Actual mass of $KMnO_4$ = moles x Rmm = 0.0061 x 158 = 0.9638g

$\% \text{ purity} = \frac{actual\ mass\ x\ 100}{sample\ mass} = \frac{0.9638\ x\ 100}{0.9875} = 97.6\%$

ADVENCED LEVEL CHEMISTRY NATIONAL EXAMINATION PAPER 2003/2004
(Biology-Chemistry)

SECTION A: Answer ALL questions /55 marks

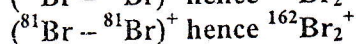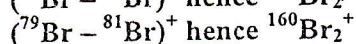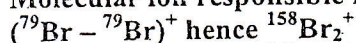01. a) The diagram below shows the mass spectrum for naturally occurring gallium (Ga).
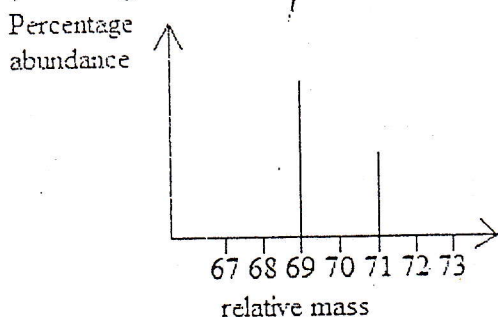
Calculate the relative atomic mass of naturally occurring gallium. **2 marks**

b) Bromine (Br) has two isotopes ^{79}Br and ^{81}Br. If Bromine is used in the mass spectrometer there are three peaks of Br_2 are responsible for these peaks. **1.5 marks**

Answer:

a) $R.A.M = \sum \frac{abundance\ x\ isotopic\ mass}{100} = \frac{60+69+71+40}{100} = 69.8$

b) Molecular ion responsible for the three peaks are:
   $(^{79}Br - ^{79}Br)^+$ hence $^{158}Br_2^+$
   $(^{79}Br - ^{81}Br)^+$ hence $^{160}Br_2^+$
   $(^{81}Br - ^{81}Br)^+$ hence $^{162}Br_2^+$

02. a) State Hess's law. **2 marks**

b) The standard enthalpy change for the combustion of carbon is -394KJmol^{-1}, and that of carbon monoxide is -111KJmol^{-1}. Calculate the standard enthalpy change for the reaction
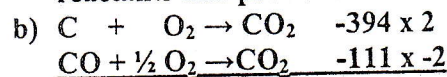$2C(s) + O_2(g) \rightarrow 2CO(g)$ **3 marks**

c) Which of the two reactions below is more likely to take place? Give a reason for your answer.

$2C(s) + O_2(g) \rightarrow 2CO(g)$
$C(s) + O_2(g) \rightarrow CO_2(g)$ **1 mark**
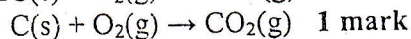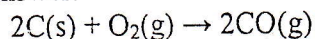
Answer:

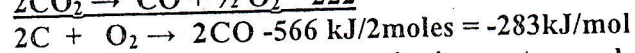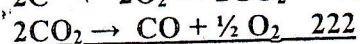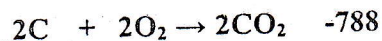a) Hess's law states that the resultant heat change for reaction is the same whether it is carried in one or several stages.
   Or That the enthalpy change of chemical reaction is the same irrespective of number of stages passed through but will depend on initial and final states of the reactants and products.
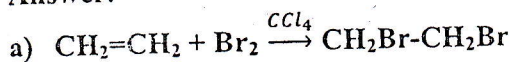
b) $C + O_2 \rightarrow CO_2$ -394 x 2
   $\underline{CO + ½O_2 \rightarrow CO_2}$ -111 x -2

$2C + 2O_2 \rightarrow 2CO_2$ -788
$2CO_2 \rightarrow CO + \frac{1}{2}O_2$ 222
$2C + O_2 \rightarrow 2CO$ -566 kJ/2moles = -283kJ/mol

c) It is $C + O_2 \rightarrow CO_2$, because it gives out more heat to the surrounding. i.e: It is more exothermic.
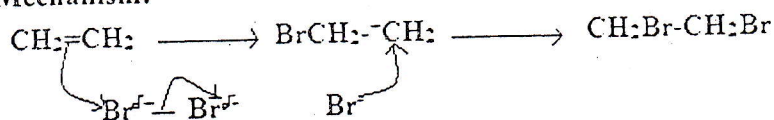
03. The compound $C_2H_4Br_2$(…) can be made by reacting ethene with bromine.
  a) Show the mechanism for the above reaction. **2 marks**
  b) What observations would you make at the end of the reaction? **1 mark**
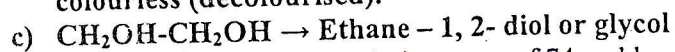 c) If $C_2H_4Br_2$ is refluxed with aqueous sodium hydroxide, an organic product B and give its systematic name. **1 mark**

Answer:

a) $CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} CH_2Br\text{-}CH_2Br$
   Mechanism:

   $CH_2=CH_2 \longrightarrow BrCH_2\text{-}^-CH_2 \longrightarrow CH_2Br\text{-}CH_2Br$

   $Br^{\delta^-} \!-\! Br^{\delta^+}$ Br^-

b) The bromine (brown) colour will be discharged. i.e: changes from brown to colourless (decolourised).

c) $CH_2OH\text{-}CH_2OH \rightarrow$ Ethane – 1, 2- diol or glycol

04. An alcohol (Alkanol) has a relative mass of 74 and has the following composition by mass: C, 64.9%; H, 13.5%; O, 21.6%
  a) Show that its empirical formula is the same as its molecular formula. **3 marks**
  b) Draw the structural formulae of four possible isomers of the alcohol. **2 marks**
  c) One of the isomers F can be oxidized to form a ketone, G. Show the structural formula of F and G. **1 mark**

Answer:

a)

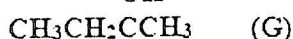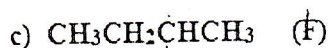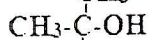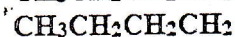| Element	C	H	O
Moles	$\dfrac{64.9}{12}$	$\dfrac{13.5}{1}$	$\dfrac{21.6}{16}$
Simplest ratio	$\dfrac{5.408}{1.35}$	$\dfrac{13.5}{1.35}$	$\dfrac{1.35}{1.35}$
	4	10	1

Empirical formula: $C_4H_{10}O$
$(C_4H_{10}O)n = 74$
$12 \times 4n + 10 \times n + 16 \times n = 74$
$74 n = 74 \Rightarrow n = 1$
Molecular formula: $(C_4H_{10}O) \times 1 = C_4H_{10}O$ it is the same as empirical formula.

b) $CH_3CH_2CH_2CH_2OH$

$CH_3CH_2CH_2\underset{|}{CH_2}$
$\quad\quad\quad\quad OH$

$CH_3\underset{|}{CH}CH_2OH$
$\quad\quad\underset{}{CH_3}$

$\underset{}{CH_3}$
$CH_3-\underset{|}{\overset{|}{C}}-OH$
$\underset{}{CH_3}$

c) $CH_3CH_2\underset{|}{CH}CH_3$ (F)
$\quad\quad\quad OH$

$CH_3CH_2\underset{||}{C}CH_3$ (G)
$\quad\quad\quad O$

05. The table below gives some data about the chlorides of elements of period 3.

| Formula	NaCl	MgCl₂	AlCl₃	SiCl₄	PCl₃	S₂Cl₂	Cl₂
Boiling point °C	1465	1418	423	57	76	136	-34
P^H of aqueous solution	7	6	2	2	2	1	1

a) Explain why the boling point of NaCl is higher than that of $MgCl_2$. **2 marks**
b) Explain why the P^H of NaCl is 7 and that of $AlCl_3$ is 2. **2 marks**

Answer:
a) NaCl is more ionic than $MgCl_2$ because the Mg^{2+} has a higher polarizing power than Na^+ and the higher the polarizing power the lesser is ionic character.
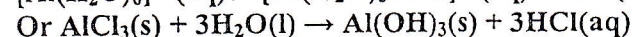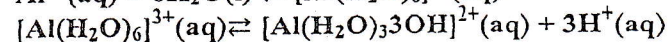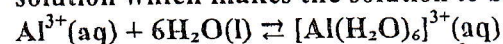
b) NaCl dissolves in water to give a neutral solution of 7.

$NaCl(s) \overset{aq}{\rightarrow} Na^+(aq) + Cl^-(aq)$
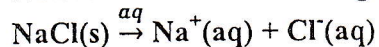
Since Na^+ does not polarize water due to its small size.

$AlCl_3(s) \overset{aq}{\rightarrow} Al^{3+}(aq) + 3Cl^-(aq)$
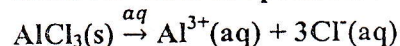
While Al^{3+} has a smaller size and big charge hence high polarizing power. Al therefore has a greater attraction for the oxygen atom in the water molecules. This weakens the oxygen-hydrogen bond in water and releases hydrogen ions in solution which makes the solution to be acidic with P^H of 2.

$Al^{3+}(aq) + 6H_2O(l) \rightleftharpoons [Al(H_2O)_6]^{3+}(aq)$

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_33OH]^{2+}(aq) + 3H^+(aq)$

Or $AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(aq)$

06. When dilute sulphuric acid is added to copper I oxide, a pink solid X and a blue solution Y are formed. The pink solid X conducts electricity.

a) Identify X and Y. **1 mark**
b) Write an equation for the reaction. **1 mark**
c) Using examples from the reaction above, explain the meaning of disproportionation. **1.5 marks**

Answer:
a) Y is $CuSO_4$ – Blue solution
   X is Cu – Pink solid
b) $Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$
c) **Disproportionation reaction is a reaction in which there is both oxidation and**
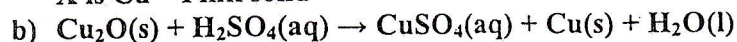
higher repulsion and the lower the bond angle.

09. Butane C_4H_{10} reacts with Cl_2 in the presence of sunlight to form a mixture of products including C_4H_9Cl which is formed as shown in the equation below

$$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$$

a) Write equations for the following stages in the mechanism of the reaction
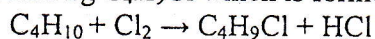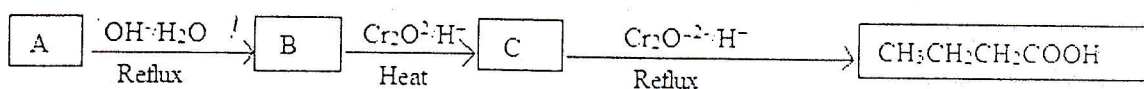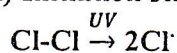   i) Equation for the initiation stage.
   ii) Equation for the propagation stage.
   iii) Equation for the termination stage. **1.5 marks**

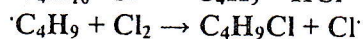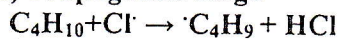b) Compound A which is one of the isomers of C_4H_9Cl was reacted in sequence as shown below

$$\boxed{A} \xrightarrow[\text{Reflux}]{OH^- H_2O} \boxed{B} \xrightarrow[\text{Heat}]{Cr_2O^{2-} H^-} \boxed{C} \xrightarrow[\text{Reflux}]{Cr_2O^{-2-} H^-} \boxed{CH_3CH_2CH_2COOH}$$

i) Write the structural formulae of A, B and C. **1.5 marks**
ii) What chemical test would you use to show that compound C has formed? **1.5 marks**
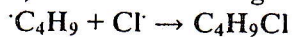
Answer:

a) i) **Initiation state**

$$Cl\text{-}Cl \xrightarrow{UV} 2Cl^{\cdot}$$

ii) **Propagation stage**

$$C_4H_{10} + Cl^{\cdot} \rightarrow {}^{\cdot}C_4H_9 + HCl$$
$${}^{\cdot}C_4H_9 + Cl_2 \rightarrow C_4H_9Cl + Cl^{\cdot}$$

iii) **Termination stage**

$${}^{\cdot}C_4H_9 + Cl^{\cdot} \rightarrow C_4H_9Cl$$
$${}^{\cdot}Cl + {}^{\cdot}Cl \rightarrow Cl_2$$
$${}^{\cdot}C_4H_9 + {}^{\cdot}C_4H_9 \rightarrow C_8H_{18}$$

b) i) A is $CH_3CH_2CH_2CH_2Cl$
      B is $CH_3CH_2CH_2CH_2OH$

   C is $CH_3CH_2CH_2C\overset{\displaystyle O}{\underset{\displaystyle H}{\big\lVert}}$
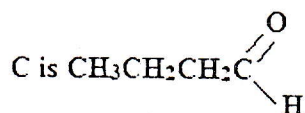
   ii) **Using Tollens reagent and heat**
      Observations: Silver mirror

10. The table below shows some bond enthalpies. Study the table below and answer the questions that follow.

Bond	Average bond energy/ $KJmol^{-1}$
F – F	+158
Cl - Cl	+244
H – F	+ 568
H- Cl	+432

Given that the enthalpy change for the reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is -184 $KJmol^{-1}$
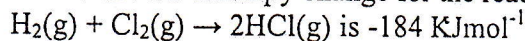
a) Calculate the bond enthalpy of the H – H bond. **2 marks**
b) Calculate the enthalpy change of reaction for the formation of HF from its elements.
   $H_{2(g)} + F_{2(g)} \rightarrow 2HF(g)$
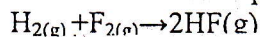
Answer:

a) $\Delta H_r = \sum \Delta H_{reactants} - \sum \Delta H_{products}$

-184 = H-H + Cl-Cl – 2 x H-Cl

-184 = H-H + 244 – 2 x 432

-184 = H-H + 244 – 864

H-H = -184 + 620

H-H = +432 kJmol^{-1}

b) $\Delta H_f = \sum \Delta H_{reactants} - \sum \Delta H_{products}$

= H-H + F-F – 2H-F

= 436 – 158 – 2x568 = -542 kJ

Enthalpy change of formation of H-F

i.4: For one mole of H-F = $\frac{-542}{2}$ = -271 kJ/mol

11. The graph below shows the Boltzmann distribution curve for the same amount of a gas sample at two different temperatures.
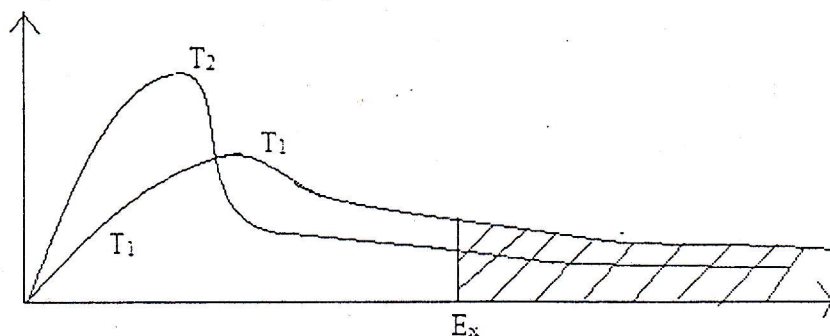
a) State what you would label on X and Y axis. **1 mark**

b) What does the shaded part represent? **1 mark**

c) Explain why a small increase in temperature increases the rate of a chemical reaction tremendously. **1 mark**

Answer:

a) On the Y axis – number of molecules

On the X axis – Kinetic energy

b) Molecules with lower activation energy.

c) Increase in temperature increases the kinetic energy of the molecules. i.e. the speed by which the molecules collide with each other increases as a result the speed of reaction increases.

On addition to that, as the temperature increases, the number of molecules that gain necessary activation energy also increases, hence increase in reaction rate.

12. The solubility of calcium phosphate $Ca_3(PO_4)_2$ is 0.0011g per 100g of water at 25^0C.

a) Calculate the solubility product of calcium phosphate.(Ca=40, P=31, O=16) 4 marks

b) What would be the effect on the solubility of calcium phosphate when a solution of sodium phosphate is added to a saturated solution of calcium phosphate? 2 marks

Answer:

a) $Ca_3(PO_4)_2 \rightleftarrows 3Ca^{2+} + 2PO_4^{3-}$, let the solubility of Ca^{2+} be x:

$$Ksp = [\overset{3x}{Ca^{2+}}]^3[\overset{2x}{PO_4^{3-}}]^2$$
$$= (3x)^3(2x)^2 = 108\ x^5$$

Solubility of $Ca_3(PO_4)_2$ in g/l

$1\ g = 1cm^3 = 1\ ml$

$1000cm^3 \rightarrow \dfrac{0.0011\ x\ 1000}{100} = 0.011g/l$

Solubility of $Ca_3(PO_4)_2$ in moles $dm^{-3} = \dfrac{concentration\ in\ g/l}{Rmm\ in\ g/l}$

Rmm of $Ca_3(PO_4)_2 = 40\ x\ 3 + (31+16)\ x\ 2 = 310$

Hence , solubility of $Ca_3(PO_4)_2$ in moles $dm^{-3} = \dfrac{0.011}{310} = 3.55\ x\ 10^{-5}\ mol\ dm^{-3}$

Solubility of Ca^{2+} which is x is $3.55\ x\ 10^{-5}\ moldm^{-3}$

$Ksp = 108\ x^5 = 108\ (3.55\ x\ 10^{-5})^5 = 6.08\ x\ 10^{-21}\ mol^{-5}dm^{-15}$

b) The solubility of $Ca_3(PO_4)_2$ decreases because of common ion effect. Addition of sodium phosphate increases the concentration of phosphate ions in equilibrium. So to restore Ksp, the excess phosphate ions from Na_3PO_4 react with Ca^{2+}.

$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$
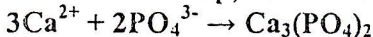
This decreases the solubility of calcium phosphate.

13. The table below shows the rates of reaction between substances A and B at different concentrations.

Experiment	[A] $moldm^{-3}$	[B] $moldm^{-3}$	Initial rate of reaction in $moldm^{-3}S^{-1}$
1	0.50	0.50	$2.0x10^{-2}$
2	1.00	0.50	$8.0x10^{-2}$
3	1.00	1.00	$16.0x10^{-2}$

a) Determine the overall order of the reaction. **2.5 marks**

b) Calculate the rate constant for the reaction showing clearly the units. **2 marks**

Answer:

a) Order with respect to A.

Using experiment 1 and 2: Let the order with respect to A be X and with respect to B be Y.

$\dfrac{Rate\ 2}{Rate\ 1} = \left[\dfrac{A_2}{A_1}\right]^X \left[\dfrac{B_2}{B_1}\right]^Y \Rightarrow \dfrac{8.10^{-2}}{2.10^{-2}} = \left[\dfrac{1.0}{0.5}\right]^X \left[\dfrac{0.5}{0.5}\right]^Y \Rightarrow 4 = 2^X.1^Y$

$\Rightarrow 2^2 = 2^X \Rightarrow X = 2$

It is the second order with respect to A.

Order with respect to B:

Using experiment 2 and 3, let the order with respect to A be X and with respect to B be Y.

$\dfrac{Rate\ 3}{Rate\ 2} = \left[\dfrac{A_3}{A_2}\right]^X \left[\dfrac{B_3}{B_2}\right]^Y \Rightarrow \dfrac{16.10^{-2}}{8.10^{-2}} = \left[\dfrac{1.0}{1.0}\right]^2 \left[\dfrac{1.0}{0.5}\right]^Y \Rightarrow 2 = 1\ .\ 2^Y$

$\Rightarrow 2 = 2^Y$, y = 1

It is the first order with respect to B.

Overall order = 2+1 = 3

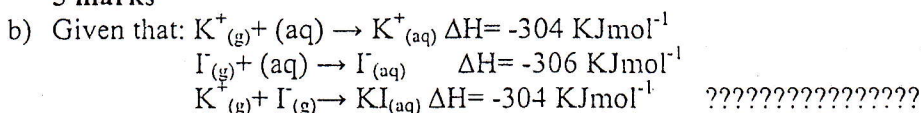b) Use the rate law: Consider experiment 1.

Rate = $K[A]^2[B]$

$$K = \frac{Rate\ 1}{[A]^2[B]} = \frac{2 \times 10^{-2}\ mol\ dm^{-3}}{[0.5\ mol dm^{-3}]^2[0.5 mol dm^{-3}]} = 0.16\ mol^2 dm^6 s^{-1}$$

SECTION B: Choose THREE questions from this section.

14. Study the table below and answer the questions that follow.

Enthalpy change	KJmol^{-1}
Atomisation of Potassium	+90
Atomisation of Iodine	+107
1stIonization energy of Potassium	+420
1stElectron affinity of Iodine	-314
Formation of Potassium Iodide	-328

a) Construct a Born Haber's cycle and calculate the lattice energy of Potassium Iodide. **5 marks**

b) Given that: $K^+_{(g)} + (aq) \rightarrow K^+_{(aq)}$ ΔH= -304 KJmol^{-1}

   $I^-_{(g)} + (aq) \rightarrow I^-_{(aq)}$ ΔH= -306 KJmol^{-1}

   $K^+_{(g)} + I^-_{(g)} \rightarrow KI_{(aq)}$ ΔH= -304 KJmol^{-1} ???????????????

   i) Calculate the enthalpy of solution of Potassium Iodide. **3 marks**

   ii) How would you confirm presence of Iodine ions in aqueous solution? **2 marks**

Answer:

a)

$\Delta H_{formation} = \Delta H_{atom}(K) + 1^{st}I.E(K) + \Delta H_{atom}(I) + 1^{st}E.A(I_2) + \Delta H_{lattice}$

$-328 = 90 + 420 + 107 - 314 + lattice\ energy$

Lattice energy = -328 -303 = -631 kJmol^{-1}

b) Draw a born haber cycle.

i) $\Delta H_{solution}$ = lattice energy + hydration energy

$$K = \frac{Rate\ 1}{[A]^2[B]} = \frac{2 \times 10^{-2}\ mol\ dm^{-3}}{[0.5\ moldm^{-3}]^2[0.5moldm^{-3}]} = 0.16\ mol^2dm^6s^{-1}$$

SECTION B: Choose THREE questions from this section.

14. Study the table below and answer the questions that follow.

Enthalpy change	KJmol^{-1}
Atomisation of Potassium	+90
Atomisation of Iodine	+107
1stIonization energy of Potassium	+420
1stElectron affinity of Iodine	-314
Formation of Potassium Iodide	-328

a) Construct a Born Haber's cycle and calculate the lattice energy of Potassium Iodide. **5 marks**

b) Given that: $K^+_{(g)} + (aq) \rightarrow K^+_{(aq)}$ ΔH= -304 KJmol^{-1}

$I^-_{(g)} + (aq) \rightarrow I^-_{(aq)}$ ΔH= -306 KJmol^{-1}

$K^+_{(g)} + I^-_{(g)} \rightarrow KI_{(aq)}$ ΔH= -304 KJmol^{-1} ??????????????????

i) Calculate the enthalpy of solution of Potassium Iodide. **3 marks**

ii) How would you confirm presence of Iodine ions in aqueous solution? **2 marks**
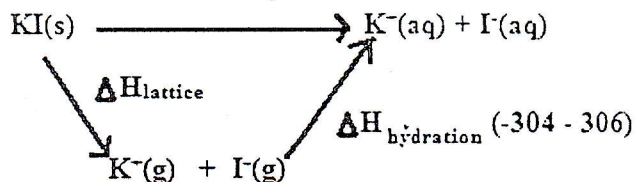
Answer:

a)

$\Delta H_{formation} = \Delta H_{atom}(K) + 1^{st}I.E(K) + \Delta H_{atom}(I) + 1^{st}E.A(I_2) + \Delta H_{lattice}$

-328 = 90 + 420 + 107 – 314 + lattice energy

Lattice energy = -328 -303 = -631 kJmol^{-1}

b) Draw a born haber cycle.

i) $\Delta H_{solution}$ = lattice energy + hydration energy

$$= -631 - (304 + 306) = -1241 kJ/mol$$
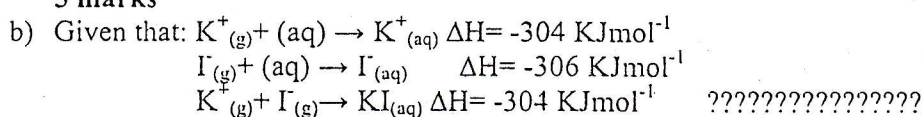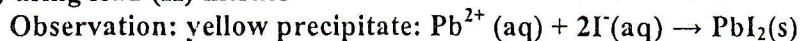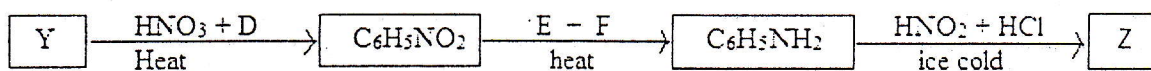
ii) using lead (II) nitrate

Observation: yellow precipitate: Pb^{2+} (aq) + $2I^-$(aq) $\rightarrow PbI_2$(s)

Or using silver nitrate solution.

15. The flow chart below shows a synthetic route for the preparation of compound Z starting with compound Y.

$$\boxed{Y} \xrightarrow[\text{Heat}]{HNO_3 + D} \boxed{C_6H_5NO_2} \xrightarrow[\text{heat}]{E - F} \boxed{C_6H_5NH_2} \xrightarrow[\text{ice cold}]{HNO_2 + HCl} \boxed{Z}$$

a) Name compounds Y, D, E, F and Z. **5 marks**

b) Show the reaction mechanism in the formation of compound $C_6H_5NO_2$ from compound Y. **3 marks**

Answer:

a) Y is benzene

D is conc. H_2SO_4 (concentrated sulphuric acid)

E is Sn (Tin)

F is Conc. Hydrochloric acid

Z is diazonium benzene salt.

b)

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

c) $C_6H_5NO_2$ contains the nitro-group which is an electron withdrawing group that reduces the availability of pi electrons in the benzene ring while it is absent in Y.

$$= -631 - (304 + 306) = -1241 kJ/mol$$

ii) using lead (II) nitrate

Observation: yellow precipitate: Pb^{2+} (aq) + $2I^-$(aq) $\rightarrow$ PbI_2(s)

Or using silver nitrate solution.

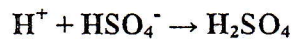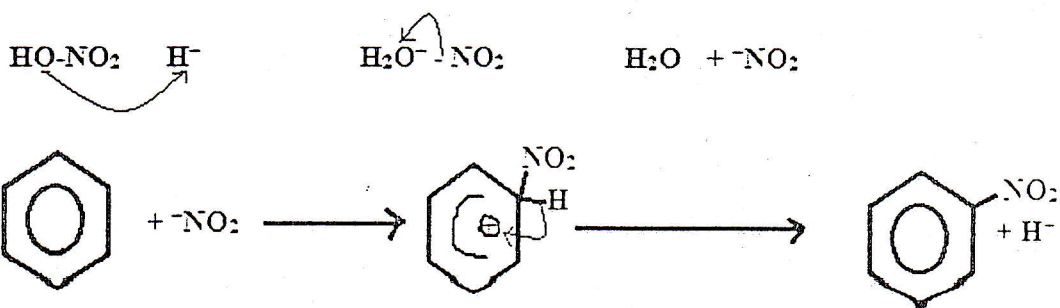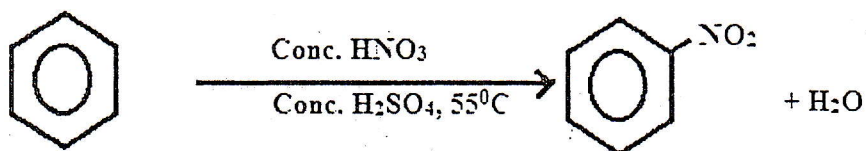15. The flow chart below shows a synthetic route for the preparation of compound Z starting with compound Y.

a) Name compounds Y, D, E, F and Z. **5 marks**

b) Show the reaction mechanism in the formation of compound $C_6H_5NO_2$ from compound Y. **3 marks**
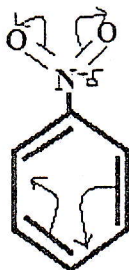
Answer:

a) Y is benzene

D is conc. H_2SO_4 (concentrated sulphuric acid)

E is Sn (Tin)

F is Conc. Hydrochloric acid
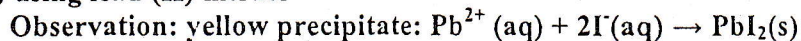
Z is diazonium benzene salt.

b)

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$
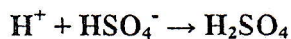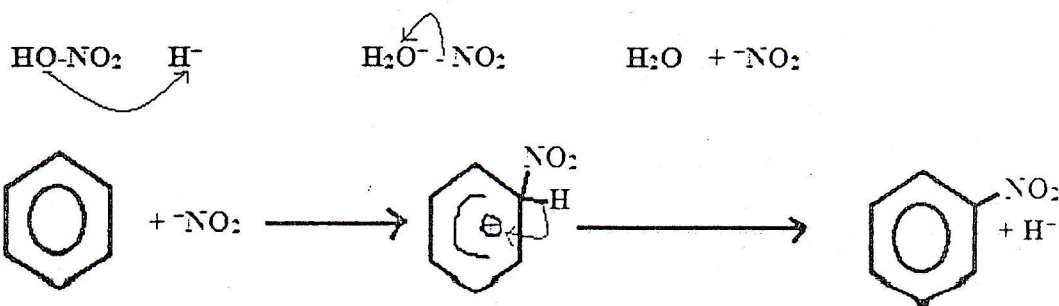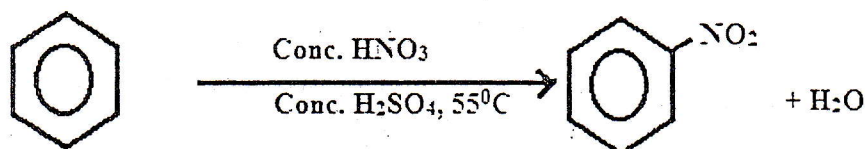
c) $C_6H_5NO_2$ contains the nitro-group which is an electron withdrawing group that reduces the availability of pi electrons in the benzene ring while it is absent in Y.
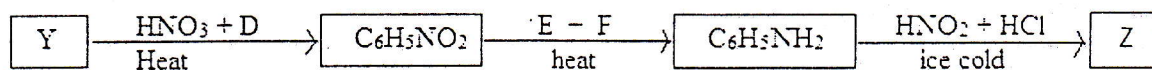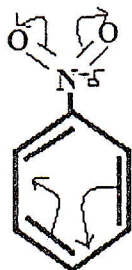
2.6 moles of N_2 and H_2 produced $\frac{2 \times 2.6}{4} = 1.3$ moles

$[N_2] = \frac{0.6\ mol}{2\ dm^3} = 0.3$ M

$[N_2] = \frac{2.0\ mol}{2\ dm^3} = 1$ M

$[N_2] = \frac{1.3mol}{2\ dm^3} = 0.65$ M

ii) $Kc = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.65^2}{0.3 \times 1^3} = 1.4\ mol^{-2}\ dm^{-6}$

iii) $Kp = \frac{P^2 NH_3}{P^2 N_2 x P^3 H_2}$

Partial pressure = molar fraction x total pressure

$= X \times Pt$, but $X = \frac{number\ of\ moles}{total\ number\ of\ moles}$, total number of moles =

$1.3 + 0.6 + 2.0 = 3.9$

$P_{NH_3} = \frac{1.3 \times 200\ kpa}{3.9} = 66.7$ kpa

$P_{N_2} = \frac{0.6 \times 200\ kpa}{3.9} = 30.8$ kpa

$P_{H_2} = \frac{2.0 \times 200\ kpa}{3.9} = 102.6$ kpa

$Kc = \frac{(66.7)^2}{(30.8)(102.6)^3} = 1.34 \times 10^{-4}\ kpa^{-2}$

18. Use the data below to answer the questions that follow.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftarrows 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\theta = +1.33V$

$Fe^{3-}(aq) + e^- \rightleftarrows Fe^{2-}(aq)$ $E^\theta = +0.77V$

$MnO_4^{2-}(aq) + 8H^+(aq) + 5e^- \rightleftarrows Mn^{2+}(aq) + 4H_2O(l)$ $E^\theta = +1.52V$

$FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightleftarrows Fe^{3+}(aq) + 4H_2O(l)$ $E^\theta = +2.2V$

$VO_3^-(aq) + 4H^+(aq) + e^- \rightleftarrows VO^{2-}(aq) + 2H_2O(l)$ $E^\theta = +1.0V$
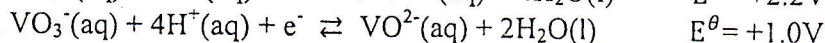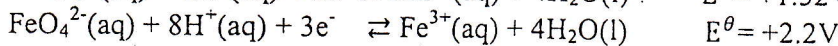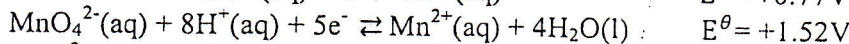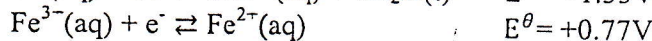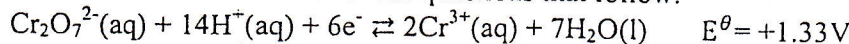
a) Which transition metal species (ions) above is the most powerful oxidizing agent and which is the most powerful reducing agent? **2 marks**

b) Identify one metal species that can reduce acidified dichromate ions. **1 mark**

c) Write an overall equation to show the reaction between acidified dichromate ions and the identified species in 18(b). **2 marks**

d) Workout the oxidation state of Cr in $Cr_2O_7^{2-}$, and of V in VO_3^-. **2 marks**

e) Suggest why acidified FeO_4^{2-} will oxidise Fe^{2+} and write the overall equation. **3 marks**

Answer:

a) Most powerful oxidizing agent FeO_4^{2-} because of highest electrode potential. Most powerful reducing agent is Fe^{2+} because of lowest electrode potential.

b) Fe^{2+} or VO^{2+}

c) $(Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O)x\ 1$

$\underline{(Fe^{2+} \rightarrow Fe^{3+} + e^-)\ x\ 6}$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$\underline{6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-}$

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

d) Let the oxidation state of Cr in $Cr_2O_7^{2-}$ be X

$2X + 7.(-2) = -2$

$2X = 12$

$X = +6$

Let the oxidation state of Mn in MnO_4^- be X

$X + 3.(-2) = -1$

$X = +5$

e) FeO_4^{2-} is a strong oxidizing agent and can oxidise Fe^{2+}

$(FeO_4^{2-} + 8H^+ + 3e^- \rightarrow 2Fe^{3+} + 4H_2O) \times 1$

$(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 3$

$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$ 2.2 V

$3Fe^{2+} \rightarrow 3Fe^{3+} + 3e^-$ -0.7V
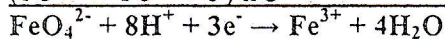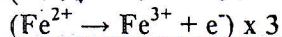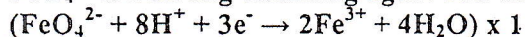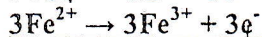
$FeO_4^{2-}(aq) + 8H^+(aq) + 3Fe^{2+}(aq) \rightarrow 4Fe^{3+}(aq) + 4H_2O(l)$ +1.43V
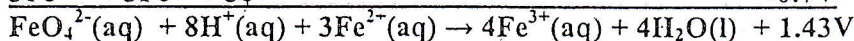
It also gives a positive electrode potential

SECTION C: Answer ONE question from this section.

19. For each of the following pairs of compounds identify the chemical test that can be used to distinguish them stating clearly the observations and writing relevant equations where possible.

               O
               ‖

a) $CH_3CH_2-C-CH_2CH_3$ and $CH_3CH_2CH_2CH_2CHO$

b) $C_6H_5CH_2OH$ and C_6H_5OH

c) $CH_3CH=CH_2$ and $CH_3CH_2CH_3$
d) $Al(NO_3)_3$ and $Cu(NO_3)_2$
e) $FeCl_2$ and $FeCl_3$
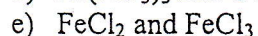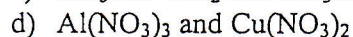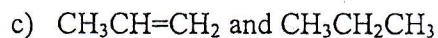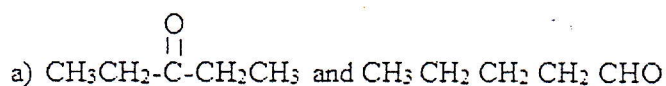
Answer:

     a) Reagent: Ammoniacal silver nitrate solution (Tollen's reagent)

        Condition: Boil

        Observations:

               O
               ‖

        $CH_3CH_2-C-CH_2CH_3$: No observable change
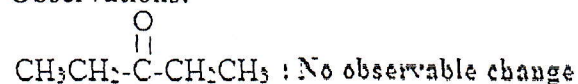
        $CH_3CH_2CH_2CH_2CHO$: silver mirror at the sides of the test tube.

        Equations:

        $CH_3CH_2CH_2CH_2CHO \xrightarrow[\text{Heat}]{AgNO_3/NH_3} CH_3CH_2CH_2CH_2COOH + Ag(s)$
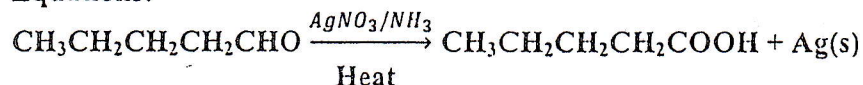
        Or using Fehling's solution.

     b) Reagent: Using bromine water

        Observations:

        C_6H_5OH – White precipitate (immediate decolourisation)

        $C_6H_5CH_2OH$ – No observable change

        Equations:

        $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$
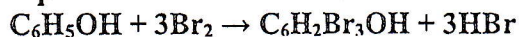
Or acidified potassium permanganate or potassium dichromate or iron (III) chloride.

c) Reagent: Bromine solution (Br_2/CCl_4)

Observations:

$CH_3CH=CH_2$: - Bromine solution changes from brown to colourless.

$CH_3CH_2CH_3$: No observable change.

Equations:

$$CH_3CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CHBr\text{-}CH_2Br$$
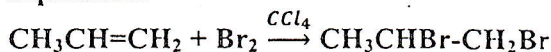
Or Using acidified potassium permanganate.

d) Reagent: Sodium hydroxide solution

Observations:

$Cu(NO_3)_2$: a pale blue precipitate insoluble in excess.

$Al(NO_3)_3$: No observable change.

Equations:

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$
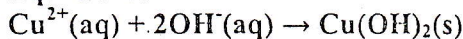
Or using ammonia solution.

e) Reagent: Sodium hydroxide

Observations:

$FeCl_2$: - a dirty green precipitate insoluble in excess

$FeCl_3$: a red-brown precipitate insoluble in excess

Equations:

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$
$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$
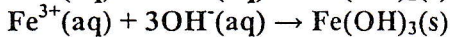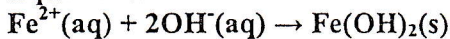
20. 0.9875 g of an impure Potassium manganate (VII) was dissolved in 250 cm^3 of water solution. 20 cm^3 of this solution was acidified with dilute sulphuric acid and titrated against sodium ethanedioate (oxalate) solution $Na_2C_2O_4$ and the volume of $Na_2C_2O_4$ required was 24.4 cm^3. Given that 1.675g fo $Na_2C_2O_4$ had been dissolved in 250 cm^3 of aqueous solution.

a) Calculate the percentage purity of potassium permanganate (manganate(VII)). 8 marks

b) Given only the solutions of $KMnO_4$, of $Na_2C_2O_4$ and of H_2SO_4 mentioned in this question, a stop watch, Na_2CO_3 solution, conical flasks, a burette and a pipette. how would you determine the order of reaction between $KMnO_4$ and $Na_2C_2O_4$? 7 marks

Answer:

a) Number of moles of $Na_2C_2O_4 = \frac{Mass}{Rmm}$, Rmm of $Na_2C_2O_4$: 23x2 + 12x2 +3x16 = 134

$$= \frac{1.675}{134} = 0.0125 \text{ moles} / 250 \text{ cm}^3$$

250 cm^3 of solution contains 0.0125 moles

24.4 cm^3 of solution contains $\frac{0.0125 \times 24.4}{250} = 0.00122$ moles of $Na_2C_2O_4$

$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$ x 2

$\underline{(C_2O_4^{2-} \rightarrow CO_2 + 2e^-) \text{ x 5}}$

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

$\underline{5C_2O_4^{2-} \rightarrow 5CO_2 + 10e^-}$

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$
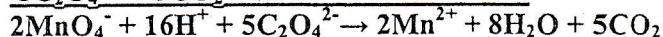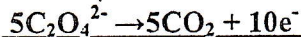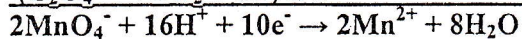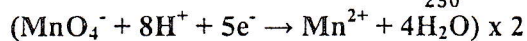
Moles of MnO_4^- that reacted $= 0.00122 \times \frac{2}{5} = 0.000488$ mol of $KMnO_4$

20 cm^3 of MnO_4^- contains 0.000488 moles

250 cm^3 of solution $\rightarrow \dfrac{0.000488 \times 250}{20} = 0.0061/250cm^3$

Actual mass of $KMnO_4$ = moles x Rmm = 0.0061 x 158 = 0.9638g

% purity $= \dfrac{actual\ mass \times 100}{sample\ mass} = \dfrac{0.9638 \times 100}{0.9875} = 97.6\%$

b) For this experiment we monitor the rate of disappearance of the purple color of potassium permanganate.

Rate $= \dfrac{KMnO_4}{t}$

You carry three experiments:

- The first trial test is for setting the standard conditions.
- A known concentration of sodium oxalate is put in the burette and potassium permanganate is acidified with sulphuric acid and then pipetted in the conical flask.
- A titration is done and the time taken for the purple colour of permanganate to disappear is recorded using a stop watch.
- Using the above, the rate of reaction is calculated and recorded in the table.
- The above experiment is repeated twice then by altering the concentrations of potassium permanganate and sodium oxalate.

Table of results:

Experiment	$[KMnO_4]M$	$[Na_2C_2O_4]M$	Rate/M minute^{-1}
1	A	A	X
2	A	B	Y
3	B	A	Z

Using the above data the orders of reactions are calculated.

21. Sodium hydroxide solution was added to 25cm^3 of 0.1M ethanoic acid and the P^H of the solution was measured at intervals of time. The results are tabled below.

Volume of NaOH (cm^3)	0	4	8	12	16	20	22	22.5	24	24	28
P^H of the mixture	2.8	3.5	4.0	4.0	5.1	5.8	7.0	9.0	10.5	11.4	12.3

a) Plot a graph P^H (y axis) against volume of NaOH. 7.5 marks

b) Explain the shape of the graph. 3.5 marks

c) Using the graph, determine the volume of NaOH required to neutralise the acid and hence calculate the molarity of NaOH. 3 marks

Answer:

a)
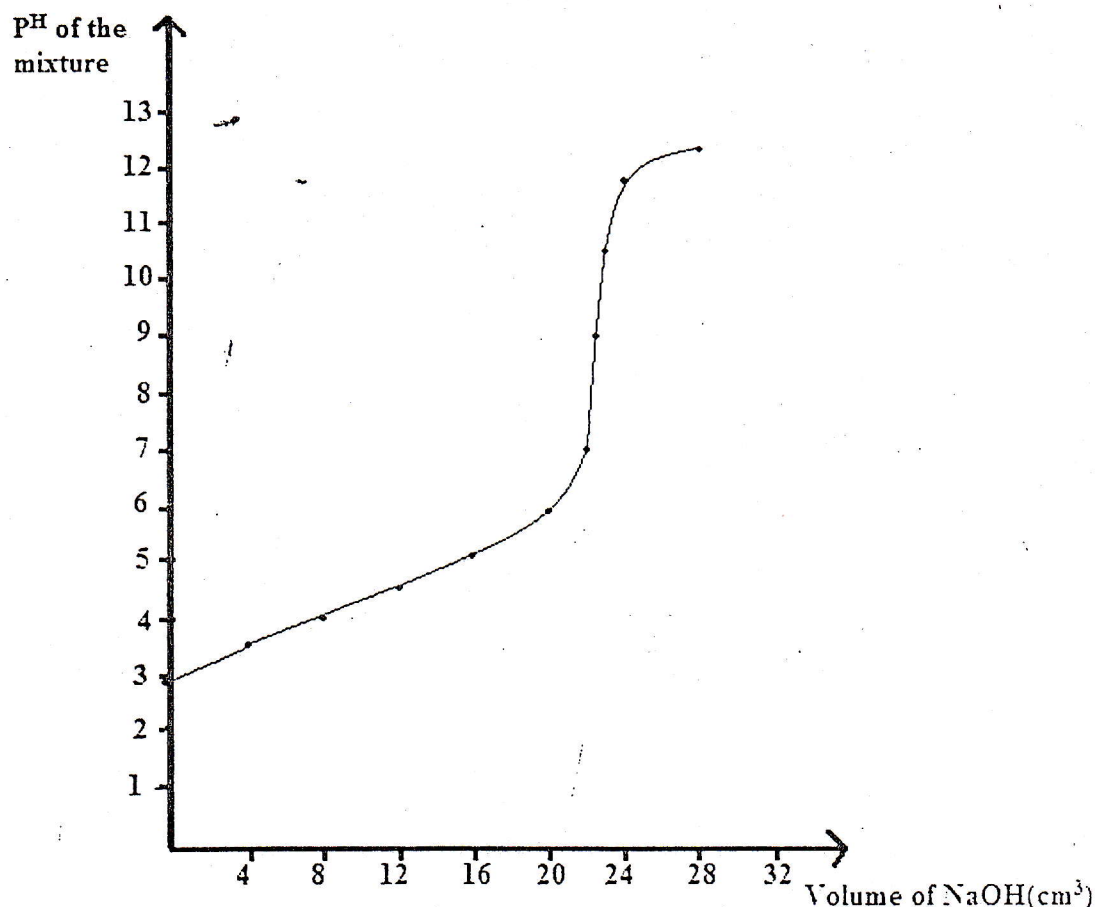
b) Initially P^H of the acid is a bit high because is a weak acid and thus not fully ionized in solution. The P^H gradually rises as the base is added because the acid is still in excess which together with the salt formed constitute a buffer that resists change in P^H.

- At the end point, a very small amount of sodium hydroxide added gives a sharp rise in P^H.

- The P^H at the end point is greater than 7 because the salt formed undergoes hydrolysis producing hydroxyl ions that make the solution more alkaline.

- Beyond the end point, the P^H rises gradually due to excess sodium hydroxide added.

c) Morality of sodium hydroxide solution:

Volume of sodium hydroxide used at end point: 22.50 cm^3

Moles of CH_3COOH that reacted $= \dfrac{25.0 \times 0.1}{1000} = 0.0025$ moles

$CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$

22.5 cm^3 of NaOH contains 0.0025 moles

1000 cm^3 of NaOH contains $= \dfrac{0.0025 \times 1000}{22.5} = 0.11$

Molarity of NaOH = 0.11M

ADVENCED LEVEL CHEMISTRY NATIONAL EXAMINATION PAPER 2005

(Biology-Chemistry)

SECTION A: Answer ALL questions /55 marks

01. The percentage abundances of the stable isotopes of chromium are:

$^{50}_{24}Cr$: 4.31%, $^{52}_{24}Cr$: 83.76%, $^{53}_{24}Cr$: 9.55%, $^{54}_{24}Cr$: 2.38%

a) What is meant by the term "isotopes" and why do isotopes of chromium show similar chemical properties? **2 marks**

b) Calculate the relative atomic mass of chromium, correct to three significant figures. **1 mark**

c) Calculate the number of neutrons in the most abundant isotope of chromium. **1 mark**

Answer:

a) Isotopes are atoms of the same element having the same atomic number but different mass number.

Isotopes of chromium show similar chemical properties because they have the same atomic number.

b) $R.A.M = \sum \frac{abundance \times isotopic\ mass}{100} = \frac{50 \times 4.31 + 52 \times 83.76 + 53 \times 9.55 + 54 \times 2.38}{100} = 52.06$

c) Number of electrons = mass number − atomic number = 52-24 = 28

02. This question concerns the following oxides

Na_2O, MgO, SiO_2, SO_3

From the list above identify the oxide that best fits the description given:

a) An oxide that is insoluble in water. **1 mark**

b) An oxide that has simple molecular structure at room temperature and pressure. **1 mark**

c) An oxide that reacts with water forming a strongly alkaline solution. **1 mark**

d) An oxide that is slightly soluble in water forming a weakly alkaline solution. **1 mark**

Answer:

a) SiO_2

b) SO_3

c) Na_2O

d) MgO

03. A possible synthetic route from benzene to benzoic acid is shown below:
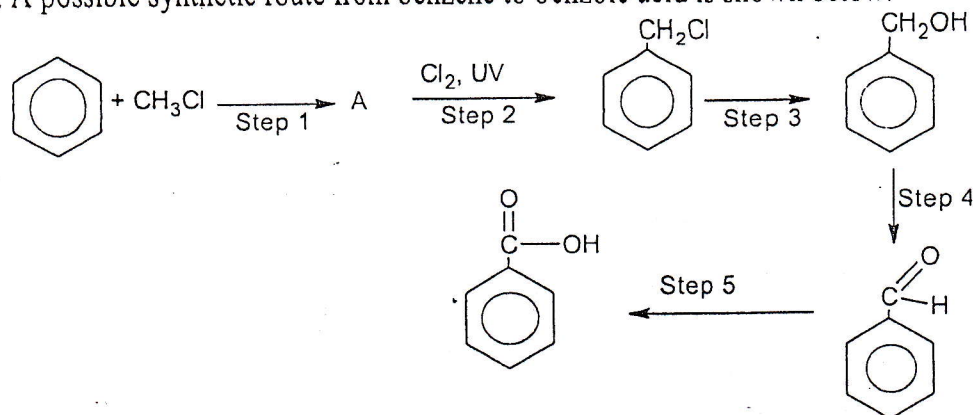
a) Give the formulae of a suitable catalyst for step 1 and give the structural formula of

compound A. **2 marks**

b) ·Give the name of the reagent used and the type of reaction in step 3. **2 marks**

c) Name the reagent used in step 4 **1 mark**

Answer:

a) Catalyst $AlCl_3$ or $FeCl_3$

CH3
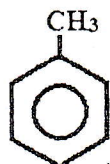
b) Sodium hydroxide or potassium hydroxide

Nucleophilic substitution reaction or SN_1

c) Acidified potassium dichromate or Acidified potassium permanganate

04. Use the bond enthalpies/bond energies in the table below to answer the questions that follow:

Bond	Average bond enthalpy KJ/mol^{-1}
F-F	158
C-H	412
Cl-Cl	242
H-Cl	432
C-Cl	338

a) Calculate the enthalpy change for the reaction:

$C_3H_8 + Cl_2 \rightarrow C_3H_7Cl + HCl$ **2 marks**
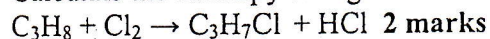
b) By considering the bonds broken and the bonds formed, calculate the average value for the S - F bond energy in the reaction:

$SF_4(g) + F_2(g) \rightarrow SF_6(g) \Delta H = -438$ KJmol^{-1}
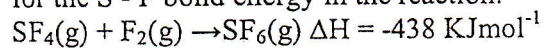
State any assumption you have made. **3 marks**

Answer:

a) $\Delta H_r = \sum \Delta H_{reactants} - \sum \Delta H_{products}$ or

$\Delta H_r = \sum \Delta H_{bond\ broken} - \sum \Delta H_{bond\ created}$

Where ΔH_r the enthalpy change for reaction and ΔH is the enthalpy change.

$$\sum \Delta H_{reactants} = \underset{H\ H\ H}{\overset{H\ H\ H}{H\text{-}C\text{-}C\text{-}C\text{-}H}} + Cl\text{-}Cl$$

$= 8(C\text{-}H) + 2(C\text{-}C) + (Cl\text{-}Cl)$

$= 8 \times 412 + 242 + 2(C\text{-}C)$

$= 3538 + 2(C\text{-}C)$

$$\sum \Delta H_{products} = \underset{H\ H\ H}{\overset{H\ H\ H}{H\text{-}C\text{-}C\text{-}C\text{-}Cl}} + H\text{-}Cl$$

$= 7(C\text{-}H) + 2(C\text{-}C) + (C\text{-}Cl) + HCl$

$= 7 \times 412 + 2(C\text{-}C) + 338 + 432$

$= 3654 + 2(C\text{-}C)$

Hence $\Delta H_r^\theta = (3538 + 2C\text{-}C) - (3654 + 2C\text{-}C) = -116$ kJ/mol

b) $\Delta H_f = \sum \Delta H_{reactants} - \sum \Delta H_{products}$

$= 4(S\text{-}F) + 158 - 6(S\text{-}F)$

$-438 = 4(S\text{-}F) + 158 - 6(S\text{-}F)$

$-438 - 158 = -2(S\text{-}F)$

S-F = +298kJ/mol

Assumption: The C-C bond is broken.

05. a) i) Explain what is meant by the standard enthalpy change of formation of a compound.
1 mark

   ii) Write a balanced equation which represents the standard enthalpy change of formation of propane. **1 mark**

   b) Calculate the standard enthalpy change of formation of propane from the standard enthalpy changes of combustion given below:

	$\Delta H_C^\theta /KJmol^{-1}$
Carbon	-393
Hydrogen	-286
Propane	- 2220

3 marks

Answer:

a) i) The standard enthalpy change of formation is the enthalpy change that occurs when one mole of a compound is formed from its constituents under standard conditions.

   ii) $3C(s) + 4H_2(g) \rightarrow$ not $C_3H_8(g)$ ΔH_f^θ

b) $C + O_2 \rightarrow CO_2$ -393 x 3
   $H_2 + 1/2 O_2 \rightarrow H_2O$ -286 x4
   $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ -2220x-1

   $3C + 3O_2 \rightarrow 3CO_2$ -393 x 3
   $4H_2 + 2O_2 \rightarrow 4H_2O$ -286 x4
   $\underline{3CO_2 + 4H_2O \rightarrow C_3H_8 + 5O_2}$ $\underline{2220}$
   $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ -103 kJ/mol

   Or

   $3C + 3\cancel{O_2} \longrightarrow 3\cancel{CO_2}$ - 393 x 3

   $4H_2 + 2\cancel{O_2} \longrightarrow 4\cancel{H_2O}$ - 286 x 4

   $\underline{3\cancel{CO_2} + 4\cancel{H_2O} \longrightarrow C_3H_8 + 5\cancel{O_2}}$ $\underline{2220}$

   $3C(s) + 4H_2(g) \longrightarrow C_3H_{8(g)}$ - 103 kJmol-1
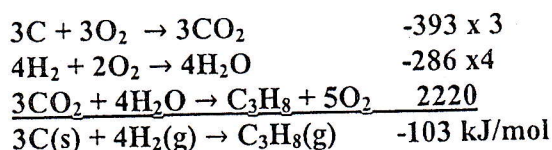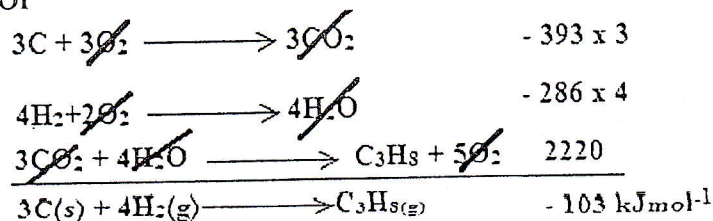
   ΔH_f^θ = -103 kJ/mol

06. This question concerns some reactions of a compound X which has the structure:
   $CH_3-CH_2-CH_2-CH_2OH$
   a) Give the systematic name of compound X. **1 mark**
   b) Is X a primary, secondary or tertiary alcohol? **1 mark**
   c) What name is given to the intermolecular forces in compound X? **1 mark**
   d) Give the structural formulae for two organic compounds which could be obtained by reacting X with a hot mixture of potassium dichromate and sulphuric acid. **2 marks**
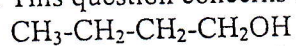
   Answer:
   a) **Butan-1-ol or 1-butanol**
   b) **X is a primary alcohol**

c) Hydrogen bonds and Van Der Waals forces

d) $CH_3-CH_2-CH_2-C$ and $CH_3-CH_2-CH_2-C$
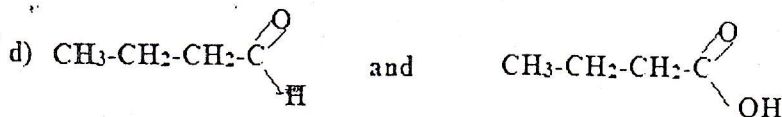
07. Boron, nitrogen and oxygen form fluorides with molecular formulae BF_3, NF_3 and OF_2.
   a) Draw the shape of each molecule and show the position of lone pairs of electrons if any. **3 marks**
   b) Give the bond angle in each case, explaining your reasons. **3 marks**

   Answer:

   a)
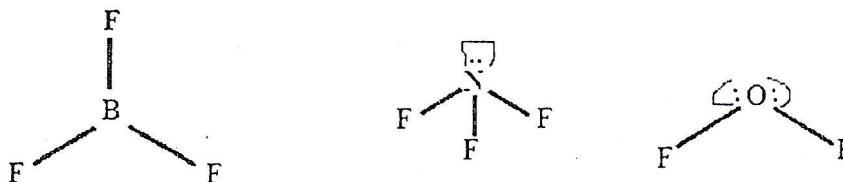
   b) BF_3 – has bond angle of 120^0 because it has three bond pairs and no lone pair of electrons.
   NH_3- has a bond angle of about 107^0 because it has three bond pairs with one lone pair of electrons.
   OF_2 – has bond angle of about 104.5^0 (102 actual) because it has two bond pairs and two lone pairs of electrons.

08. a) Write down the electronic configuration of a calcium atom and of a calcium ion in terms of s.p.... .. orbitals. (The atomic number of calcium = 20) **2 marks**
   b) Why is the atomic radius of calcium significantly greater than the ionic radius of the calcium ion. **1 mark**
   c) Explain why the hydration energy (enthalpy change of hydration) of Mg^{2-} is more exothermic than that of Ca^{2+}?

   Answer:
   a) $Ca = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
      $Ca^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6$
   b) Calcium ion has lost two electrons which reduces the shielding effect and increases the effective nuclear charge on the outermost shell electrons, hence reduced in ionic radius.
   c) Both Mg^{2+} and Ca^{2+} have the same charge but Mg^{2+} has a smaller ionic radius which causes a higher charge density (polarizing power).
      Therefore Mg^{2+} will have a greater attraction for water molecules (higher hydration energy) than Ca^{2+}.

09. Over one million tons of manganese are produced in the world each year.
   a) Write the electronic configuration of manganese (atomic number = 25) and use it to explain why manganese is a transition element. **2 marks**
   b) State, with specific examples, two properties of manganese or its compounds which are typical of transition elements. **2 marks**
   c) Calculate the oxidation number of manganese in the ion MnO_4^-. **1 mark**

   Answer:

a) Mn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

Or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Mn is a transition metal element because it has partially filled 3d-orbitals.

b) - Mn has variable oxidation states. i.e: +2, +4, +6, +7

- Mn shows different colours in its compounds.

E.g: Mn^{2+} solutions are pink and MnO_4^- solutions are purple.

-Mn is capable of complex ion formation. E.g: MnO_4^-, MnO_4^{2-}, $[Mn(H_2O)_6]^{2+}$

c) Let oxidation state of Mn be X;

$X + 4.(-2) = -2$

$X = +6$

10. Explain the following: !

a) The boiling point of water (H_2O) is higher than that of hydrogen sulphide (H_2S). 1 mark

b) The boiling points of ethane, water and sodium hydride increase in the order: $C_2H_6 <$ H_2O <NaH. 2 marks

Answer:

a) Oxygen is more electronegative than sulphur.

Water molecules are therefore held together by stronger hydrogen bonds which are broken at higher temperature while hydrogen sulphide molecules are held together by weak Van Der Waals forces which are broken at lower temperature.

b) The boiling points depend on bonding and structure.

Ethane has a simple molecular structure held together by weak Van Der Waals force hence the least boiling point.

Water consists of stronger hydrogen bonds hence higher boiling point than ethane. Sodium hydride has the highest boiling point because it forms a giant ionic structure held together by strong ionic bonds.

11. Consider the following equilibrium reactions:

Reaction I: $3Fe(s) + 4H_2O(l) \rightleftarrows Fe_3O_4(s) + 4H_2(g)$

Reaction II: $CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$
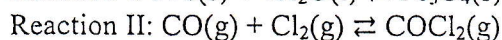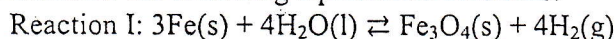
a) Write expressions for the equilibrium constant, Kp

i) for reaction I

ii) for reaction II 2 marks

b) State, giving reasons, how an increase in pressure affects the the position of equilibrium in each reaction above. 2 marks

Answer:

a) i) $Kp = \dfrac{P_{H_2}^4}{P_{H_2O}^4}$

ii) $Kp = \dfrac{P_{COCl_2}}{P_{CO} \times P_{Cl_2}}$

b) Reaction I: Increase in pressure will shift to the right where is few number of moles.

Reaction II: Increase in pressure has no effect on the equilibrium position since the number of moles of gases on the left hand side is equal to the number of moles on the left hand side.

12. A radioactive isotope X decays by emitting beta particles. It was found that only $\dfrac{1}{32}$ of the

original isotope remained after 100 days. Calculate the half-life of the radioactive isotope.
2 marks

Answer:

a) By simple method:

$$1 \xrightarrow{1t_{1/2}} \frac{1}{2} \xrightarrow{2t_{1/2}} \frac{1}{4} \xrightarrow{3t_{1/2}} \frac{1}{8} \xrightarrow{4t_{1/2}} \frac{1}{16} \xrightarrow{5t_{1/2}} \frac{1}{32}$$

$t_{1/2} = \frac{T}{n}$ where, n-number of half-lives and T-time

$$= \frac{100}{5} = 20 \text{ days}$$

Or from $Nt = \frac{No}{2^n} \Rightarrow \frac{Nt}{No} = \frac{1}{2^n} \Rightarrow \frac{1}{32} = \frac{1}{2^n} \Rightarrow 2^n = 32 \Rightarrow 2^n = 2^5 \Rightarrow n = 5$

$t_{1/2} = \frac{T}{n} = \frac{100}{5} = 20 \text{ days}$

13. An electric current was passed through two beakers containing aqueous silver nitrate and aqueous copper (II) sulphate connected in series. After 30 minutes 0.100g of silver was deposited in the first beaker
    a) Write an equation for the deposit of silver. 1 mark
    b) Calculate the current passed (Ag = 108, F = 96500 C mol^{-1}) 2 marks

Answer:

a) $2Ag^+(aq) + e^- \rightarrow 2Ag(s)$
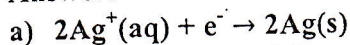
b) Using the general formula

$M = \frac{Mm \times 1 \times t}{n \times f}$, where M- mass, Mm- molar mass, I- Current(A), t-times(s), f-

Faraday constant

$I = \frac{M \times n \times f}{Mm \times t} = \frac{0.1 \times 2 \times 96\,500}{108 \times 30 \times 60} = 0.099A$ per two moles of Silver.

$= 0.0495A$ for one mole of Silver.

SECTION B: Choose THREE questions from this section /30 Marks.

14. Some foodstuffs contain "acidity regulators" which have a buffering action on the pH. Mixtures of citric acid and its sodium salt are often used for this purpose.

    $C_5H_7O_4COOH \rightleftharpoons C_5H_7O_4COO^- + H^+$

    Citric acid $Ka = 7.4 \times 10^{-4} moldm^{-3}$
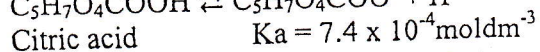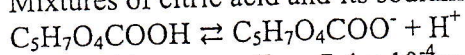
    a) The concentration of citric acid in lemon juice is 0.23 mol dm^{-3}. Assuming that no other acid is present, calculate the pH of lemon juice. 3 marks
    b) Write equations to show how citric acid and sodium citrate buffer system regulates the acidity on the addition of:
       i) H$^+$ ions
       ii) OH$^-$ ions   2 marks
    c) Calculate the pH of a solution containing 0.20 mol dm^{-3} citric acid and 0.3 mol dm^{-3} sodium citrate. 2 marks
    d) Define the term Kw and explain why, at 25°C, water has a pH of 7. 3 marks

Answer:

a) $P^H = -\log[H^+]$

$H^+ = \sqrt{ka \times Ca} = \sqrt{7.4 \times 10^{-4} \times 0.23} = \sqrt{1.72 \times 10^{-4}} = 1.305 \times 10^{-2} moldm^{-3}$

$P^H = -\log(1.305 \times 10^{-2}) = 1.88$

b) i) The addition of H$^+$ reacts with excess $C_5H_7COO^-$ to form C_5H_7COOH to

maintain the equilibrium hence the P^H remains constant.
Equation: $C_5H_7COO^- + H^+ \rightarrow C_5H_7O_4COOH$

ii) The addition of OH^- reacts with C_5H_7COOH to form $C_5H_7COO^-$ and water to maintain the equilibrium, hence the P^H remains constant.
Equation: $C_5H_7COOH + OH^- \rightarrow C_5H_7COO^- + H_2O$

c) $P^H = Pka + \log\frac{[salt]}{[acid]} = -\log(7.4 \times 10^{-4}) + \log\frac{0.3}{0.2} = 3.131 + 0.176 = 3.3$

d) Kw is the dissociation constant for water, $Kw = [H^+][OH^-]$
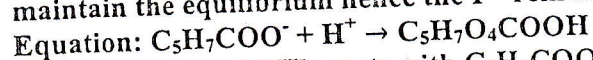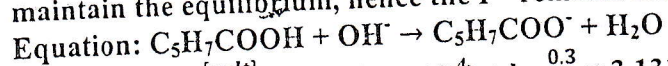Water has P^H of 7 because it is a neutral molecule.

15. a) Give the formulae of the three structural isomers of C_4H_8 which are non-cyclic. 3 marks

b) One of these isomers shows a type of stereoisomerism.
  i) Give the structures of the stereoisomers and name them. 2 marks
  ii) Give a chemical test for the functional group present in the isomers and describe the expected observation. 2 marks

c) One of the isomers of C_4H_8 in (a) reacts with HBr to give two different products, the major one of which is a chiral molecule.
  i) Identify this isomer of C_4H_8. 1 mark
  ii) Give the mechanism for the reaction of this isomer with HBr. 2 marks

Answer:

a)
$CH_3CH_2CH=CH_2$
$CH_3CH=CHCH_3$
$CH_3C=CH_2$
$\quad \; CH_3$
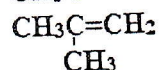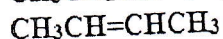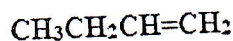
b) Using bromine water or bromine in an organic solution.
Observations: Bromine water is decolourised. i.e: changes from brown to colourless.

c) i) $CH_3CH_2CH=CH_2$

ii)

Mechanism (major product)
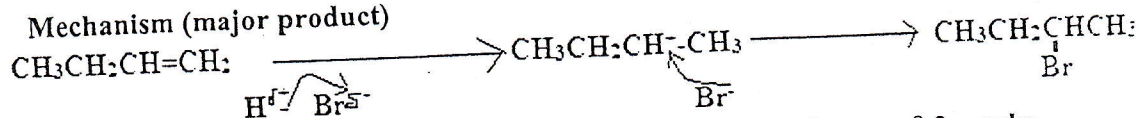
16. a) What reagents and conditions are used to prepare nitrobenzene from benzene? 2 marks
b) The reaction in (a) is described as electrophilic substitution. Describe the mechanism of this reaction, clearly indicating how the electrophile is formed and its role in all the steps. 2 marks
c) The local pain killer labelled as X below is synthesized from the aromatic compound 4 - nitromethylbenzene as shown in the following steps.
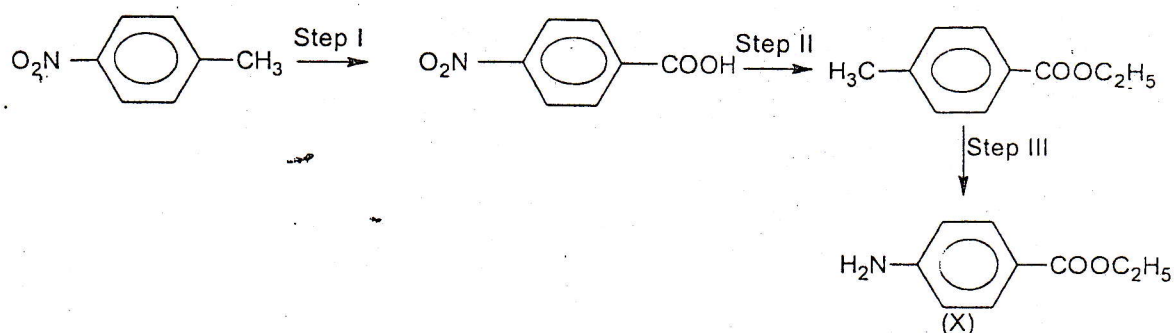
Suggest reagents and conditions for:

   Step I

   Step II

   Step III   6 marks

Answer:

a) Reagents: Conc. HNO_3

   Conditions: Conc. H_2SO_4 and 55^0C.

b)

Mechanism:

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$HO-NO_2 \quad H^- \longrightarrow H_2O^- - NO_2 \longrightarrow H_2O + ^-NO_2$

$H^+ + HSO_4^- \rightarrow H_2SO_4$
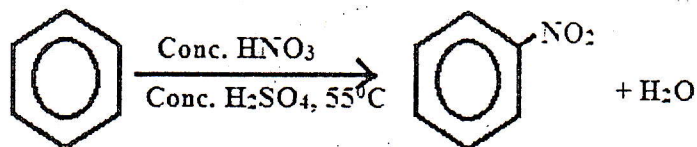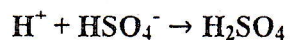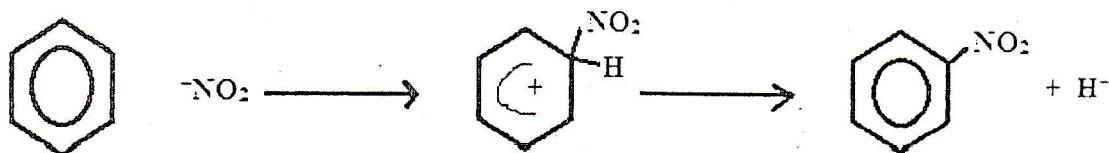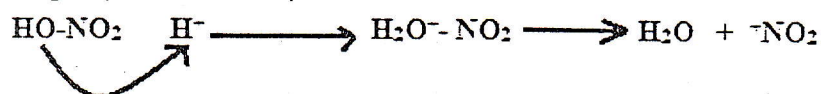
$^+NO_2$ = is the electrophile that substitutes H atom in benzene.

c)

Steps	Reagents	Conditions
Step I	$H^+/KMnO_4$ or $H^+/K_2Cr_2O_7$	Heat
Step II	CH_3CH_2OH	Heat/H^+
Step IIII	Sn/HCl	heat
	$LiAlH_4$	

17. The reversible reaction: $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$ is used in the Contact process for the manufacture of sulphuric acid, using V_2O_5 catalyst.

a) i) Calculate the enthalpy of reaction, ΔH, of the forward reaction, assuming it goes to completion. You are given the enthalpies of formation of SO_2 (g) and SO_3 (g) which are -297 and -395 KJ mol-1 respectively. **2 marks**
ii) State and explain the effect of raising the temperature on the position of equilibrium of this reaction. **2 marks**
iii) The optimum temperature used in this industrial process is 450°C. Basing your answers on economics and chemical principles, suggest two reasons which determine the choice of this operating temperature. **2 marks**
iv) What is the effect of the catalyst on the position of equilibrium in this reaction? **1 mark**

b) i) Write an expression for the equilibrium constant Kc for the reaction. **1 mark**
ii) What is the effect of increasing the concentration of oxygen (at the same temperature) on:
I : the equilibrium constant, Kc.
II : the position of equilibrium. **2 marks**

Answer:

a) **i) Enthalpy of reaction:**
$$\Delta H_f = \sum \Delta H_{reactants} - \sum \Delta H_{products} = \text{-395 x 2} - (\text{-297 x 2}) = \text{-196 kJ/mol}$$
ii) The effect of temperature depends on either exothermic or endothermic reaction. Increase of temperature for the exothermic reaction will shift the equilibrium position to the left. Increase of temperature for the endothermic reaction will shift the equilibrium position to the right.
iii) It is economical because it increases the rate of reaction.
iv) Catalyst has no effect on equilibrium position.

b) **i) $Kc = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$**
ii) I: increase in concentration of oxygen has no effect on the value of Kc.
II: Increase in concentration of oxygen shift the equilibrium position to the right so as to reduce its concentration on the left hand side, according to lechaterier's principle.

18. The following list gives standard electrode potentials for various half cells:

	E^θ/volts
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+ 0.54
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+ 0.80
$F_2(aq) + 2e^- \rightleftharpoons 2F^-(aq)$	+ 2.87
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.36
$Cu^{2-}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34

a) Draw a labeled diagram of a cell which can be used to measure the standard electrode potential of the. Cu^{2+}/Cu half-cell. **4 marks**
b) From the list above, identify the
i) Strongest reducing agent
ii) Strongest oxidizing agent **2 marks**
c) Calculate the standard cell e.m.f (E^θ cell) corresponding to the cell reaction:
$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)$ **1 mark**

d) When a constant current was passed through an aqueous solution of copper (II) nitrate for one hour the mass of the copper cathode increased by 15.24g. Calculate the current in amperes which was used. ($F = 96500C$ mol^{-1}, $Cu = 63.5$)

Answer:

a)
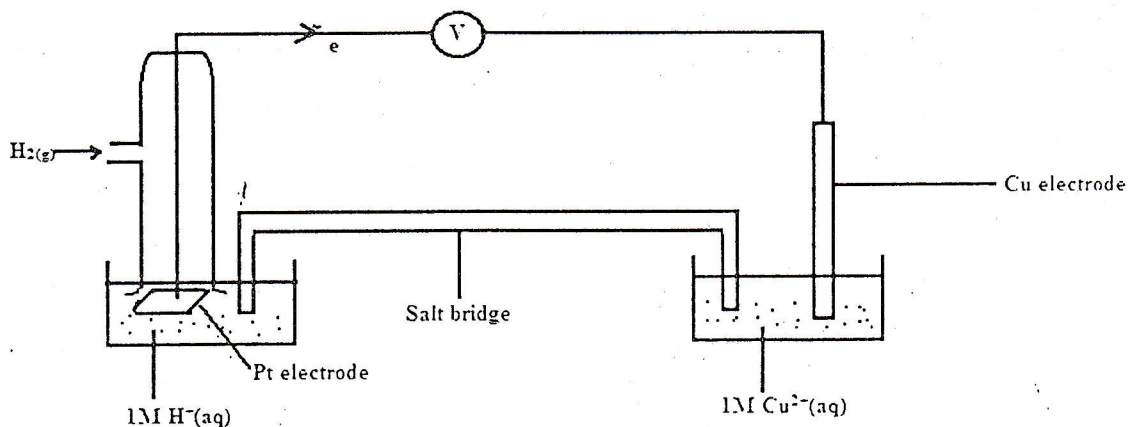
b) i) Strongest reducing agent is Mg.
   ii) Strongest oxidizing agent is F_2.

c) $Emf = E^{\theta}_{right} - E^{\theta}_{left} = 0.34 - 1.23 = -0.89V$

d) Using the general formula
$$M = \frac{M \times n \times f}{Mn \times t} = \frac{15.24 \times 2 \times 96\,500}{63.5 \times 3600} = 12.8 \text{ A}$$

SECTION C: Answer ONE question from this section /15 Marks.

19. For each of the following pairs of compounds identify the chemical test which can be used to distinguish between them. State clearly the expected observations and write relevant equations for the reactions involved.
    a) $CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2CH_2CHO$
    b) $CH_3CH_2CH_2CO_2H$ and $CH_3CH_2CH(OH)CH_3$

    c) $CH_3CH(OH)CH_3$ and $(CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH)$ $(CH_3)_3COH$

    d) $Zn(NO_3)_2$ and $Pb(NO_3)_2$
    e) Na_2SO_3 and Na_2SO_4 3 marks

Answer:

a) Reagent: Ammoniacal silver nitrate solution (Tollens reagent)
   Condition: Heat
   Observations:
   $CH_3CH_2CH_2CH_2OH$: No observable change.
   $CH_3CH_2CH_2CHO$: Silver mirror at the sides of the test tube.

By KAYIRANGA S....

Equations:

$$CH_3CH_2CH_2CHO \xrightarrow{AgNO_3/NH_3} CH_3CH_2CH_2COOH + Ag(s)$$
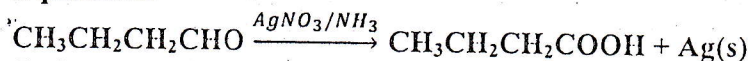
Or Using Fehlings solutions, brady's reagent, sodium hydrogen sulphite.

b) Reagent: Sodium carbonate

Observations:

$CH_3CH_2CH_2CO_2H$: bubbles of a colourless gas that turns lime water milky.

$CH_3CH_2CH(OH)CH_3$: no observable change.

Equations:

$$2CH_3CH_2CH_2CO_2H + Na_2CO_3 \rightarrow 2CH_3CH_2CH_2COO^-Na^+ + CO_2 + H_2O$$
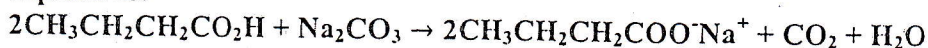
Or Using sodium hydrogen carbonate, acidified potassium permanganate or acidified potassium dichromate, Lucas reagent.

c) Reagent: A mixture of anhydrous Zinc (II) chloride and concentrated hydrochloric acid (Lucas reagent)

Observations:

$CH_3CH_2CH(OH)CH_3$: Cloudiness after 5 minutes at room temperature.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C-OH}}$$ - Immediate cloudiness at room temperature

Equations:

$$\underset{\underset{OH}{|}}{CH_3CH_2CHCH_3} + \text{Conc. HCl} \xrightarrow{ZnCl_{2(s)}} \underset{\underset{Cl}{|}}{CH_3CH_2CHCH_3} + H_2O$$

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C-OH}} + \text{Conc. HCl} \xrightarrow{ZnCl_2(s)} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-C-Cl}} + H_2O$$
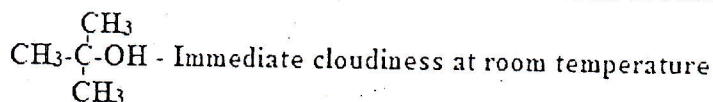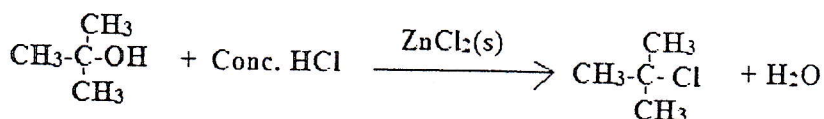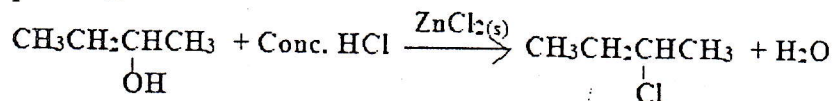
Or using acidified potassium permanganate or potassium dichromate.

d) Reagent: Potassium iodide solution

Observations:

$Pb(NO_3)_2$: Yellow precipitate

$Zn(NO_3)_2$: No observable change.

Equations:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$
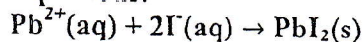
Or using ammonia solution

e) Reagent: Barium chloride and hydrochloric acid.

Observations:

Na_2SO_4: white precipitate insoluble in acid.

Na_2SO_3: white precipitate soluble in acid.

Equations:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons BaSO_4(s)$$

$$Ba^{2+}(aq) + SO_3^{2-}(aq) \rightleftharpoons BaSO_3(s)$$
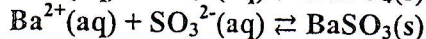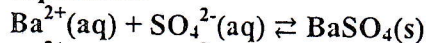
Or Barium nitrate and nitric acid.

20. A 25.0 cm^3 portion of a solution containing Fe^{2+} ions and Fe^{3+} ions was acidified and titrated against potassium manganate (VII) (potassium permanganate) solution. 15.0 cm^3 of a 0.0200 mol dm^{-3} (0.0200M) solution of potassium manganite (VII) were required. In

this titration only Fe^{2+} ions react with MnO_4^- ions in an acidic solution. A second $25.0 cm^3$ portion was reacted with zinc to reduce Fe^{3+} to Fe^{2+}. After the reduction, the sample of $25.0 \ cm^3$ portion was titrated against the same manganate (VII) solution. $19.0 \ cm^3$ of the manganate (VII) solution were required.

a) Explain why no indicator is required in this titration. **1 mark**
b) Use the half-equations below to write the overall redox equation for the reaction between Fe^{3+} and MnO_4^- in an acidic medium:
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$Fe^{3+} \rightarrow Fe^{2+} + e^- \qquad \textbf{2 marks}$$
c) Calculate the number of moles of MnO_4^- in $15.0 \ cm^3$ of $0.0200 \ mol \ dm^{-3}$ solution of $KMnO_4$. **1 mark**
d) Calculate the concentration in $mol \ dm^{-3}$ of Fe^{2+} in the original sample of the solution. **3 marks**
e) Calculate the number of moles of MnO_4^- in $19.0 \ cm^3$ (if $0.0200 \ mole \ dm^{-3}$ (0.0200M) $KMnO_4$. **1 mark**
f) Calculate the total concentration of Fe^{2+} in $mol \ dm^{-3}$ after the reduction of Fe^{3+} in the second portion of the solution. **3 marks**
g) Hence calculate the concentration of Fe^{3+} in the original sample of the solution in $mol \ dm^{-3}$. **1 mark**
h) Calculate the ratio of concentrations of Fe^{3+} : Fe^{2+} in the original sample. **2 marks**
i) The final ratio of concentrations of Fe^{3+} : Fe^{2+} is higher after several hours of exposure of the solution to the atmosphere. Suggest an explanation for this. **1 mark**

Answer:
a) **Because potassium permanganate acts as its own indicator.**
b) $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$ x1
$\underline{(Fe^{2+} \rightarrow Fe^{3+} + e^-)x5}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
$\underline{5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-}$
$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
c) **Moles of MnO_4^- in $15.0 cm^3 = \frac{0.0200 \ x \ 15}{1000} = 3 \ x \ 10^{-4} moles$**
d) **Moles of Fe^{2+} that reacted $= 3 x 10^{-4} x 5 = 0.0015$ moles**
Moles/dm^3 of $Fe^{2+} = \frac{0.0015 \ x \ 1000}{24} = 0.06 mol dm^{-3}$
e) **Moles of MnO_4^- in $19.0 cm^3 = \frac{0.0200 \ x \ 19}{1000} = 3.8 \ x \ 10^{-4} moles$**
f) **Moles of Fe^{2+} that reacted $= 3.8 \ x \ 10^{-4} \ x \ 5 = 0.0019$ moles**
Moles/dm^3 of $Fe^{2+} = \frac{0.0019 \ x \ 100}{25} = 0.76 \ mol/dm^3$
g) **Concentration of $Fe^{3+} = 0.076 - 0.06 = 0.016 \ mol dm^{-3}$**
h) $\frac{Fe^{2+}}{Fe^{3+}} = \frac{0.016}{0.06}$
$= \frac{4}{15}$
$Fe^{3+}:Fe^{2+} = 4:15$ or 1:3.75
i) **Fe^{2+} is unstable and is easily oxidized to Fe^{3+} in the presence of air.**

ADVENCED LEVEL CHEMISTRY NATIONAL EXAMINATION PAPER 2006

(Biology-Chemistry)

SECTION A: Answer ALL questions /55 marks

01. The atomic number of sulphur is 16
    a) In terms of s, p, d electrons, Write the electronic configuration of sulphur. **1 mark**
    b) In which block of the Periodic Table is sulphur located? **1 mark**
    c) Explain briefly why the first ionisation energy of sulphur is lower than that of phosphorus (atomic number 15) **2 marks**
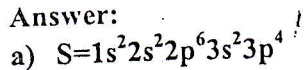
Answer:
a) $S = 1s^2 2s^2 2p^6 3s^2 3p^4$
b) P-block
c) This caused by different electronic structures of the two atoms
    $P = 15: 1s^2 2s^2 2p^6 3s^2 3p^3$
    $S = 1s^2 2s^2 2p^6 3s^2 3p^4$
    In sulphur, the outermost electron is removed form a partially filled 3p orbital which is less stable.
    While in phosphorus an electron is being removed from a half-filled 3p orbital which is more stable and will require high energy to remove, hence high first ionization energy.
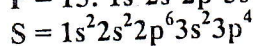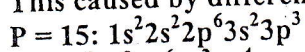
02. $^{238}_{92}U$ undergoes radioactive decay as shown below:

$$^{238}_{92}U \xrightarrow{\alpha\text{-}emission} A \xrightarrow{\beta\text{-}emission} \quad \xrightarrow{\beta\text{-}emission} X$$

$$X \xrightarrow{\alpha\text{-}emission} Y$$
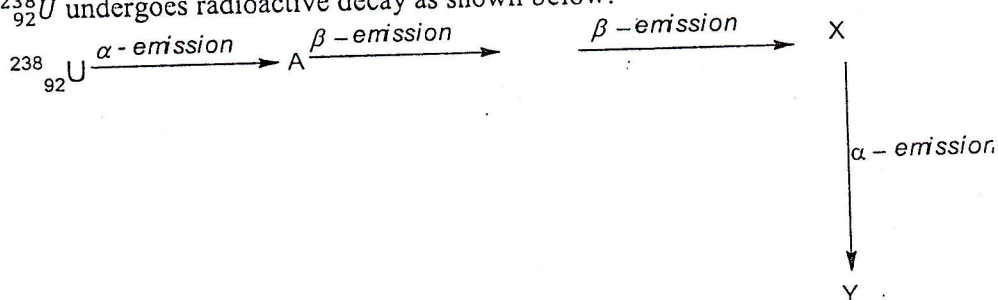
a) Calculate the mass number and atomic number of element Y. **2 marks**
b) State one medical use of radioactive isotopes. **1 mark**
c) A radioactive isotope has a half-life of 15 days. What fraction of the original amount of the isotope would remain after 75 days? **2 marks**
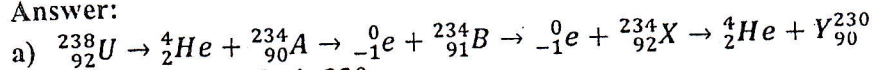
Answer:
a) $^{238}_{92}U \rightarrow {}^4_2He + {}^{234}_{90}A \rightarrow {}^0_{-1}e + {}^{234}_{91}B \rightarrow {}^0_{-1}e + {}^{234}_{92}X \rightarrow {}^4_2He + Y^{230}_{90}$
    Mass number of y is 230
    Atomic number of y is 90
b) Radioactive isotopes are used in x-rays
    Radioactive isotopes are used in sterilization of medical equipment instruments.
c) $t^{1/2} = \frac{T}{n}$, T= time taken, $t^{1/2}$=half-life, n = number of half-life
    $n = \frac{T}{t^{1/2}} = \frac{75}{15} = 5$
    From $Nt = \frac{No}{2^n}$, where Nt = amount remained after decay, No = original amount
    $\frac{Nt}{No} = \frac{1}{2^5} = \frac{1}{32}$

Give the names of the substances A, B, C and D. **4 marks**

Answer:

A is cyclohexane

B is hydrogen

C is Chloroethane

D is ethylbenzene

06. Esters are widely used and some esters occur naturally.

   a) Draw the structural formulae of any three different esters that have the molecular formula $C_5H_{10}O_2$. **3 marks**

   b) Write an equation for the hydrolysis of one of these esters by hot, aqueous sodium hydroxide. **1 mark**

   Answer:

   a) $CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_2CH_3$

   $CH_3\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_2CH_2CH_3$

   $H\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_2CH_2CH_2CH_3$

   $CH_3CH_2CH_2CH_2\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}CH_3$

   b) $CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OCH_2CH_3 + NaOH \longrightarrow CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O^-Na^- + CH_3CH_2OH$
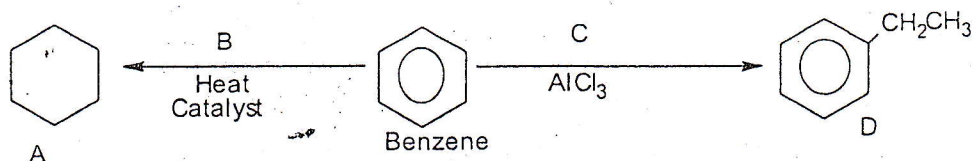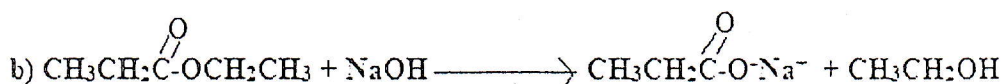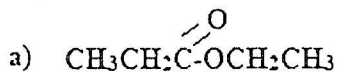
07. The standard enthalpy change of the reaction:

   $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$ can be calculated from standard enthalpy changes of combustion given below:

   $C_2H_4(g)$ $\Delta H_c^\theta = -1411 kJmol^{-1}$

   $C_2H_5OH(l)$ $\Delta H_c^\theta = -1367 kJmol^{-1}$
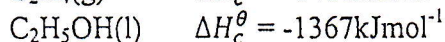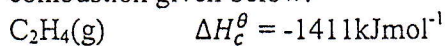
   a) What is meant by standard enthalpy change of combustion? **2 marks**

   b) Calculate the standard enthalpy change of the above reaction. **2 marks**

   Answer:

   a) Standard enthalpy of combustion is the enthalpy change when one mole of substance is completely burnt in oxygen at standard conditions (at temperature of 298K and a pressure of 1atm)·

   b) $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH$ I

   $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$............II

   $C_2H_4OH(l) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$ III

   The standard enthalpy change for (I) equation: I=II-III

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O\ (l) \ldots\ldots\ldots -1411 kJmol^{-1}$$
$$2CO_{2(g)} + 3H_2O(l) \longrightarrow C_2H_5OH(l) + 3O_{2(g)} \ldots\ldots\ldots 1367\ kJmol^{-1}$$

$$C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l) \qquad \ldots\ldots\ldots -44 kJmol^{-1}$$
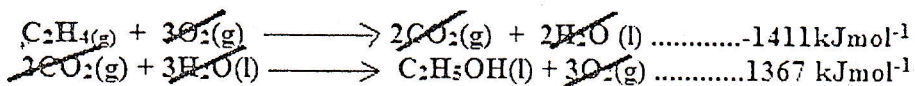
08. a) Write a balanced equation to show the thermal decomposition of calcium nitrate, $Ca(NO_3)_2$. **2 marks**

b) Which one has a higher thermal stability, $Mg(NO_3)_2$ or $Ca(NO_3)_2$. Give a reason for your answer. **2 marks**

Answer:

a) $2Ca(NO_3)_2(g) \to 2CaO(s) + 4NO_2(g) + O_2(g)$

b) $Ca(NO_3)_2$ is more thermodynamically stable. Ca^{2+} has larger ionic radius than Mg^{2+} and both cations have the same charge.
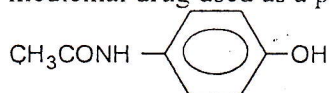Ca^{2+} has a lower polarizing power than Mg^{2-} and the lower the polarizing power the greater the ionic character. Therefore, $Ca(NO_3)_2$ is more ionic and more thermodynamically stable.

09. A common medicinal drug used as a pain killer has the following structure.

CH_3CONH —⬡— OH

a) Name two functional groups in the above molecule. **2 marks**

b) The medicinal drug can be produced by using the reaction

H_2N—⬡— $OH + X \longrightarrow$
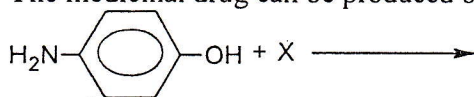
i) Suggest the identity of X. **1 mark**

ii) What reagent would you use to convert ethanoic acid, CH_3COOH into X. **1 mark**

Answer:

a) – Phenol
   - Amide

b)

i) X is $CH_3\text{-}\overset{O}{C}\text{-}Cl$

ii) PCl_5 or $SOCl_2$

10. a) State and explain the trend of acid strength of the hydrogen halides HCl, HBr and HI. **2 marks**

b) A test-tube containing hydrogen chloride gas is inverted in water. Describe what you would observe. **1 mark**

Answer:

a) The acidic strength of hydrogen halides increases down the group. The acidic strength depends on the ease of release of a proton which depends on the bond strength. The bond strength of hydrogen halides decreases from HF to HI due to a decrease in electronegativity from F to I. Therefore, since bond strength decreases there will be an increase in the ease of release of H^+ ions.

b) Hydrogen chloride gas dissolves in water forming a solution which turns blue litmus red. Water will rise inside the inverted test tube.

11. Explain the following observations, clearly showing chemical principles involved.
    a) Ammonia forms complex ions with cobalt (II) ions but methane does not. **1 mark**
    b) A blue solution of copper (II) sulphate turns green, then yellow when concentrated hydrochloric acid is added. **2 marks**

Answer:

a) Ammonia forms complexes with cobalt (II) due to the presence of a lone pair of electrons in ammonia which is donated to the empty orbitals of cobalt (II) to form a complex. While methane does not have any lone pair of electrons.

b) There is first formation of $CuCl_2$ which is green then finally formation of tetrachlorocopper (II) complex.
$Cu^{2+}(aq) + 2Cl^-(aq) \rightarrow CuCl_2(aq) -$ green
$CuCl_2(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-} -$ yellow
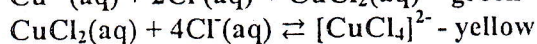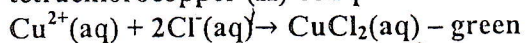
12. A reaction between A and B was investigated to determine its rate equation. The results of the investigation are shown in the following table. The temperature was kept constant during the investigation.

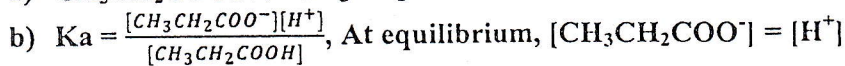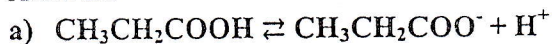| [A] (mol dm^{-3})	[B] (mol dm^{-3})	[C] (mol dm^{-3})
0.2	0.2	3.2×10^{-4}
0.2	0.2	1.3×10^{-3}
0.4	0.4	1.3×10^{-3}

a) Deduce the order of the reaction with respect to:
   i) A ii) B **2 marks**
b) Write the rate equation for the reaction **1 mark**

Answer:

a) i) Using experiment 1 and 2, doubling the concentration of A and the concentration of B is kept constant multiplies the rate by 4, the order of reaction with respect to A is 2.
   ii) Using experiment 2 and 3, doubling the concentration of B and the concentration of A is kept constant does not have any effect on rate. The order of reaction with respect to B is 0.

b) $R=K[A]^2[B]^0$ where R is rate and k is rate constant.
   $R = K[A]^2$

13. Ka for propanoic acid (CH_3CH_2COOH) is 1.3×10^{-5} mol dm^{-3}.
    a) Write an equation for the dissociation of propanoic acid in aqueous solution **1 mark**
    b) Calculate the pH of a 0.10 mol dm^{-3} (0.10M) solution of propanoic acid. **1 mark**

Answer:

a) $CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$

b) $Ka = \dfrac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$, At equilibrium, $[CH_3CH_2COO^-] = [H^+]$

$Ka = \dfrac{[H^+]^2}{[CH_3CH_2COOH]}$

$1.3 \times 10^{-5} = \dfrac{[H^+]^2}{0.10}$, $[H^+]^2 = 1.3 \times 10^{-5} \times 0.10 = 1.3 \times 10^{-6}$

$[H^+] = \sqrt{1.3 x 10^{-6}} = 1.14 \times 10^{-3}$ mol dm^{-3}

$P^H = -\log[H^+] = -\log(1.14 \times 10^{-3}) = 2.94$

14. The decomposition of dinitrogen tetroxide is represented by the equation.
    $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (ΔH is positive)
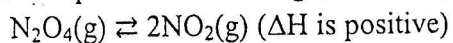
a) Write an expression for the equilibrium constant, Kp, for this reaction. **1 mark**

b) Explain the effect on the equilibrium mixture when the pressure is doubled at a constant temperature. **2 marks**

Answer:

a) $Kp = \dfrac{P_{NO_2}^2}{P_{N_2O_4}}$

b) Using Boyle's law and Avogadro's theory, increase in pressure favours the direction which has less volume and thus doubling the pressure at constant temperature favours the backward reaction.

15. An electrochemical cell is represented as shown below:

Mn(s) l Mn^{2+}(aq) ll Ni^{2+}(aq) l Ni(s)

Use the following data to answer the questions:

Mn^{2+}(aq)+2e$^-$ ⇌ Mn(s) $E^\theta = -1.18$ V

Ni^{2+}(aq)+2e$^-$ ⇌ Ni(s) $E^\theta = -0.23$ V

a) Calculate cell e.m.f(E^θ cell). **1 mark**

b) State and explain how the cell e.m.f would change if the concentration of Mn^{2-} is increased in the left hand half- cell. **2 marks**
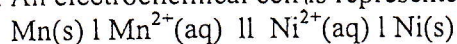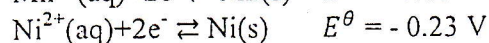
Answer:

a) $Emf = E^\theta_{right} - E^\theta_{left} = -0.23 - (-1.18) = +0.95V$

b) **From the cell reaction:**

Mn(s) + Ni^{2+}(aq) ⇌ Mn^{2+}(aq) + Ni(s)
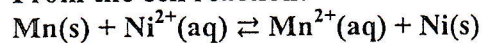
Thus increasing the concentration of Mn^{2+} shifts the equilibrium position to the left. Hence the value of emf decreases.

SECTION B: Answer THREE questions from this section /30 marks

16. Dyes can be made from aromatic amines and are widely used in textile industries. One synthetic route for making a dye is shown as follows:
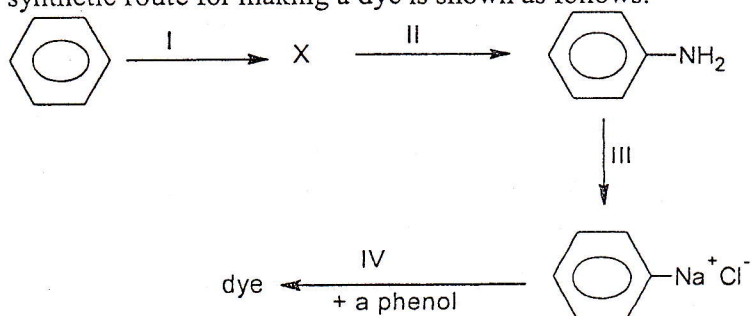
a) Draw the structural formula of the intermediate compound X. **1 mark**

b) State the rea8ents and conditions for
   i) step I **2 marks**
   ii) step II **2 marks**
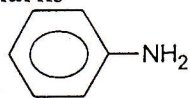
c) Phenylamine ⬡—NH₂ is a weak base.
   i) Write an equation to show phenylamine acting as a base. **1 mark**
   ii) Which one is a stronger base, phenylamine or ammonia? Explain your reasoning **2**

, marks

d) State the reagent for step III. **1 mark**

e) Give the structural formula of the dye formed when benzene diazonium chloride reacts with phenol. **1 mark**

Answer:

a)
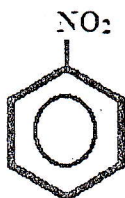
b) i) Conc. HNO_3 and H_2SO_4 with heat (55^0C)

ii) Sn/HCl plus NaOH and heat.

c) i)
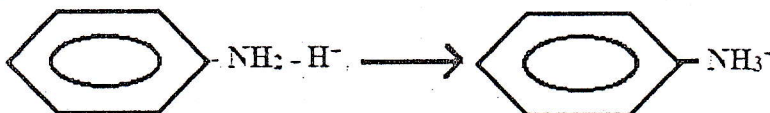
ii) Ammonia is stronger base than

Basic strength of amines depends on the availability of the lone pair of electrons on the nitrogen atom. In phenylamine the lone pair of electrons on the nitrogen atom interacts with the delocalized pi-electrons in benzene ring making the lone pair less available. Ammonia has three hydrogen atoms bonded to nitrogen and hydrogen atoms have no inductive effect, thus no effect on availability of the lone pair of electrons on nitrogen atom.

d) $NaNO_2$/ Conc. HCl at 0^0C.

e)
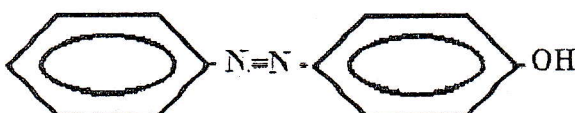
17. Zinc is extracted from zinc sulphide in a series of steps. The first step is to roast the sulphide ore in air:

$$2ZnS(s) + 3O_2(g) \rightarrow 2\ ZnO(s) + 2SO_2(g)$$
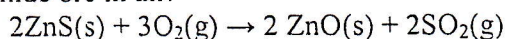
The final step is to convert ZnO to Zn.

a) Use the data below to calculate ΔH^θ for the above reaction:

$\Delta H_f^\theta (ZnS_{(s)}) = -200kJmol^{-1}$

$\Delta H_f^\theta (ZnO_{(s)}) = -348kJmol^{-1}$

$\Delta H_f^\theta (SO_{2(s)}) = -297kJmol^{-1}$ **3 marks**

b) Is the reaction exothermic or endothermic? **1 mark**

c) What environmental problem could arise from this process of extraction? **1 mark**

d) Suggest one method that can be used to eliminate this environmental problem. **1**

, mark

·e) Suggest a compound or an element which can reduce zinc oxide to zinc. Write an equation for the reaction. **2 marks**

f) You are provided with a solution containing zinc ions and lead ions. Suggest a reagent you could use to separate the two ions. Explain the chemical principles involved in this separation. **2 marks**

Answer:

a) $2ZnS(s) + 3O_2(g) \rightarrow ZnO(s) + 2SO_2(g)$ i

$ZnO(s) \rightarrow Zn(s) + 1/2O_2(g)$ ii

Given;

$Zn(s) + S(s) \rightarrow ZnS(s)$ -200 kJ/mol..............iii

$Zn(s + \frac{1}{2} O_2(g) \rightarrow ZnO(s)$ -348 kJ/mol............iv

$S(s) + O_2(g) \rightarrow SO_2(g)$ -297kJ/mol.................v
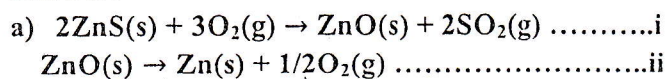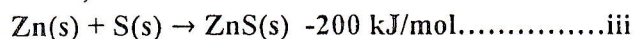
(i) = -2(iii) + 2(iv) + 2(v)

(i) = -2(-200) + 2(-348) + 2(-297) = -890 kJ/ 2 moles

For one mole, it is -445 kJ/mol

b) It is exothermic because enthalpy change is negative.

c) Sulphur dioxide pollutes the environment and can lead to greenhouse effect which rises the global warming. It also leads to acidic rain.
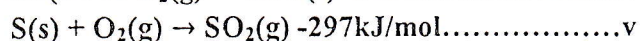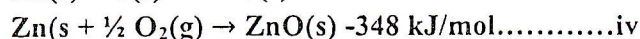
d) Treatment of waste gases before disposal by dissolving the sulphur dioxide gas in alkalis.

e) Carbon monoxide

$ZnO(s) + CO(g) \rightarrow Zn(s) + CO_2(g)$

f) Reagent used to distinguish Zn^{2+} and Pb^{2+} is potassium iodide (KI).

Pb^{2+}: yellow precipitate observed.

Zn^{2+}: No observable change.

$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

Or use aqueous ammonia.

18. Two organic compounds X and Y both have the molecular formula C_4H_8O. Both compounds give yellow precipitates when added to 2,4 - dinitrophenylhydrazine (Brady's reagent).

a) What can you deduce about X and Y? **1 mark**

b) Compound X gives a red precipitate when warmed with Fehling's solution but Y shows no reaction when treated this way.

i) What further deductions can you make about the natures of X and Y? **1 mark**

ii) Give the name or the formula of the red precipitate. **1 mark**

c) Draw the structural formula of compound Y and give its systematic name. **2 marks**
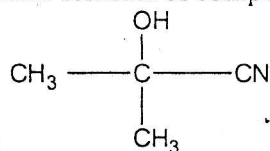
d) The compound   CH₃   is a product of the reaction between an organic compound and hydrogen cyanide (HCN).

i) Give the structural formula of the original organic compound. **1 mark**

ii) Give the mechanism for the reaction between HCN and the original organic

compound. **3 marks**

e). Give the structural formula of the organic compound formed when

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - CN$$
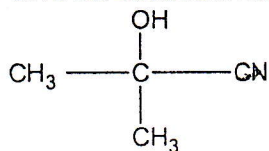
is reacted with Lithium aluminium hydride ($LiAlH_4$). **1 mark**

Answer:

a) X and Y are carbonyl compounds (aldehydes and ketones)

b) i) X is an aldehyde

   Y is a ketone

   ii) Copper (I) oxide or Cu_2O

c)

$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \quad Butanone$$

d) i)

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

ii) $HCN \rightarrow H^+ + CN^-$

$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CN^-}{}}{C}}-CH_3 \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_3 + H^- \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

e)

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2NH_2$$
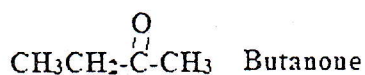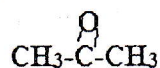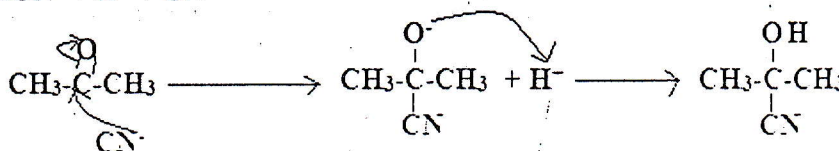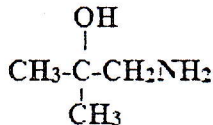
19. a) What is meant by the term acid according to the Bronsted – Lawry theory of acids and bases? **1 mark**

    b) Identify two substances acting as acids in the following reaction:

    $$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + OH^- \quad \textbf{2 marks}$$
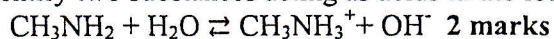
    c) Write an expression for the solubility product (Ksp) of calcium hydroxide. **1 mark**

    d) A 20.0cm^3 sample of saturated, aqueous calcium hydroxide required 18.2 cm^3 of 0.050 mol dm^{-3} hydrochloric acid for neutralization. Calculate:

    i) the concentration of OH$^-$ in the saturated solution. **1 mark**

    ii) A value for the solubility product of calNcium hydroxide, stating the units. **3 marks**

    e) Explain why calcium hydroxide is more soluble in water than potassium hydroxide. **1 mark**

Answer:

a) Acid is proton donor according to Bronsted-Lowry theory of acids and bases.

b) H_2O and $CH_3NH_3^+$ are acting as acids.

c) $Ksp = [Ca^{2+}][OH^-]^2$

d) i) $Ca(OH)_2$ (aq) + 2HCl(aq) → $CaCl_2$(aq) + $2H_2O$(l)

$1000cm^3$ contain 0.050 moles of HCl

18.2 cm^3 contain $\frac{0.050 \times 18.2}{1000}$ = 0.00091 moles of HCl

2 moles of HCl → 1 mole of $Ca(OH)_2$

0.00091 moles of HCl → $\frac{1 \times 0.00091}{2}$ of $Ca(OH)_2$ = 0.000455mol of $Ca(OH)_2$

20 cm^3 contain 0.000455 mol of $Ca(OH)_2$

$1000cm^3$ contain $\frac{0.000455 \times 1000}{20.0}$ = 0.02275 M of $Ca(OH)_2$

But one moe of $Ca(OH)_2$ is produced by 2 moles of OH^-

Thus concentration of OH^- = 2 × 0.02275 $moldm^{-3}$ = 0.0455 $moldm^{-3}$

ii) $[Ca^{2+}]$ = 0.02$moldm^{-3}$

$[OH^-]$ = 0.0455 $moldm^{-3}$

$Ksp = [Ca^{2+}][OH^-]^2$

$Ksp = (0.02275\ moldm^{-3})(0.0455 moldm^{-3})$ = 4.7 × 10^{-5} mol^3dm^{-9}

e) Calcium hydroxide is less soluble in potassium hydroxide due to the common ion effect of OH^- which reduces the solubility of calcium hydroxide.

20. Electrolysis has many applications in industry. One such application is the manufacture of hydrogen, chlorine and sodium hydroxide by electrolysis of brine (concentrated sodium chloride solution)

a) Briefly outline, using relevant equations how the above products are formed by electrolysis of brine. **5 marks**

b) A current of 0.200 A is passed through Copper II) sulphate solution for 10 hours.
i) Calculate the mass of copper deposited on the cathode. (Cu = 63.5, F = 96,500 C mol^{-1}) **3 marks**
ii) Calculate the volume of oxygen evolved at the anode (measured at room temperature and pressure). You may use the following data:

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
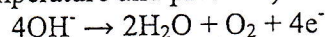
Molar volume of a gas at r.t.p. = 24 dm^3 **2 marks**

Answer:

a) During electrolysis of Conc.NaCl, the ions present in solution are Na^+, Cl^-, H^+, OH^-

Anode: Cl_2 formed because Cl^- is being discharged in preference to OH^-.

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
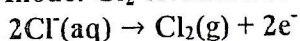
Cathode: H_2 formed because H^+ is being discharged in preference to Na^+

$2H^+(aq) + 2e^- \rightarrow H_2(g)$
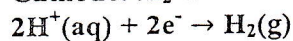
Remaining solution will form NaOH.

Hence, products are: $Cl_2(g)$, $H_2(g)$ and NaOH.

b) i) Total quantity (Q) = Ixt = 0.200 × 10 × 60 × 60 = 7200C

c) At cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

2 faradays deposit 1 mole of Cu

2×96500C deposit 63.5 g of copper.

7200C deposit $\frac{63.5 \times 7200C}{2 \times 96500c}$ = 2.36g of copper.

ii) 4faradays liberates 24dm^3 of $O_2(g)$

4×96500 liberates 32 g

7200C liberates $\frac{24 \times 7200}{4 \times 96500}$ = 0.448 dm^3 or 448cm^3

SECTION C: Answer ONE question from this section /15 marks

21. a) What mass of potassium iodate (V) (KNO_3) would be required to make 250 cm^3 of a solution containing one sixtieth (1/6) of a mole per dm^{-3} (K= 39, I= 127, O = 16) **2 marks**

b) When 25 cm^3 of the solution of potassium iodate (V) of the above concentration in (a) was added to excess of acidified potassium iodide solution, the iodine produced reacted with 20 cm^3 of a solution of sodium thiosulphate. Use these equations to answer the questions that follow:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

i) Calculate the number of moles of iodate (IO_3^-) ions in 250cm^3 of the solution. **1 mark**

ii) Deduce the number of moles of $2S_2O_3^{2-}$ ions in 20 cm^3. **1 mark**

iii) Calculate the concentration of the thiosulphate solution in mol dm^{-3}. **2 marks**

iv) Give the name of a suitable indicator to use in the titration of iodine solution with the thiosulphate solution. **1 mark**

c) Concentrations of chlorine in treated water for domestic use can be monitored by testing water samples. In one such test, excess potassium iodide [KI] was added to a 1000 cm^3 sample of water. The liberated iodine reacted with 14.0 cm^3 of 0.00100 mol dm^{-3} sodium thiosulphate solution (0.00100M).

i) Calculate the number of moles of sodium thiosulphate, $Na_2S_2O_3$ used in the reaction and hence the number of moles of iodine liberated. **2 marks**

ii) Write an equation for the reaction between Cl_2(aq] and I^-(aq) ions. Identify the reducing agent in this reaction. **2 marks**

iii) Calculate the number of moles of Cl_2 and hence the mass of chlorine molecules in the original sample of Water (Cl = 35.5). **2 marks**

iv) Write an equation for the reaction between Cl_2 and water and show that this is a disproportionation reaction. **2 marks**

Answer:

a) Concentration/molarity $= \frac{1}{60} = 0.017$ M

1000cm^3 contain 0.017 moles of KIO_3

250 cm^3 contain $\frac{0.017 \times 250}{1000} = 0.00425$ moles of KIO_3

Number of moles $= \frac{mass}{molar\ mass}$, molar mass of KIO_3 = 39 + 127 + 3x16 = 214g/mol

Mass = n x molar mass= 0.00425 moles x 214g/mol = 0.9095g of KIO_3

b) i) 1000cm^3 contain 0.017 moles of IO_3^-.

25 cm^3 contain $\frac{0.017 \times 25}{1000} = 0.000425$ moles of IO_3^-

ii) 1mole of IO_3^- liberated 3 moles of I_2

0.000425 of IO_3^- liberated $\frac{0.000425 \times 3}{1} = 0.001275$ moles of I_2

But 1 mole of iodine is reacted with 2 moles of $S_2O_3^{2-}$.

0.001275 moles of I_2 reacted with $\frac{2 \times 0.001275}{1} = 0.00255$ moles of $S_2O_3^{2-}$

iii) 20cm^3 contain 0.00255 moles of $S_2O_3^{2-}$

1000cm^3 contain $\frac{0.00255 \times 1000}{20} = 0.1275$ moldm^{-3} of $S_2O_3^{2-}$

iv) Starch indicator

c) i) 1000 cm^3 contain 0.001 moles of $S_2O_3^{2-}$

14 cm^3 contain $\frac{0.001 \times 14.0}{1000} = 0.000014$ moles of $S_2O_3^{2-}$

2 moles of $S_2O_3^{2-}$ reacted with 1 mole of I_2

0.000014 moles of $S_2O_3^{2-}$ reacted $\frac{0.00014 \times 1}{2} = 0.000007$ moles of I_2

ii) $Cl_2(g) + 2I^-(aq) \rightarrow I_2 + 2Cl^-(aq)$

Iodide ion is reducing agent since it has reduced Cl_2 from oxidation state of 0 to -1.

iii) 1 mole of I_2 liberated by 1 mole of Cl_2

0.000007 moles of Iodine liberated by 0.000007 moles of Cl_2

Mass of pure chlorine = number of moles x molar mass of chlorine.

Mass of pure chlorine = $0.000007 \text{ mol} \times 70 \text{g/mol} = 0.00049\text{g}$ of Cl_2

iv) $Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$

$\quad\quad 0 \quad\quad\quad\quad\quad -1 \quad\quad\quad +1$

Cl_2 undergoes both oxidation and reduction in the same reaction. i.e: disproportionation reaction. Or Add NaOH.

22. Describe a chemical test to distinguish between each of the pairs of the following compounds. Include in your description the expected observation and give relevant equations for the reactions involved.

a) NH_4NO_3 and $Mg(NO_3)_2$ **3 marks**

b) $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2CH_2CHO$ **3 marks**

c) $CH_3CH_2CH_2Cl$ and $CH_3\,CH_2\overset{\overset{\displaystyle O}{\|}}{C}\!\!-\!\!Cl$ **3 marks**

d) $CH_3CH=CH_2$ and $CH_3CHBrCH_3$ **3 marks**

e) Cu_2O and CuO
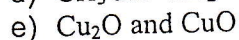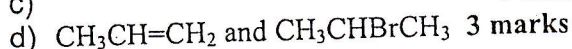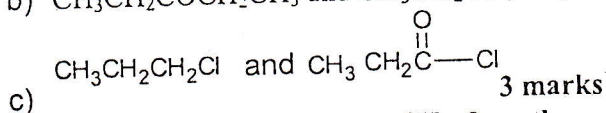
Answer:

a) Reagent used is aqueous sodium carbonate

For $Mg(NO_3)_2$, a white precipitate is observed and no observable change with NH_4NO_3.

$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$ (white precipitate)

Or using sodium hydroxide solutions.

b) Reagent ammoniacal silver nitrate (Tollen's reagent)

No observable change with $CH_3CH_2COCH_2CH_3$

Silver mirror observed with $CH_3CH_2CH_2CH_2CHO$

Equation:

$CH_3CH_2CH_2CH_2CHO(aq) + 2NH_4OH + 2AgNO_3 \rightarrow CH_3CH_2CH_2CH_2COOH + 2Ag(s) + 2NH_4NO_3(aq)$

Or using Fehling's solution or acidified potassium dichromate or permanganate.

c) To both compounds separately add H_2O (water), then test P^H of mixture/ use litmus paper.

Observations:

CH_3CH_2COCl: fumes of HCl and turns litmus paper red/ P^H will be 1 to 3.

$CH_3CH_2CH_2Cl$: Solution of two layers.

Or using silver nitrate and ammonia.

d) To both compounds separately add bromine solutions (Br_2 dissolved in an

By KAVIRANGA S

organic solvent)

. Observations:

$CH_3CH=CH_2$: decolourises bromine solutions (red-brown to colourless)

$CH_3CHBrCH_3$: No observable change.

Equation: $CH_3CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CHBrCH_2Br$

Or To both compounds separately add acidified permanganate or Using silver nitrate and ammonia.

e) Using Sulphuric acid

Observations:

For Cu_2O: The red-brown solid gives a blue solution and a brown solid.

For CuO: The black solid gives a blue solution.

$Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$

$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

ADVENCED LEVEL CHEMISTRY NATIONAL EXAMINATION PAPER 2007

(Biology-Chemistry)

SECTION A: Answer ALL questions /55 marks

01. a) With reference to sodium, Na, state what is meant by the term ionization energy. Include an equation with state symbols in your answer. **2 marks**

b) Why is the second ionization energy of Na much higher than the first ionization energy? (Atomic number of Na = 11) **1 mark**

Answer:

a) Ionisation is the minimum energy required to remove one mole of electrons from one mole of free gaseous atoms or cations to form one mole of positively charged gaseous cations for example.

$Na(g) \rightarrow Na^+(g) + e^-$
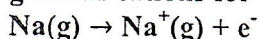
b) The second electron is closer to the nucleus and experiences greater nuclear attraction. On addition the second electron is removed from a stable full 3p orbital.

02. The ions F^-, Na^+ and Mg^{2+} all have the same number of electrons. (Atomic numbers = F (9), Na (11), Mg (12)).

a) Using the s, p, d... notation, write the electronic configuration (arrangement) of F^-. **1 mark**

b) Arrange the above ions in order of increasing size (ionic radius). Explain why they are in that order of size. **2 marks**

c) Briefly explain why F^- has a larger size than F. **1 mark**

Answer:

a) F^-: $1s^2 2s^2 2p^6$

b) The order of increasing ionic radius is $Na^+ > Mg^{2+} > F^-$

Across the period nuclear charge increases hence higher attraction of the outside electrons.

This leads to a decrease in size from Na^+, Mg^{2+}, then to F^-.

c) F^- has a larger size than F because there is an extra electron gained by F^-

resulting into increased screening effect and thus larger size.

03. Three isomers which are all alcohols are represented by the molecular formula $C_4H_{10}O$.
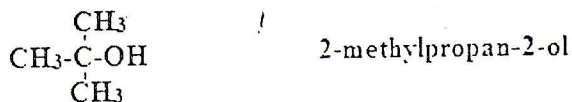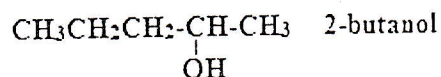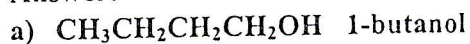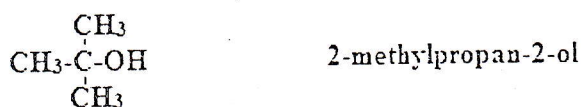   a) Give the structural formulae of the isomers and name them. **3 marks**
    b) One of the alcohols does not react with hot acidified potassium dichromate. $K_2Cr_2O_7$. Identify the alcohol. **1 mark**

Answer:
a) $CH_3CH_2CH_2CH_2OH$ 1-butanol

$CH_3CH_2CH_2-CH-CH_3$ 2-butanol
$\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad OH$

$\quad\quad CH_3$
CH_3-C-OH 2-methylpropan-2-ol
$\quad\quad |$
$\quad\quad CH_3$

b)
$\quad\quad CH_3$
CH_3-C-OH 2-methylpropan-2-ol
$\quad\quad |$
$\quad\quad CH_3$

04. Hydrogen chloride is a gas at room temperature while sodium fluoride is a solid of high melting point.
    a) State the type of bonding present in each compound. **1 mark**
    b) Briefly explain in terms of bonding why their melting points are different. **2 marks**

Answer:
a) **Hydrogen chloride has covalent bonding**
   Sodium fluoride has ionic bonding
b) **Hydrogen chloride associates through Van Der Waal's forces of attraction which is easily broken at room temperature, thus the lower melting point.**
   While sodium fluoride associates through a strong ionic bond which is hard to break and thus higher melting point.

05. Give brief explanations for the following trends in the Periodic Table:
    a) Atomic radius decreases across the period. **2 marks**
    b) Electronegativity decreases down the group. **2 marks**

Answer:
a) **Across the period, increase in nuclear charge outweighs increase in screening effect hence effective nuclear charge increases.**
   The electrons are therefore more attracted to the nucleus which decreases atomic radius (size).
b) **As you move down the group, an extra shell of electrons is added, hence screening effect outweighs nuclear charge resulting to less attraction of electrons, thus a decrease in electronegativity.**

06. State and explain what might be observed in the following reactions:
    a) Ethanoic acid solution is mixed with magnesium powder. **2 marks**
    b) Ethanal is warmed with potassium permanganate. **2 marks**

Answer:
a) **Effervecence of a colourless gas which is neutral to litmus and burns with a ''pop''sound in presence of a glowing splint.**

By KAVIRANGA S.

$$2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$$
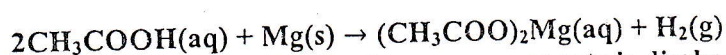
b) The purple colour of potassium permanganate is discharged.

$$CH_3CHO \xrightarrow[\text{Heat}]{MnO_4^-/H^+} CH_3COOH$$

07. a) How does the acid-base character of oxides of period 3 (Na-Cl) change across the period? **1 mark**

b) Use balanced chemical equations to support your answer in (a) to show how the oxides MgO, Al_2O_3, and SO_3 react with HCl or NaOH. **4 marks**

Answer:

a) The acid-base character increased as you move across period.

b) The basic character decreases as you move across period.

MgO is a basic oxide, it reacts with acids. e.g:

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

Al_2O_3 is an amphoteric oxide and it reacts with both acids and bases.

$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$
$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightleftarrows 2NaAl(OH)_4$$
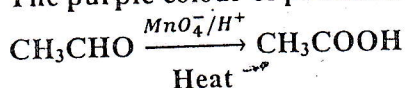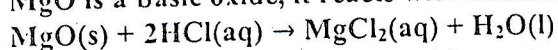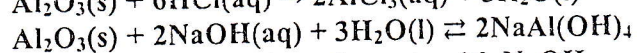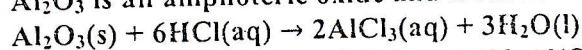
SO_3 is an acidic oxide and reacts with NaOH

$$SO_3 + NaOH(aq) \rightarrow NaHSO_4(aq)$$
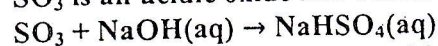
08. a) One of the characteristics of transition elements is the ability to form complex ions such as $[Cr(NH_3)_4Cl_2]^+$. Use this complex ion to explain the terms :

i) ligand

ii) Coordination number **2 marks**

b) State the oxidation number of Cr in the above complex ion **1 mark**

Answer:

a) i) A ligand is a molecule or ion or group of atoms that donate a lone pair of electrons to the central metal ion to form a complex.

For example in $[Cr(NH_3)_4Cl_2]^+$ the ligands are NH_3 and Cl^-.

ii) Coordination number is the number of coordinate bonds from ligands to the central ion. For example, since there are six bonds form the ligand to the central metal ion in $[Cr(NH_3)_4Cl_2]^+$, the coordinate number is 6.

b) Let the oxidation number of Cr be X:

$$X+4(0) + 2(-2) = 1$$
$$X = +3$$

09. Some reactions of phenol are represented in the scheme below :
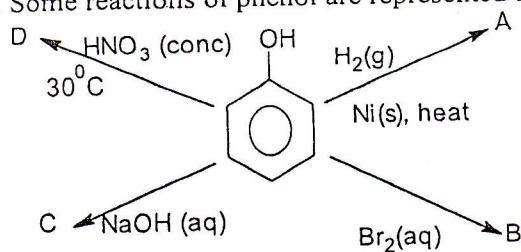
Identify by structural formulae the products A, B, C and D. **4 marks**

Answer:

A: OH (cyclohexanol structure)

B: OH Br (phenol with Br)

C: O⁻Na⁺ (sodium phenoxide)

D: OH NO₂ (nitrophenol)

10. Some magnesium powder was mixed with excess hydrochloric acid. The temperature rose by 10°C.
    a) Write a balanced equation for the reaction that took place. **1 mark**
    b) Draw an energy profile/ diagram for the reaction clearly showing the energy of the reactants, the products and the activation energy of the reaction. **3 marks**
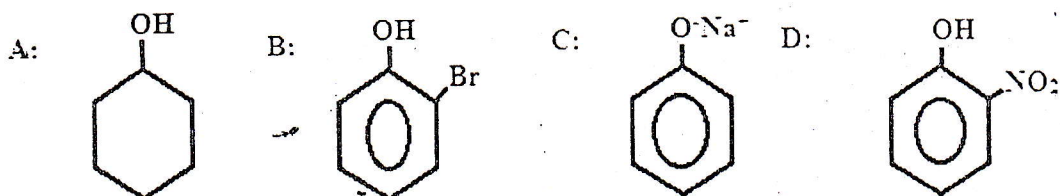
Answer:

a) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

b) Since the temperature rose by 10^0C the reaction is exothermic and thus we have the energy diagram like below. Energy profile diagram:
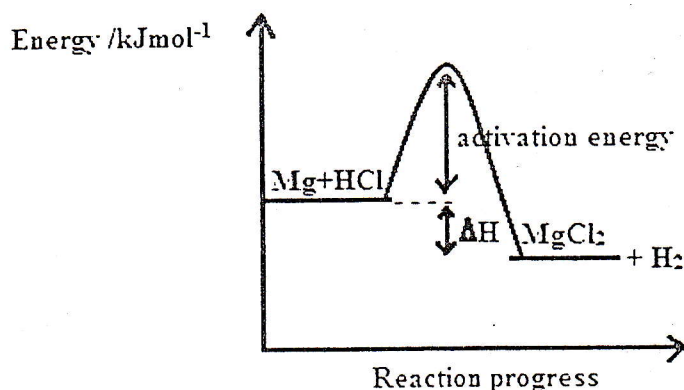
11. The structures of two amino acids are given below :

$NH_2 - CH - CO_2H$
         |
         CH_3
Alanine

$NH_2 - CH - CO_2H$
         |
         CH_2OH
Serine
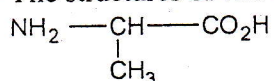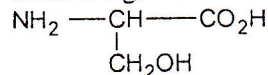
    a) Write equations to show :
       i) the reaction between alanine and HCl (aq)
       ii) the reaction between serine and NaOH (aq) **2 marks**
    b) What type of polymer is formed by amino acids? **1 mark**
    c) Draw the structure of the linkage group found in the type of polymer mentioned in (b). **1 mark**

Answer:

a)

i) $NH_2\text{-}CH\text{-}COOH + HCl(aq) \longrightarrow {}^-NH_3\text{-}CH\text{-}COOH(aq) + Cl^-(a)$
         CH_3 CH_3

ii) $NH_2\text{-}CH\text{-}COOH + NaOH(aq) \longrightarrow NH_2\text{-}CH\text{-}COO^-Na^-(aq) + H_2O(l)$
         CH_2OH CH_2OH

b) Condensation polymer

c)

Linkage group

12. The reaction A + B → C, is first order with respect to A and to B.
    a) Write a rate equation for the reaction. **1 mark**
    b) Given that the initial concentrations are :
       [A]= 1.5×10^{-2} mol dm^{-3}, [B]= 2.5×10^{-3} mol dm^{-3} and the initial rate is 3.75×10^{-4} mol dm^{-3}S^{-1};
       i) Calculate the rate constant for the reaction.
       ii) Give the units of the rate constant. **2 marks**

   Answer:
   a) $R = k[A][B]$
   b) i) $K = \dfrac{[R]}{[A][B]}$

   $K = \dfrac{3.75 \times 10^{-4} moldm^{-3}s^{-1}}{(1.5 \times 10^{-2})(2.5 \times 10^{-3})(moldm^{-3})} = 10 mol^{-1}dm^{3}S^{-1}$

   ii) Units of K: $mol^{-1}dm^{3}s^{-1}$

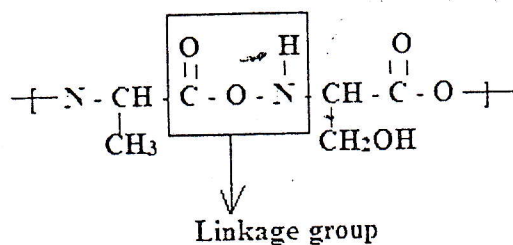13. Hydrogen and iodine react together to give an equilibrium mixture according to the equation: $H_2(g) + I_2(g) \rightleftarrows 2HI (g)$.
    a) Write an expression for Kp for this equilibrium **1 mark**
    b) 0.50 mol of I_2 and 0.50 mol of H_2 were reacted in a closed versel at 450°C and 2 atm. After attaining equilibrium, the mixture was found to contain 0.11 mol of I_2.
       i) Calculate the number of moles of I_2 which reacted and hence the number of moles of HI. **1 mark**
       ii) Calculate the partial pressures of I_2, H_2 and HI in the equilibrium mixture. **2 marks**
       iii) Calculate the value of Kp at 450°C. **1 mark**

   Answer:
   a) $Kp = \dfrac{P^2_{HI}}{P_{I_2}P_{H_2}}$

   i) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

	H_2	I_2	$2HI$
Initial amount	0.5	0.5	0
Amount reacted	x	x	2x
Amount at equilibrium	0.5-x	0.5-x	2x

   Total amount in moles at equilibrium
   But at equilibrium, there was 0.11 moles of I_2
   Thus, 0.5-x = 0.11
         X = 0.5 − 0.11 = 0.39 moles
   Number of moles of I_2 = 0.11 moles
   Number of moles of H_2 = 0.11 moles
   Number of moles of HI = 2 x 0.39 = 0.78 moles

ii) Total moles = 0.11 + 0.11 + 0.78 = 1 mole
Partial pressure = mole fraction x pressure of system

$$P_{I_2} = \frac{0.11 \times 2}{1} = 0.22 \text{ atm}$$

$$P_{H_2} = \frac{0.11 \times 2}{1} = 0.22 \text{ atm}$$

$$P_{HI} = \frac{0.74 \times 2}{1} = 1.56 \text{ atm}$$

$$Kp = \frac{(1.56)^2}{0.22 \times 0.22} = 50.28$$

14. A fruit juice has a pH of 3.5

a) Define pH using a mathematical expression. **1 mark**
b) Calculate the concentration of hydrogen ions in the juice. **1 mark**

Answer:

a) $P^H = -\log[H^+]$
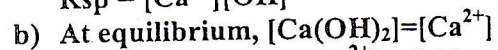b) $3.5 = -\log[H^+] \Rightarrow [H^+] = 0.000316 \text{ moldm}^{-3}$

15. Calcium hydroxide has low solubility in water.

a) Write an expression for the solubility product (Ksp) of Calcium hydroxide. **1 mark**
b) A saturated solution of Calcium hydroxide has a concentration of Calcium hydroxide of 0.011 mol dm^{-3}. Calculate the solubility product of calcium hydroxide in water. **1 mark**

Answer:

a) $Ca(OH)_2(s) \rightleftarrows Ca^{2+}(aq) + 2OH^-(aq)$
   $Ksp = [Ca^{2+}][OH]^2$
b) At equilibrium, $[Ca(OH)_2] = [Ca^{2+}]$
   $[Ca^{2+}] = 0.11 \text{ moldm}^{-3}$
   $[OH^-] = 2 \times 0.11 = 0.022 \text{ moldm}^{-3}$
   $Ksp = (0.011)(0.022)^2 = 5.3 \times 10^{-5} \text{mol}^3\text{dm}^{-9}$

Section B: Choose THREE questions from this section. (30 marks)

16. Some reactions of 2-hydroxybenzoic acid are shown in the scheme below.
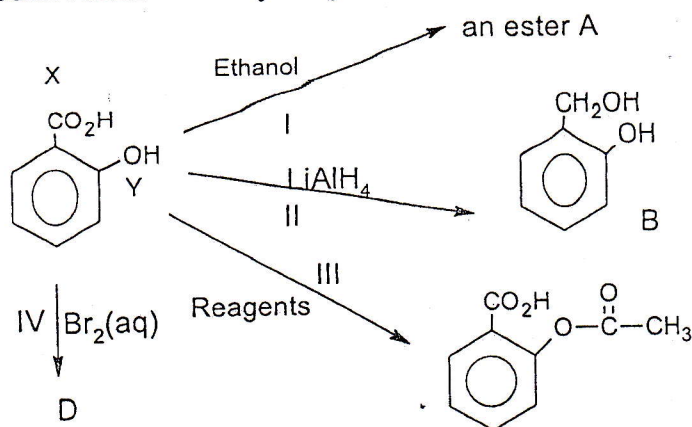
a) Give the names of the functional groups X and Y (encircled) **2 marks**
b) What type of reaction is reaction ll ? **1 mark**
c) Suggest the structural formula of ester A. **1 mark**
d) Give the structural formula of the organic compound formed by warming compound

, C with NaOH(aq). **2 marks**

- e) Suggest the structural formula of compound D. **1 mark**
- f) Suggest the intermolecular force that would be between functional groups X and Y. **1 mark**
- g) Give the reagents and conditions for converting

to

2 marks

Answer:

a) X is carboxylic acid group
   Y is phenol

b) Reduction

c)
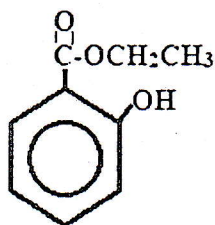
d)
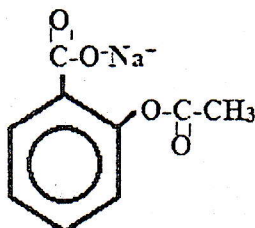
e)
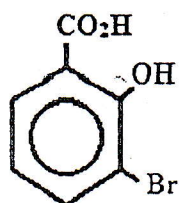
f) **Intra-molecular hydrogen bonding**

g) **MnO_4^-/H^+ and heat**

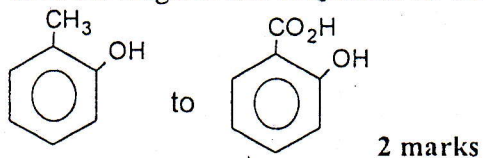17. a) An acidified solution of copper (II) sulphate, $CuSO_4(aq)$, was electrolysed using platinum electrodes.

Use the standard electrode potentials below to answer the following questions:

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad\qquad E^{\theta \cdot} = 0.00V$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad\qquad E^{\theta} = +0.34V$$
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^{\theta} = +0.34V$$

i) Sketch and label an apparatus that can be used for such an experiment. **2 marks**

ii) Write an equation for the reaction that occurs at the cathode. **2 marks**

iii) Write an equation for the reaction at the anode. **2 marks**

. iv) What happens to the pH of the solution as electrolysis proceeds? Explain why. **2 marks**

b) The platinum electrodes are replaced by copper electrodes. State and explain two differences in the observations that would be made. **2 marks**

Answer:

a) i)

ii) Cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

iii) Anode: $4OH^-(aq) \longrightarrow 2H_2O(l) + O_2 + 4e^-$

iv) The P^H of the solution reduces. i.e: the solution becomes more acidic. Discharge of OH^- ions leaves H^+ ions in solution hence reacting with the remaining SO_4^{2-} forming sulphuric acid.

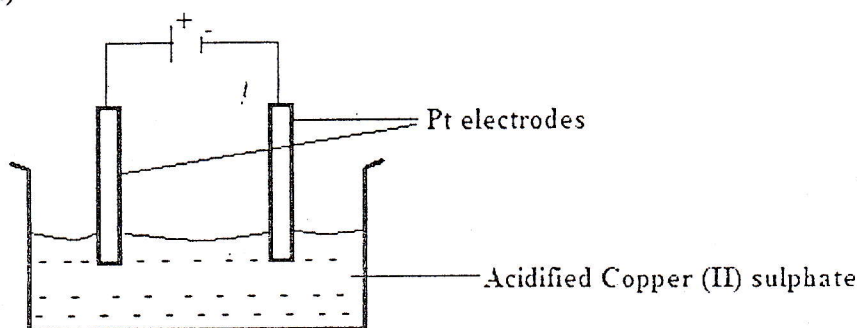$2H^+(aq) + SO_4^{2-} \longrightarrow H_2SO_4(aq)$

b)

Pt electrodes	Cu electrode
The blue colour of copper (II) sulphate fades	The blue colour of copper (II) sulphate remains because the anode continues to break down
The anode does not change size	The anode reduces in size because it breaks down
Bubbles of a colourless gas at the anode because hydrogen is evolved.	No bubbles of a gas at the anode

18. The table below shows the first, second, and third ionization energies (in kJmol⁻) of six successive elements in the periodic table.

Element	1^{st}I.E	2^{nd}I.E	3^{rd}I.E
A	1060	1900	2920
B	1000	2260	3390
C	1260	2300	3850
D	1520	2660	3950
E	418	3,070	4600
F	590	1150	4940

NB : The elements are not in one period.

a) For a given element, M, write equations to represent 1st, 2nd and 3rd ionization

energies. **3 marks**

b) ·From the above table, identify the letter corresponding to an alkaline earth metal (Group ll). Explain your answer. **2 marks**

c) Which element is most likely to be a noble gas? Explain your answer. **2 marks**

d) Suggest the formula of a compound formed between elements F and C. Explain your answer. **2 marks**

e) Suggest from the above table which elements are metals. **1 mark**

Answer:

a) $M(g) \rightarrow M^+(g) + e^-$ 1st ionization energy
   $M^+(g) \rightarrow M^{2+}(g) + e^-$ 2nd ionization energy
   $M^{2+}(g) \rightarrow M^{3+}(g) + e^-$ 3rd ionization energy

b) F is in group II due to a large difference between the second and the third ionization energy. This means that the third electron comes from a stable energy level.

c) D is mostly likely to be a noble gas due to the highest value of first ionization energy caused by its stability.

d) FC_2

e) This is because F is in group II of the periodic table

f) E and F

19. Production of ammonia by the Haber process is one of the major chemical industries. The equation for the reversible exothermic reaction is:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
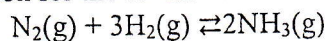
a) State the optimal conditions of temperature, pressure and catalyst which are used in this process. **3 marks**

b) Using the principles of equilibrium, kinetics and economic costs, justify the use of the above conditions in (a). **3 marks**

c) One of the major uses of ammonia is to manufacture nitric acid. Use equations to outline how nitric acid is manufactured from ammonia. **3 marks**

d) Suggest why potassium nitrate, KNO_3 might be a better fertilizer than ammonium nitrate (NH_4NO_3) **3 marks**

Answer:

a) **Optimum conditions:**
   - **Pressure of 200 atm**
   - **Temperature of 450^0C**
   - **Catalyst is iron**

b) A low temperature would give a higher yield but the rate would be too slow, hence not economical. A higher temperature of 500^0C increases the rate.
   A high pressure increases the yield but if it is higher than 200 atm, it becomes very expensive because of the higher cost of repairing broken parts.
   The catalyst increases the rate of reaction because it provides an alternative pathway for activation energy hence reducing the cost.

c) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$
   $2NO + O_2 \rightarrow 2NO_2(g)$
   $3NO_2(g) + 2H_2O(l) + 2O_2(g) \rightarrow HNO_3(aq)$

d) KNO_3 contains potassium and nitrogen minerals which are needed by soil.
   NH_4NO_3 contains basically nitrogen as the mineral required by the soil

By KAYIRANGA Serge. Chemist... ....

20. a) The enthalpy change of combustion of butane gas is -3000 KJmol⁻¹. 1.2 dm³ of butane gas (measured at room temperature and pressure) was used to heat water from 20°C to the boiling point (100°C).

    i) Write a balanced equation for the complete combustion of butane. (C_4H_{10}) 2 marks

    ii) 1 mole of gas has a volume of 24dm³ at room temperature and pressure. Calculate the number of moles of C_4H_{10} in 1.2 dm³. **1 mark**

    iii) If 80% of the heat produced by burning 1.2 dm³ of butane was absorbed by water, calculate the mass of water that was heated up to the boiling point. (Specific heat capacity of water = $4.2 Jg^{-1}K^{-1}$)

b) Given that the enthalpies of combustions of hydrogen and carbon are 286KJmol⁻¹ and -394KJmol⁻¹ respectively, calculate the enthalpy change of formation of butane. 3 marks

Answer:

a) i) $C_4H_{10}(g) + \frac{13}{2}O_2 \longrightarrow 4CO_2(g) + 5H_2O(l)$
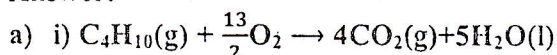
    ii) 24cm³ of C_4H_{10} at r.t.p. contains 1mole

    1.2 cm³ of C_4H_{10} at r.t.p. contains $\frac{1 \times 1.2}{24} = 0.05$ moles

    iii) (heat produced by C_4H_{10}) $\times \frac{80}{100}$ = heat absorbed by water

    1 mole of C_4H_{10} produces 3000kJ

    0.05 moles of C_4H_{10} produces $\frac{3000 \times 0.05}{1} = 150$ kJ

    $\frac{80}{100} \times 150kJ = MC\Delta\theta$ where M = mass, C = specific heat capacity

    $120kJ = M \times 4.2 \times (100-20)$, $1kJ = 1000J$

    $120kJ \times 1000J = 336 \times M$

    $M = \frac{120\,000}{336} = 357g = 0.357kg$

    Mass of water is 0.357Kg

b) $C + O_2 \longrightarrow CO_2$

    $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ -286 ......(ii)

    $C_4H_{10}(g) + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$ -3000(iii)

    Solution:

    $4C(s) + 5H_2(g) \longrightarrow C_4H_{10}(g)$ ....(iv)

    Iv = 4(ii) + 5(i) – (iii)

    $4C + 4O_2 \longrightarrow 4CO_2$ -394 x 4

    $5H_2 + \frac{5}{2}O_2 \longrightarrow 5H_2O$ -286 x 5

    $4CO_2 + 5H_2O \longrightarrow C_4H_{10} + \frac{13}{2}O_2$

    $4C(s) + 5H_2(g) \longrightarrow C_4H_{10}(g)$ $\Delta H_f^\theta = -6kJ/mol$
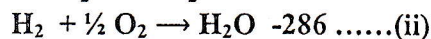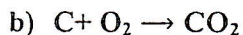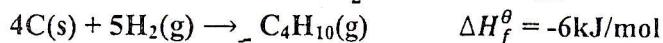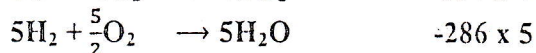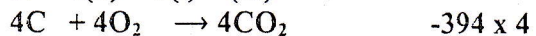
    The enthalpy change of formation of butane is 6kJmol⁻¹

Section C : Answer one question from this section. (15 marks)

21. An organic compound, A, of molecular formula $C_2H_4O_2$ contains two functional groups.

    a) The first functional group was tested as follows :

    i) The dry compound, A, reacts with sodium to give hydrogen gas and a compound of molecular formula $C_2H_3O_2Na$.

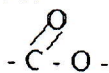ii) When A was heated with ethanoic acid and a few drops of concentrated sulphuric acid the product, of molecular formula $C_4H_6O_3$, had a sweet smell.

Give the formula and name of the first functional group **2 marks**

Give the name of the functional group formed in (a) (ii) above. **1 mark**

b) The second functional group was tested as follows =

i) A few drops of A were added to 2,4-dinitrophenyl hydrazine which gave a yellow/orange precipitate.

ii) One drop of A was mixed with a solution containing $[Ag(NH_3)_2]^+$ (Tollen's reagent) and warmed. A deposit of silver was formed on the inner sides of the test tube.

Give the name and the formula of the second functional group. **2 marks**

c) Give the structural formula for compound A. **2 marks**

d) Give the structural formulae of two possible geometric isomers of molecular formula $C_2H_4O_2$. **2 marks**

e) Compound A is oxidized to give an acid of molecular formula $C_2H_2O_4$. Give the structural formula of $C_2H_2O_4$ **2 marks**

f) Compound A is reduced to give a compound of molecular formula $C_2H_6O_2$. Give the structural formula of $C_2H_6O_2$. **1 mark**

g) Suggest the formula of the compound formed by reacting $C_2H_6O_2$, with excess HBr. **1 mark**

h) Give the structural formula of a possible compound formed when one mole of $C_2H_6O_2$, reacts with two moles of ethanoic acid. **2 marks**

Answer:

a) **First functional group;**
   Alcohol
   In a (ii), An ester is formed:

$$-\overset{\overset{O}{\|}}{C}-O-$$

b)

$$-\overset{\overset{O}{\|}}{C}-H \text{ aldehyde group}$$

c)

$$H-\overset{\overset{O}{\|}}{C}-CH_2OH \text{ is A}$$

d) HO-CH=CH-OH

Isomers

$$\overset{H}{\underset{OH}{\diagdown}}C=C\overset{OH}{\underset{H}{\diagup}} \quad \text{and} \quad \overset{HO}{\underset{H}{\diagdown}}C=C\overset{OH}{\underset{H}{\diagup}}$$

e)

$$\begin{array}{ccc} O & & O \\ \diagdown & & \diagup \\ & C=C & \\ \diagup & & \diagdown \\ HO & & OH \end{array}$$
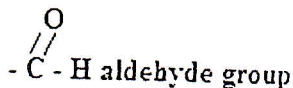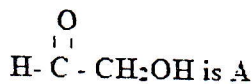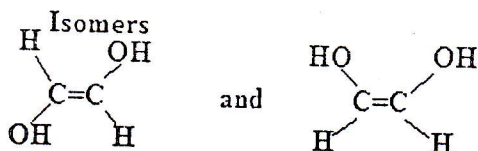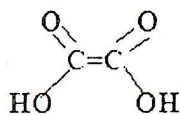
f) $HO\text{-}CH_2\text{-}CH_2\text{-}OH$

g) $Br\text{-}CH_2\text{-}CH_2\text{-}Br$

h)

$$\begin{array}{ccc} & O & & O \\ & \| & & \| \\ CH_3\text{-}C\text{-}OCH_2CH_2\text{-}C\text{-}OCH_3 \end{array}$$

22. The following experimental method was used in the laboratory to determine the percentage of copper in a sample of impure copper metal :

Nitric acid was added to a sample of impure copper metal. The resulting copper (II) nitrate solution was reacted with an excess of potassium iodide to produce iodine. The iodine liberated was titrated with a solution of sodium thiosulphate of concentration 0.480 mol dm^3. The volume of sodium thiosulphate required was 23.7cm^3. Use the following equations in your calculations.

$Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI_{(s)} + I_2(aq)$

$I_2(aq) + 2S_2O_3{}^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$
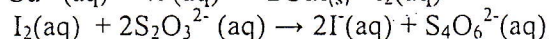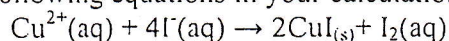
a) Calculate the number of mole of thiosulphate ions ($S_2O_3{}^{2-}$) in 23.7cm^3 of the solution. **2 marks**

b) Deduce the number of moles of Cu^{2+} in the copper (II) nitrate solution. **1 mark**

c) The mass of the impure copper was 0.900 g. Calculate the percentage of copper in the sample of impure copper. (Cu = 63.5) **3 marks**

d) Give the oxidation number and the electronic configuration of copper in CuI (Atomic number of Cu = 29). **2 marks**

e) Using equations and a simplified labeled diagram, describe how impure copper is purified by electrolysis. **5 marks**

f) Copper is widely used in electrical gadgets and also in alloys to make money coins. State two characteristics of copper which are related to the above uses. **2 marks**

Answer:

a) 1000cm^3 contain 0.48 moles of $S_2O_3{}^{2-}$

23.7 cm^3 contain $\dfrac{0.48 \times 23.7}{1000}$ = 0.011376 moles of $S_2O_3{}^{2-}$

b) 2 moles of $S_2O_3{}^{2-}$ react with 1 mole of I_2

0.011376 moles of $S_2O_3{}^{2-}$ react with $\dfrac{1 \times 0.011376}{2}$ = 0.005688 moles of I_2

But one mole of Iodine is produced by 1 mole of Cu^{2+}

0.005688 mol of I_2 are produced by $\dfrac{1 \times 0.005688}{1}$ of Cu^{2+} = 0.005688 moles

c) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

1 mole of Cu^{2+} produces 1 mole of Cu

0.005688 moles of Cu^{2+} produce 0.005688 moles of Cu.

Mass of pure copper = number of moles x molar mass of copper

Mass of pure copper = 0.005688 mol x 63.5g/mol = 0.36 g

Percentage purity = $\dfrac{pure\ mass}{impure\ mass}$ x 100 = $\dfrac{0.361 \times 100}{0.900}$ = 40.132%

d) The oxidation state is +1

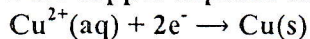Electronic configuration of Cu^+ is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

e) Electrolysis of aq. $CuSO_4$ using impure copper as anode and the fine strips pure copper as cathode.
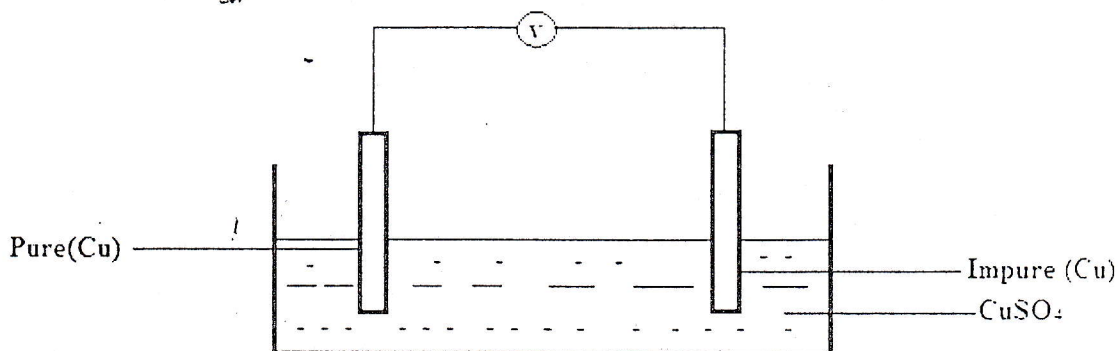
Anode dissolves and impurities drop to the bottom.

$Cu(s) \rightarrow Cu^{2+}(aq) + e^-$
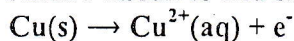
Pure copper deposits on the cathode

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

f) Copper has mobile electrons thus can conduct electricity and has thermal conductivity hence it is malleable, ductile and able to form alloys.

ADVENCED LEVEL CHEMISTRY NATIONAL EXAMINATION PAPER 2007

(Math-Physics)

Questions and their answers which are not in this paper, check from 2007-Biology chemistry questions and answers because they are the same.

Section A: Answer all questions. (55 marks)

12. The melting points of some group IV elements are given below.

CO_2 melting point ; = -78°c

SO_2 melting point = 1610°C

Describe the bonding in each oxide and how it relates to its melting point.**3 marks**

Answer;

CO_2 is a discrete molecule which is simple structure with weak van der waal's force of attraction which broken with less energy resulting to low boiling points.

SiO_2 has a giant covalent structure with strong covalent bonds which broken at high energy hence resulting high boiling points.

13. a) Write a balanced equation to represent the thermal decomposition of calcium nitrate, $Ca(NO_3)_2$ **2 marks**

b) How does the thermal stability of group II nitrates change down the group? Briefly explain this trend. **2 marks**

c) How does the thermal decomposition of KNO_3 differ from that of $Ca(NO_3)_2$. **1 mark**

Answer:

a) $2Ca(NO_3)_2 \rightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$

b) Trend: **Thermal stability increases down the group.**

Explanation: **Down the group the size of the cation increases and charge is constant**

By KAYIRANGA Serge. Chemistr...