NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **15 September 2017**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A

Answer **all** questions. Marks [60]

Section B

Answer **one** question. Marks [20]

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **XX** printed pages (including this page).

Section A

Answer **all** the questions in this section.

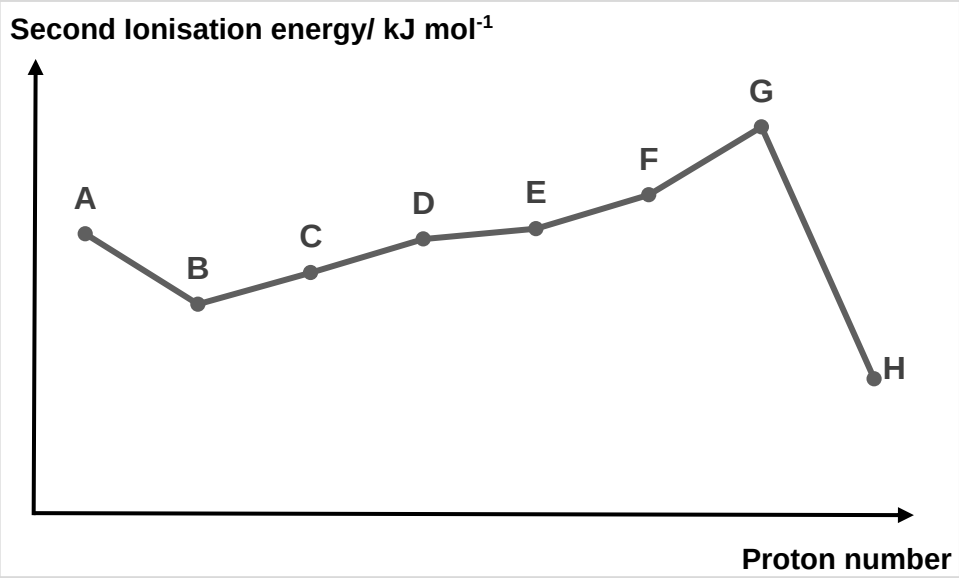
1 (a) Iodine is a lustrous purple-black solid at standard conditions that sublimes readily to form a violet gas.

(i) Give the equation that represents the *second ionisation energy* of *iodine*. [1]

$I^+(g) \rightarrow I^{2+}(g) + e^-$ [1]

$\Delta H > 0$ is not required since this is not a definition question.

(ii) The graph below shows the second ionisation energies of eight elements with consecutive atomic number. [2]



Which of the above elements, **A** to **H**, is iodine? Explain your answer.

Element **E**. [1] The sharp drop from **G** to **H** indicates that **G** is from Group 1 where the second ionisation energy involves the removal of an electron from the **inner** principal **quantum shell**, which is nearer to the nucleus, requiring more energy. [1] Hence Element **E** is in Group 17 and is iodine.

(iii) Explain the trend in second ionisation energies from elements **A** to **G**, including the irregularity for element **B**. [4]

The second IE generally increases from **A** to **G** because from **A** to **G**, there is an increase in proton number and hence nuclear charge while shielding effect is almost constant as electrons are added to the same quantum shell. [1] Hence effective nuclear charge increases and the attraction for the outermost electron becomes increasingly stronger. [1] More and more energy is required to remove the strongly attracted valence electron as we move across the period.

Second IE of **B** is lower than that of **A** because the electron is removed from the valence 5p subshell which is further away from the nucleus compared to the 5s subshell in **A**. [1] It also experiences additional screening effect by the two 5s. These factors outweigh the effect of increase in nuclear charge from A to B, resulting in a weaker attraction by the nucleus.[1]
Less energy is required to remove the outermost electron in **B** than that in **A**.

(iv) Suggest, with reason, which of the above elements, **A** to **H**, can form an amphoteric oxide. [2]

Hence, write an equation to show the reaction of this amphoteric oxide with hydrochloric acid. (You are not required to provide the identity of the element in the equation.)

Element **A** has amphoteric oxide since it is in Group **13** [1] and its oxide would have both ionic and covalent character.

$\mathbf{A}_2O_3 + 6HCl \rightarrow 2ACl_3 + 3H_2O$ [1]

or

$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O$ [1]

No ecf from part (ii)

(b) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to $[H^+]$.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial $[H_2O_2(aq)]$ / mol dm^{-3}	Initial $[I^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.020	0.040	1.2×10^{-4}
2	0.020	0.050	1.5×10^{-4}
3	0.050	0.040	3.0×10^{-4}
4	0.020	0.500	1.5×10^{-3}
5	0.050	1.000	7.5×10^{-3}

(i) What is understood by the terms *order of reaction* and *half-life*. [2]

The order of reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation. [1]

Or Let the Rate = $k[A]^m[B]^n$, where m and n are the order of reaction wrt [A] and [B] respectively. [1]

Half-life, $t_{½}$, is the time taken for the reactant concentration to decrease to half of its original value.[1]

(ii) Determine the order of the reaction with respect to $[H_2O_2]$ and $[I^-]$ and hence suggest the units of the rate constant of this reaction. [3]

Let rate= $k[H_2O_2(aq)]^m[I^-(aq)]^n$

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ constant

$$\frac{1.2x10^{-4}}{1.5x10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.020)^m(0.050)^n}$$ (or use inspection method)

n = 1

Rate of reaction is 1st order with respect to [I^-(aq)] [1]

Compare experiments 1 & 3, keeping [I^-(aq)] constant

$$\frac{1.2x10^{-4}}{3.0x10^{-4}} = \frac{k(0.020)^m(0.040)^n}{k(0.050)^m(0.040)^n}$$ (or use comparing method)

m = 1

Rate of reaction is 1st order with respect to [H_2O_2(aq)] [1]

Hence,

rate= k[H_2O_2(aq)][I^-(aq)]

units of k = mol^{-1} dm^3 min^{-1} [1]

(iii) The half-life of hydrogen peroxide in experiment 4 was 9.24 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]

For Expt 4 and 5, since [I^-(aq)] >> [H_2O_2(aq)], [I^-(aq)] is approximately constant.

Thus, rate = k'[H_2O_2(aq)] (a pseudo first order reaction) where

k' = k[I^-(aq)]

$$t_{1/2} = = \frac{\ln 2}{k'} = \frac{\ln 2}{k[I^-]}$$

$t_{1/2}$ of H_2O_2 in experiment 4 = 9.24 min (for [I^-(aq)] = 0.500 mol dm^{-3})

$t_{1/2}$ of H_2O_2 in experiment 5 = **4.62 min** (for [I^-(aq)] = 1.00 mol dm^{-3}) [1]

To investigate the rate of the above reaction, a teacher suggested titrating the iodine formed with sodium thiosulfate solution at specified time intervals.

(iv) Write an equation for the reaction between iodine and thiosulfate. [1]

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

State symbols not required but penalized when wrong ones are provided.

(v) Suggest how the reaction can be quenched at specified time intervals. [1]

The reaction can be quenched by:

- adding $NaOH/NaHCO_3/Na_2CO_3$ to remove the $H^+(aq)$
- sudden cooling of the reaction mixture
- sudden dilution through the addition of large volume of water

any of the above method [1]

(vi) With reference to the *Data Booklet*, explain why hydrochloric acid is not a suitable acid used for the reaction between hydrogen peroxide and iodide. [2]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^\ominus = +1.36\ V$

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \quad E^\ominus = +1.77\ V$

$E^\ominus_{cell} = +1.77 - 1.36 = +0.41\ V$ [1 for quoting and calculating]

H_2O_2 can oxidise chloride to chlorine[1] while it itself is reduced to H_2O. Hence, the oxidation of iodide may not be complete.

[Total:19]

2 Metals have been used widely since ancient times.

(a) An electrochemical cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes.

The relevant half reactions are:

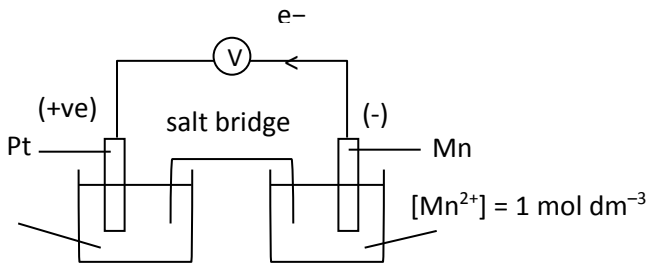
HSO_4^- (aq) + $3H^+$(aq) + $2e^-$ $\rightleftharpoons$ H_2SO_3(aq) + H_2O $E^\ominus$ = +0.17 V

Mn^{2+}(aq) + $2e^-$ $\rightleftharpoons$ Mn(s) $E^\ominus$ = –1.18 V

(i) Draw a fully labelled diagram of the above electrochemical cell to measure the cell potential under standard conditions, indicating clearly the direction of the electron flow in the external circuit. [3]

T= 298 K

$[H^+] = [HSO_4^-] = [H_2SO_3]$ = 1 mol dm^{-3}



[1] – e^- flow

[1] – voltmeter, salt bridge (can BOD from diagram) + Mn and Pt electrodes

[1] – label all the solutions (HSO_4^- , H_2SO_3, H^+) & 1 mol dm^{-3} and temperature

(ii) Write a balanced equation for the reaction that would take place if the electrodes of the cell were connected together by an external circuit. [1]

$Mn + HSO_4^- + 3H^+ \rightarrow Mn^{2+} + H_2SO_3 + H_2O$ [1]

(iii) Calculate the standard cell potential for this cell [1]

$E^\ominus_{cell}$ = + 0.17 – (−1.18) = + 1.35 V [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the cell above. [1]

$\Delta G^{\ominus} = -nFE^{\ominus}$, where n = 2 electrons transferred

$= -2 \times 96500 \times (+1.35) = -260550$ J mol^{-1} $= -261$ kJ mol^{-1} [1]

(v) Suggest, with reasons, what happens to the $E^{\ominus}_{cell}$ when the following are done to the electrochemical cell above. [4]

1) The pH of the HSO_4^- /H_2SO_3 half−cell is increased.

2) A solution of sodium hydroxide to the Mn^{2+} /Mn half−cell.

HSO_4^- (aq) + $3H^+$ (aq) + $2e^-$ $\rightleftharpoons$ H_2SO_3 (aq) + H_2O

1. When [H^+] is reduced /pH increases , equilibrium position shifts to the left to replenish the [H^+], hence $E^{\theta}_{cathode}$ becomes less positive [1]. As E_{cell} = E (cathode) - E (anode), and E (cathode) become less positive, hence, the E_{cell} of the cell becomes less positive. [1]

Mn^{2+}(aq) + $2e^-$ $\rightleftharpoons$ Mn(s) E_{anode}

2. When NaOH is added, $Mn(OH)_2$ (s) will be formed and [Mn^{2+}] will decrease. Position of equilibrium will shift left to increase [Mn^{2+}], hence E_{anode} becomes more negative.[1] E_{cell} becomes more positive. [1]

(b) In an electrolytic cell, a current of 0.250 A is passed through a concentrated solution of a chloride of iron, producing iron metal and gas, **Y**.

(i) Write the equation for the half-reaction take occurs at the anode. [1]

$2\ Cl^- \rightarrow Cl_2 + 2e^-$ [1]

(ii) When the cell operates for 2 hours, 0.521 g of iron is deposited at one of the electrodes. Determine the formula of the chloride of iron in the original solution. [2]

Charge = 0.25 x 2 x 60 x 60 = 1800 C

Amt of electrons = 1800/96500 = 0.0187 mol

Amt of iron formed= 0.521/55.8 = 0.009336 mol

Mole ratio of electrons taken in: iron deposited = 0.0187: 0.009336 ≈2:1 [1]

Formula of iron chloride = $FeCl_2$ [1]

(iii) Write a balanced equation for the overall reaction that occurs in the cell. [1]

$Fe^{2+} + 2Cl^- \rightarrow Cl_2 + Fe$ [1]

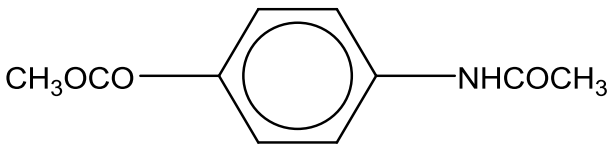
(iv) Calculate the current that would produce the gas **Y** from the solution at a rate of 2.50 g per hour. [2]

Amt of chlorine gas liberated per hour = 2.5/ 71 = 0.03521 mol

Charge required per hour= 2 x 96500 x 0.03521 = 6795 C[1]

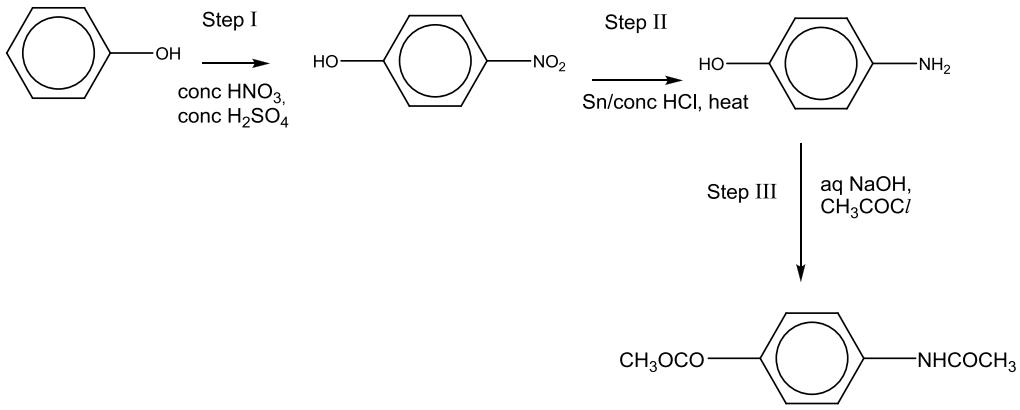
Current = Charge / time = 6795 /(60 x 60) = 1.89 A [1]

(c) Metals are also used as catalysts in organic synthesis. The derivative of acetaminophene is investigated for the treatment of headaches.



Derivative of acetaminophene

(i) A student suggested a flawed synthesis of the derivative of acetaminophene starting from phenol. Identify and explain the error in each step. [3]



Step I: Only dilute HNO_3 instead of conc H_2SO_4 and conc HNO_3 need to be used as phenol is more reactive than benzene/ or –OH group is an activating substituent.

OR conc H_2SO_4 and conc HNO_3 will produce a tri-substituted product.

OR the reagents will result in multiple substituted products.

[1]

Step II: HCl will neutralise phenylamine and form a salt instead

OR There is need to perform careful neutralisation of NaOH to remove the proton from phenylammonium ion.

[1]

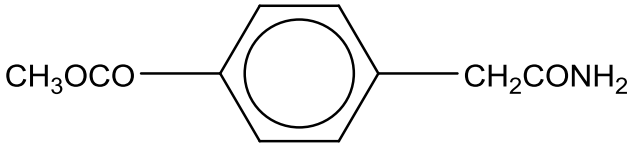
Step III: Acid chloride will hydrolyse to give CH_3CO_2H and HCl which will be neutralised by aq NaOH, hence not able to react with the phenol and phenylamine.

OR Acid chloride will react with aq NaOH, hence not able to react with the phenol and phenylamine.

OR Neutralisation takes place between acid chloride and NaOH and hence condensation will not take place.

[1]

(ii) Compound **Z** is an isomer of the derivative of acetaminophene. Suggest a simple chemical test to distinguish between the derivative of acetaminophene and compound **Z**. [2]



compound **Z**

Test: aq NaOH, heat. [1]

Observations: Compound **Z** produces pungent NH_3 gas that turns **moist** red litmus paper blue but derivative of acetaminophene does not produce pungent NH_3 that turns moist red litmus paper blue.

OR

Compound **Z** gives pungent NH_3 that forms white fumes with concentrated HCl but derivative of acetaminophene does not give pungent NH_3 that forms white fumes with concentrated HCl [1]

[Total:21]

3 **(a)** Blood obtains its colour from its respiratory proteins which occur as octahedral metal complexes. It is different in different organisms.

Protein	Source	Metal per subunit	De-oxygenated colour	Oxygenated colour
Haemoglobin	Mammals, birds, fish, reptiles, insects	1 Fe	red-purple	red

Haemocyanin	mollusks, crustaceans, spiders	2 Cu	colourless	blue

(i) Explain why oxygenated haemoglobin and haemocyanin are coloured. [3]

The oxygenated haemoglobin and haemocyanin contains transition metals ion in the centre of the complexes.
In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the presence of ligand such as oxygen, the 3d orbitals split into 2 groups with a small energy gap between them. [1]
An electron from the lower energy d orbital absorbs energy from the visible region (or visible spectrum) of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed and get promoted to a higher energy d orbital.[1]
The light energy not absorbed is reflected and observed as colour of its the oxygenated blood. (Or the colour observed is complementary to the colour absorbed.) [1]

(ii) Using the Cartesian axes, like those shown in Figure 3.1, draw **fully labelled** diagrams of the following. [2]

- One of the d-orbitals at the lower energy level in an octahedral complex. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in an octahdral complex. Label this diagram “upper”.

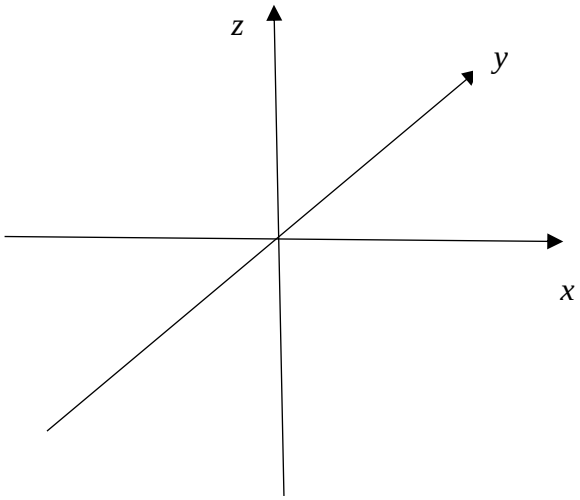
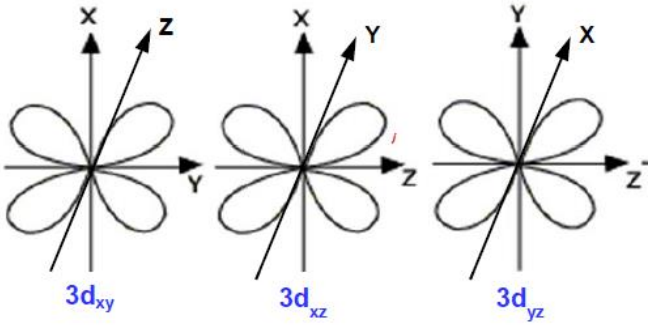
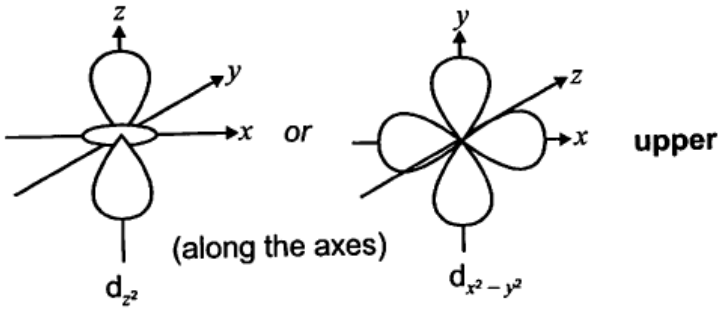


Figure 3.1

Lower: any



Upper: either



Students can change the position of x, y and z axes in their respective diagrams. Orbitals must be labelled.

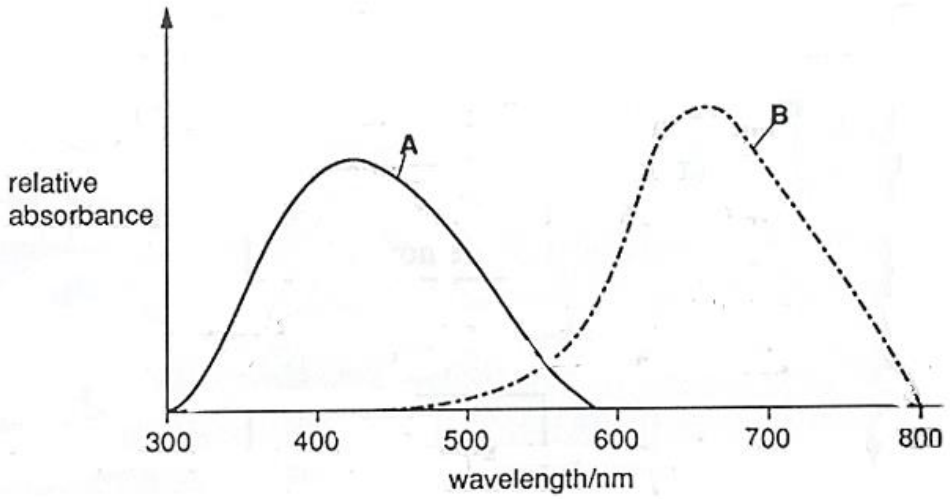
(iii) Explain why the splitting of the d subshell occurs in an octahedral complex using your answer in **(a)(ii)**. [2]

The electrons in the upper d orbitals are pointing towards the lone pairs of electrons on the ligands,[1] hence will be repelled by them and resulting in higher energy. [1]

OR

In octahedral complexes, the lone pairs of electrons on the 6 ligands approach the central ion along the axes. Thus, the energy of an electron in either the upper d orbitals ($3d_{x^2-y^2}$ or $3d_{z^2}$) experience greater electronic repulsion, resulting in higher energy. [1]

(b) Oxygenated haemoglobin and haemocyanin were analysed and the absorption spectrum was observed.



Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	**Yellow**	560 – 580
Blue	400 – 490	**Orange**	580 – 620
Green	490 – 560	**Red**	620 – 800

(i) Which graph represents the absorption spectrum of oxygenated haemocyanin? Explain your answer. [2]

Graph B. [1] The wavelength not absorbed is ~380 – 470 nm. This means that the light reflected is blue/violet (accept indigo). [1]

(ii) Which oxygenated blood (haemoglobin or haemocyanin) has a larger energy gap between the d subshells after splitting? Explain your answer. [2]

Haemoglobin has a larger energy gap [1] as $\Delta E = hc/\lambda$, haemoglobin absorbs as a lower wavelength, hence it has a larger energy gap. [1]

(iii) The deoxygenated haemocyanin has a Cu^+ central ion. State the electronic configuration of Cu^+. Hence, suggest why the deoxygenated haemocyanin is colourless? [2]

Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]
Cu^+ has a fully filled 3d-subshell or fully filled 3d-orbitals. Hence, d-d transition of electrons from the lower d-orbitals to the higher orbital is not possible. [1] Hence, no energy from the visible region of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed or reflected.

(c) Carbon monoxide, chlorine and phosgene are the best known toxic gases. Many of these gases are assigned an NFPA 704 health rating of 4 (may be lethal) or 3 (may cause serious or permanent injury).

Toxic Gas	Chemical formula	Colour	Odour	NFPA 704 Health Rating
carbon monoxide	CO	colourless	No	3

chlorine	Cl_2	green	Yes	4
phosgene	CCl_2O	colourless	No	4

(i) Describe, in terms of bonding, what happens when carbon monoxide is absorbed in the human blood and hence, explain why it is given a NFPA 704 health rating of 3. [2]

Carbon monoxide (CO) forms dative bond with Fe^{2+} in haemoglobin more readily than O_2 molecule (since Fe-CO bond is stronger than Fe-O_2 bond); or

CO displaces the oxygen in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).

Or

Being a stronger ligand, carbon monoxide, CO can be bonded less reversibly to the metal centre. [1]

$$HbO_2 + CO \rightarrow HbCO + O_2$$

This consequently cuts down the supply of oxygen to the body and so, accounts for the toxic nature of carbon monoxide, resulting in suffocation. This could lead to serious or permanent injury or death. [1]

Hence, it is given a NFPA 704 health rating of 3.

(ii) Chlorine was widely used as a chemical warfare in World War I. However, it was replaced by phosgene as a more effective chemical warfare. [1]
Suggest one possible reason why chlorine was replaced by phosgene.

Chlorine has a distinct odour and is green in colour while phosgene is colourless and have a more subtle smell. Hence, it is more difficult for troops to detect and take counter measure. [1]

Other reasons:

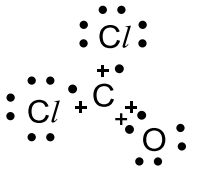
Chlorine is water-soluble and so the effect would be minimised by placing a water-soaked rag over mouth and nose.[1]

Do not accept "Phosgene is much more toxic and deadly than chlorine"; same NFPA value.

(d) Phosgene reacts with water to release hydrogen chloride and carbon dioxide gas.

$$CCl_2O + H_2O \rightarrow CO_2 + 2HCl$$ ----------Reaction **1**

(i) Draw the dot-and-cross diagram of phosgene and suggest its bond angle. [2]



[1]

Bond angle= 120° [1]

(ii) Suggest the type of reaction involved in Reaction **1**. [1]

Nucleophilic substitution or Hydrolysis [1]

(The water acts as a nucleophile; the lone pair on O of water attacks the δ+ C of phosgene)

(ii) Gaseous spills of phosgene can be removed using ammonia. The reaction is similar to Reaction **1**. Suggest how phosgene reacts with ammonia, using a chemical equation . [1]

$CCl_2O + 4NH_3 \rightarrow CO(NH_2)_2 + 2NH_4Cl$

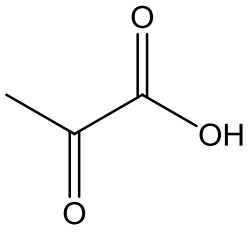
Or $CCl_2O + 2NH_3 \rightarrow CO(NH_2)_2 + 2HCl$ [1]

[Total:20]

Section B

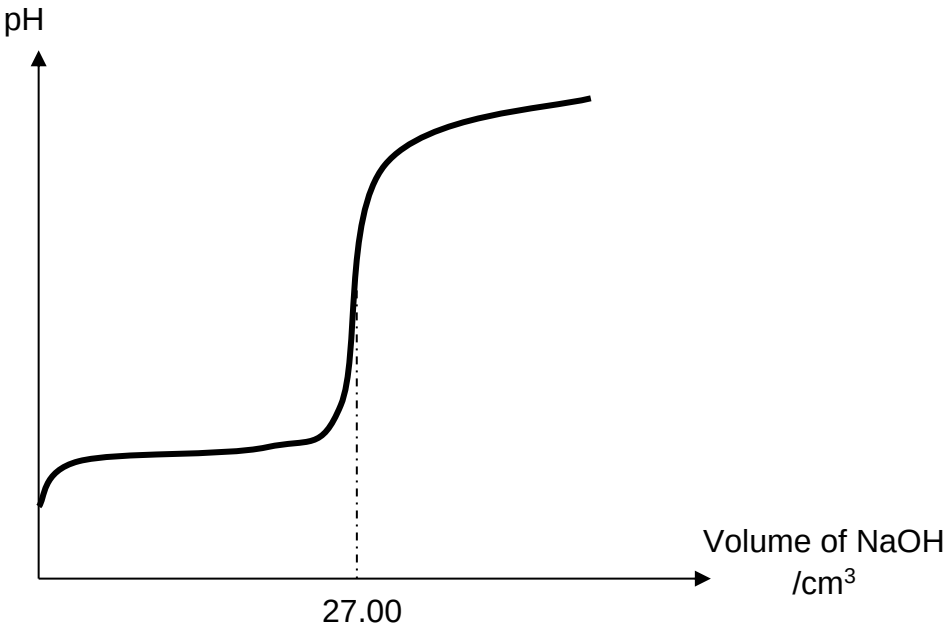
Answer **one** question from this section.

4. Pyruvic acid is an important component in the human body. It is involved in various processes such as the Krebs Cycle.



Pyruvic acid

(a) 30.0 cm^3 of pyruvic acid was titrated against 0.15 mol dm^{-3} of NaOH. The following titration curve was obtained.



(i) Given that the solution of pyruvic acid is only 15.3 % dissociated, calculate the value of K_a for pyruvic acid, stating clearly its units. [2]

[Pyruvic acid] = $\frac{0.15 \times 0.027}{0.03}$ = 0.135 mol dm^{-3}

[H$^+$] = 0.135 x 0.153 = 0.02065 mol dm^{-3} [1]

K_a = $\frac{0.02065^2}{0.135}$ = 3.16 x 10^{-3} mol dm^{-3} [1 with units]

Or

K_a = (0.135)(0.153)^2 = 3.16 x 10^{-3} mol dm^{-3} [2 with units]

(ii) Calculate the volume of NaOH added to obtain a solution of pH 12. [2]

pOH = 2

[OH$^-$] = 0.01 mol dm^{-3} [1]

Let the volume of NaOH added be x dm^3.

[OH$^-$] = $\frac{0.15(x-0.027)}{x+0.03}$ = 0.01

x = 0.0311 dm^3

31.1cm^3 of NaOH was added. [1]

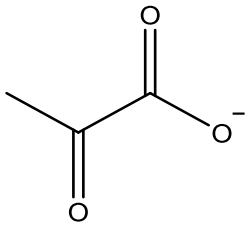
(iii) Suggest a suitable indicator for this titration. [1]

Phenolphthalein [1]

Penalise for wrong spelling

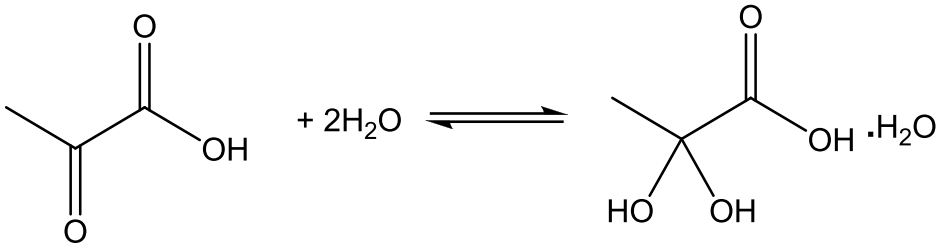
(iv) Blood has a working pH of 7.35 to 7.45. Suggest why pyruvic acid is found in trace amounts in blood. Hence, draw the major species of pyruvic acid in blood. [2]

Pyruvic acid is a weak acid. Since its pK_a value (as calculated based on (a)(i) calculation is 2.50) is less than 7 ,[1] its tendency to remain as pyruvic acid molecule in blood (which has working pH of 7.35 to 7.45) is low, hence it is only found in trace amounts in blood. [1] Hence, in blood, pyruvic acid will exist in the pyruvate(salt/conjugate base) form.



[1]

(b) An experiment to study the equilibrium between pyruvic acid and its hydrated form was done by Y. Pocker in 1969. The following data was obtained.



pyruvate hydrate

Temperature/ K	[pyruvate hydrate] / [pyruvic acid]
278	3.47
294	1.75
304	1.06
324	0.47

(i) Deduce whether the hydration of pyruvic acid is an endothermic or exothermic reaction. [2]

Temperature increases, more pyruvic acid is present. Backward and forward reaction both increases. However, rate (constant) of backward reaction increases more that of forward reaction. [1] Backward reaction is the endothermic reaction. Thus hydration of pyruvic acid is exothermic. [1]

Or

Temperature increases, more pyruvic acid is present. This implies that position of equilibrium shifts left.[1] Since increase in temperature always favours the endothermic reaction, the backward reaction is endothermic.

Thus hydration of pyruvic acid is exothermic. [1]

Conclusion must be supported by correct reason. 0 if say exothermic but reason contradicts.

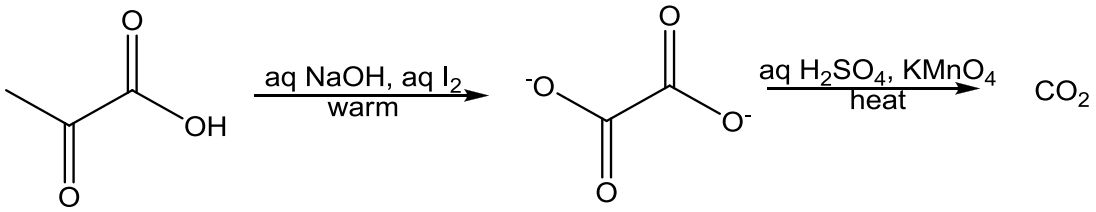
BOD and give 1 mark if only state exothermic but no reason provided.

(ii) The pyruvate hydrate has a higher pK_a value than pyruvic acid. Explain. [2]

Higher pK_a indicates that pyruvate hydrate is less acidic than pyruvic acid.[1] The -C=O group is more electron-withdrawing than the 2-OH groups, hence stabilising the conjugate base of the pyruvic acid more.[1] Hence, pyruvic acid is more acidic.

Alternate answer: Conjugate base of pyruvic acid is more resonance-stabilised due to the C=O and COO^-.

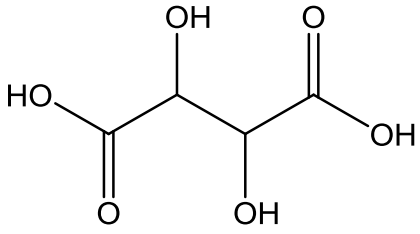
(c) Suggest a 2-step synthesis for the formation of carbon dioxide from pyruvic acid. [3]



Each reagent and condition –[1]

Intermediate – [1]

(d) Pyruvic acid was first synthesised in the laboratory through the distillation of tartaric acid with potassium hydrogen sulfate. The structure of tartaric acid is shown below.



Tartaric acid

(i) Suggest why tartaric acid has a much higher melting point than pyruvic acid. [2]

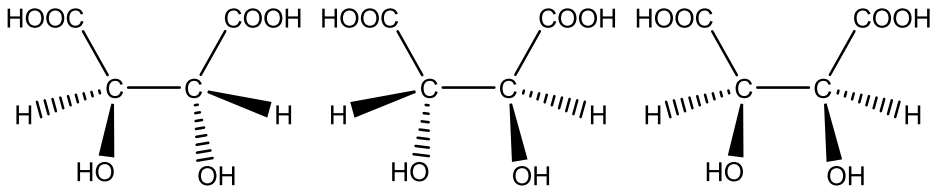
Tartaric acid and pyruvic acid are both polar simple covalent molecules with intermolecular hydrogen bonding.[1] However, tartaric acid can form more extensive intermolecular hydrogen bonding (since it has more –COOH and –OH groups). More energy required to break the more extensive intermolecular hydrogen bonding.[1]

OR

Pyruvic acid would dimerise while tartaric acid would polymerise [1] and hence id-id between the tartaric acid polymers is stronger than the id-id between pyruvic acid dimers. [1]

(ii) There are three stereoisomers present in tartaric acid. Two of them rotate plane of polarised light in opposite direction, whereas one has no effect on plane of polarised light. [4]

Draw **all** the stereoisomers of tartaric acid and explain why one of the stereoisomers does not rotate the plane of polarised light.



[1m each]

There is a plane/line of symmetry present in that stereoisomer

Or it is a meso compound. [1]

[Total: 20]

5 (a) Thallium(I) chromate, Tl_2CrO_4, has a solubility product of 8.67×10^{-13} mol^3 dm^{-9} at 25 ^oC.

(i) Calculate the solubility of Tl_2CrO_4 in 0.05 mol dm^{-3} K_2CrO_4. [2]

$K_{sp} = [Tl^+]^2[CrO_4^{2-}]$ units mol^3 dm^{-9}

Let the solubility be x mol dm^{-3}

$8.67 \times 10^{-13} = [2x]^2[0.05]$ [1]

$x = 2.08 \times 10^{-6}$ mol dm^{-3} [1]

(ii) Given that the numerical K_{sp} value of $BaCrO_4$ is 1.17×10^{-10}, deduce which precipitate will be formed first if K_2CrO_4 was added slowly into a solution containing 0.015 mol dm^{-3} of Ba^{2+} and 0.015 mol dm^{-3} Tl^+. [2]

For $BaCrO_4$ ppt to form, $[CrO_4^{2-}] = \frac{1.17x10^{-10}}{0.015} = 7.8 \times 10^{-9}$ mol dm^{-3}

For Tl_2CrO_4 ppt to form, $[CrO_4^{2-}] = \frac{8.67\times10^{-13}}{0.015^2} = 3.85 \times 10^{-9}$ mol dm^{-3}

[1 for both calculations]

Since less $[CrO_4^{2-}]$ is required to form Tl_2CrO_4, it will precipitate first. [1]

(b) Transition elements are known to form coloured complexes. Chromium is one of the common transition element used today.

(i) An equilibrium exists between chromate(VI) ion and dichromate(VI) ions. [2]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Explain why changes in pH will cause changes in the colour of the solution.

When pH increases, the equilibrium position will shift left as OH^- will react with H^+. More yellow CrO_4^{2-} formed. [1] When pH decreases, the equilibrium position will shift right to remove the excess H^+. More orange $Cr_2O_7^{2-}$ formed. [1]

(ii) When gallium, Ga, is added to an acidified $Na_2Cr_2O_7$ solution, a series of colour changes takes place until a blue solution is obtained. [3]

Using relevant data from the *Data Booklet* and the data given below, explain the observation of the colour changes.

$$Ga^{3+} + 3e^- \rightleftharpoons Ga \qquad E^\ominus = -0.53V$$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33V$

$Cr^{3+} + e \rightleftharpoons Cr^{2+}$ $\quad E^\ominus = -0.41V$

[1 for quote]

$Cr_2O_7^{2-} + 2Ga + 14H^+ \rightarrow 2Cr^{3+} + 2Ga^{3+} + 7H_2O$ $E^{\ominus} = +1.86V$ [1]

Orange *green [1]*

$3Cr^{3+} + Ga \rightarrow 3Cr^{2+} + Ga^{3+}$ $E^{\ominus} = +0.12V$ [1]

Green *blue*

$3Cr^{2+} + 2Ga \rightarrow 3Cr + 2Ga^{3+}$ $E^{\ominus} = -0.382V$

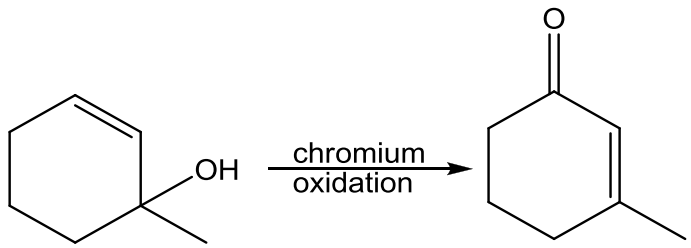
Cr^{2+} cannot be further reduced to Cr by Ga.

(iii) Suggest why the blue solution slowly changes to a green solution when it is left standing in air. [1]

Cr^{2+} is oxidised to Cr^{3+}.

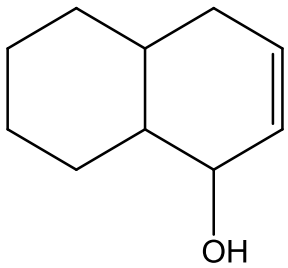
$4Cr^{2+} + O_2 + 2H_2O \rightarrow 4Cr^{3+} + 4OH^-$ $E^{\ominus}_{cell} = +0.81V$ [1]

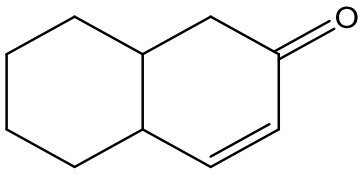
(c) Chromium oxidation is a special type of reaction in which oxidation and a rearrangement takes place. An example of a chromium oxidation is as shown.



1-methylcyclohex-2-enol 3-methylcyclohex-2-enone

(i) Draw the structure of the product when the following compound undergoes chromium oxidation. [1]





[1]

(ii) Suggest a simple chemical test to distinguish between [2]

1-methylcyclohex-2-enol and 3-methylcyclohex-2-enone.

2,4-DNPH, warm [1] No penalty for missing 'warm'

Orange ppt for 3-methylcyclohex-2-enone and no orange ppt for 1-methylcyclohex-2-enol [1]

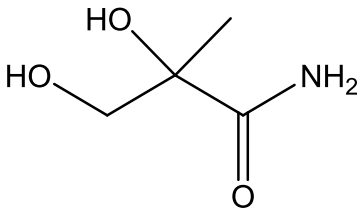
(d) Compound **F**, $C_4H_9O_3N$, is a neutral and chiral compound which is soluble in water. When compound **F** is heated with dilute sulfuric acid and potassium dichromate(VI), compound **G**, $C_4H_6O_5$, is formed. 1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2. If compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), compound **H**, $C_4H_4O_4$, is formed instead. When compound **F** reacts with $LiAlH_4$ in dry ether, a compound **J** which is no longer neutral is formed. [7]

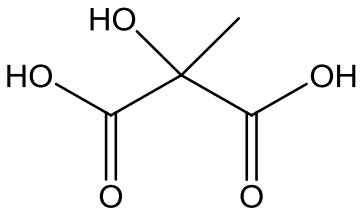
Deduce the structures of compounds **F**, **G H** and **J**, and explain the reactions involved.

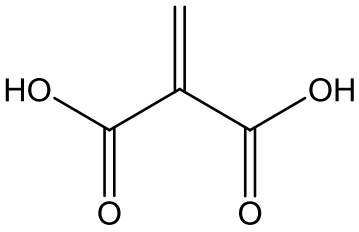
	Deduction [cap at 3 marks]
Compound **F**, $C_4H_9O_3N$, is a neutral compound which is soluble in water.	F is not a carboxylic acid or amine since it is neutral. [1] OR F can be an amide, ester or contains alcohol groups since it can form H bonding with water, making it soluble. [1]
When Compound **F** is heated with acidified potassium dichromate(VI), Compound **G**, $C_4H_6O_5$, is formed	-oxidation of primary alcohol and hydrolysis - $-CONH_2$ in **F*/*** Amide is present in **F** [1]
1 mol of compound **G** reacts with aqueous sodium carbonate to produce 1 mol of CO_2.	-acid-carbonate reaction (accept acid-base reaction) **G** contains two –COOH groups [1]

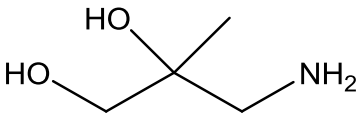
Compound **F** is heated with concentrated sulfuric acid and potassium dichromate(VI), Compound **H**, $C_4H_4O_4$, is formed instead	-elimination of water -alkene in **H** [1]
Compound **F** reacts with $LiAlH_4$ in dry ether, Compound **J** is formed	-reduction - $-CONH_2$ in F becomes $-CH_2NH_2$ in J[1]

Max 2 marks

F: 

G: 

H: 

J: 

1 mark each structure

[Total: 20]

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