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UACE chemistry 2023

PAPER 2

DURATION: 2 HOUR 30 MINUTES

Instruction to candidates

*Answer **five** questions including **three** questions from section A and any **two** from section B.*

Use equations where necessary to illustrate your answer.

Mathematical tables and squared papers are provided

Silent non-programmable scientific calculators may be used

Where necessary use the following:

(H = 1, C = 12, O = 16)

SECTION A (60MARKS)

Answer any three questions from this section

Any additional question answered will **not** be marked.

1. (a) Define the term homogeneous and heterogeneous systems (02marks)

(b) Ammonia can be formed according to the following equation

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g}); \Delta H = -92,4\text{kJmol}^{-1}$$
 - (i) Derive an expression to show the relationship between K_p and K_c . (03marks)
 - (ii) Explain how the position of equilibrium of the system can be affected by temperature and pressure. (06marks)

(c) The esterification of ethanol by ethanoic acid is reversible reaction.

 - (i) Write an equation and expression for the equilibrium constant for the reaction. (02marks)
 - (ii) When 1.0 mole of ethanoic acid and 1.0 mole of ethanol were reacted in a 1.0dm^3 vessel, 0.67moles of ethylethanoate and 0.67 moles of water were formed. Calculate the equilibrium constant at this temperature. (02marks)
 - (iii) 1.5 moles of ethanoic acid were reacted with 2.0 moles of ethanol under similar conditions as in (c)(ii). Calculate the mass of ethylethanoate formed. (05marks)

2. Compounds W, X, Y and Z with molecular formulae $\text{C}_3\text{H}_8\text{O}$, $\text{C}_3\text{H}_6\text{O}$, C_4H_6 and $\text{C}_2\text{H}_7\text{H}$ respectively, react as follows

W gives white fumes of hydrogen chloride with phosphorus (V) chloride,
 X gives an orange precipitates with 2, 4-dinitrophenylhydrazine,
 Y decolorizes bromine water slowly and
 Z dissolves in water to give alkaline solution

 - (a) For each of the compounds;
 - (i) Identify the functional group. (04marks)
 - (ii) Write the structural formulae of two possible isomers (04marks)
 - (b) Write a mechanism for the reaction of one of the isomers of X with 2,4-dinitrophenylhydrazine (06marks)
 - (c) Name one reagent that can be used to differentiate between the isomers of the following compounds, and in each case state what would be observed if each of the isomers was treated with the reagent you have named: (06marks)
 - (i) W
 - (ii) Z

3. (a) State what is meant by the term **eutectic mixture**. (01marks)

- (b) Table 1 shows how the melting points of the mixtures of copper and silver vary with composition

Table 1

Percentage of copper in the mixture	0	20	40	70	80	100
Melting point ($^{\circ}\text{C}$)	961	830	830	960	1000	1085

- (i) Draw a fully labeled diagram for the copper-silver system. (05marks)
- (ii) Determine the eutectic temperature and the composition of the eutectic mixture, (1 ½ marks)
- (c) Describe the changes that would take place when a liquid mixture of the above system containing 50% copper is cooled from 1000°C to 700°C . (4 ½ marks)
- (d) Equations for some half-cell reactions are shown below
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad E^{\circ} = +0.80\text{V}$
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}) \quad E^{\circ} = +0.34\text{V}$
- (i) Write an equation for overall cell reaction. (01mark)
- (ii) Calculate the E°_{cell} in (d)(i) (01mark)
- (iii) Calculate the Gibb's free energy of the cell and state whether the reaction is feasible or not. Give a reason for your answer. ($1F = 96500\text{C}$) (02marks)
- (e) Discuss the reaction of copper with sulphuric acid (04marks)
4. Cobalt, copper, iron and manganese are d-block elements.
- (a) State what is meant by the term **d-block element**. (01mark)
- (b) (i) Write the electronic configurations of copper, iron (II) ions and Manganese (II) ions. (1½ marks) (The atomic number of manganese, Iron and copper are 25, 26 and 29 respectively.)
 (ii) Explain why iron (II) ions are readily oxidized to iron (III) ions but manganese (II) ions are not readily oxidized to manganese (III) ions. (5½ marks)
- (c) (i) Write the formula of a compound or ion in which manganese is in oxidation state of +7 (01mark)
 (ii) Explain why it is possible for manganese to form compounds or ions in which manganese is in the +7 oxidation state (02 marks)
- (d) Explain the following observations
 (i) Manganese can be magnetized whereas copper cannot. (04 marks)
 (ii) Iron is used as a catalyst in many reactions (02 marks)
- (e) State three properties of cobalt which show that it is a transition element and give one example in each case. (03marks)

SECTION B (40MARKS)

Answer any two questions from this section

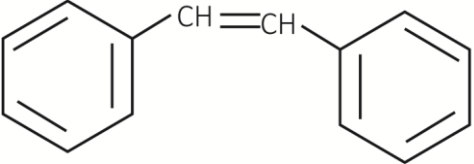
Any additional question(s) answered will not be marked

5. (a) Define each of the follow terms:
- Molar enthalpy of combustion (01marks)
 - Standard enthalpy of atomization. (01marks)
- (b) Describe an experiment that can be used to determine the molar enthalpy of combustion of ethanol (10 marks)
- (you answer should include treatment of results but not diagram; specific heat capacity of water = $4.2\text{Jg}^{-1}\text{K}^{-1}$)
- (c) Carbon burns in air to produce carbon monoxide and carbon dioxide. The enthalpy of combustion of carbon is -393kJmol^{-1} and that of carbon monoxide is -283kJmol^{-1} .
- Construct a Born Haber cycle to show reactions leading to the enthalpies of combustion of carbon, carbon monoxide and formation of carbon dioxide. (03marks)
 - Using the diagram in (c) (i), calculate the enthalpy of formation of carbon monoxide. (02marks)
- (d) How is the enthalpy change used to predict the feasibility of a reaction? (03marks)
6. (a) The E^0 for some half-cell reaction are shown below.
- $$\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq}) \quad E^0 = + 0.77\text{V}$$
- $$\text{Cl}_2(\text{aq}) + 2\text{e} \rightarrow 2\text{Cl}^-(\text{aq}) \quad E^0 = + 1.36\text{V}$$
- Explain what would be observed if to a solution containing iron (II) ions was added aqueous chlorine followed by dilute sodium hydroxide solution (06marks)
- (b) Explain what would be observed if excess potassium iodide was added to aqueous copper (II) Sulphate and a mixture shaken with hexane. (05 marks)
- (c) The color of dilute copper (II) Sulphate is blue but when excess concentrated hydrochloric acid is added to it, it changes to yellow. Explain (3 ½ marks)
- (d) Explain why chromium hydroxide reacts with both dilute hydrochloric acid and sodium hydroxide solutions. (5 ½ marks)

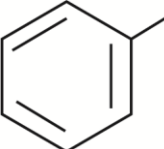
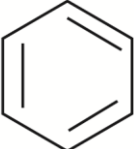
7. Write equations to show how each of the following compounds can be synthesized. Indicate reagents and conditions for the reactions in each case

(a) CH_4 from $\text{CH}_2 = \text{CH}_2$ (03marks)

(b) $\text{CH}_3\text{CH}_2\text{NH}_2$ from CH_3OH (05marks)

(c)  from benzene (04marks)

(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ from $\text{CH}_3\text{CH} = \text{CH}_2$ (4 ½ marks)

(e)  from  (3 ½ marks)

8. Fluorine, chlorine, bromine and iodine are elements in group (VII) of the periodic table

(a) Explain why fluorine shows different properties from the rest of the elements (2 ½ marks)

(b) With the exception of fluorine, describe a general method for preparing the elements in group (VII) in the laboratory and write equations for the reactions. (3 ½ marks)

(c) The lattice energies of silver halides are shown in table 2.

Table 2

Silver halide	Lattice energy (kJmol^{-1})
AgF	-943
AgCl	-890
AgBr	-877
AgI	-867

Explain the trend in the lattice energy (3 1/2marks)

(d) Explain why;

(i) Chlorine is more soluble in dilute sodium hydroxide solution than water (04marks)

(ii) Iodine is more solution in potassium iodide than in water (4 ½ marks)

(e) State what would be observed when alkaline iodide is added to butanone and write an equation for the reaction that takes place (02marks)

END

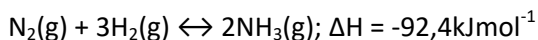
Proposed answers

1. (a) Define the term homogeneous and heterogeneous systems (02marks)

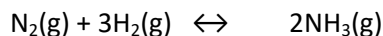
A homogeneous system has properties that are either the same throughout the system, or vary continuously from point to point with no discontinuities

A heterogeneous system consists of two or more homogeneous systems separated by physical boundaries or surfaces of discontinuity.

- (b) Ammonia can be formed according to the following equation



- (iii) Derive an expression to show the relationship between K_p and K_c . (03marks)



$$P = \frac{n}{V}RT$$

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$

From $PV = nRT$

$$P = \frac{n}{V}RT = [\text{gas}]RT$$

$$\begin{aligned} \Rightarrow K_p &= \frac{[\text{NH}_3(\text{g})]^2 (\text{RT})^2}{[\text{N}_2(\text{g})] \text{RT} \times [\text{H}_2(\text{g})]^3 [\text{RT}]^3} \\ &= \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} \times [\text{RT}]^{-2} \\ &= K_c (\text{RT})^{-2} \end{aligned}$$

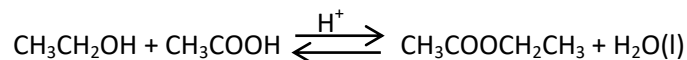
- (iv) Explain how the position of equilibrium of the system can be affected by temperature and pressure. (06marks)

Increasing pressure shift equilibrium from left to right to produce fewer moles of a gas to fit in a smaller volume to resist change in pressure while reducing pressure shifts the equilibrium from right to left producing more moles of gases

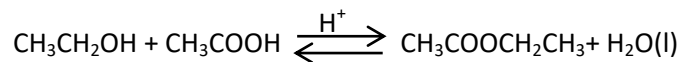
Increases temperature shifts equilibrium from right to left to absorb heat lower change in temperature.

- (c) The esterification of ethanol by ethanoic acid is reversible reaction.

- (i) Write an equation and expression for the equilibrium constant for the reaction. (02marks)



- (ii) When 1.0 mole of ethanoic acid and 1.0 mole of ethanol were reacted in a 1.0dm³ vessel, 0.67moles of ethylethanoate and 0.67 moles of water were formed. Calculate the equilibrium constant at this temperature. (02marks)

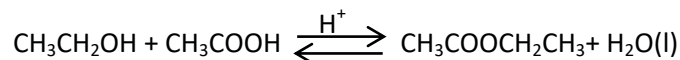


Initially	1.0	1.0	0	0
At eqbm.	0.33	0.33	0.67	0.67

$$K_c = \frac{0.67 \times 0.67}{0.33 \times 0.33} = 4$$

(iii) 1.5 moles of ethanoic acid were reacted with 2.0 moles of ethanol under similar conditions as in (c)(ii). Calculate the mass of ethylethanoate formed. (05marks)

Let x moles of ethylethanoate be formed



Initially	1.5	2.0	0	0
At eqbm.	1.5 - x	2.0 - x	x	x

$$K_c = \frac{x^2}{(1.5-x)(2-x)} = 4$$

$$x^2 = 4(1.5-x)(2-x)$$

$$3x^2 - 14x + 12 = 0$$

$$x = 1.13 \text{ or } 3.35$$

Since the concentration of ethylethanoate cannot be greater than the concentration of the reactants; moles of ethylethanoate produced = 1.13

Formula mass of ethylethanoate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) = 15 + 12 + 32 + 14 + 15 = 88

Mass of ethylethanoate produced = 1.13 x 88 = 99.44g

2. Compounds W, X, Y and Z with molecular formulae $\text{C}_3\text{H}_8\text{O}$, $\text{C}_3\text{H}_6\text{O}$, C_4H_6 and $\text{C}_2\text{H}_7\text{N}$ respectively, react as follows

W gives white fumes of hydrogen chloride with phosphorus (V) chloride,

X gives an orange precipitates with 2,4-dinitrophenylhydrazine,

Y decolorizes bromine water slowly and

Z dissolves in water to give alkaline solution

(e) For each of the compounds;

- (i) Identify the functional group. (04marks)

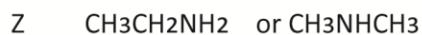
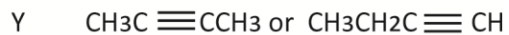
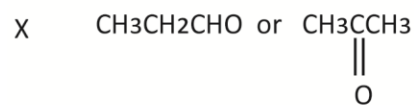
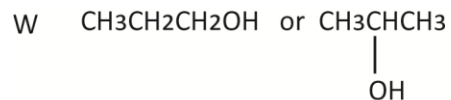
W is -OH or alcohol

X is -CO- or carbonyl group

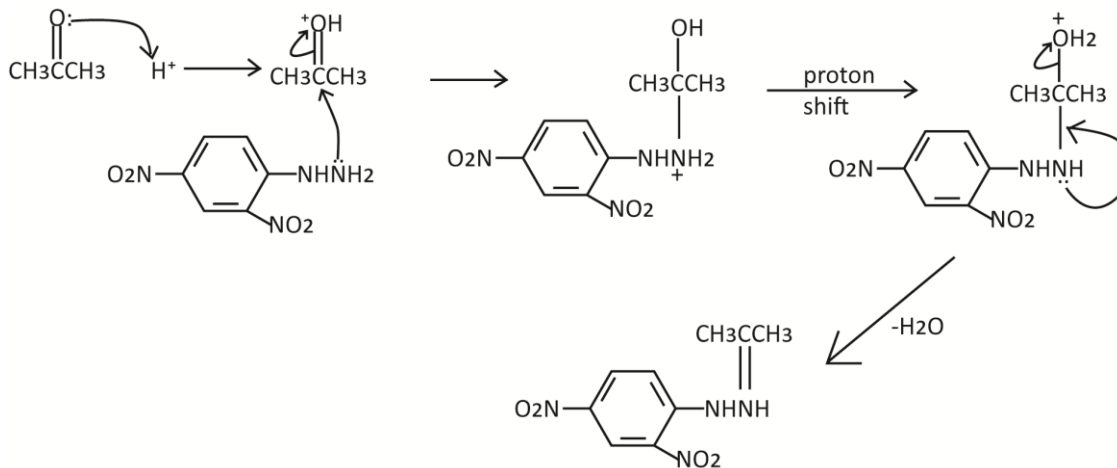
Y is $\text{C}\equiv\text{C}$ or alkyne

Z is - NH_2 or amine

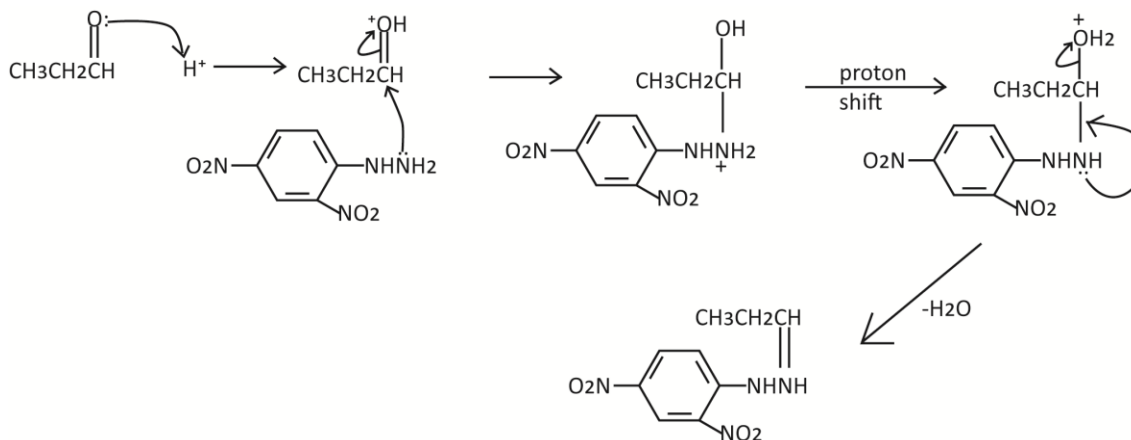
(ii) Write the structural formulae of two possible isomers (04marks)



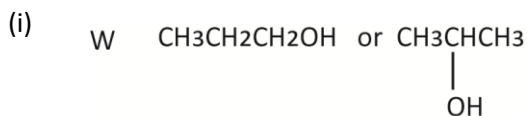
(f) Write a mechanism for the reaction of one of the isomers of X with 2,4-dinitrophenylhydrazine (06marks)



Or



(g) Name one reagent that can be used to differentiate between the isomers of the following compounds, and in each case state what would be observed if each of the isomers was treated with the reagent you have named: (06marks)

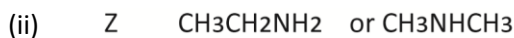


Reagent: anhydrous $\text{ZnCl}_2/\text{Conc HCl}$ (Lucas reagent)

Observation

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ no observable change

$\text{CH}_3\underset{\text{OH}}{\text{C}}\text{CH}_3$ turbidity in 5 minutes



Reagent: $\text{NaNO}_2/\text{HCl} < 5^\circ\text{C}$

Observations

$\text{CH}_3\text{CH}_2\text{NH}_2$ colorless solution with effervescence

CH_3NHCH_3 yellow oily ppt.

3. (a) State what is meant by the term **eutectic mixture**. (01marks)

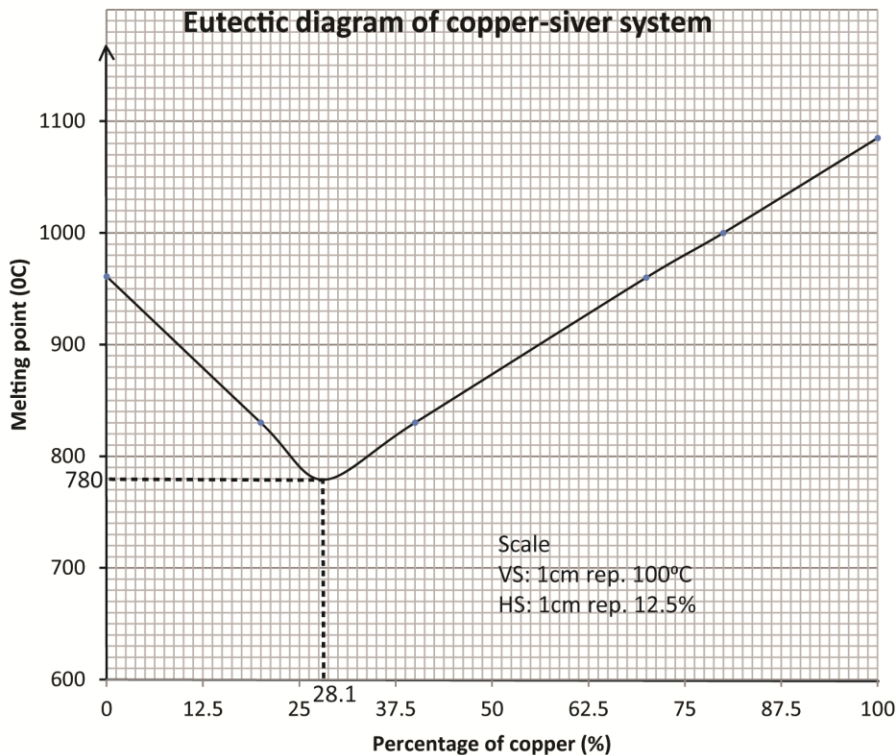
It is mixture which at constant pressure freezes at constant temperature to give a solid of the same composition.

(b) Table 1 shows how the melting points of the mixtures of copper and silver vary with composition

Table 1

Percentage of copper in the mixture	0	20	40	70	80	100
Melting point (°C)	961	830	830	960	1000	1085

(i) Draw a fully labeled diagram for the copper-silver system. (05marks)



- (ii) Determine the eutectic temperature and the composition of the eutectic mixture, (1 ½ marks)
 Eutectic temperature = 780°C
 Eutectic composition = 28.1% copper and 71.9% silver
- (c) Describe the changes that would take place when a liquid mixture of the above system containing 50% copper is cooled from 1000°C to 700°C. (4 ½ marks)
- Temperature drops from 1000°C to 770°C.
 - Between 870°C and 780°C copper solidifies out and its composition in solution falls to 28.1%
 - The mixture of constant 28.1% copper freezes at a constant temperature of 780°C.
 - The temperature of the solid falls from 780°C to 770°C.
- (d) Equations for some half-cell reactions are shown below
- $$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad E^{\circ} = +0.80\text{V}$$
- $$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}) \quad E^{\circ} = +0.34\text{V}$$
- (i) Write an equation for overall cell reaction. (01mark)
- $$\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$$
- (ii) Calculate the E°_{cell} in (d)(i) (01mark)
- $$E_{\text{cell}} = E_{\text{red}} - E_{\text{oxid}}$$
- $$= 0.80 - 0.34$$
- $$= 0.46\text{V}$$
- (iii) Calculate the Gibb's free energy of the cell and state whether the reaction is feasible or not. Give a reason for your answer. (1F = 96500C) (02marks)

$$\begin{aligned}\Delta G^{\circ} &= -nFE^{\circ} \\ &= -2 \times 96500 \times 0.46 \\ &= -88,780 \text{ J mol}^{-1}\end{aligned}$$

The reaction is feasible because Gibbs free energy is negative

(e) Discuss the reaction of copper with sulphuric acid (04marks)

Copper does not react with dilute sulphuric acid

It reacts with concentrated sulphuric acid to give copper sulphate, sulphur dioxide and water

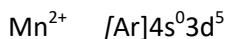
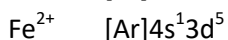


4. Cobalt, copper, iron and manganese are d-block elements.

(a) State what is meant by the term **d-block element**. (01mark)

d-block element has its outer electron configuration in d-orbital

(b) (i) Write the electronic configurations of copper, iron (II) ions and Manganese (II) ions. (1½ marks) (The atomic number of manganese, Iron and copper are 25, 26 and 29 respectively.)

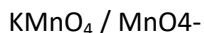


(ii) Explain why iron (II) ions are readily oxidized to iron (III) ions but manganese (II) ions are not readily oxidized to manganese (III) ions. (5½ marks)

iron (II) ions $\{[\text{Ar}]4s^13d^5\}$ has unstable electron configuration and is readily oxidized to iron (III) ions $\{[\text{Ar}] 3d^5\}$ with stable electron configuration of half d-orbital.

Manganese (II) ions $\{[\text{Ar}]3d^5\}$ has stable electron configuration of half d-orbital and is not readily oxidized to manganese (III) ions $\{[\text{Ar}]3d^4\}$ with stable electron configuration.

(c) (i) Write the formula of a compound or ion in which manganese is in oxidation state of +7 (01mark)



(ii) Explain why it is possible for manganese to form compounds or ions in which manganese is in the +7 oxidation state (02 marks)

Manganese has 7 electrons in outermost orbital which interact in chemical bonding

(d) Explain the following observations

(iii) Manganese can be magnetized whereas copper cannot. (04 marks)

Manganese has unpaired d-electrons while copper does not

(iv) Iron is used as a catalyst in many reactions (02 marks)

Iron has variable oxidation states exchange between which lowers the activation energy of reactions

(e) State three properties of cobalt which show that it is a transition element and give one example in each case. (03marks)

- Forms colored compounds; for instance Co^{2+} is pink
- Has variable oxidation states; +2, +3,
- Forms complexes, e.g. CoCl_4^{2-} .

SECTION B (40MARKS)

Answer any two questions from this section

Any additional question(s) answered will not be marked

5. (a) Define each of the follow terms:

(i) Molar enthalpy of combustion (01marks)

The standard molar enthalpy of combustion of a substance is the enthalpy changes when 1 mole of it is completely burn in oxygen under standard conditions.

(ii) Standard enthalpy of atomization. (01marks)

Standard enthalpy of atomization is enthalpy change when 1 mole of gaseous atoms is formed from an element under standard conditions of 1 atmosphere and 298K.

(b) Describe an experiment that can be used to determine the molar enthalpy of combustion of ethanol (10 marks)

(you answer should include treatment of results but not diagram; specific heat capacity of water = $4.2\text{Jg}^{-1}\text{K}^{-1}$)

m_1 g of ethanol is burnt completely and heat liberated used to raise the temperature of m_2 g water in a calorimeter of negligible heat capacity through $\theta^\circ\text{C}$.

Treatment of results

Heat produced by combusting fuel = heat gained by water

Heat gained by water = $m_2c\theta = 4.2m_2\theta$ joules

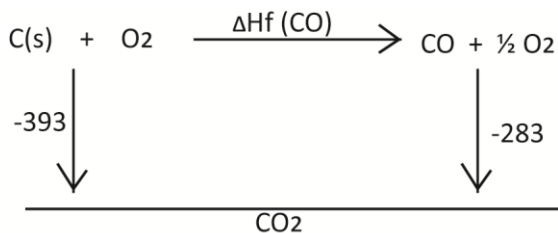
It implies that

m_1 g of ethanol produce = $4.2m_2\theta$ joules

Molecular ethanol = 46

46 g (of ethanol) produces = $\frac{46 \times 4.2m_2\theta}{m_1} = \frac{193.2m_2\theta}{m_1}$ joulesmol⁻¹

- (c) Carbon burns in air to produce carbon monoxide and carbon dioxide. The enthalpy of combustion of carbon is -393kJmol^{-1} and that of carbon monoxide is -283kJmol^{-1} .
- (i) Construct a Born Haber cycle to show reactions leading to the enthalpies of combustion of carbon, carbon monoxide and formation of carbon dioxide. (03marks)

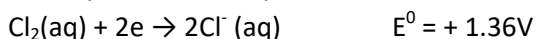
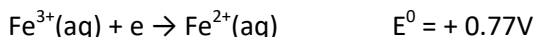


- (ii) Using the diagram in (c) (i), calculate the enthalpy of formation of carbon monoxide. (02marks)
- $$\Delta H_f(\text{CO}) + (-283) = -393$$
- $$\Delta H_f(\text{CO}) = -110\text{kJmol}^{-1}$$
- Therefore enthalpy of formation of carbon monoxide = -110kJmol^{-1}

- (d) How is the enthalpy change used to predict the feasibility of a reaction? (03marks)

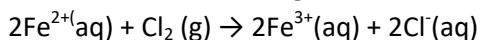
Feasible reactions have negative enthalpy change or they are exothermic.

6. (a) The E^0 for some half-cell reaction are shown below.

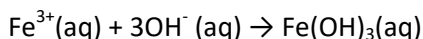


Explain what would be observed if to a solution containing iron (II) ions was added aqueous chlorine followed by dilute sodium hydroxide solution (06marks)

When chlorine is added to iron (II) ions solution, iron (II) ions are oxidized to Iron (III) ions and the solution turns from green to brown.

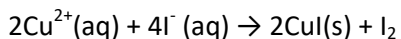


When sodium hydroxide is then added to the resultant solution, a brown ppt. is formed



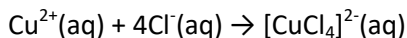
- (b) Explain what would be observed if excess potassium iodide was added to aqueous copper (II) Sulphate and a mixture shaken with hexane. (05 marks)

A white ppt. of CuI is formed and a brown hexane layer due to extraction of iodine from solution



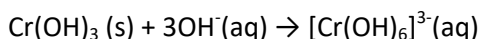
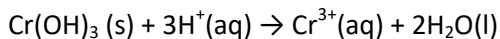
- (c) The color of dilute copper (II) Sulphate is blue but when excess concentrated hydrochloric acid is added to it, it changes to yellow. Explain (3 ½ marks)

Copper (II) ions react with excess concentrated hydrochloric acid to form a yellow tetrachlorocopper complex.



- (d) Explain why chromium hydroxide reacts with both dilute hydrochloric acid and sodium hydroxide solutions. (5 ½ marks)

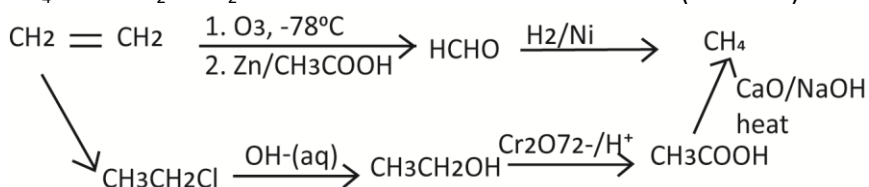
Chromium hydroxide is amphoteric thus, reacts with both acids and bases



7. Write equations to show how each of the following compounds can be synthesized. Indicate reagents and conditions for the reactions in each case

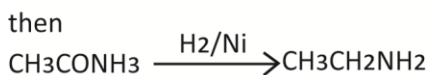
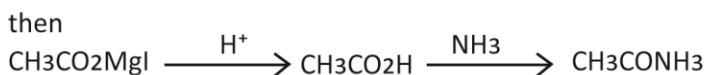
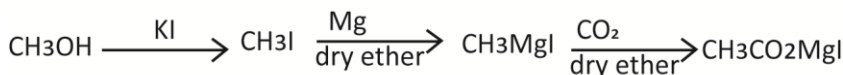
- (a) CH_4 from $\text{CH}_2 = \text{CH}_2$

(03marks)

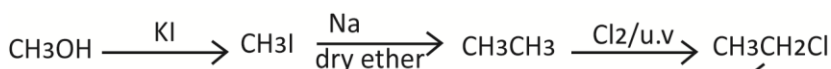


- (b) $\text{CH}_3\text{CH}_2\text{NH}_2$ from CH_3OH

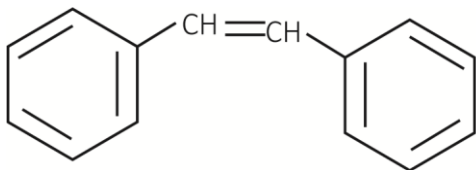
(05marks)



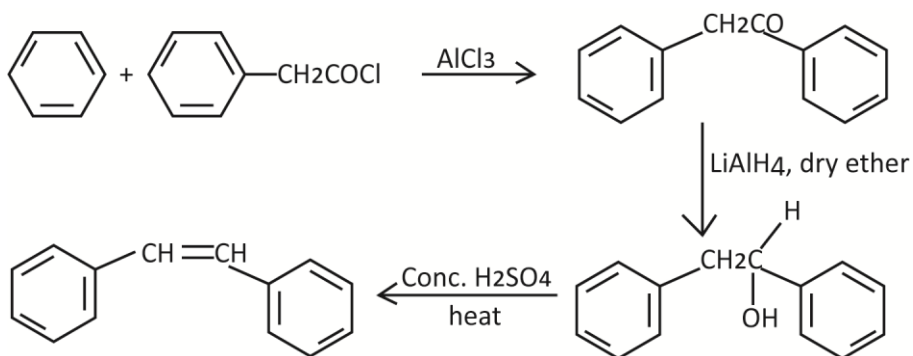
Or



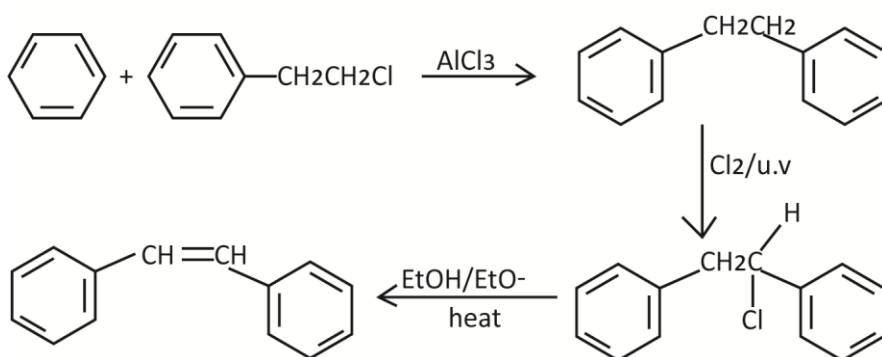
- (c)



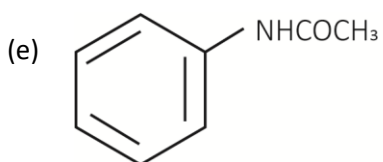
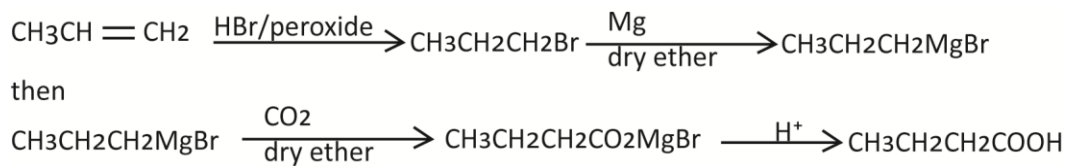
from benzene (04marks)



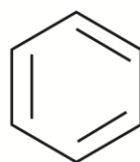
Or

(d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ from $\text{CH}_3\text{CH}=\text{CH}_2$

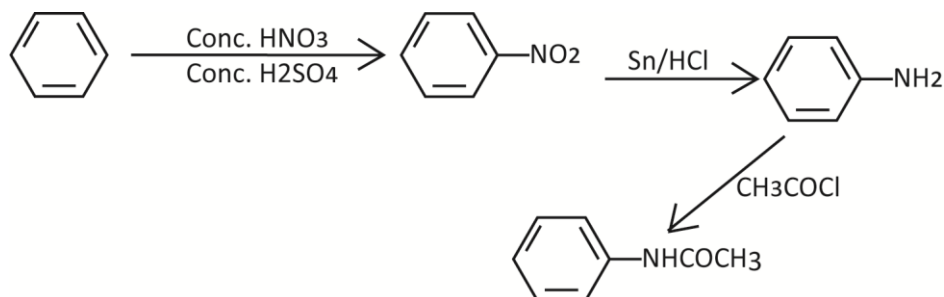
(4 ½ marks)



from



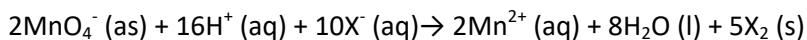
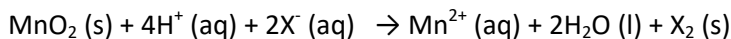
(3 ½ marks)



8. Fluorine, chlorine, bromine and iodine are elements in group (VII) of the periodic table
- (a) Explain why fluorine shows different properties from the rest of the elements (2 ½ marks)
- Fluorine has high electronegativity
 - Fluorine has small atomic radius
 - Fluorine has very low F-F bond

- (b) With the exception of fluorine, describe a general method for preparing the elements in group (VII) in the laboratory and write equations for the reactions. (3 ½ marks)

By oxidation of acidified solutions of the halides with manganese dioxide or potassium permanganate (VII).



(where X = Cl, Br, I)

- (c) The lattice energies of silver halides are shown in table 2.

Table 2

Silver halide	Lattice energy (kJmol ⁻¹)
AgF	-943
AgCl	-890
AgBr	-877
AgI	-867

Explain the trend in the lattice energy (3 ½ marks)

The lattice energy decreases in order AgF > AgCl > AgBr > AgI because of the decrease in the electronegativity of the halides in the order F > Cl > Br > I

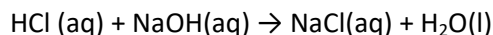
- (d) Explain why;

- (i) Chlorine is more soluble in dilute sodium hydroxide solution than water (04marks)

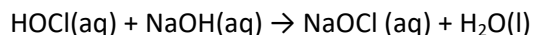
Chlorine dissolves in water to form a weak acid of HOCl and HCl



The acids react with sodium hydroxide to form salts which drives the equilibrium to the right.

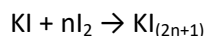


And



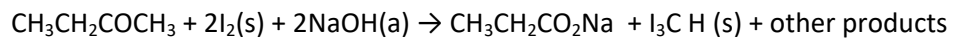
- (ii) Iodine is more solution in potassium iodide than in water (4 ½ marks)

Iodine is more soluble in KI than in water due to formation of soluble complexes with KI.



- (e) State what would be observed when alkaline iodide is added to butanone and write an equation for the reaction that takes place (02marks)

A yellow ppt. is formed



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Thanks

END