2016

Part I *(Answer all questions)*

Question: 1

a. Fill in the blanks by choosing the appropriate word/words from those given in the brackets: [5]
(Henry's, aldol condensation, absence, do not, ohm, Raoult's, increases, common ion effect, easily, three, solubility product, ohm^{-1}, two, four, $ohm^{-1}cm^{2}$, cannizzaro, $ohm^{-1}cm^{-1}$, zero, decreases, presence)

1. Ideal solutions obey _____ law and they _____ form azeotropic mixtures.

Answer:
Raoult's , do not.

2. Benzaldehyde undergoes _____ reaction due to _____ of a-hydrogen atom.

Answer:
Cannizzaro, absence

3. The solubility of silver chloride _____ in the presence of sodium chloride because of _____.

Answer:
Decreases, common ion effect

4. The unit of conductance is _____ and that of specific conductance is _____ .

Answer:
Ohm^{-1}, $ohm^{-1}cm^{-1}$

5. When the concentration of a reactant of first order re n is doubled, the rate becomes _____ times, but for _____ order reaction, the rate remains same.

Answer:
Two, zero

b. Complete the following statements by selecting the correct alternative from the choices Given:

1. Electrochemical equivalent is the amount of substance which gets deposited from its solutions on passing electrical charge equals to:

    a. 96,500 Coulombs
    b. 1 Coulombs
    c. 60 Coulombs
    d. 965 Coulombs

Answer:
1 Coulombs

2. The complex ion $[Ni(CN_4)]^{2-}$ is:

a. Square planar and diamagnetic

b. Tetrahedral and paramagnetic

c. Square planer and paramagnetic

d. Tetrahedral and diamagnetic

Answer:
Square planer and diamagnetic.

3. Wohler's synthesis is used for the preparation of:

a. Glycine

b. Amino acids

c. Urea

d. Proteins

Answer:
Urea.

4. When SO_2 gas is passed through acidified $K_2Cr_2O_7$ solution, the color of the solution changes to:

a. Red

b. Black

c. Orange

d. Green

Answer:
Green.

5. In the equation $CH_3COOH + Cl_2 \xrightarrow[-HCl]{Red\ P} A$ the compound A is:

a. CH_3CH_2Cl

b. $ClCH_2COOH$

c. CH_3Cl

d. CH_3COCl

Answer:
$ClCH_2COOH$

c. Answer the following questions: [5]

1. What is the order of reaction whose rate constant has the same unit as the rate of reaction?

Answer:
Zero order reaction, rate = k $[A]^o$.

$k = \frac{rate}{[A]^o} = rate = k$

2. What is the pH value of a solution whose hydroxyl ion concentration is 1×10^{-2} M?

Answer:

$pOH = -\log_{10}[OH^-]$.
$[OH^-] = 1 \times 10^{-2}$ M
pOH = 2
pH = 14 – 2 =12

3. Calculate the number of coulombs required to deposit 5.4g f Al when the electrode reaction is: $Al^{3+} + 3e^- \rightarrow Al$ [Atomic weight of Al = 27g/ mol].

Answer:

$Al^{3+} + 3e^- \rightarrow Al$
1 mole 3 mole 1 mole
27g 3 Faraday 27 g
$\therefore$27g if Al is deposited by 3F
$\therefore$5.4g Al is deposited by $\frac{3 \times 5.4}{27} = 0.6$ F
Coulomb = Faraday x 96,500 = 0.6 x 96,500
= 57,900 coulomb.

4. Write the reaction to prepare acetaldehyde from hydrogen gas and an acid chloride.

Answer:

$$CH_3COCL + H_2 \xrightarrow[BaSO_4]{Pd} CH_3CHO + HCl$$

5. The edge length of unit cell of a body centered cubic (bcc) crystal is 352 pm. Calculate the radius of the atom.

Answer:

For bcc structure radius of sphere = r = $\frac{\sqrt{3}a}{4}$.

a = 352 pm (edge length of unit cell)

Radius of atom (r)= $\frac{\sqrt{3}}{4} \times 352 = 152.42$ pm.

d. Match the following: [5]

1. Weak electrolyte	a. pH of a solution
2. Color in crystals	b. Iodoform
3. Acetone	c. Tollen's reagent
4. Sorensen	d. Ostwald dilution law
5. Ammonical silver nitrate	e. F-centre

Answer:

Weak electrolyte - Ostwald dilution law
Color in crystals - F-centre
Acetone - Iodoform

Sorensen - pH of a solution
Ammonical silver nitrate - Tollen's reagent

Part II *(Answer six questions choosing two from section A, two from section B. And two from section C)*

Section A *(Answer any two questions)*

Question: 2

a.

i. A 10% aqueous solution of cane sugar (mol. Wt. 342) is isotonic with 1.754% aqueous solution of urea. Find the molecular mass of urea. [2]

Answer:

No. of moles of cane sugar = $\frac{10}{342} = 0.0292$

No. of moles of urea = $\frac{1.754}{x}$

π cane sugar = π urea (isotonic solution)
n_1 RT/V = n_2 RT/V
0.0292 = 1.754/x
X=60.06

ii. The molecular weight of an organic compound is 58g mol^{-1}. What will be the boiling point of a solution containing 48grams of the solute in 1200 grams of water? [K_b for water = 0.513^{0}C kg $mole^{-1}$; Boiling point of water = 100^0 C.] [2]

Answer:

1200 g of water contains 48g of solute

1000 g contains $\frac{48 \times 1000}{1200}$ = 40g of solute

Molality = $\frac{48}{58}$ = 0.689 mol/kg

$\Delta T_b = k_b$ molality= 0.513 x 0.689 = 0.353^{0}C
B.P = 100+0.353 = 100.353^{0}C

iii. What will be the value of van't Hoff factor (i) of benzoic acid if it dimerises in aqueous solutions? How will the experimental molecular weight vary as compared to the normal molecular weight? [1]

Answer:

Van't Hoff factor (i) = $\frac{\text{observed colligative property}}{\text{normal colligative property}}$

Since benzoic acid dimerised, $i = \frac{1}{2}$ or 0.5

Experimental mol. wt. = twice the normal mol. wt.

b.

i. Determine the pH value of 0.001 M acetic acid solution if it is 2% ionized at this concentration. How can the degree of dissociation of this acetic acid solution be increased? [2]

Answer:

$\alpha = \frac{2.0}{100} = 0.02$

pH = -log C α

pH = -log 0.001 x 0.02

= =log 2 x 10^{-5}

pH = 4.69

The degree of dissociation of this acetric acid can be increased by diluting the solution.

ii. The solubility product of $PbCl_2$ at 298 K is 1.7 x 10^{-5}. Calculate the solubility of $PbCl_2$ in g/lit. at 298K. [2]
Atomic weights: [Pb = 207 and Cl = 35.5]

Answer:

Solubility product (K_{sp}) = $4S^3$= 1.7 x 10^{-5}

Solubility (S) = 0.01619 mol L^{-1}

Mol mass of $PbCl_2$ = 278

Solubility in g/lit = 0.01619 x 278 = 4.50 g/lit

c. Graphite is anisotropic with respect to condition of electric current. Explain [1]

Answer:

Graphite exists in the form of layer structure. The electrical conductivity is more parallel to the layer whereas the electrical conductivity is less perpendicular to the layer.

Question: 3

a.

i. In a body centred and face centred arrangement of atoms of an element, what will be the number of atoms presents in respective unit cells? Justify your answer with calculation. [2]

Answer:

BCC corner atoms = 8 x $\frac{1}{8}$ = 1

Body centered atom = 1 x 1 = 1

Total number of atoms 1 +1 = 2

FCC corner atoms = 8 x $\frac{1}{8}$ = 1

Face centred atoms = 6 x $\frac{1}{2}$ = 3

Total number of atoms 1 + 3 = 4

ii. A compound AB has a simple cubic structure and has molecular mass 99. Its density is 3.4 cm^{-3}. What will be the edge length of the unit cell?

Answer:

$$\rho = \frac{Z \times M}{\alpha^3 \times N_A}$$

Simple cubic structure Z = 1

M = 99, $N_A = 6.023 \times 10^{23}$, density = $3.4 g/cm^3$

$$a^3 = \frac{Z \times M}{\rho \times N_A} = \frac{1 \times 99}{3.4 \times 6.023 \times 10^{23}}$$

$$a^3 = 4.834 \times 10^{-23} \text{ cm}$$

$$a^3 = 3.64 \times 10^{-8} \text{ cm}$$

b.

i. For the reaction : $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}; \Delta H = -\text{heat}$ [2]

$$K_e = 2.5 \times 10^2 \text{ at } 298K$$

What will happen to the concentration of N_2 if:

a. Temperature is decreased to 273K.
b. Pressure is reduced.

Answer:

a. The reaction is exothermic hence decrease in temperature will favour the forward reaction, i.e concentration of N_2 will increase.
b. Pressure has no effect on equilibrium.

ii. In a first order reaction, 10% of the reactant is consumed in 25 minutes. Calculate: [2]

a. The half-life period of the reaction.
b. The time required for completing 87.5 % of the reaction.

Answer:

a. $$k = \frac{2.303}{t} \log 10 \frac{\alpha}{\alpha - x}$$

$$k = \frac{2.303}{25} \log 10 \frac{100}{90}$$

$k = 0.0042 \text{ min}^{-1}$

$$t\frac{1}{2} = \frac{0.693}{k} = \frac{0.693}{0.0042} = 165 \text{min}$$

b. $$t = \frac{2.303}{0.0042} \log 10 \frac{100}{12.5}$$

$t = 495.14$ min

c. Water acts as Bronsted acid as well as a Bronsted base. Give one example each to illustrate this statement. [2]

Answer:

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

acid – 1 base – 2 acid – 2 base – 1

$$H_2O_{(l)} + NH_{3(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

acid – 1 base – 2 acid – 2 base – 1

Question: 4

a.

1. Consider the following cell reaction at 298 K:
   $2Ag^{+}+Cd \rightarrow 2Ag+Cd^{2+}$ [3]

   The standard reaction potentials (E^{0}) for $\frac{Ag^{+}}{Ag}$ and $\frac{Cd^{2+}}{Cd}$ are 0.80 V and -0.40V respectively:

   a. Write the cell representation.

Answer:

$Cd_{(s)} / Cd^{2+}_{(aq)} / / Ag^{+}_{(aq)} / Ag$

   b. What will be the emf of the cell if the concentration of Cd^{2+} is 0.1 M and that of Ag^{+} is 0.2 M.

Answer:

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

$= 0.80-(-0.40)$

$=1.2V$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log_{10}\frac{[cd^{2+}][Ag]^{2}}{[Ag^{+}]^{2}[cd]}$$

$$= 1.2 - \frac{0.0591}{n}\log\frac{[0.1]}{[0.2]^{2}}$$

$=1.18$ V

   c. Will the cell work spontaneously for the condition given in (2) above?

Answer:

$\Delta G = -nFE^{o}$

Since E^{o} is positive, ΔG will be negative so the cell will work spontaneously.

2. What is a buffer solution? How is it prepared? Explain the buffer action of a basic buffer with a suitable example. [2]

Answer:

Buffer solutions are those solutions which resist the change in their pH value when small quantity of acid or alkali is added to it.

Preparation of buffer

- By taking aqueous solution of a weak acid and its salt with a strong base. or
- By taking aqueous solution of a weak base and its salt with a strong acid.

Buffer action of basic buffer

$NH_4OH_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$

$NH_4Cl_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + Cl^{-}_{(aq)}$

On adding NaOH

$NH4^+ + OH^- \rightarrow NH_4OH_{(aq)}$

from buffer from NaOH

On adding HCl

$OH^-_{(aq)} + H_3O^+ \rightarrow 2H_2O(l)$

From buffer from HCl

Hence, there is no change in pH of buffer solution.

Buffer action of any basic buffer solution may be given

b. Explain the following: [2]

1. When NaCl is added to $AgNO_3$ solution, a white precipitate is formed.

Answer:

$NaCl\overline{aq} \rightarrow Na^+ + Cl^-$

$AgNO_3\overline{aq} \rightarrow Ag^+ + NO_3^-$

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

white ppt

2. An aqueous solution of ammonium chloride is acidic in nature.

Answer:

Ammonium chloride is a salt of strong acid and weak base, hence due to cationic hydrolysis, the aq solution of ammonium chloride is acidic in nature.

c. A 0·05 M NH_4OH solution offers the resistance of 50 ohms to a conductivity cell at 298K. If the cell constant is 0·50 cm^{-1} and molar conductance of NH_4OH at infinite dilution is 471·4 $ohm^{-1}\ cm^2\ mol^{-1}$, calculate: [3]

i. Specific conductance

Answer:

$$\text{Specific conductance } k = \frac{1}{R} \text{ x cell constant}$$

$$= \frac{1}{50} \text{ x } 0.50$$

$= 0.01\ ohm^{-1}\ cm^{-1}$

ii. Molar conductance

Answer:

$$\text{Molar conductance } (^{\wedge}m) = \frac{1000 \text{ x } K}{C} = \frac{1000 \text{ x } 0.01}{0.05}$$

$= 200 ohm^{-1}\ cm^2\ mol^{-1}$

iii. Degree of dissociation

Answer:

$$\text{Degree of dissociation } (\alpha) = \frac{^{\wedge}m}{^{\wedge}m_{\infty}} = \frac{200}{471.4} = 0.4242$$

Section B *(Answer any two questions)*

Question: 5

a. Write the IUPAC names of the following: [2]

1. $[Co(NH_3)_4SO_4]NO_3$

Answer:

Tetra ammine sulphato cobalt (III) nitrate

2. $K[Pt(NH_3)Cl_3]$

Answer:

Potassium ammine trichloridoplatinate (II)

b. What type of isomerism is exhibited by the following pairs of compounds: [1]

i. $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$.

Answer:

Ionisation isomerism

ii. $[Cr(SCN)(H_2O)_5]^{2+}$ and $[Cr(NCS)(H_2O)_5]^{2+}$.

Answer:

Linkage isomerism.

c. How does $K_2[Pt\ Cl_4]$ get ionised when dissolved in water? Will it form precipitate when $AgNO_3$ solution is added to it? Give a reason for your answer.

Answer:

$$K_2[Pt\ \ Cl_4] \rightarrow 2K^+ + [Pt\ \ Cl_4]^{2-}$$

It will not form white precipitate with $AgNO_3$ solution because Cl^- ion is not free to form white precipitate of AgCl.

Question: 6

a. Give balanced chemical equation for the following: [3]

i. Silver nitrate is added to dilute solution of sodium thiosulphate

Answer:

$$2AgNO_3 + Na_2S_2O_3 \rightarrow \underset{\text{white ppt}}{Ag_2S_2O_3} + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{black}}{Ag_2S} + H_2SO_4$$

ii. Potassium dichromate is treated with acidified ferrous sulphate solution.

Answer:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

iii. Phosphorous reacts with conc. sulphuric acid.

Answer:

$$P_4 + 10H_2SO_4 \rightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

b. How will you obtain pure potassium permanganate (KMnO4) crystals from its ore. pyrolusite? Give the steps involved and the reactions [2]

Answer:

Conversation of pyrolusite (MnO_2) to potassium manganite

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$$

Or, $2MnO_2 + 2K_2CO_3 + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2CO_2$

Oxidation of potassium manganite to potassium permanganate.

$$3K_2MnO_4 + CO_2 \rightarrow 2KMnO_4 + 2K_2CO_3$$

Or, $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

Question 7

a. [3]

1. Sulphur dioxide acts as an oxidizing agent as well as a reducing agent. Give one reaction each to show its oxidizing nature and its reducing nature.

Answer:

The oxidation state of S in SO_2 is +4

Which is an intermediate state and may increase or decrease. Hence, SO_2 can act both as an oxidizing and reducing agent.

Example of oxidizing agent $\rightarrow 3Fe + SO_2 \rightarrow 2FeO + FeS$

Example of reducing agent $\rightarrow SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$

2. Explain why an aqueous solution of potassium hexacyanoferrate (II) does not give the test for ferrous ion.

Answer:

Aqueous solution of $K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

Fe^{2+} ion is not in free state, hence it does not give the test of Fe^{2+} ion.

b. What is meant by Lanthanide contraction? Write the general electronic configuration of inner transition elements.

Answer:

On moving from La^{3+} (At. No. 57) to Lu^{3+} (At. No. 71) the size of the atoms and ions decreases regularly due to increase in nuclear change. This decrease in size is called Lanthanide contraction.

The general electronic configuration of inner transitional elements is $ns^2\ (n\text{-}1)\ d^{0\text{-}1}\ (n\text{-}\ 2)f^{1\text{-}14}$

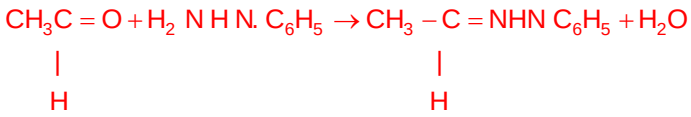
Section C *(Answer any two questions)*

Question: 8

a. How can the following conversions be brought about

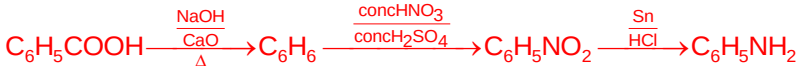
i. Acetaldehyde to acetamide phenyl hydrazone. [1]

Answer:



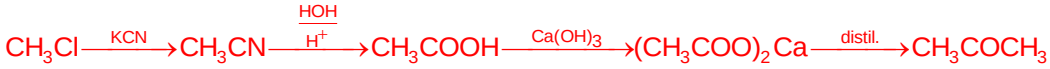
ii. Benzoic acid to aniline [1]

Answer:



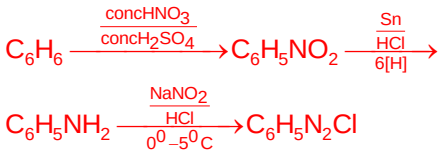
iii. Methyl chloride to acetone. [2]

Answer:



iv. Benzene to benzene diazonium chloride. [1]

Answer:



b.

1. Glycerol (propane 1, 2, 3 triol) is more viscous than ethylene glycol (ethane 1, 2, diol). Explain. [1]

Answer:

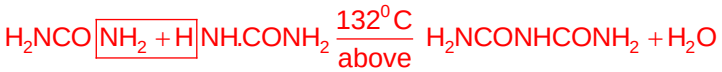
Glycerol is more viscous than ethane 1, 2 diol because, in glycerol, there are three OH groups as cpmpared to two OH groups in ethane 1, 2 diol. Therefore, the extent of hydrogen bonding is more, hence glycerol is more viscous.

2. How can urea be detected by Biuret test? [1]

Answer:

Biuret test:

2 moles of urea when heated above 132^0C



Biuret

When alkaline solution of Biuret is treated with copper sulphate solution, a violet color is produced.

c. Identify the compounds A, B and C:

i. $C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C_2H_5COOH \xrightarrow[\Delta]{NH_3} C$

Answer:

$C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow{H_3O^+} C_2H_5COOH \xrightarrow[\Delta]{NH_3} C_2H_5CONH_2$

ii. $C_6H_5COOH \xrightarrow{SOCl_2} A \xrightarrow{NH_3} B \xrightarrow[KOH]{Br_2} C$

Answer:

$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{NH_3} C_6H_5CONH_2 \xrightarrow[KOH]{Br_2} C_6H_5NH_2$

Question: 9

a. Give balanced equations for the following name reactions: [3]

1. Benzoin condensation.

Answer:

$$C_6H_5\overset{\overset{O}{\|}}{C}H - \overset{\overset{O}{\|}}{C} - C_6H_5 \xrightarrow[\Delta]{KCN(alc)} C_6H_5 - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - \overset{\overset{O}{\|}}{C} - C_6H_5$$

Benzoin

2. Wurtz-Fittig reaction.

Answer:

$C_6H_5Cl + 2Na + ClCH_3 \xrightarrow{\text{dry ether}} C_6H_5.CH_3 + 2NaCl$

3. Carbylamine reaction.

Answer:

$RNH_2 + CHCl_3 + 3KOH_{(alc)} \xrightarrow{\Delta} R - N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$

b. Give chemical test to distinguish: [3]

i. Formaldehyde and acetaldehyde.

Answer:

Formaldehyde and acetaldehyde:

Acetaldehyde on reaction with iodine and alkali gives yellow precipitate of iodoform which has a characteristic odour. Formaldehyde does not give this test. (or any other suitable test.)

ii. Dimethyl ether and ethyl alcohol

Answer:

Dimethyl ether and ethyl alcohol:

Ethyl alcohol when reacts with iodine and alkali gives yellow precipitate of iodoform which has characteristic odour. Diethyl ether does not give this test. *(or any other suitable test)*

c. [4]

1. Write the structure of three ethers with molecular formula $C_4H_{10}O$.

Answer:

$CH_3 - O - CH_2 - CH_2 - CH_3$

$CH_3\ CH_2 - O - CH_2 - CH_3$

$$CH_3 - O - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$$

2. Starting with Grignard's reagent, how will you prepare propanoic acid?

Answer:

$$C_2H_5MgBr + O = C = O \rightarrow O = \underset{\displaystyle C_2H_5}{\underset{|}{C}} - O\ MgBr \xrightarrow{+HOH} O = \underset{\displaystyle C_2H_5}{\underset{|}{C}} - OH + Mg\begin{matrix} Br \\ \diagup \\ \diagdown \\ OH \end{matrix}$$

Question: 10

a. An organic compound A has the molecular formula C_7H_6O. When A is treated with NaOH followed by acid hydrolysis, it gives two products B and C. when B is oxidized it gives A, when A and C are each treated separately with PCl_5, they give two different products D and E. [3]

i. Identify A, B, C, D and E.

Answer:

$A = C_6H_5CHO$

$B = C_6H_5CH_2OH$

$C = C_6H_5COOH$

$D = C_6H_5CHCL_2$

$E = C_6H_5COCl$

ii. Give the chemical reaction when A is treated with NaOH and name the reaction.

Answer:

$2C_6H_5CHO + NaOH \rightarrow C_6H_5COONa + C_6H_5CH_2OH$

Or Cannizzaro reaction

b. Answer the following: [4]

i. What do you observe when glucose solution is heated with Tollen's reagent?

Answer:

$(CHOH)_4 + 2[Ag(NH_3)_2]^+ OH^- \xrightarrow{\Delta} (CHOH)_4 + 2Ag + 3NH_3 + H_2O$

| Tollen's reagent |
CH_2OH CH_2OH
glucose Silver mirror

Or,

CHO COOH
| |
$(CHOH)_4 + Ag_2O \xrightarrow{\Delta} (CHOH)_4 + 2Ag$

| Tollen's reagent |
CH_2OH CH_2OH
glucose Silver mirror

ii. Name the monomers and the type of polymerization in each of the following polymers:
a. Terylene

Answer:
Terylene: Ethylene glycol + terephthalic acid
Condensation polymerization

b. Polyvinyl chloride

Answer:
Polyvinyl chloride: Vinyl chloride
Additiontion polymerization

c. Give balanced equations for the following reactions: [3]

i. Ethylamine with nitrous acid

Answer:
$C_2H_5NH_2 + HONO \rightarrow C_2H_5OH + N_2 + H_2O$

ii. Diethyl ether with phosphorous pentachloride.

Answer:
$C_2H_5 - O - C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$

iii. Aniline with acetyl chloride

Answer:
$CH_3CO\boxed{Cl + H}NHC_2H_5 \rightarrow CH_3CONHC_6H_5 + HCl$