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## Scholarship 2015 Chemistry

9.30 a.m. Friday 27 November 2015

Time allowed: Three hours

Total marks: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

Pull out Resource Sheet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–20 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

**YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.**

Question	Mark
ONE	
TWO	
THREE	
FOUR	
<b>TOTAL</b>	/32

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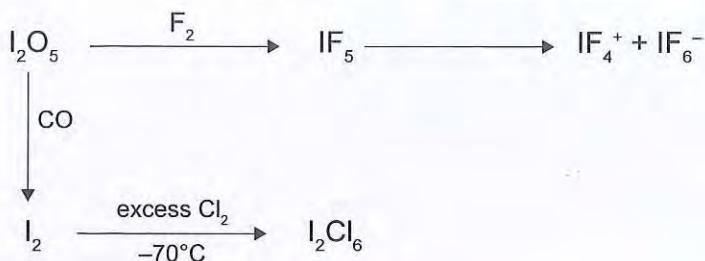
## QUESTION ONE

Almost all the elements of the periodic table form halides, which may be simple molecular compounds, ionic compounds or infinite atomic arrays. When interhalogen compounds form, there is often more than one possible product, depending on the temperature of the reaction or the relative proportions of the halogens.

- (a)  $\text{IF}_5$  can be formed by the action of  $\text{F}_2$  on diiodine pentoxide,  $\text{I}_2\text{O}_5$ .  $\text{IF}_5$  self-ionises to  $\text{IF}_4^+$  and  $\text{IF}_6^-$ .

$\text{I}_2$  can be extracted from  $\text{I}_2\text{O}_5$  with  $\text{CO}$ .

$\text{I}_2\text{Cl}_6$  is produced by reacting  $\text{I}_2$  with excess  $\text{Cl}_2$  at  $-70^\circ\text{C}$ .



- (i) Predict, with reasoning, the shape of the ions  $\text{IF}_4^+$  and  $\text{IF}_6^-$ .

Include a diagram and suggested bond angles in your answer.

$\text{IF}_4^+$   $7 \times 5 - 1 = 34$  electrons in total.

$\left[ \begin{array}{c} :\text{F}: \\ | \\ \text{I} \\ | \\ :\text{F}: \end{array} \right]^+$  If we have iodine in the centre with the 4 fluorines around

F regions of electrons hence the base shape is

$\text{F} \quad \begin{array}{c} \text{F} \quad \text{I} \quad \text{F} \\ / \quad \backslash \\ \text{I} \quad \text{C} \quad \text{I} \\ \backslash \quad / \\ \text{F} \quad \text{F} \end{array} \quad \text{F}$   $180^\circ$  a trigonal bipyramidal. Iodine can have 10 electrons

in its valence shell due to having empty d-orbitals to place the electrons. Since there is a lone pair, the shape is a see-saw with the angle between the top and bottom fluorine being  $180^\circ$  (vertical axis).

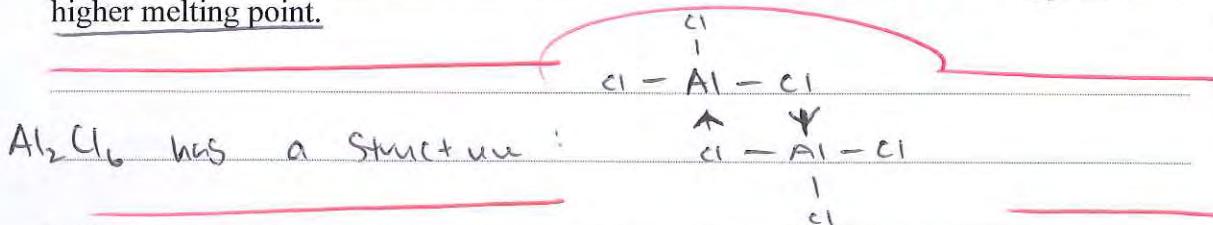
The angle between the fluorines on the horizontal axis is slightly less than  $120^\circ$  due to the lone pair repelling the bonding electrons. The angle between horizontal-planned and vertical-

planned fluorines is  $90^\circ$ .

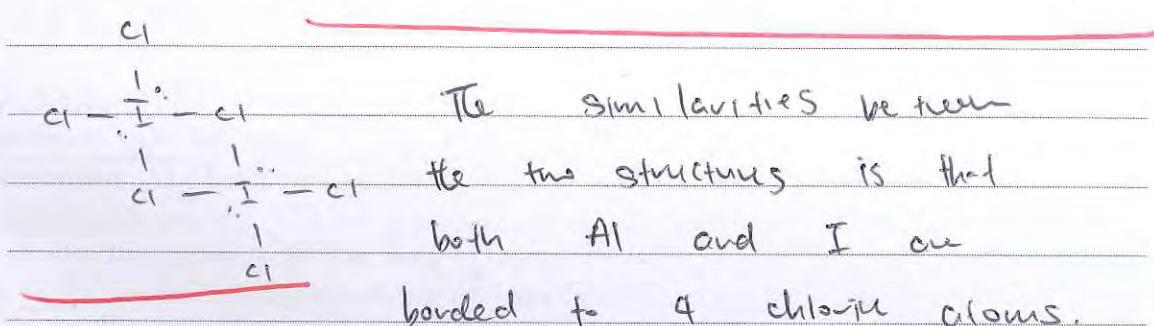
| See Page 18 |

- (ii)  $I_2Cl_6$  is a molecular compound. Molecules of  $I_2Cl_6$  are symmetrical with no I-I bonds.  $Al_2Cl_6$  is also a molecular compound, containing symmetrical molecules with no Al-Al bonds.

Compare and contrast the geometry around the I and Al atoms in these molecules, and predict, on the basis of the molecular structure, which of the compounds would have the higher melting point.



$I_2Cl_6$  also has a similar structure .f:



However, differences are that, in  $Al_2Cl_6$ , the four only 4 regions of electrons around can Al atom hence the shape will be tetrahedral with a bond angle of  $109^\circ$  apart between  $\text{Cl}-\text{Al}-\text{Cl}$  bonds. Around the I however, there are 6 regions of electrons so the basic shape will be octahedral. The lone pairs separate as far as possible to leave a square-planar shape between the I-Cl bonds resulting in a bond angle of  $90^\circ$ .

The molecular mass of  $I_2Cl_6$  is  $467 \text{ g mol}^{-1}$  (with 208 electrons). That of  $Al_2Cl_6$  is  $267 \text{ g mol}^{-1}$  (with 128 electrons). As  $I_2Cl_6$  has a greater electron cloud it will have stronger temporary dipoles and hence greater melting point. Furthermore, the whole shape of the  $I_2Cl_6$  molecule is

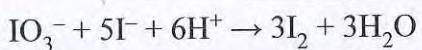
- (b) Diiodine pentoxide ( $I_2O_5$ ) can be used to determine quantitatively the concentration of carbon monoxide in air. The iodine resulting from the reaction of CO and  $I_2O_5$  is titrated with thiosulfate, and the end point is detected by the disappearance of the blue-black colour produced by starch and iodine.

Thiosulfate ions,  $S_2O_3^{2-}$ , are oxidised to tetrathionate ions,  $S_4O_6^{2-}$ , by iodine.

Thiosulfate solutions can be standardised using a primary standard, potassium iodate,  $KIO_3$ .

In order to standardise a thiosulfate solution, a standard solution of potassium iodate was prepared by dissolving 0.5466 g of  $KIO_3(s)$  in sufficient water to make 250.00 mL of solution.

10.00 mL of this  $KIO_3$  solution was pipetted into a conical flask, and 10 mL of 2 mol L<sup>-1</sup> sulfuric acid was added, followed by the slow addition of 10 mL of 0.25 mol L<sup>-1</sup> potassium iodide solution. A red-brown solution is formed. The equation for the reaction is:



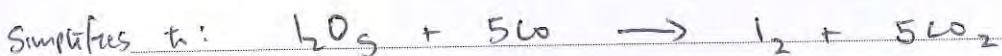
The iodine generated was then titrated against the unknown thiosulfate solution using a starch indicator. The average titre for three concordant results was 25.48 mL.

To determine the concentration of carbon monoxide in a sample of air, 23.20 L samples were passed through a series of cold traps to remove nitrogen oxides, water and other interfering compounds. The remaining gas was passed through a sample of acidified  $I_2O_5$ , which reacted quantitatively with the CO fraction of the gas to produce  $I_2$  and  $CO_2$ . The resulting iodine was flushed with nitrogen into a reaction flask, and titrated with the standardised sodium thiosulfate solution described above. The average titre for the samples tested was 17.23 mL.

Determine the concentration of CO in the air sample, in g L<sup>-1</sup>.

$$M(KIO_3) = 214.0 \text{ g mol}^{-1}$$

$$M(CO) = 28.00 \text{ g mol}^{-1}$$



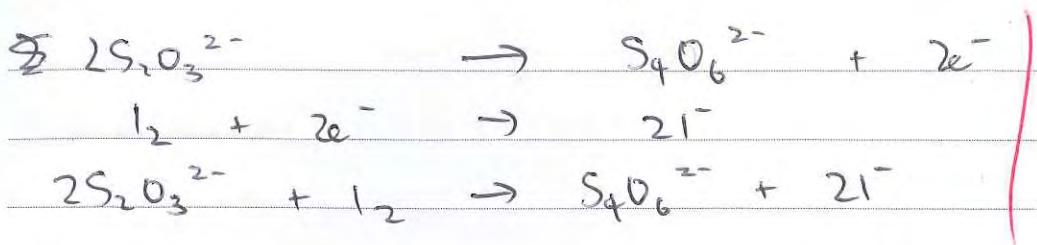
$$[KIO_3] = \left( \frac{0.5466}{214.1} \right) \div \left( \frac{250}{1000} \right) = 0.0102121 \text{ mol L}^{-1}$$

In 10mL,  $1.02121 \times 10^{-4}$  mol of  $I_2$ .

$$n(I_2 \text{ produced}) = 1.02121 \times 10^{-4}$$

In 10mL of 1<sup>-</sup>, 0.0025 mL 1<sup>-</sup>.  $I_2$  is the limiting reagent.

$$n(I_2 \text{ produced}) = 1.02121 \times 10^{-4} \times 3 = 3.063615 \times 10^{-4} \text{ mol}$$



$$n(S_2O_3^{2-} \text{ reacted}) = n(I_2) \times 2 = 6.12723 \times 10^{-4} \text{ mol}$$

$$c(S_2O_3^{2-}) = \frac{6.12723 \times 10^{-4}}{\frac{25.48}{1000}} = 0.0240472 \text{ mol L}^{-1}$$

Determining CO:

$$n(\pm S_2O_3^{2-} \text{ used}) = 0.0240472 \times \frac{17.23}{1000} = 4.143335 \times 10^{-4} \text{ mol}$$

$$n(I_2 \text{ reacted}) = \frac{1}{2} n(S_2O_3^{2-}) : 2.0716675 \times 10^{-4} \text{ mol}$$

$$n(I_2) = 5 \times n(I_2) = 1.03583 \times 10^{-3} \text{ mol}$$

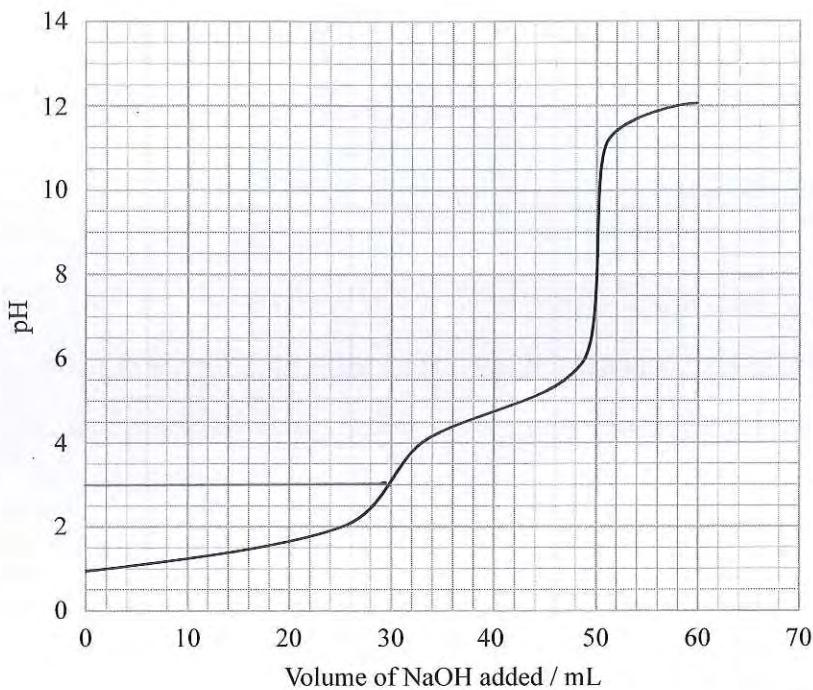
$$m(I_2) = 1.03583 \times 10^{-3} \times (12 + 16) = 0.029 \text{ g}$$

$$[I_2] = \frac{0.029}{23.2} = \underline{\underline{1.25 \times 10^{-3} \text{ g L}^{-1}}}$$

**QUESTION TWO**

A mixture of 15.00 mL of 0.200 mol L<sup>-1</sup> HCl and 10.00 mL of 0.200 mol L<sup>-1</sup> CH<sub>3</sub>COOH is titrated against 0.100 mol L<sup>-1</sup> NaOH solution.

The titration curve shows two equivalence points, one at 30.0 mL and one at 50.0 mL of added NaOH.



- (a) (i) Calculate the pH after the addition of 5 mL, 29 mL, and 50 mL of NaOH.

Comment on the validity of any assumptions made for the calculations.

Note: The pK<sub>a</sub> of the acid should be approximated from the graph.

15 mL of 0.2 mol L<sup>-1</sup> HCl

10 mL of 0.2 mol L<sup>-1</sup> CH<sub>3</sub>COOH

0.1 mol L<sup>-1</sup> NaOH

mol (HCl) :  $3 \times 10^{-3}$  mol

mol (CH<sub>3</sub>COOH) :  $2 \times 10^{-3}$  mol

Initial pH = 0.92

After the addition of 5 mL NaOH :

$$\frac{5}{1000} \times 0.1 = 5 \times 10^{-4} = n(\text{NaOH})$$

$$n(\text{HCl}) = 2.5 \times 10^{-3} \quad V = 30 \text{ mL}$$

$$[\text{H}^+] = 0.083 \quad \text{pH} = 1.079$$

When 50 mL of NaOH is added ( $5 \times 10^{-3}$  mol)

~~All~~ of the species present is  $\text{Cu}_3\text{W}_2\text{O}_2^-$  and  $\text{Cl}^-$ . The NaOH has neutralised  $\text{HCl}$  and  $\text{Cu}_3\text{W}_2\text{O}_2\text{H}$ .

At 30mL of NaOH, all of the HCl has been neutralised. The pH of 3 is due to  ~~$\text{Cu}_3\text{W}_2\text{O}_2\text{H}$~~ .

$$\frac{(10^{-3})^2}{\left(\frac{0.062}{55}\right)} = \frac{0.0275}{2.75 \times 10^{-5}} \quad \text{pK}_a(\text{Cu}_3\text{W}_2\text{O}_2) = 1.56$$

$$\text{pK}_a = 4.56$$

$$\text{pK}_a(\text{Cu}_3\text{W}_2\text{O}_2) = 4.56$$

∴ at 30mL of NaOH,  $[\text{Cu}_3\text{W}_2\text{O}_2^-] = 0.0267 \text{ mol L}^{-1}$

$$\text{pK}_b = 14 - 4.56 = 9.44$$

$$[\text{OH}^-] = \sqrt{0.0267 \times 10^{-9.44}} = 3.11 \times 10^{-6}$$

$$\text{pH} = 14 - 5.51 = 8.49. \quad (\text{at } 30\text{mL of NaOH})$$

( See page 19 )

- (ii) Account for the variation in pH, in terms of the species present in the solution, between the addition of 30 mL and 60 mL of NaOH solution.

Include balanced equations in your discussion.

At 30mL of NaOH, all of the HCl has been neutralised, so the only acid remaining is  $\text{Cu}_3\text{W}_2\text{O}_2\text{H}$ .



At 30mL, the pH is 3 and the  $[\text{Cu}_3\text{W}_2\text{O}_2\text{H}] = 0.0364 \text{ mol L}^{-1}$



The ethanolic acid is a weak acid & only partially dissociates.

As NaOH is added,

the  $\text{Cu}_3\text{W}_2\text{O}_2\text{H}$  gets converted

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to  $\text{CH}_3\text{CO}_2^-$ .



Thus ~~result~~ For a few mL after 30mL of NaOH, the pH rises rapidly as the conjugate base is formed.

When the amount of NaOH added is 40mL, half of the ethanoic acid has been converted to ethanate. Hence the  $\text{pH} = \text{pKa}$  which is 4.76. ~~between  $\text{pKa} \pm 1$  (3.56 to 5.56)~~

~~there~~ Normally between  $\text{pKa} \pm 1$  ~~there~~ is a buffer region.

However, the graph suggests more like  $\text{pKa} \pm 0.5$  as the buffer region in this case. Once between pH 4.06 and 5.06 the pH remains relatively similar due to ~~it~~ and is called a buffer region.

$$\text{At } \text{pH} = \text{pKa} \quad [\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2^-]$$

$\therefore$

$$\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{1}{K_a} \rightarrow [\text{H}^+] = K_a \rightarrow \text{pH} = \text{pKa}$$

In the ~~buffer~~ buffer region, the solution resists pH change as the conjugate base reacts with any acid added and the conjugate acid reacts with any base added to keep the pH similar.

As NaOH is continued to be added,  $\text{CH}_3\text{CO}_2\text{H}$  is converted to  $\text{CH}_3\text{CO}_2^-$ . When 50mL of NaOH added, all of the  $\text{CH}_3\text{CO}_2\text{H}$  is converted to  $\text{CH}_3\text{CO}_2^-$ . Hence the pH is determined by the concentration and ~~pKa~~  $\text{pK}_b$  of the conjugate base.

continued:

base which is 8.49 as shown in 2(a)i).

Afterwards, the ~~is~~ the extra NaOH added (until 60mL) doesn't react with  $\text{H}_3\text{O}^+$  to form water and hence determines the pH. The ~~final~~ pH approaches the pH of the NaOH solution but ~~is~~ will be less as the  $\text{OH}^-$  is diluted by the volume of the solution.

At 60mL of NaOH added:

$$10 \text{ mL of } 0.1 \text{ mol/L } \text{OH}^- = 1 \times 10^{-3} \text{ mol}$$
$$[\text{OH}^-] = \frac{1 \times 10^{-3}}{\frac{85}{1000}} = 0.01176$$

$$\text{pH} = 14 - 1.929 = 12.07$$

e2.

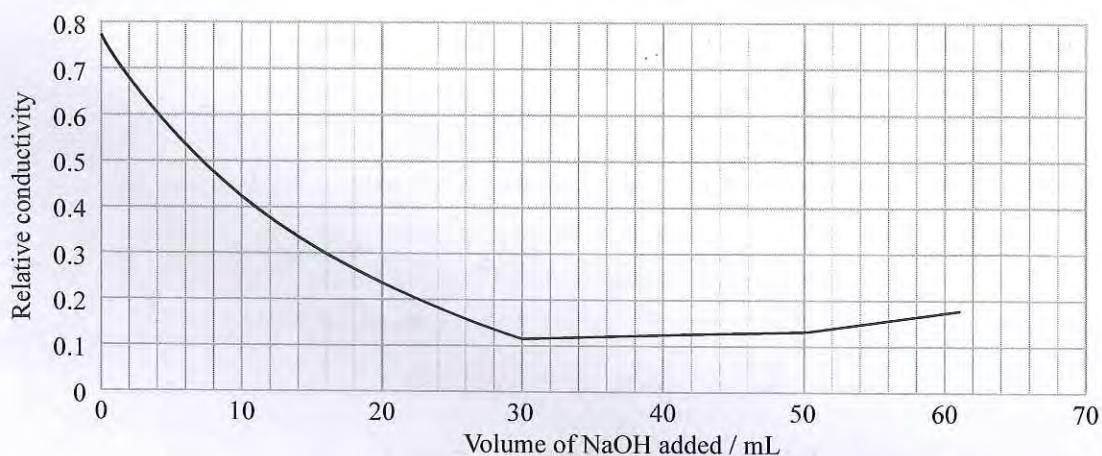
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- (b) Solutions of mixed strong and weak acids are often analysed using a conductometric titration. In a conductometric titration, the equivalence points are determined by monitoring changes in the conductivity of the solution. These changes depend on the concentration and the relative conductivities of the ions in solution.

The relative conductivities of some ionic species are shown in the table below.

Ionic species	Relative conductivity
$\text{Na}^+$ , $\text{Cl}^-$ , $\text{CH}_3\text{COO}^-$	1
$\text{OH}^-$	3
$\text{H}_3\text{O}^+$	5

The conductivity curve for the titration described in part (a) is given below.



Account for the shape of the conductivity curve as the volume of NaOH increases from 0 mL to 60 mL by commenting on why the conductivity decreases or increases in each phase of the plot. Link your answers to the relative concentrations of the species present in the solution in the reaction flask.

It can be assumed that the total conductivity in a solution is the sum of the conductivities of the ions present.

At 0 mL of NaOH added, there was  $3 \times 10^{-3}$  mol of  $\text{HCl}$  which dissociates to  $\text{H}_3\text{O}^+$ .  $\text{H}_3\text{O}^+$  has a very high conductivity hence the conductivity of the solution is high.  $\text{CH}_3\text{CO}_2\text{H}$  has no conductivity so doesn't contribute to the overall conductivity. As NaOH is added, the  $\text{H}_3\text{O}^+$  is converted to  $\text{H}_2\text{O}$  ( $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ ) which has no conductivity. Hence the overall conductivity decreases as //

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$\text{OH}^-$  is added (due to decreasing  $\text{Cu}_3\text{O}_2^{+}$ ).

The slight curve in conductivity between 0 and 30 mL of NaOH can be attributed to the increase  $\uparrow$  in  $\text{pH}$  which causes  $\text{Cu}_3\text{O}_2\text{H}$  to dissociate more to  $\text{Cu}_3\text{O}_2^-$  which has a conductivity of 1. Hence the rate of decrease in conductivity decreases as pH increases (which is proportional to  $\text{OH}^-$  added).

At 30 mL of NaOH added, all of the  $\text{Cu}_3\text{O}_2^+$  has been converted to  $\text{H}_2\text{O}$ . Hence the total overall conductivity of around 0.11 is due to the presence of  $\text{Na}^+$ ,  $\text{Cl}^-$  and the small amount of  $\text{Cu}_3\text{O}_2^-$  present.

These species all have a relative conductivity of 1 hence the overall conductivity is low.

As NaOH is added from 30 mL to 50 mL, the increase in conductivity is due to the increasing concentration of  $\text{Na}^+$  and  $\text{Cu}_3\text{O}_2^-$ .

The  $\text{OH}^-$  added converts  $\text{Cu}_3\text{O}_2\text{H}$  to  $\text{Cu}_3\text{O}_2^-$ .

→ There is only a small increase as the conductivity of  $\text{Cu}_3\text{O}_2^-$  and  $\text{Na}^+$  is 1.

At 50 mL of NaOH added, all of the  $\text{Cu}_3\text{O}_2\text{H}$  is converted to  $\text{Cu}_3\text{O}_2^-$  and as there is no acid to neutralise  $\text{OH}^-$ .



Hence from 50 mL to 60 mL, the increase in overall conductivity is due to the increase in  $\text{OH}^-$  ions. The rise is steeper than from 30 mL to 50 mL as  $\text{OH}^-$  has a greater concentration.

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2b) continued :

conductivity of 3 compared to that of  
 ~~$Mg^{2+}$~~  which is 1.  $Na^+$  is also  
added between some of rows and boats.

But the difference is steepness is due to  
the difference in conductivity between  $Mg^{2+}$   
and  $Na^+$  as  $Na^+$  is added in both

## QUESTION THREE

- (a) A solution is made by adding 42.69 g of a mixture of the aldehydes methanal, HCHO, and ethanal, CH<sub>3</sub>CHO, to 76.59 g of water.

Addition of excess ammoniacal silver nitrate solution to 2.18 g of the mixed aldehyde solution results in the precipitation of 4.64 g of silver metal.

Determine, by carrying out the appropriate calculation, the mass, in g, of each of the aldehydes, methanal, and ethanal, in the mixture.

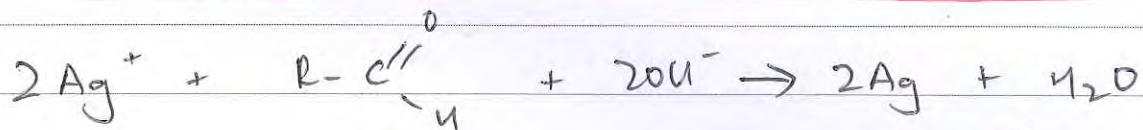
$$M(\text{Ag}) = 107.9 \text{ g mol}^{-1} \quad M(\text{HCHO}) = 30.03 \text{ g mol}^{-1} \quad M(\text{CH}_3\text{CHO}) = 44.05 \text{ g mol}^{-1}$$

$$42.69 + 76.59 = 119.28 \text{ g}$$

$$\text{Aldehyde mixture \%} = \frac{42.69}{119.28} = 35.78974\% \quad 0.35$$

$$\text{Water \%} = \frac{76.59}{119.28} = 64.21026\%$$

In 2.18 g, there is 0.780216 g of aldehyde mixture.



This is Tollen's reaction.

$$n(\text{Ag}) = 4.64 / 107.9 = 0.043 \text{ mol}$$

$$n(\text{aldehyde}) = \frac{1}{2} n(\text{Ag}) = 0.0215 \text{ mol}$$

$$n(\text{ethanal}) + n(\text{methanal}) = 0.0215 \text{ mol}$$

$$\text{let } x = n(\text{ethanal})$$

$$x \times 44.05 + (0.0215 - x) \times 30.03 = 0.780216 \text{ g}$$

$$44.05x + 6.6456867 - 30.03x = 0.780216 \text{ g}$$

$$14.02x = 0.13453 \quad 9.66 \times 10^{-3} \text{ mol}$$

$$x = 9.596 \times 10^{-3} \text{ mol} = 9.596$$

$$m(\text{ethanal}) \rightarrow m(\text{ethanal in } 2.18 \text{ g}) = 0.423 \text{ g}$$

continued :

✓

mass (methanol)

$$\text{mass (methanol in } 2.18\text{ g)} = 0.780216 - 0.423 = 0.357\text{ g}$$

$$\% \text{ ethanol} = \frac{0.423}{0.780} = 54.23\%$$

$$\% \text{ methanol} = \frac{0.357}{0.780} = 45.77\%$$

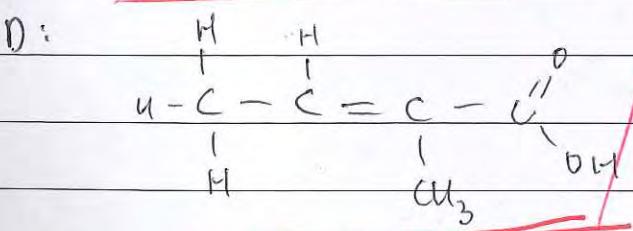
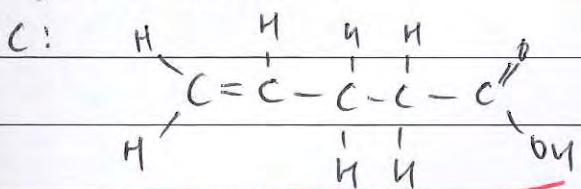
In the 42.69 g mixture:

mass (ethanol)

$$\text{mass (ethanol)} = 42.69 \times 0.5423 = 23.15\text{ g}$$

$$\text{mass (methanol)} = 42.69 \times 0.4577 = 19.54\text{ g}$$

3b) continued :



(b)

**INFORMATION**

The reaction of an alkene with acidified potassium permanganate results in the breaking of the double bond. The reaction product depends on the number of hydrogen atoms present on the double-bonded carbon atoms. If there are no hydrogen atoms, a ketone is formed; if one hydrogen atom is present, a carboxylic acid is formed; if there are two hydrogen atoms present, carbon dioxide gas is produced. Oxalic acid (ethanedioic acid) also reacts with warmed, acidified, potassium permanganate to give two mole equivalents of  $\text{CO}_2$  gas.

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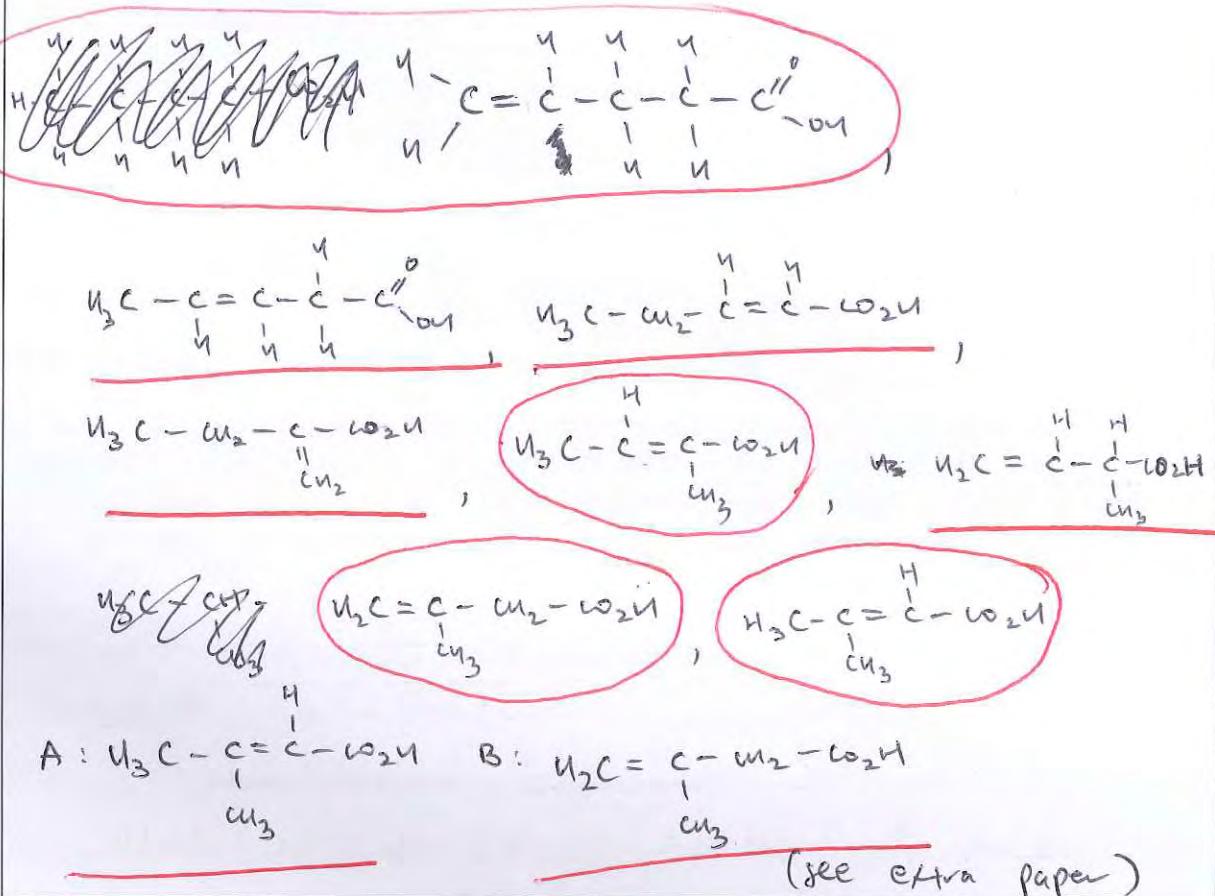
*Acetate*  
 Four compounds, A, B, C, and D, have the molecular formula  $\text{C}_5\text{H}_8\text{O}_2$ . They all turn moist blue litmus paper red. Spectral data indicate that none of the compounds is cyclic. Each compound is reacted with warmed, acidified, potassium permanganate and, for some compounds or reaction products, further reactions are carried out as outlined below.

- Compound A, on reaction with warmed, acidified, potassium permanganate, produces Compound E,  $\text{C}_3\text{H}_6\text{O}$ , and a colourless gas is observed. Compound E does not react with sodium carbonate solution. Compound A also reacts with water in the presence of an acid catalyst to give Compound F,  $\text{C}_5\text{H}_{10}\text{O}_3$ , as the major product. Compound F is not optically active, and does not react with acidified potassium dichromate.
- Compound B, on reaction with warmed, acidified, potassium permanganate, produces a colourless solution containing Compound G, and a colourless gas is observed. Compound B reacts with water in the presence of an acid catalyst to give Compound F as the major product.
- Compound C, on reaction with warmed, acidified, potassium permanganate, produces a colourless solution containing Compound H. Bubbles of gas are also observed. Compound H does not exist as enantiomers. One mole of Compound H reacts with 2 mol equivalents of a standard solution of sodium hydroxide. Compound C reacts with water in the presence of an acid catalyst to give Compound I,  $\text{C}_5\text{H}_{10}\text{O}_3$ , as the major product. Compound I exists as enantiomers, and in the presence of concentrated sulfuric acid, produces Compound J,  $\text{C}_5\text{H}_8\text{O}_2$ . Compound J is neutral to litmus paper, and does not rapidly decolourise bromine water.
- Compound D reacts with warmed acidified potassium permanganate to give a colourless solution containing two compounds, K and L. Titration of this mixture requires 2 mol equivalents of a standard solution of sodium hydroxide. Compound K distils first from the mixture of compounds. Neither compound reacts further with Tollens' reagent.

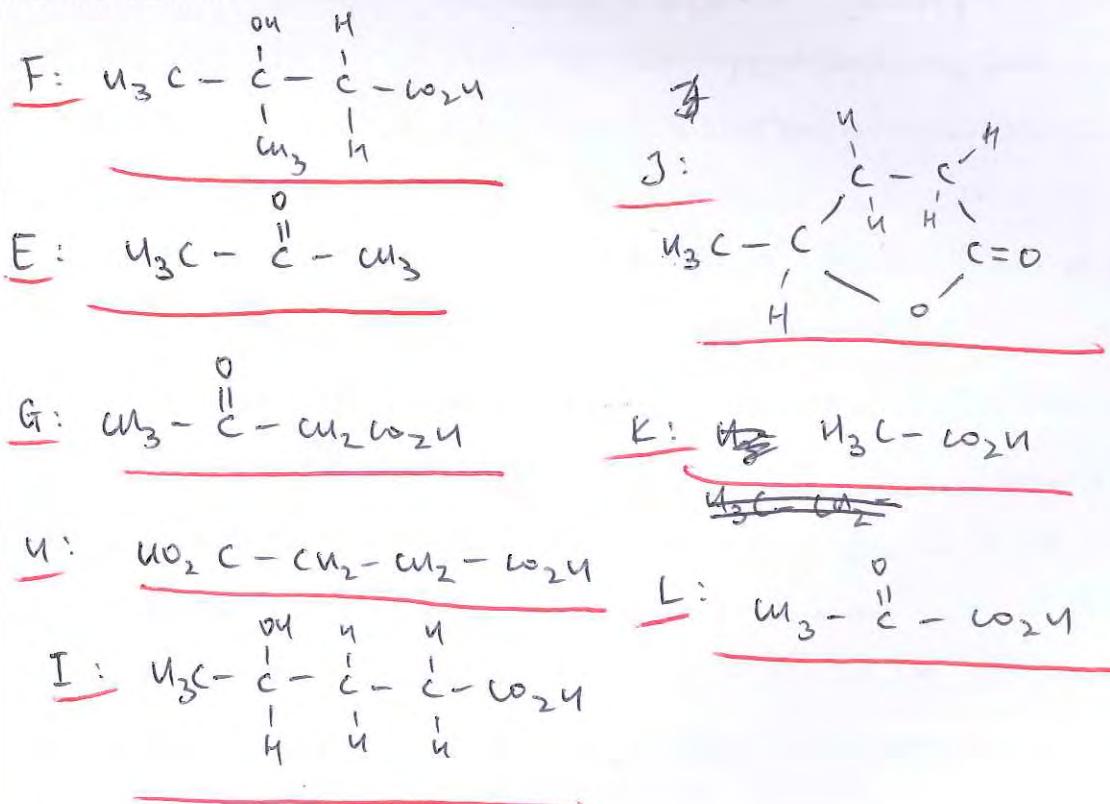
Draw the structures of ALL the possible isomers of  $\text{C}_5\text{H}_8\text{O}_2$  that turn moist blue litmus paper red, and select the best match for Compounds A, B, C, and D.

Draw structures for all the reaction products E to L. Ignore any geometric isomer possibilities.

*Extra pages for planning/working are provided at the back of this booklet.*

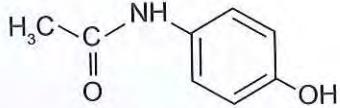
Isomers of  $C_5H_8O_2$ :

Structures E to L:

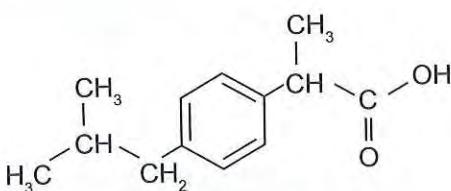


## QUESTION FOUR

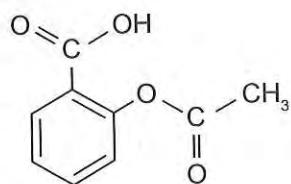
- (a) The structural formulae for the molecules of three common pain relievers found on the market today are shown below.



Paracetamol



Ibuprofen



Aspirin

In order for the pain relievers to have their physiological effect, they need to be carried in the bloodstream. Blood is mostly water. Of the three pain relievers, paracetamol is the most soluble at  $13 \text{ mg mL}^{-1}$ , aspirin is slightly less at  $3 \text{ mg mL}^{-1}$ , while ibuprofen has limited solubility at  $0.021 \text{ mg mL}^{-1}$ . The solubility of aspirin and ibuprofen can be increased by supplying each as its calcium salt.

Account for the trend in the solubilities of the pain relievers described above.

$$M(\text{paracetamol}) = 151.2 \text{ g mol}^{-1}, M(\text{ibuprofen}) = 206.3 \text{ g mol}^{-1}, M(\text{aspirin}) = 180.2 \text{ g mol}^{-1}$$

Water molecules form hydrogen bonds with each other. For the substances to be soluble, the bonds between water and the pain reliever ~~substances~~ compound must be strong ~~so~~ so that ~~enough~~ enough energy ~~can be~~ released the bonds between water molecules can be broken (with the energy released when water - pain relieve bond is formed). As water bonds by hydrogen bonding, compounds that can hydrogen bond are more soluble. The groups present in the ~~substances~~ compounds given that can form hydrogen bonds are the ~~amide, ester, and keto~~ carboxylic acid, ~~and~~ ketone groups, and alcohols. Furthermore, solubility is decreased if ~~there~~ ~~is~~ there are a lot of regions non-polar regions are present in the compound. Paracetamol is the most soluble at  $13 \text{ mg mL}^{-1}$  as it has an alcohol group, a ketone group and an ~~amide~~.

amide group (ketone is part of amide group).

As the for the alcohol, it has two lone pairs and hence can form 2 hydrogen bonds with water molecules. ( $\text{H}_3\text{O}^+ \cdots \text{O}=\text{N}-\text{H}$ ). Also, due to the high electro negativity of the oxygen, the oxygen is  $\delta^-$  and the hydrogen is  $\delta^+$ .

The hydrogen can also form hydrogen bonds with the lone pairs on the ~~the~~ oxygen on the water molecules hence one -OH group forms 3 hydrogen bonds. The -N=O on the amide is also polar. The Nitrogen is electronegative hence the hydrogen is  $\delta^+$  (delta positive) and can form hydrogen bonds with water. Also, the oxygen on the carbonyl part of the amide group is  $\delta^-$  due to <sup>oxygen</sup> being electronegative.

The lone pair on the  $\text{C}=\text{O}$  can form hydrogen bonds with the hydrogens in water ( $\text{H}_3\text{O}^+ \cdots \text{O}=\text{C}-\text{H}$ ). Also, paracetamol has ~~the~~ the lowest number of non-polar groups (and hence mass  $\rightarrow$  its low) so overall solubility is high.

Aspirin is the second most soluble at  $3\text{ mg mL}^{-1}$ .

Aspirin has an ester group and a carboxylic acid group. The ~~oxygen~~-OH group on the carboxylic acid group can form hydrogen bonds as described above. However, due to the  $\text{C}=\text{O}$  group, the ~~the~~ lone pairs on the  $-\text{O}-\text{H}$  group are drawn out making them less available.

Hence, the -OH group on a carboxylic acid don't form hydrogen bonds as strong as an

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4a) continued:

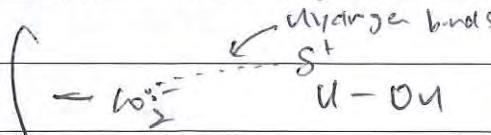
~~alcohol group group.~~

Also, the  $\text{C=O}$  on the carboxylic acid can also form hydrogen bonds. The oxygen on the ester group also form hydrogen bonds. Aspirin is less soluble than paracetamol as the alcohol group on paracetamol ~~is a single~~ forms stronger hydrogen bonds, and Aspirin also has more carbons  $\therefore$  greater non-polar region.

b) For that isoprofer, there is only 1 group able to form hydrogen bonds which is the - $\text{HO}_2\text{C}$  group. The rest of the molecule consists of carbons that are non-polar and cannot form hydrogen bonds. ~~These~~ These non-polar ~~water~~ regions are repelled by water and hence overall ~~isoprofer~~ is very insoluble.

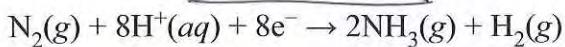
Solubility of paracetamol:  $0.086 \text{ g/L}$ Solubility of aspirin:  $0.0166 \text{ g/L}$ Solubility of isoprofer:  $0.000102 \text{ g/L}$ 

Adding  $(\text{CaCO}_3)$  makes all the  $-\text{HO}_2\text{C}$  groups on isoprofer and aspirin into  $-\text{HO}_2\text{C}^+$ . Due to the ~~water~~ ions and the charges, they are able to form much stronger ~~hydrogen~~ bonds with water and hence are more soluble.



- (b) Nitrogenase is an enzyme present in rhizobia (soil bacteria) that live in the root nodules of legumes. Nitrogenase catalyses the reduction of dinitrogen, N<sub>2</sub>, to two equivalents of ammonia, with additional production of one equivalent of dihydrogen, H<sub>2</sub>.

A balanced half-equation for this reaction is:



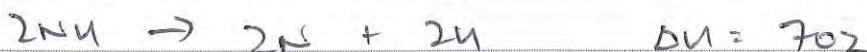
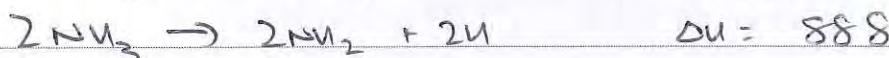
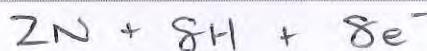
Discuss the enthalpy and entropy of this half-reaction, with reference to the data below.

Bond Dissociation Reaction	Bond Dissociation Enthalpy (kJ mol <sup>-1</sup> )
N <sub>2</sub> → 2N	945
H <sub>2</sub> → 2H	436
NH <sub>3</sub> → NH <sub>2</sub> + H	444
NH <sub>2</sub> → NH + H	385
NH → N + H	351

Atom	First Ionisation Enthalpy (kJ mol <sup>-1</sup> )
H	1312

Ion	**Hydration Enthalpy (kJ mol <sup>-1</sup> )
H <sup>+</sup> (g)	-1150

\*\* Hydration enthalpy is the enthalpy change when 1 mole of gaseous ions dissolve in sufficient water to give an infinitely dilute solution. It is a measure of the energy released when attractions are set up between positive or negative ions and water molecules.



Answering

The enthalpy change of the reaction is :

~~Gross~~

$$(94S - 10496 + 9200) - (888 + 770 + 702 + 436) \\ = -3147 \text{ kJ mol}^{-1}$$

The total enthalpy change of this half reaction is ~~not~~ exothermic indicating energy is released. (energy released when forming the bonds of the ~~prod~~ products is greater than the energy used when breaking the bonds of the reagents).

As the enthalpy change is exothermic, it suggests a high chance of being spontaneous.

Regarding the ~~entrop~~ entropy, there ~~is~~ is only 1 mol of gas on the left compared to 3 mols of gas on the right. The left side has 8 mols of ~~c~~ aqueous  $\text{U}^+$  which has a low entropy than a gas. So overall, the entropy of the right side is greater than the left (this difference in entropy would be small however as there are 9 mols of compound on the left (excluding  $e^-$ ) and 3 on the right).

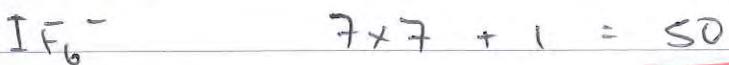
Since  $\text{U}^+$  is aqueous and low entropy we would include that the right has greater entropy but only by a small amount.) Since the entropy ~~change~~ increases, we ~~can~~ can conclude that the reaction is likely to be spontaneous.

(see extra page)

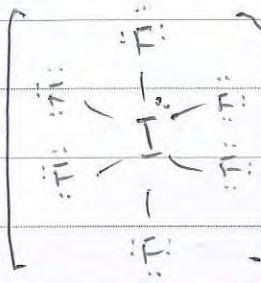
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1(a)i) (continued):

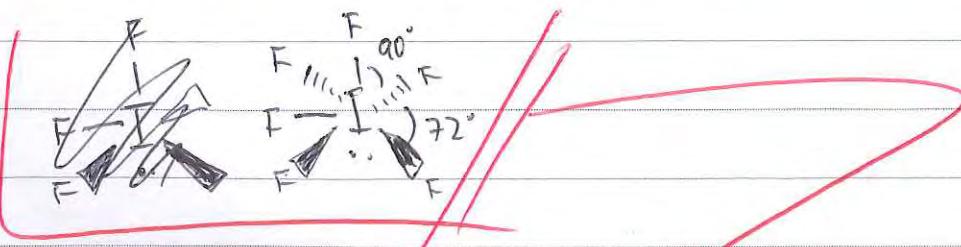


50 electrons in total.



With iodine central, we can place the fluorines around the central iodine. With a total of 50 electrons, all the fluorines have a full valence shell (of 8 electrons) with iodine having 14 electrons. It is able to have more than 8 due to having ~~of~~ empty d orbitals into which electrons can be placed.

There are 7 regions of electrons so it is likely to have a base shape ~~of~~ of a pentagon-based bipyramidal. And so the single lone pair will occupy one of the ~~the~~ positions on the vertical axis. Hence the angle between the ~~the~~ fluorines on the horizontal axis is  $72^\circ$ . The angle between the fluorine on the horizontal axis and the vertical axis will be  $90^\circ$ .



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1(a)iii)

continued:

a planar hence it has a whereas the molecule of  $\text{Al}_2\text{Cl}_6$  is much more bent and has a low surface area due to having a tetrahedral shape around the Al. Hence  $\text{I}_2\text{Cl}_6$  has a greater surface area meaning it is more likely to ~~be~~ form temporary dipoles ~~to~~ and therefore have a higher melting point. whilst  $\text{Al}_2\text{Cl}_6$  is polar due to the they all cancel out due to the tetrahedral shape hence permanent dipoles don't contribute to the total inter-molecular force in  $\text{Al}_2\text{Cl}_6$ .

2(a)ii)

continued:

At 29 ml NaOH ( $2.9 \times 10^{-3}$  mol)

$$\text{The } n(\text{UCl}) = 0.1 \times 10^{-3}, \quad n(\text{Cu}_2\text{Cl}_2\text{O}_2\text{H}) = 2 \times 10^{-3}$$

$$[\text{UCl}] = \frac{0.1 \times 10^{-3}}{\frac{(25+29)}{1000}} = 1.85 \times 10^{-3}$$

$$\text{pH} = 2.73 \cancel{\text{at}}$$

because UCl is a strong acid it ~~is~~ fully dissociates and hence affects towards pH.

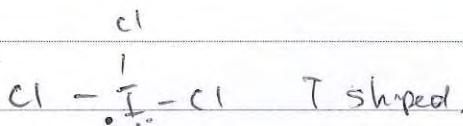
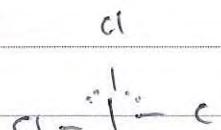
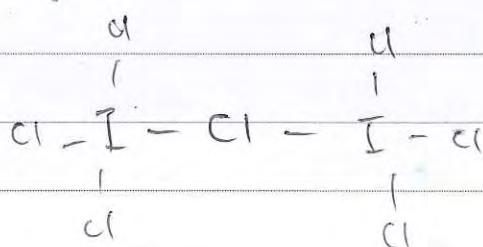
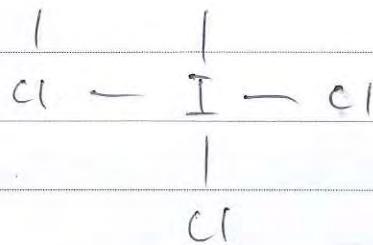
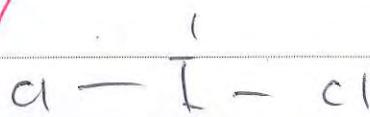
Using  $\text{Cu}_2\text{Cl}_2\text{O}_2\text{H}$  we would get a pH of 3 which is incorrect. Since  $K_a$  of  $\text{Cu}_2\text{Cl}_2\text{O}_2\text{H}$

is high i. it doesn't contribute significantly to the pH.

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Sh) Spontaneous reactions have negative Gibbs free energy.  $\Delta G = \Delta H - T\Delta S$ . Since  $\Delta H$  is negative and  $\Delta S$  is positive we can conclude that the reaction will be spontaneous (or have an  $E^\circ$  value that is at a large positive value). However, since an enzyme is needed for this reaction, we can conclude that this half reaction has a high activation energy, seems that a catalyst is needed. ~~To break~~ (To break the strong N≡N bond) Entropy is the measure of disorder and so gases have greater entropy than liquids and aqueous compounds. Spontaneous reactions are most likely ones that result in an increase in entropy.