IIT-JEE-1999

CHEMISTRY

[Time allowed: 3 hours] [Maximum Marks: 200]

General Instructions :

1. Do not break the seal of the question paper before you are instructed to do so by the invigilator.
2. This question paper is in two sections. Section I has 35 objective type questions. Sections II has 12 regular questions.
3. Answer Section I only the special machine-graded OBJECTIVE RESONSE SHEET (ORS) that is inserted in this booklet. Questions of Section I will not be graded if answered anywhere else.
4. Answer problems of Sections II in the answer-book.
5. Without breaking the seal of this booklet, take out the Response Sheet (ORS) for Section I. Make sure that the ORS has the SAME QUESTIONPAPER CODE, printed on its as on the top of this page.
6. Write your name, registration number and name of the Centre at the specified locations on the right half of the ORS for Section I.
7. Using s soft HB pencil darken the appropriate bubble under each digit of your registration number.
8. The Objective Response Sheet will be collected back after 75 minutes have expired from the start of the examination. In case you finish Section I before the expiry of 75 minutes, you may start answering Section II.

INSTRUCTIONS FOR SECTION I

1. Questions are to answered by darkening with a soft HB pencil the appropriate bubble (marked A, B, C and D) against the question number on the left-hand side of the Objective Response Sheet.
2. In case you wish to change an answer, erase the old answer completely using a good soft eraser.
3. The answer sheet will be collected back after 75 minutes from the start of the examination.
4. There is no negative marking.
5. Question numbers 1-25 carry 2 marks each and have only one correct answer.
6. Question Numbers 26-35 carry 2 marks each, and may have more than one correct answers. All the correct answers must be marked in these questions to get any credit.

IMPORTANT INFORMATION

1. Logarithmic tables is can be allowed.
2. Use of calculator is not allowed

Useful data :

Gas constant, R = 0.Q82 L atm K–1 = 8.314 J K–1 mol–1
= 1.987 cal K–1 mol–1

1 Faraday constant = 96.500 C mol–1

Avagadro number, NA = 6.02 × 1023

Atomic number : Ni = 28

Relative atomic mass : H = 1;

CI = 35.5; Cr = 52; Cu = 63.5; Xe = 131

SECTION I

DIRECTIONS: Select the most appropriate alternative A, B, C or D in questions 1-25.

1. The electrons, identified by quantum numbers n and l, (i) $n=4,\ l=1$, (ii) $n=4,\ l=0$, (iii) $n=3,\ l=2$, and (iv) $n=3,\ l=1$ can be placed in order of increasing energy, from the lowest to highest, as:

   (A) (iv) < (ii) < (iii) < (i)

   (B) (ii) < (iv) < (i) < (iii)

   (C) (i) < (iii) < (ii) < (iv)

   (D) (iii) < (i) < (iv) < (ii)

2. The number of neutrons accompanying the formation of $139Xe54$ and $94Sr38$ from the absorption of a slow neutron by $235U92$, followed by nuclear fission is:

   (A) 0

   (B) 2

   (C) 1

   (D) 3

3. The correct order of increasing $C-O$ bond length of CO, CO2-3, CO2 is:

   (A) CO2-3 < CO2 < CO

   (B) CO2 < CO2-3 < CO

   (C) CO < CO2-3 < CO2

   (D) CO < CO2 < CO2-3

4. A gas will approach ideal behaviour at:

(A) low temperature and low pressure

(B) low temperature and high pressure

(C) high temperature and low pressure

(D) high temperature and high pressure

5. The normality of $0.3M$ phosphorus acid $(H3PO3)$ is

(A) 0.1

(B) 0.9

(C) 0.3

(D) 0.6

6. The coordination number of a metal crystallizing in a hexagonal close-packed structure is:

(A) 12

(B) 4

(C) 8

(D) 6

7. A gas X at $1atm$ is bubbled through a solution containing a mixture of $1M\,Y-$ and $1M\,Z-$ and $250C$. If the reduction potential of $Z < Y > X$, then:

(A) Y will oxidize X and not Z

(B) Y will oxidize Z and not X

(C) Y will oxidize both X and Z

(D) Y will reduce both X and Z

8. The pH of 0.1M solution of the following salts increases in the order:

(A) $NaCI < NH3CI < NaCN < HCI$

(B) $HCI < NH4CI < NaCI < NaCN$

(C) $NaCN < NH4CI < NaCI < HCI$

(D) $HCI < NaCI < NaCN < NH4CI$

9. For the chemical reaction $3X(g) + Y(g) <--> X3Y(g)$, the amount of $X3Y$ at equilibrium is affected by:

(A) temperature and pressure

(B) temperature only

(C) pressure only

(D) temperature, pressure and catalyst

10. In the dichromate dianion:

(A) 4 Cr—O bonds are equivalent

(B) 6 Cr—O bonds are equivalent

(C) all Cr—O bonds are equivalent

(D) all Cr—O bonds are non-equivalent

11. One mole of calcium phosphide on reaction with excess water gives:

(A) one mole of phosphine

(B) two moles of phosphoric acid

(C) two moles of phosphine

(D) one mole of phosphorus pentoxide

12. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are:

(A) $0, +1$ and -2

(B) $+2, +1$ and -2

(C) $0, +1$ and $+2$

(D) $-2, +1$ and -2

13. On heating ammonium dichromate, the gas evolved is:

(A) oxygen

(B) ammonia

(C) nitrous oxide

(D) nitrogen

14. In the commercial electrochemical process for aluminium extraction, the electrolyte used is:

(A) $AI(OH)3$ in $NaOH$ solution

(B) an aqueous solution of $AI2(SO4)3$

(C) a molten mixture of $AI2O3$ and $Na3AIF6$

(D) a molten mixture of $AIO(OH)$ and $AI(OH)3$

15. The geometry of $H2S$ and its dipole moment are:

(A) angular and non-zero

(B) angular and zero

(C) linear and non-zero

(D) linear and zero

16. The geometry of $Ni(CO)4$ and $Ni(PPh3)2CI2$ are:

(A) both square planar

(B) both tetrahedral and square planar, respectively

(C) both tetrahedral

(D) square planar and tetrahedral, respectively

17. In compounds of type $ECI3$, where $E = B, P$ As or Bi, the angles $CI - E - CI$

(A) $B > P = As = Bi$

(B) $B > P > As > Bi$

(C) $B < P = As = Bi$

(D) $B < P < As < Bi$

18. In the compound $CH2 = CH—CH2—CH2—C^{\circ}CH$, the $C2 = C3$ bonds is of

(A) $sp - sp2$

(B) $sp3 - sp3$

(C) $sp - sp3$

(D) $sp2 - sp3$

19. When propionic acid is treated with aqueous sodium bicarbonate, $CO2$ is liberated the '*C*' of $CO2$ comes from:

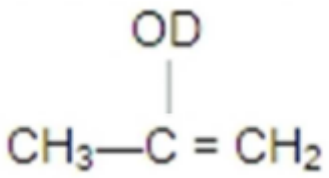
(A) methyl group

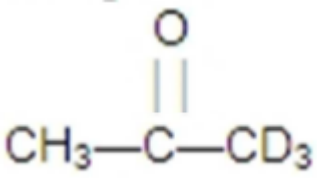
(B) carboxylic acid group

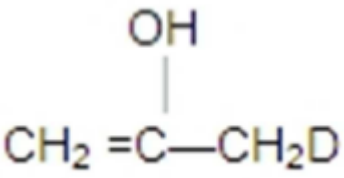
(C) methylene group

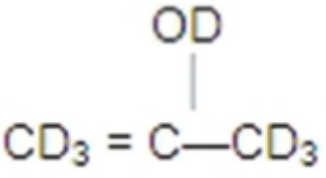
(D) bicarbonate

20. The enol form of acetone, after treatment with D_2O, gives:

(A) 

(B) 

(C) 

(D) 

21. A positive carbylamines test is given by:

(A) $N, N-$ dimethylaniline

(B) $2,4-$ dimethylaniline

(C) N-methyl-o-methylaniline

(D) p-methylbenzylamine

22. The optically active tartaric acid is named as $D-(+)-$ tartaric acid because it has a positive:

(A) optical rotation and is derived from D -glucose

(B) pH in organic solvent

(C) optical rotation and is derived from $D-(+)-$ glyceraldehyde

(D) optical rotation only when substituted by deuterium

23. A solution of $(+)-2-$ chloro $-2-$ phenylethane in toluene racemises slowly in the presence of small amount of $SbCI5$,due to the formation of:

(A) carbanion

(B) carbine

(C) free-radical

(D) carbocation

24. The product(s) obtained via oxymercuration $(HgSO4 + H2SO4)$ of 1-butyne would be:

$O_{1/21/2}$

(A) $CH3 - CH2 - C - CH3$

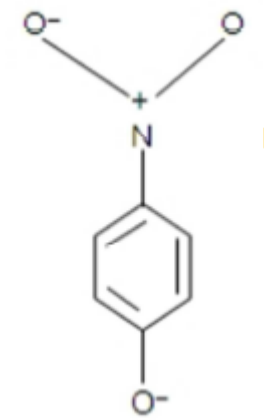
(B) $CH3 - CH2 - CH2 - CHO$

(C) $CH3 - CH2 - CHO + HCHO$

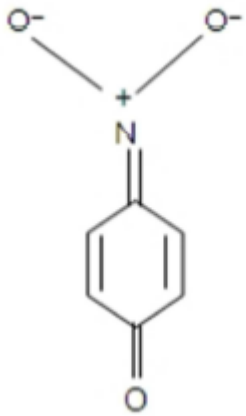
(D) $CH3 - CH2 - COOH + HCOOH$

25. the most unlikely representation of resonance structures of *p* -nitrophenoxide ion is:

(A)



(B)



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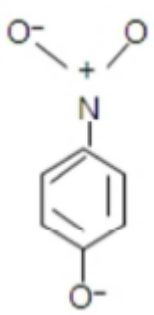
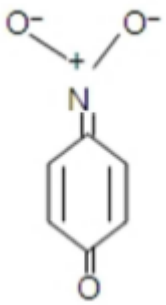
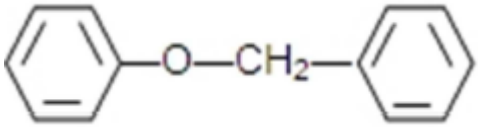
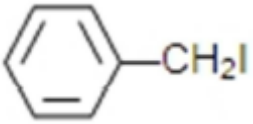


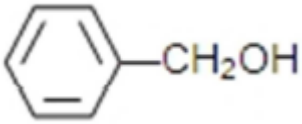
(D)

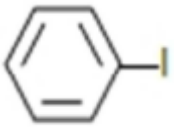


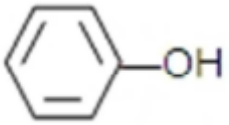
DIRECTIONS: Question numbers 26-35 carry 3 marks each and may have more than one correct answer. All correct answers must be marked to get any credit in these questions.

26. The ether  when treated with HI produces:

(A) 

(B) 

(C) 

(D) 

27. Toluene, when treated with $Br2/Fe$, gives p-bromotoulene as the major product because the $CH3$ group:

(A) is para directing

(B) is meta directing

(C) actives the ring by hyperconjugation

(D) deactivates the ring

28. The following statement(s) is(are) correct:

(A) A plot of log Kp versus $1/T$ is linear

(B) A plot of log $[X]$ versus time is linear for a first order reaction, $X \dashrightarrow P$

(C) A plot of log p versus $1/T$ is linear at constant volume

(D) A plot of p versus $1/V$ is linear at constant temperature

29. The following is(are) endothermic reaction(s):

(A) Combustion of methane

(B) Decomposition of water

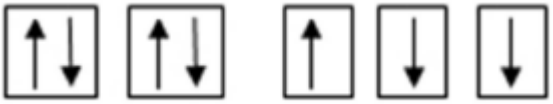
(C) Dehydrogenation of ethane of ethylene

(D) Conversion of graphite to diamond.

30. Ground state electronic configuration of nitrogen atom can be represented by:

(A) 

(B) 

(C) 

(D) 

31. In the depression of freezing point experiment, it is found that the:

(A) vapour pressure of the solution is less than that of pure solvent

(B) vapour pressure of the solution is more than that of pure solvent

(C) only solute molecules solidify at the freezing point

(D) only solvent molecules solidify at the freezing point

32. Ionic radii of:

(A) $Ti^{4+} < Mn^{7+}$

(B) $35CI^{-} < 37CI^{-}$

(C) $K^{+} > CI^{-}$

(D) $P^{3+} > P^{5+}$

33. Ammonia, on reaction with hypochlorite anion, can form:

(A) NO

(B) NH4CI

(C) N2H4

(D) HNO2

34. A buffer solution can be prepared from a mixture of:

(A) sodium acetate and acetic acid in water

(B) sodium acetate and hydrochloric acid in water

(C) ammonia and ammonium chloride in water

(D) ammonia and sodium hydroxide in water

35. An aromatic molecule will:

(A) have $4n\,p$ electrons

(B) have $(4n+2)p$ electrons

(C) be planar

(D) be cyclic

SECTION II

INSTRUCTIONS

(i) There are 12 questions in this section.

(ii) At the end of the answer to a question, leave about 3 cm blank space, draw a horizontal line and start answer to the next question. The corresponding question number must be written in the left margin. Answer all parts of a question at one place only.

(iii) The use of Arabic numerals (0, 1, 2, ……..9) only is allowed in answering the question at one place only.

1. (a) A white solud is either $Na2O$ or $Na2O2$. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.

   (i) Identify the substance and explain with balanced equation.

   (ii) Explain what would happen to the red litmus if the white solid were the other compound.

(b) A, B and C are three complexes of chromium (III) with the empirical formula $H12O6CI3Cr$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated $H2SO4$, whereas complexed B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated $H2SO4$. Identify A, B and C.

3. (a) An aqueous solution containing one mole of $HgI2$ and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of $NaOCI$. Explain with equations.

   (b) How many millilitres of $0.5M$ $H2SO4$ are needed to dissolve $0.5g$ of copper (II) carbonate?

   (c) Give reasons for the following in one or two sentences only.

   (i) $BeCI2$ can be easily hydrolysed.

   (ii) $CrO3$ is an acid anhydride.

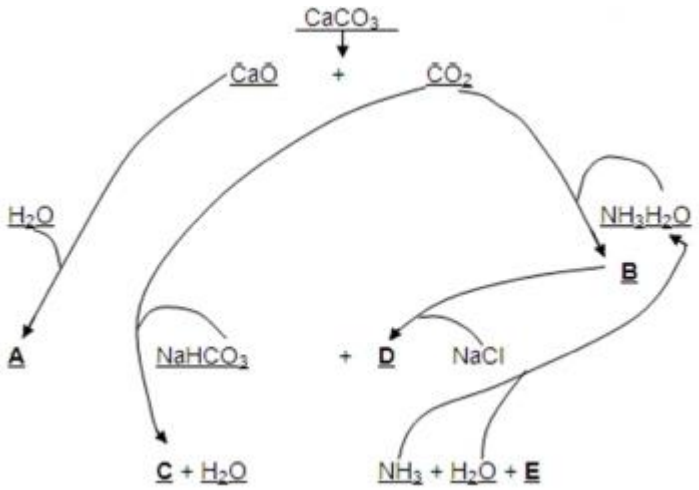
3. (a) In the following equation,

   $A + 2B + H2O \text{--} > C + 2D$

   $(A = HNO2, B = H2SO3, C = NH2OH)$. Identify D. Draw the structures of A, B, C and D.

(b) In the Contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of $SO2$?

4 (a) The Haber process can be represented by the following scheme:



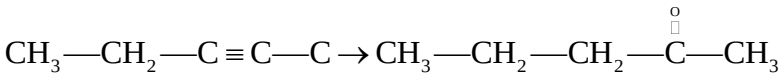
Identify A, B, C, D and E.

(b) Discuss the hybridization of carbon atoms in allene $(C3H4)$ and show the $p-$orbital overlaps.

(c) Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

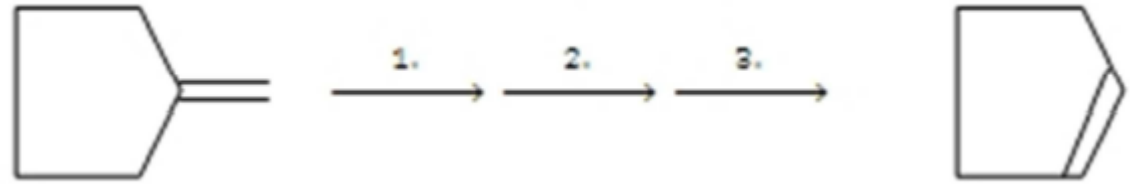
5. (a) Compound $A(C8H8O)$ on treatment with $NH2OH.HCI$ given B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B,C,D and E are all isomers of molecular formula $(C8H9NO)$. When D is boiled with alcoholic KOH, an oil $F(C6H7N)$ separates out. F reacts rapidly with $CH3COCI'$ to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid $G(C7H6O2)$. Identify A-G.

(b) Carry out the following transformation in not more than three steps.



6. Complete the following reactions with appropriate reagents.

(a)



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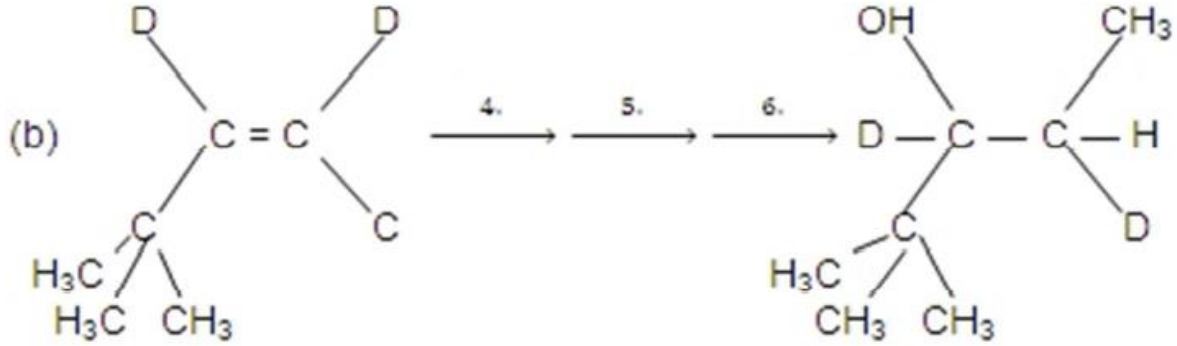

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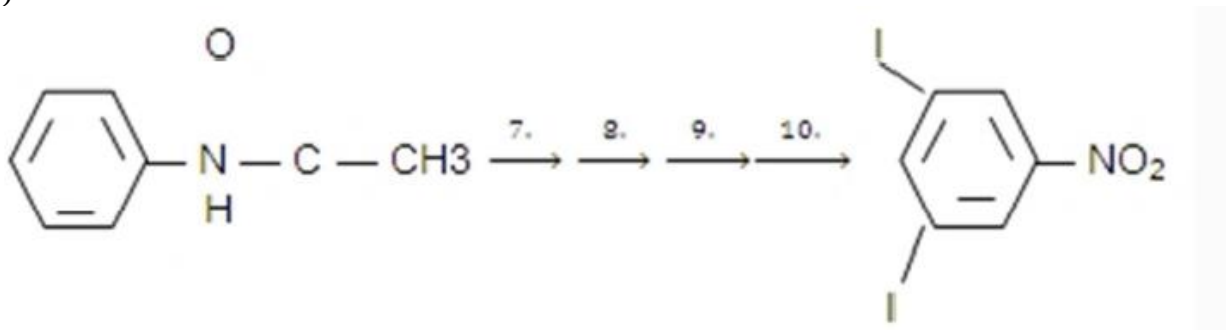
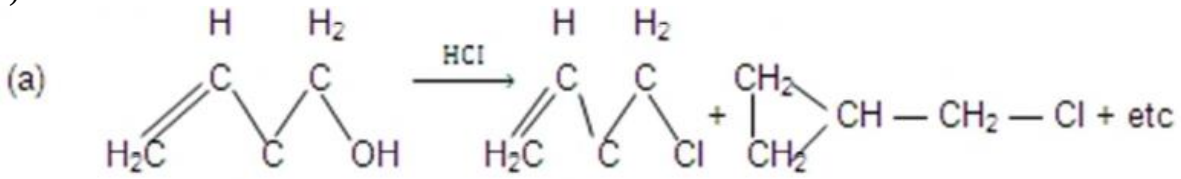
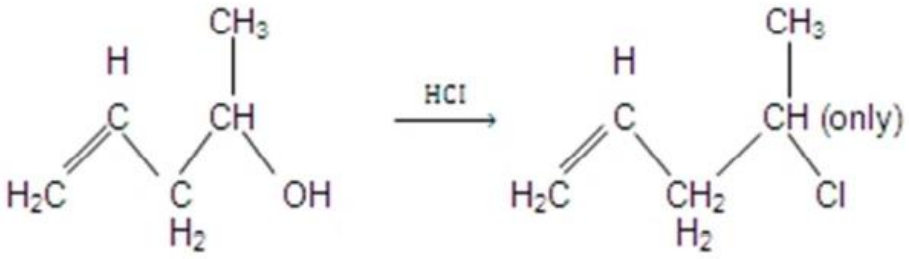


7. Explain briefly the formation of the products giving the structures of the intermediates.

(A)

(a)





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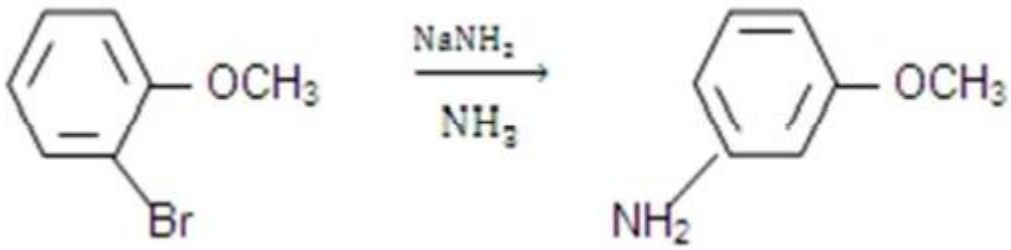

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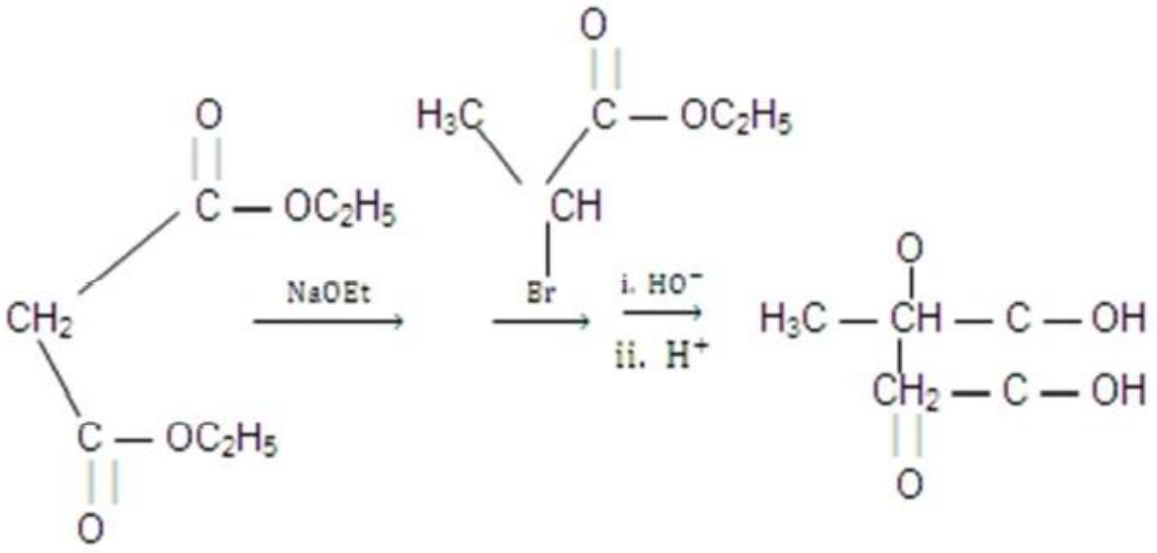

8. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon: 42.86%, hydrogen: 16.67%, and oxygen: 38.07%,

(i) Calculate the empirical formula of the minor product.

(ii) When $5.5\,g$ of the minor product is dissolved in $45\,g$ of benzene, the boiling point of the solution is $1.840C$ higher than that of pure benzene. Calculate the molar mass of the minor product is dissolved in $45\,g$ of benzene, the boiling point of the solution is $1.840C$ higher than that of pure benzene. Calculate the molar mass of the minor product the determine its molecular and structural formula.

(Molal boiling point elevation constant of benzene is $2.53\,K\,kg\,mol-1.$)

9. (a) A plant virus is found to consist of uniform cylindrical particles of $150\,A$ in diameter and $5000\,A$ long. The specific volume of the virus is $0.75\,cm3/g$.

If the virus is considered to be a single particle, find its molar mass.

(b) When $3.06\,g$ of solid $NH4HS$ is introduced into a two-litre evacuated flask at $270C$, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate Kc and Kp for the reaction at $270C$.

(ii) What would happen to the equilibrium when more solid $NH4HS$ is introduced into the flask?

10.(a) One mole of nitrogen gas at $0.8\,atm$ takes $38\,s$ to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at $1.6\,atm$ takes $57\,s$ to diffuse through the samel hole. Calculate the molecular formula of the compound.

(b) The pressure exerted by $12\,g$ of an ideal gas at temperature t^0C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas $=120$)

11.(a) A cell, $Ag|Ag+||Cu2+|Cu$, initially contains $1M\,Ag+$ and $1M\,Cu2+$ ions. Calculate the change in the cell potential after the passage of $6.95\,A$ of current for $1h$.

(b) The solubility of $Pb(OH)2$ in water is $6.7\times10-6\,M$. Calculate the solubility of $Pb(OH)2$ in a buffer solution of $pH=8$.

12.(a) Estimate the average $S-F$ bond energy in $SF6$. The values F standard enthalpy of formation of $SF6(g), S(g)$ and $F(g)$ are: $1100, 275$ and $80\,kJ\,mol-1$ respectively.

(b) The rate constant for an isomerisation reaction, $A-->B$ is $4.5\times10-3\,min$. If the initial concentration of A is $1M$, calculate the rate of the reaction after $1h$.

(c) A metal crystallizes into two cubic phases, face centered cubic (FCC) and body centered cubic (BCC), whose unit cell lengths are 3.5 and $3.0\,A$, respectively. Calculate the ratio of densities of FCC and BCC.