioisotope disintegrates in such a rate that $\frac{1}{4}$th of its initial remains after 68 minutes. Calculate decay constant and half-life period. $\qquad 3+3+2+2=10$
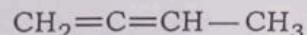
UNIT—III

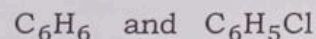### (Organic Chemistry)

5. (a) Explain tautomerism with example.

(b) Which one is more basic and why?

N(CH₃)₂ ... and ... N(CH₃)₂ with H₃C and CH₃

(Turn Over)

(c) Write down the state of hybridization and bond angle (C—C—C) with respect to C_2 and C_3 carbons :

$$CH_2\!=\!C\!=\!CH\!-\!CH_3$$

(d) Which one has higher dipole moment and why?

$$C_6H_6 \quad \text{and} \quad C_6H_5Cl$$

$$(1\tfrac{1}{2}+1\tfrac{1}{2})+3+2+2=10$$

6. (a) Complete the reaction by writing the reactants :

$$A + B \xrightleftharpoons{Al(OR)_3} \underset{R^I \quad R^{II}}{\overset{O}{\|}} \quad \underset{R^{III} \quad R^{IV}}{\overset{OH \; H}{\cdots}}$$
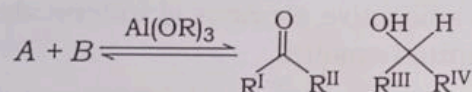
(b) Complete the reaction by writing the reagents :

$$\underset{R \quad Cl}{\overset{O}{\|}} \xrightarrow{C} \underset{R \quad H}{\overset{O}{\|}} \xrightarrow{C} \underset{H}{\overset{OH}{R-\!\!\!\!-\!H}}$$

(c) Complete the reaction by writing the product :

$$CH_3C\!\equiv\!CH \xrightarrow[NH_3/THF]{Li, \; (CH_3)_3COH} D$$
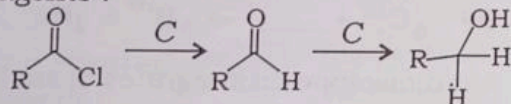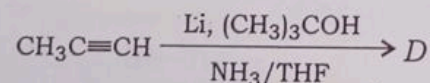
(d) Complete the reaction by writing the product :

$$CH_3\!-\!CH\!=\!CH\!-\!NO_2 \xrightarrow[HCl]{Pd, \; H_2, \; 0\,°C} E$$
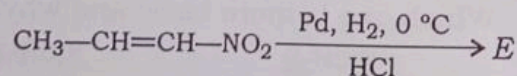
(e) What species will you get from the reaction of sodium hydroxide and chloroform?

$$2+2+2+2+2=10$$

(Continued)

UNIT—IV

(Physical Chemistry)

7. (a) Write down the Maxwell's equation for the distribution of molecular velocities and explain different terms involved in it.

(b) Write down the van der Waals' equation for n-moles of a gas.

(c) Explain collision number, collision frequency and collision diameter of molecules in a gas.

(d) Calculate the most probable velocity of N_2 gas at 27 °C. $\quad (1+2)+2+3+2=10$

8. (a) Explain the following terms with suitable examples :

(i) Entropy

(ii) Enthalpy

(b) Thermodynamically prove that for 1 mole ideal gas, $C_P - C_V = R$.

(c) 2 moles of a perfect gas expand reversibly and isothermally at 27 °C from 1 litre to 10 litre. Calculate the work done.

$$(1\tfrac{1}{2}\times2)+4+3=10$$

★★★

2014

CHEMISTRY

(General)

FIRST PAPER

(Part—I / 2008 Syllabus)

Full Marks : 100

Time : 3 hours

The figures in the margin indicate full marks for the questions

Use separate answer script for each Group

GROUP—A

(Organic Chemistry)

(*Marks* : 34)

Answer Question No. **1** and **two** more questions, taking **one** from each Unit

1. Answer/Choose the correct answer (any *four*) :

$1 \times 4 = 4$

(a) Which of the following is obtained by addition polymerization?

   (i) PVC

   (ii) Terylene

   (iii) Nylon

   (iv) Polyamide
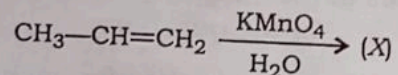
(b) Ethylene reacts with cold, dil. alkaline $KMnO_4$ solution to give

   (i) HCHO

   (ii) oxalic acid

   (iii) glycol

   (iv) ethyl alcohol

(c) 2-hydroxybutanoic acid is optically active but butanoic acid is not. Explain.

(d) Write the name and structure of (X) :

$$CH_3-CH=CH_2 \xrightarrow[H_2O]{KMnO_4} (X)$$

(e) How many optical isomers will be possible for 2,4-dibromo-3-hydroxy pentane?

(f) The general molecular formula of alkyne is

   (i) C_nH_{2n+2}

   (ii) C_nH_{2n}

   (iii) C_nH_{2n-2}

   (iv) $C_nH_{2n+1}OH$

(g) Assign E/Z for
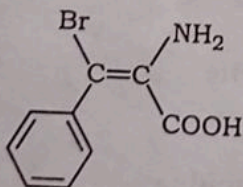
14M—1660/**801**

(h) Which of the following compounds is used in Wöhler's experiment in the synthesis of urea?

   (i) Ammonium cyanate

   (ii) Sodium cyanate

   (iii) Ammonium isocyanate

   (iv) None of the above

UNIT—I

2. (a) What do you mean by 'sigma bond' and 'pi bond'? Indicate the sigma bonds and pi bonds in 2-methyl-1,3-butadiene.

(b) What do you understand by 'optical activity' and 'optically active substance'?

(c) What are the necessary and sufficient conditions for a compound to be optically active?

(d) Write the mechanism of the reaction of methane with chlorine under proper irradiation.

(e) Explain with examples the 'inductive effect' and 'electromeric effect'.

(f) Acetophenone oxime exhibits geometrical isomerism but benzophenone oxime does not. Explain.   4+2+1+3+3+2=15

14M—1660/**801**

(4)

3. (a) What do you understand by 'configuration' and 'conformation'?

(b) Explain with examples the formation of a carbocation and a free radical.

(c) What is meant by resonance energy? Indicate the conditions of resonance.

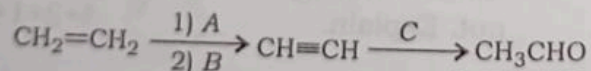(d) What do you mean by hybridization? Explain with examples.

(e) Give an example for each of neutral nucleophile and neutral electrophile.

$$2+3+(1+3)+(1+3)+2=15$$

UNIT—II

4. (a) Explain 1,4-addition reaction with suitable example.

(b) Why according to Markownikoff's rule, HBr when reacts with propene gives 2-bromopropane as a major product?

(c) Explain the ozonolysis reaction of propyne.

(d) Identify A, B and C for the following reaction :

$$CH_2=CH_2 \xrightarrow[2)\ B]{1)\ A} CH\equiv CH \xrightarrow{C} CH_3CHO$$

14M—1660/**801**

(Continued)

(5)

(e) Which one is more stable and why?

$$CH_3-CH=CH-CH=CH_2 \quad \text{and}$$
$$CH_2=CH-CH_2-CH=CH_2$$
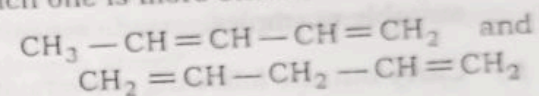
(f) Write the mechanism for the following reaction :

$$CH_3CH_2-OH \xrightarrow[\Delta]{H^+} CH_2=CH_2$$
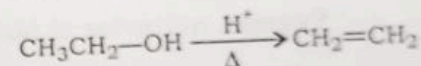
$$2\tfrac{1}{2}+2\tfrac{1}{2}+2\tfrac{1}{2}+3+2\tfrac{1}{2}+2=15$$

5. (a) Identify (A), (B), (C), (D) and (E) in the following reaction chain :

$$CH_2=CH-CH_3 \xrightarrow{O_3} (A) \xrightarrow{H_2O} (B)+(C)$$
$$\downarrow H_2O/Zn$$
$$(D)+(E)$$
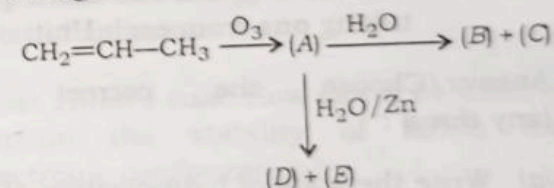
(b) How would you identify chloroform? State with equation, what happens when chloroform is kept open to air.

(c) Identify (A), (B) and (C) in the following reaction sequence :

$$CH_3COCH_3 + H-C\equiv C-H \xrightarrow[\text{liq. } NH_3]{1)\ NaNH_2} (A)$$
$$2)\ H_2O$$

$$\xrightarrow[\substack{\text{heat} \\ \text{(partial} \\ \text{reduction)}}]{H_2/Ni} (B) \xrightarrow[\text{heat}]{Al_2O_3} (C)$$

14M—1660/**801**

(Turn Over)

(6)
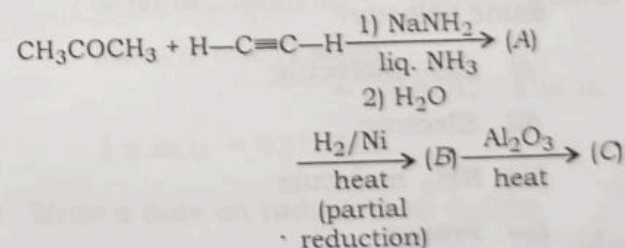
(d) Explain S_N1 and S_N2 reactions with suitable examples.

(e) Carry out the following conversion :
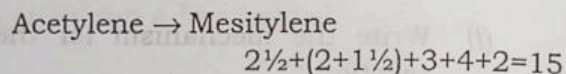
Acetylene → Mesitylene

$$2½+(2+1½)+3+4+2=15$$

GROUP—B

(Inorganic Chemistry)

(Marks : 33)

Answer Question No. 6 and two more questions, taking one from each Unit

6. Answer/Choose the correct answer (any three) : $1×3=3$

(a) Write the state of hybridization of both N atoms in NH_4NO_3 molecule.

(b) Give one example of artificial radioactivity.

(c) Which one of the following has maximum de Broglie's wavelength if all of them have same velocity?

(i) CO_2 molecule

(ii) Electron

(iii) NH_3 molecule

(iv) Proton

(7)

(d) Under what condition the lines of Balmer series are observed in the line spectrum of hydrogen atom?

(e) Give one example of innermetallic complex.

(f) What is solvation energy?

UNIT—I

7. (a) Deduce the necessary relation to determine the energy of an electron in nth orbit of an atom.

(b) State Hund's rule. How can it be used to explain the stability of Mn(II) ion electronic configuration?

(c) Calculate the mass defect and binding energy per nucleon in helium atom ($_2He^4$) from the following data :

Mass of a helium atom
$$= 4·00260 \text{ a.m.u.}$$

Mass of a neutron $= 1·008665$ a.m.u.

Mass of one H atom
$$= 1·007825 \text{ a.m.u.}$$

1 a.m.u. = 931 MeV

(d) Write a note on radiocarbon dating.

$$5+3+4+3=15$$

8. (a) Explain why slow neutrons are more suitable than fast neutrons for nuclear fission.

(b) Show that half-life period of a radioactive element does not depend on the initial amount of that element.

(c) Describe the phenomenon of Compton effect.

(d) A cricket ball weighing 100 gm is to be located within $0 \cdot 1 \text{Å}$. What is the uncertainty in its velocity? Comment on your result.

(e) Complete the following artificial transmutations :

(i) $Al^{27}_{13} (n, p) \rightarrow$

(ii) $Cr^{50}_{24} (\alpha, n) \rightarrow$

$$3+3+3+4+2=15$$

UNIT—II

9. (a) Explain the structures of NH_3 and ClF_3 molecules in the light of VSEPR theory.

(b) AlF_3 is ionic but $AlCl_3$ is covalent. Explain.

(c) What are ambidentate ligands? Give an example.

(d) Discuss stereoisomerism in four-coordinated complex compounds.

(e) Write a note on intermolecular force.

$$4+3+2+4+2=15$$

10. (a) How will you detect the complexes formed in solution according to the following reactions?

(i) $CuSO_4 + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]SO_4$

(ii) $Fe(CN)_2 + 4KCN \rightleftharpoons K_4[Fe(CN)_6]$

(b) Find out the primary and secondary valency of cobalt in the complex $[Co(NH_3)_5Cl]Cl_2$.

(c) Explain Bent's rule with an example.

(d) In between NH_3 and NF_3, which one has higher dipole moment and why?

(e) Write the IUPAC names of the following compounds :

(i) $[Co(en)_3]Cl_3$

(ii) $Na_2[Fe(CN)_5NO]$

(f) Write the coordination number of iron in the complex $K_3[Fe(C_2O_4)_3]$.

$$4+2+3+3+2+1=15$$

GROUP—C

(Physical Chemistry)

(Marks : 33)

Answer Question No. **11** and **two** more questions, taking **one** from each Unit

11. Answer/Choose the correct answer (any *three*) : $1 \times 3 = 3$

(a) The value of C_p / C_v for diatomic gas is

    (i) $1 \cdot 66$

    (ii) $1 \cdot 40$

    (iii) $1 \cdot 29$

    (iv) $1 \cdot 51$

(b) $C_2H_5 (l) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (l)$

If heat of the reaction at constant volume for the above reaction is ΔE, then expression of heat of the reaction at constant pressure will be

    (i) $\Delta H = \Delta E + RT$

    (ii) $\Delta H = \Delta E - RT$

    (iii) $\Delta H = \Delta E - 2RT$

    (iv) $\Delta H = \Delta E + 2RT$

(c) Write the units of van der Waals' constant a and b.

(d) Give an example of enzyme catalysed reaction.

(e) Write the unit of rate constant of second-order reaction.

(f) The normal strength of 5% (wt/vol) NaOH solution is

    (i) $4/5 (N)$

    (ii) $5 (N)$

    (iii) $0 \cdot 125 (N)$

    (iv) $1 \cdot 25 (N)$

UNIT—I

12. (a) From kinetic theory of gas, prove that

$$PV = \frac{1}{3} m \bar{n} c^2$$

where gas of mass m have the volume V, pressure P and $\bar{n}$, no. of molecules with velocity c.

(b) How does viscosity change with the change of temperature for (i) gas and (ii) liquid?

(c) Draw the Amagat's curve and explain the nature of plot with the help of van der Waals' equation.

(d) Draw the plot between $\frac{1}{n} \cdot \frac{dn_c}{dc}$ against c, using Maxwell distribution of molecular speed at a particular temperature. How does this plot change with the increase of temperature?

(e) Calculate average kinetic energy of 1 mole CO_2 gas at 300 °C.

$$4+(1\frac{1}{2}+1\frac{1}{2})+(1+3)+2+2=15$$

13. (a) Thermodynamically prove that for 1 mole ideal gas, $C_p - C_v = R$.

(b) State the law of corresponding state.

(c) What is inversion temperature? Show that inversion temperature $(T_i) = \frac{2a}{Rb}$ for real gas.

(d) At 227 °C, 10 mole of ideal gas expanded isothermally and reversibly from volume 10 lit. to 100 lit. Calculate the work done.

(e) The pressure of gas during adiabatic expansion decreases more rapidly than isothermal expansion. Why?

$$4+2+(1+2)+3+3=15$$

UNIT—II

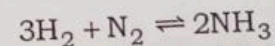14. (a) $$A \rightarrow \text{Products}$$
Derive the expression of rate constant (K_0) for the above reaction if the reaction follows zero-order kinetics.

(b) Write down the expression of reaction rate in terms of reactant and product concentration for the following reaction :

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

(c) Write down Arrhenius equation and indicate the terms used in this equation. What will be the nature of plot and value of slope, when $\log K$ plotted against $\frac{1}{T}$?

(d) Calculate the order of the reaction, where dissociation of ammonia involved, using following data at constant temperature :

Pressure of NH_3 (P) in mm	50	100	200
Half-life period $(t_{\frac{1}{2}})$ in min	3·64	1·82	0·91

(e) Define the terms phase, component and degrees of freedom.

$$3+2+(2+2)+3+3=15$$

15. (a) Given

$$H_2 + I_2 \rightleftharpoons 2HI, \text{ equilibrium constant is } K_{C_1}$$

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI, \text{ equilibrium constant is } K_{C_2}$$
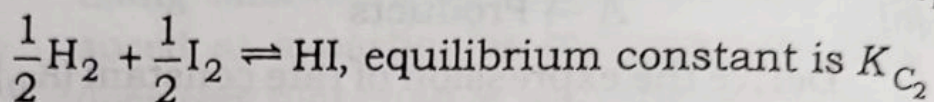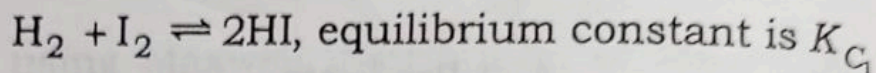
Find out the relationship between K_{C_1} and K_{C_2}.

(b) In what conditions vapourisation of water will be faster for the system $H_2O\,(l) \rightleftharpoons H_2O\,(g)$ and why?

(c) Human blood is isotonic with $0 \cdot 1$ (N) NaCl solution. If the value of van't Hoff factor for NaCl is $1 \cdot 82$, then calculate the value of osmotic pressure of blood at $37\,°C$ temperature.
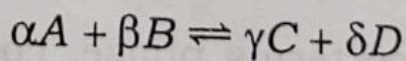
(d) Define molal boiling point constant. State its unit.

(e) Derive the relation $\pi = cRT$.

$\pi = $ osmotic pressure

$c = $ molar concentration

(f) Establish the relationship between K_p and K_x for the reaction

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

$2+(1+1)+3+2+3+3=15$

2 0 1 3

CHEMISTRY

(General)

FIRST PAPER

(Part—I / 2008 Syllabus)

Full Marks : 100

Time : 3 hours

The figures in the margin indicate full marks
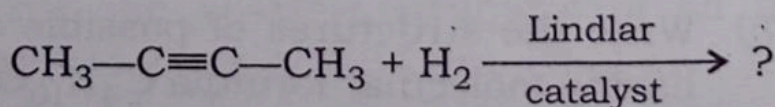*for the questions*

GROUP—A

(Organic Chemistry)

(*Marks* : 34)

Answer Question No. **1** and **two** more questions,
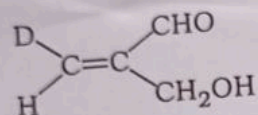taking **one** from each Unit

1. Answer any *four* of the following :   1×4=4

   (a) Write the configuration of the product
   formed in the following reaction :

   $$CH_3—C\equiv C—CH_3 + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} ?$$

(2)

(b) Identify whether the following compound is E or Z :

$$D\!\!-\!\!\underset{H}{\overset{}{C}}\!=\!\underset{CH_2OH}{\overset{CHO}{C}}$$

(c) Give an example of a geometrical isomer having no double bond.

(d) Write down the structure of an optically active compound having molecular formula $C_3H_8O_2$.

(e) What is heat of hydrogenation of alkene?

(f) Lactic acid is optically active but propanoic acid is not. Explain.

(g) Identify X in the following :

$$CH_3\!\!-\!\!CH\!=\!\!CH_2 \xrightarrow{\text{HOBr}} X$$

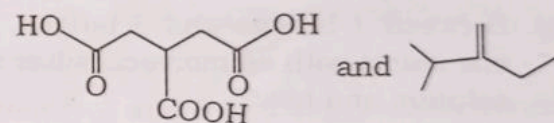(h) Maleic acid forms anhydride easily but fumaric acid does not. Explain.

UNIT—I

2. (a) Write the difference between resonance and tautomerism.

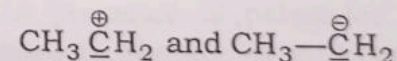(b) Write the structures of possible isomers having molecular formula $C_4H_{10}O$.

(3)

(c) What is plane of symmetry? Why molecules having such symmetry are optically inactive?

(d) "Resonance energy of 1,3-butadiene is 3·61 kcal/mole." What do you mean by the statement?

(e) Between o-NO_2-phenol and p-NO_2-phenol, which one is more acidic and why?

(f) Write down the IUPAC name of

$$HO\!\!-\!\!\underset{O}{\overset{}{C}}\cdots\underset{\underset{COOH}{|}}{C}\cdots\underset{O}{\overset{}{C}}\!\!-\!\!OH \quad \text{and} \quad \text{(structure)}$$

$$2+4+2+2+2\tfrac{1}{2}+2\tfrac{1}{2}=15$$

3. (a) By salt forming process, how would you resolve 1:1 mixture of d- and l-tartaric acid?

(b) Write the hybridisation of carbon in the following (underlined carbon) :

$$CH_3\,\overset{\oplus}{\underline{C}}H_2 \text{ and } CH_3\!\!-\!\!\overset{\ominus}{\underline{C}}H_2$$

(c) Write the difference between optical isomers and geometrical isomers.

(d) Write the possible structure of all the stereoisomers of 2,3-butanediol and also write the relation between them.

(e) Arrange the following with respect to stability with proper reasoning :

cis-2-butene, *trans*-2-butene and 2-methyl-2-butene

(f) Between phenol and phenoxide ion, which one is more stable and why?
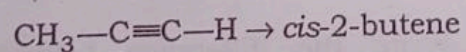
$$3+2+2+3+3+2=15$$

UNIT—II

4. (a) Between 1-butyne and 2-butyne, which one reacts with ammoniacal silver nitrate solution and how?
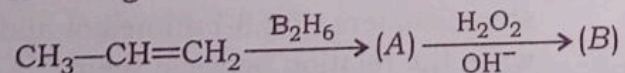
(b) Identify (A) and (B) from the following :

$$\text{(cyclopentene)} \xrightarrow[\text{Zn, H}_2\text{O}]{\text{O}_3} (A) + (B)$$
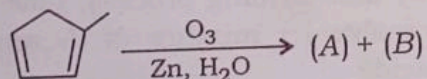
(c) From 2-chlorobutane, how would you prepare 2-butene and butan-2-ol?

(d) Convert :

$$CH_3\text{—}C\equiv C\text{—}H \to \text{cis-2-butene}$$

(e) Write the structure of (A) and (B) from the following :

$$CH_3\text{—}CH=CH_2 \xrightarrow{B_2H_6} (A) \xrightarrow[\text{OH}^-]{H_2O_2} (B)$$

(Continued)

(f) How would you prepare $CH_3CH_2CH_3$ from CH_3I?

(g) Convert : $CHI_3 \to CH\equiv CH$.

$$2+2+2+2+2+3+2=15$$

5. (a) Between isobutane and neopentane, which one has higher boiling point and why?

(b) Write the value of bond angles a, b and c in the following compound :

$$CH_3\overset{c}{\text{—}}CH_2\text{—}CH=C\overset{a}{\text{—}}C\equiv C\text{—}CH_3$$
$$\underset{b}{\quad}\underset{CH_3}{\mid}$$
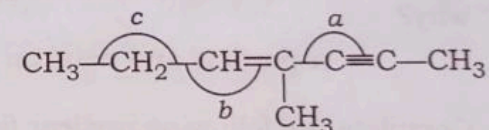
(c) Identify A and B and suggest mechanism for the following reaction :

$$CH_2=CH\text{—}CH=CH_2 + Br_2 \xrightarrow{CCl_4} A + B$$
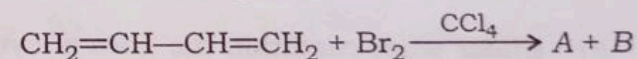
(d) When $H_3C\text{—}CH=CH_2$ undergoes addition reaction with HBr, which compound will form as a major product? What happens if the reaction is carried out in presence of peroxide? Write the mechanism of reaction with peroxide.

(e) Write the mechanism of the following reaction :
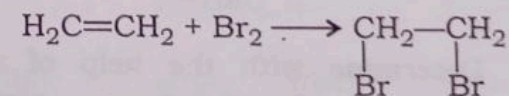
$$H_2C=CH_2 + Br_2 \longrightarrow \underset{\underset{Br}{\mid}}{CH_2}\text{—}\underset{\underset{Br}{\mid}}{CH_2}$$

$$2+3+3+5+2=15$$

(Turn Over)

GROUP—B

(Inorganic Chemistry)

(Marks : 33)

Answer Question No. 6 and **two** more questions, taking **one** from each Unit

6. Answer any *three* of the following : $1 \times 3 = 3$

(a) Which one of the following is more effective in causing nuclear fission and why?

α-particle and neutron

(b) Complete the following nuclear fission :

$$_{37}Rb^{85} + {_0}n^1 \rightarrow ? + {_{37}}Rb^{84}$$
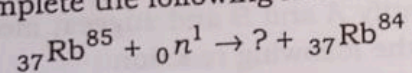
(c) Under what condition the lines of Lyman series are observed in the spectrum of hydrogen?

(d) Explain why an excess of NH_3 solution converts the blue colour of Cu(II) salt into deep blue.

(e) Write the structure of EDTA.

UNIT—I

7. (a) Determine with the help of quantum numbers the maximum number of electrons in the third shell of an atom.

(Continued)

(b) Explain the $(n + l)$ rule.

(c) Give examples of two isotones.

(d) State the defects of the Bohr's postulates about the structure of an atom.

(e) How many α and β particles will be emitted in the following nuclear change?

$$_{84}Po^{208} \rightarrow {_{82}}Pb^{206} \qquad 3+3+1+3+5=15$$
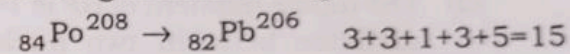
8. (a) What is meant by radioactive equilibrium? How does it differ from chemical equilibrium?

(b) What is meant by artificial radioactivity? Give example.

(c) What is spallation? How does it differ from nuclear fission?

(d) Give an example of radioactive isotope.

(e) A piece of wood was found to have C^{14}/C^{12} ratio 0·7 times that in a living plant. Calculate the period when the plant died. (Half-life of C^{14} is 5700 years)

$$(1\frac{1}{2}+1\frac{1}{2})+(1+1)+(1\frac{1}{2}+1\frac{1}{2})+2+5=15$$

UNIT—II

9. (a) What is lattice energy? Write its mathematical expression. On what factors does it depend?

(Turn Over)

(b) Starting from Ca and F_2, construct the Born-Haber cycle for formation of CaF_2 and mention the meaning of the terms used in it.

(c) Explain why $CaCl_2$ is soluble in water but CaF_2 is not.

(d) The dipole moment of HF is 1·98 D and the distance between two nuclei is 0·92 Å. Calculate the percentage of ionic character of H—F bond. $\qquad$ 3+5+2+5=15

10. (a) $K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$ are different classes of compounds. Explain.

(b) Give example of each of ambident and chilating ligands.

(c) What are chelate compounds? Write the name and structure of a chelate compound. Mention the use of chelate compounds in analytical chemistry.

(d) Calculate the EAN of $K_3[Cr(C_2O_4)_3]$.

(e) Write the IUPAC names of the following :

(i) $K[Pt(NH_3)Cl_5]$

(ii) $[Co(NH_3)_6][Cr(CN)_6]$

(f) Give examples of linkage and coordination isomerism.

$$2+2+(1+2+2)+2+2+2=15$$

GROUP—C

(Physical Chemistry)

(Marks : 33)

Answer Question No. **11** and **two** more questions, taking **one** from each Unit

11. Answer any *three* questions : $\qquad$ 1×3=3

(a) Define mole fraction of a solute in a solution.

(b) Write the dimension of universal gas constant, R.

(c) What is the number of components of the following system?

$$NH_3 \text{ (g, 1 mole)} + HCl \text{ (g, 2 mole)} \rightleftharpoons NH_4Cl(s)$$

(d) Which of the following is not an extensive property?

(i) Density

(ii) Viscosity

(iii) Surface tension

(iv) Number of moles

(e) Kinetic energy of gas depends on

(i) P and n

(ii) T and V

(iii) T and n (Choose the correct answer)

(f) Give one example of pseudounimolecular reaction.

(10)

UNIT—I

12. (a) Derive van der Waals' equation for n gm mole of a real gas. What are the drawbacks of this equation?

(b) Define viscosity and viscosity coefficient of a liquid.

(c) Determine the mean free path of argon (Ar) at normal temperature and pressure. Given the diameter of argon atom is 2·24 Å.

(d) Why is the specific heat at constant pressure greater than that of the specific heat at constant volume?

$$(5+2)+(1½+1½)+3+2=15$$

13. (a) State the first law of thermodynamics and express it by a simple equation.

(b) Distinguish between isothermal and adiabatic processes.

(c) The volume of 45 gm N_2 is expanded isothermally and reversibly at 25 °C from 10 lit to 20 lit. Considering the gas as ideal, calculate the work done for the given expansion.

(11)

(d) Write a short note on Joule-Thomson effect.

(e) For an adiabatic change of an ideal gas, derive the relationship between pressure (P) and temperature (T). $(1+1)+3+3+3+4=15$

UNIT—II

14. (a) Compare between order and molecularity of a reaction.

(b) Derive the expression for rate constant of a second-order reaction.

(c) Determine the unit of rate constant (k) for zero-order reaction.

(d) In the dissociation process of HI, 20% of HI dissociates at equilibrium

$$HI\,(g) \rightleftharpoons \frac{1}{2}H_2\,(g) + \frac{1}{2}I_2\,(g)$$
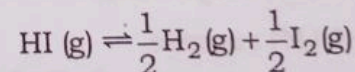
Calculate K_p for the above equilibrium.

(e) What is catalyst poison? Give example. Give one example of each of homogeneous and heterogeneous catalysts.

$$3+4+1+3+(1×4)=15$$

15. *(a)* By giving example, state Nernst distribution law.

(b) What do you mean by elevation of boiling point of a liquid? State Raoult's law of elevation of boiling point. Show that boiling point of a solution is greater than that of a pure solvent.

(c) The vapour pressure of a solution becomes 756·2 mm, when 5 gm of a solute be dissolved in 100 gm water at 100 °C. Calculate the molecular weight of the solute.

(d) At constant temperature, arrange the following solutions according to increasing order of their osmotic pressure and explain them :

(i) 0·1 (*M*) Na_2SO_4

(ii) 0·1 (*M*) CH_3COOH

(iii) 0·1 (*M*) sucrose

$$2+(2+3+2)+3+(1+2)=15$$

(Continued)

2012

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CHEMISTRY

(General)

FIRST PAPER

(Part—I / 2008 Syllabus)

Full Marks : 100

Time : 3 hours

The figures in the margin indicate full marks
for the questions

Write the answers to each Group in a separate book
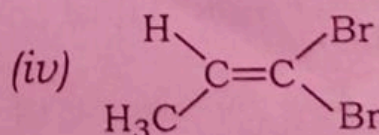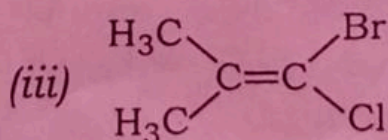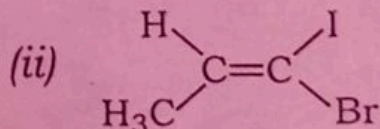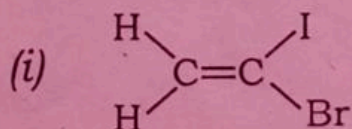
GROUP—A.

(Organic Chemistry)

(*Marks* : 34)

Answer Question No. **1** and **two** more questions,
taking **one** from each Unit

1. Answer/Choose the most correct answer
   (any *four*) :   1×4=4

   (a) Which of the following compounds will
   exhibit geometrical isomerism?

   (i) $\underset{H}{\overset{H}{\diagdown}} C = C \underset{Br}{\overset{I}{\diagup}}$ (ii) $\underset{H_3C}{\overset{H}{\diagdown}} C = C \underset{Br}{\overset{I}{\diagup}}$

   (iii) $\underset{H_3C}{\overset{H_3C}{\diagdown}} C = C \underset{Cl}{\overset{Br}{\diagup}}$ (iv) $\underset{H_3C}{\overset{H}{\diagdown}} C = C \underset{Br}{\overset{Br}{\diagup}}$

ch of the following compounds will nibit optical isomerism?

(i) C_2H_5—O—C_2H_5

(ii) CH_3—O—CH_3

(iii) $CH_3CH_2CH_2CH_2OH$

(iv) $CH_3CHOHCH_2CH_3$

(c) The IUPAC name of

$$H—C≡CCH_2—CH=CH_2 \text{ is}$$
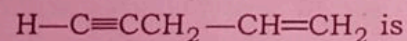
(i) 1-propyn-ethene

(ii) propene acetylene

(iii) pent-4-yne-1-ene

(iv) pent-1-en-4-yne

(d) In which of the following compounds are all the carbon atoms in the sp^3 state of hybridisation?

(i) CH_4

(ii) C_3H_8

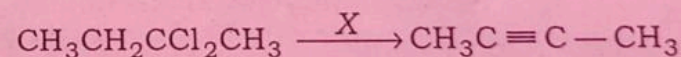(iii) C_4H_{10}

(iv) All of the above

(v) None of the above

(e) Which of the following will react with sodium to give hydrogen gas?

(i) Methane

(ii) Ethane

(iii) Ethylene

(iv) Acetylene

(f) 1-Buten-3-yne contains

(i) six sigma and four pi bonds

(ii) five sigma and three pi bonds

(iii) seven sigma and three pi bonds

(iv) eight sigma and two pi bonds

(g) In the reaction

$$CH_3CH_2CCl_2CH_3 \xrightarrow{\ X\ } CH_3C≡C—CH_3$$

the reagent X is

(i) KOH/C_2H_5OH

(ii) Zn

(iii) HCl/H_2O

(iv) Na

(h) Maleic acid forms anhydride easily but fumaric acid does not. Why?

(4)

UNIT—1

2. (a) Under what conditions a compound would be optically active?

(b) What do you understand by enantiomer and diastereoisomer? Explain with example.

(c) Write a note on hyperconjugation.

(d) Explain the hydrogen bond with an example.

(e) Between $CH_2=CH-\overset{+}{C}H_2$ and $CH_3-\overset{+}{C}H-CH_3$ carbocations, which one is more stable and why?
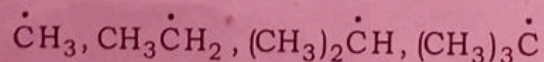
(f) Give one example for each of neutral neucleophile and neutral electrophile.

$$2+3+3+3+2+2=15$$

3. (a) Give an example of geometrical isomer having C=N.

(b) What is meant by resonance energy? Mention the conditions for resonance.

(c) What is free radical? Arrange the following in increasing order of stability :

$$\overset{\cdot}{C}H_3,\ CH_3\overset{\cdot}{C}H_2,\ (CH_3)_2\overset{\cdot}{C}H,\ (CH_3)_3\overset{\cdot}{C}$$
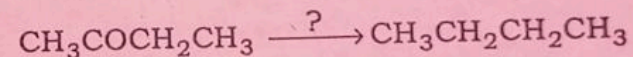
Give the reason.

(5)

(d) What is racemic mixture? How can you separate the racemic mixture?

(e) How do conformation and configuration differ from each other?

$$2+(1+3)+(1+3)+3+2=15$$

UNIT—2

4. (a) Complete the following reaction :

$$CH_3COCH_2CH_3 \xrightarrow{?} CH_3CH_2CH_2CH_3$$

(b) Write down the mechanism of photochemical chlorination of methane.
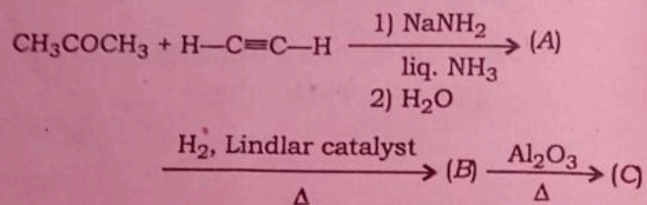
(c) When treated with ammoniacal silver nitrate, acetylene forms silver acetylide but ethylene does not. Explain.

(d) Chemically distinguish between propyne and 2-butyne.

(e) What happens when ethylene gas is passed into cold and dil. $KMnO_4$ solution? Give the reaction.
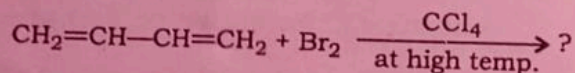
(f) Predict the products (A), (B) and (C) in the following reaction chain:

$$CH_3COCH_3 + H\!-\!C\!\equiv\!C\!-\!H \xrightarrow[\text{liq. } NH_3]{\text{1) } NaNH_2} (A)$$

2) H_2O

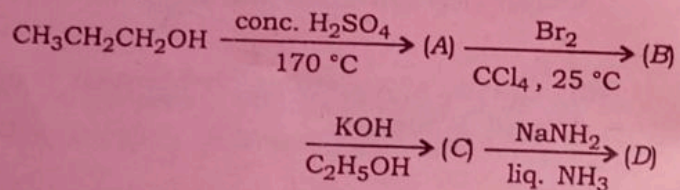$$\xrightarrow[\Delta]{H_2, \text{ Lindlar catalyst}} (B) \xrightarrow[\Delta]{Al_2O_3} (C)$$

Write down the IUPAC name of the compound (C).　　　$1+3+3+2+2+(3+1)=15$

5. (a) Predict the product and suggest a suitable mechanism for the following :

$$CH_2\!=\!CH\!-\!CH\!=\!CH_2 + Br_2 \xrightarrow[\text{at high temp.}]{CCl_4} ?$$

(b) Identify (A), (B), (C) and (D) in the following reaction-sequence :

$$CH_3CH_2CH_2OH \xrightarrow[170\,°C]{\text{conc. } H_2SO_4} (A) \xrightarrow[CCl_4,\, 25\,°C]{Br_2} (B)$$

$$\xrightarrow[C_2H_5OH]{KOH} (C) \xrightarrow[\text{liq. } NH_3]{NaNH_2} (D)$$
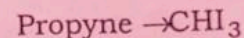
(c) What happens when 1,3-butadiene and maleic anhydride are heated together? Give the equation.

(Continued)

(d) Write down the structure of an alkene which on ozonolysis gives two molecules of propanal.

(e) Transfer the following :

Propyne $\rightarrow CHI_3$

(f) Give the mechanism of E_1 reaction with suitable example.　　$3+4+2+2+2+2=15$

GROUP—B

(Inorganic Chemistry)

(Marks : 33)

Answer Question No. 6 and two more questions, taking one from each Unit

6. Answer any three of the following :　　$1\times3=3$

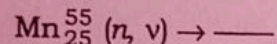(a) Write the IUPAC name of $[Co(NH_3)_5ONO]SO_4$.

(b) How many series of lines are observed in the line spectrum of hydrogen atom?

(c) On hydrolysis, NCl_3 and PCl_3 gives different kinds of products. Why?

(d) What type of hybridisation of P atom is found in PCl_3F_2?

(Turn Over)

(e) Write down the formula of potassium-dicyanoargentate(I).

(f) Complete the artificial transmutation

$$Mn_{25}^{55} (n, v) \rightarrow \underline{\hspace{1cm}}$$

UNIT—1

7. (a) Explain, with example, the wave-particle duality.

(b) Explain the origin of line spectrum of hydrogen atom, on the basis of Bohr's theory.

(c) What is the Heisenberg's uncertainty principle?

(d) Describe artificial transmutation of nuclei with example.

(e) Calculate the wavelength of a body of mass 10^{-6} kg moving with a velocity of 3 ms^{-1} [$h = 6 \cdot 624 \times 10^{-34}$ J-s]. $3 \times 5 = 15$

8. (a) Derive a mathematical formulation of the law of radioactive disintegration.

(b) β-Particle comes from the nucleus. Explain.

(c) What is nuclear binding energy? How is it related to mass defect?

(d) Draw the shapes of d-orbitals.

(e) $$U_{92}^{238} \xrightarrow[\text{6 β-particle}]{\text{8 α-particle}} {}_{?}X^{?}$$
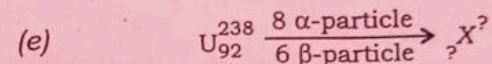
Find the atomic number and atomic mass of daughter element. $4+2+(2+2)+2+3=15$

UNIT—2

9. (a) Explain the structure of NH_3 and H_2O molecule from VSEPR theory.

(b) Explain the shapes of $BeCl_2$ and PCl_5 using the concept of hybridisation.

(c) "Metals are good conductors." Explain on the basis of band theory.

(d) $CaCO_3$ is insoluble in water. Why?

(e) Explain the association of liquid ammonia molecule. $4+4+3+2+2=15$

10. (a) What do you mean by perfect and imperfect complexes? Give one example of each type.

(b) What is inner metallic complex? Give two examples of analytical importance.

(c) State the postulates of Werner's theory of coordination complex.

(d) Discuss the isomerism of coordination complex of the type ML_4. $3+4+4+4=15$

GROUP—C

(Physical Chemistry)

(Marks : 33)

Answer Question No. **11** and **two** more questions, taking **one** from each Unit

11. Answer/Choose the most correct answer (any *three*) of the following : $1 \times 3 = 3$

(a) What is meant by collision number?

(b) What is triple point?

(c) Which of the following properties is not a state function?

(i) Concentration

(ii) Internal energy

(iii) Enthalpy

(iv) Entropy

(Continued)

(d) What is van't Hoff factor?

(e) Write the mathematical formulation of the zeroth law of thermodynamics.

(f) Define colligative property with examples.

UNIT—1

12. (a) What is meant by mean free path of a gas molecule? How does it depend upon temperature and pressure?

(b) Write down the expression for the Maxwell's distribution of molecular speed in a gas and discuss its characteristics using a graphical representation.

(c) What do you observe if a glass capillary tube is dipped into (i) water and (ii) mercury? Give reason.

(d) Calculate the kinetic energy of 1 gm CO_2 gas at 27 °C in SI unit. $(2+2)+(3+3)+3+2=15$

13. (a) Write down and deduce the Kirchhoff's equation regarding the effect of temperature on the heat of reaction.

(Turn Over)

(b) For a reversible adiabatic expansion of an ideal gas, show that $TV^{\gamma-1} = $ constant (where the terms have their usual meanings).

(c) Explain reversible and irreversible processes with illustrations.

(d) $4 \cdot 2$ gm N_2 is expanded isothermally and reversibly at $27\,°C$ from 10 atm to 1 atm. Calculate q, ΔE and W. $\qquad 3+5+(2+2)+3=15$

UNIT—2

14. (a) Deduce an expression for the rate constant of a first-order reaction and hence establish an expression for half-life of it.

(b) What are enzyme-catalysed reactions? Give an example, indicating the name of the enzyme involved in it.

(c) Draw the phase diagram of water and mention its important features.

(d) A first-order reaction is 25% complete at the end of 20 minutes. How long will it take to complete 75%? $\qquad 5+3+4+3=15$

15. (a) State Henry's law of the effect of pressure on the solubility of a gas in a liquid and write its mathematical form.

(b) State and explain the van't Hoff laws of osmotic pressure. Show that a dilute solution behaves as an ideal gas.

(c) What is meant by 'molal cryoscopic constant'? What type of thermometer is used for measurement of elevation of boiling point? Can an ordinary thermometer be used for such purpose? Give reason.

(d) Human blood is isotonic with $0 \cdot 1$ (M) NaCl solution at $27\,°C$. If the value of van't Hoff factor of NaCl is $1 \cdot 82$, calculate the osmotic pressure of human blood. $\qquad 3+5+4+3=15$