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TOP SCHOLAR



NEW ZEALAND QUALIFICATIONS AUTHORITY
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Scholarship 2011 Chemistry

9.30 am Saturday 19 November 2011

Time allowed: Three hours

Total marks: 40

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

You should answer ALL the questions in this booklet.

A periodic table is provided on page 2.

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 2–26 in the correct order and that none of these pages is blank.

You are advised to spend approximately 35 minutes on each question.

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

PERIODIC TABLE OF THE ELEMENTS

Atomic number		Molar mass/g mol ⁻¹																			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18				
Li 6.9	Be 9.0	Na 23.0	Mg 24.3	K 39.1	Ca 40.1	Sc 45.0	Ti 47.9	V 50.9	Cr 52.0	Mn 54.9	Fe 55.9	Co 58.9	Ni 58.7	Cu 63.5	Zn 65.4	Ga 69.7	Ge 72.6	As 74.9	Se 79.0	Br 79.9	Kr 83.8
11	12	19	20	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Na	Mg	K	Ca	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
23.0	24.3	39.1	40.1	85.5	87.6	88.9	91.2	92.9	95.9	98.9	101	103	106	108	112	115	119	122	128	127	131
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Th
133	137	175	179	181	184	186	190	192	195	197	201	204	207	209	210	210	222	223	226	227	232
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112	113	114	115	116	117	118	119	120	121	122
223	226	262	261	262	263	264	265	268	271	272	273	274	275	276	277	278	279	280	281	282	283

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
139	140	141	144	147	150	152	157	159	163	165	167	169	173
Lanthanide Series													
89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
227	232	231	238	237	239	241	244	249	251	252	257	258	259
Actinide Series													

You have three hours to complete this examination.

QUESTION ONE

- (a) (i) Discuss how the charges on subatomic particles contribute to the size of atoms and their ions.

Subatomic particles in an atom include positively charged protons that are held in the nucleus, and negatively charged electrons that ~~are~~ orbit in discrete energy levels around the nucleus. Electrostatic attractions between the positively charged protons and the electrons in the outer valence shell primarily define the size of atoms. The greater the electrostatic attraction between them, the closer the outer electrons are to the nucleus and thus the smaller the atom. Greater electrostatic attraction arises from a greater positive charge in the nucleus, which is proportional to the number of protons. Shielding from inner shells of electrons also act to make the atom larger, as the electron-electron repulsion means that the effective nuclear charge acting on valence electrons is reduced. Similarly, ^{greater} electron-electron repulsion in the valence shell means a larger atom, as the overall atomic radius is increased to reduce repulsion. The same factors apply to the size of ions - the greater the nuclear charge, the smaller the ion, and the more shielding from inner electrons ~~and~~ and the more electron-electron repulsion from electrons occupying the outer shell, the larger the ion. ~~For~~ Hence, for positive cations, they are comparably smaller than their atoms due to loss of electrons, and for anions they are comparably larger than their atoms due to gain in electrons.

(ii) Explain the trends in the atom and ion sizes (in pm) in Figure 1 below.

Relate your answer to your discussion in part (i).

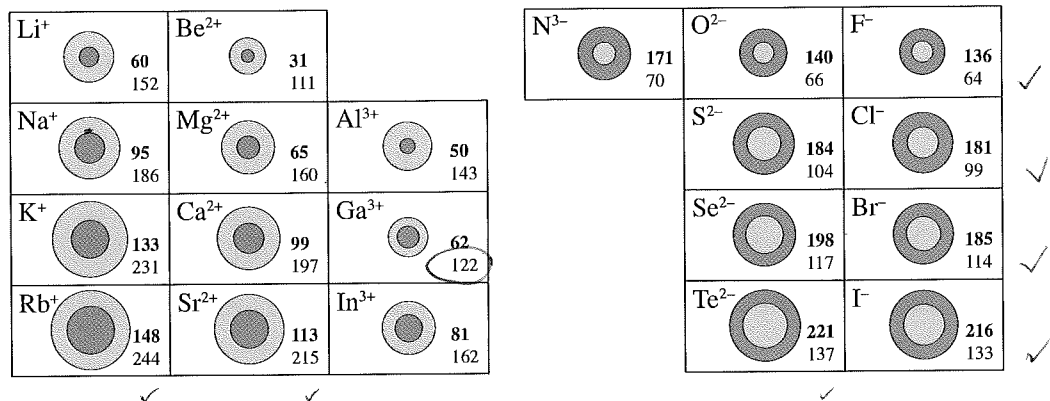


Figure 1: Atomic and ionic radii (pm)

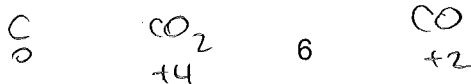
Note:

- The dark circles represent the ions.
- The bolded numbers are the ionic radii.

The trend across a period for atomic radii is decreasing i.e. from Li to F, the atoms get smaller, and this trend is ^{the same} ~~continued~~ across all periods. This is due to the increasing nuclear charge ~~of~~ of the nucleus ~~as~~ along the period (from left to right), and as electrons are being added to the same valence shell there is overall a greater electrostatic attractions between the outer electrons and the more positive nucleus.

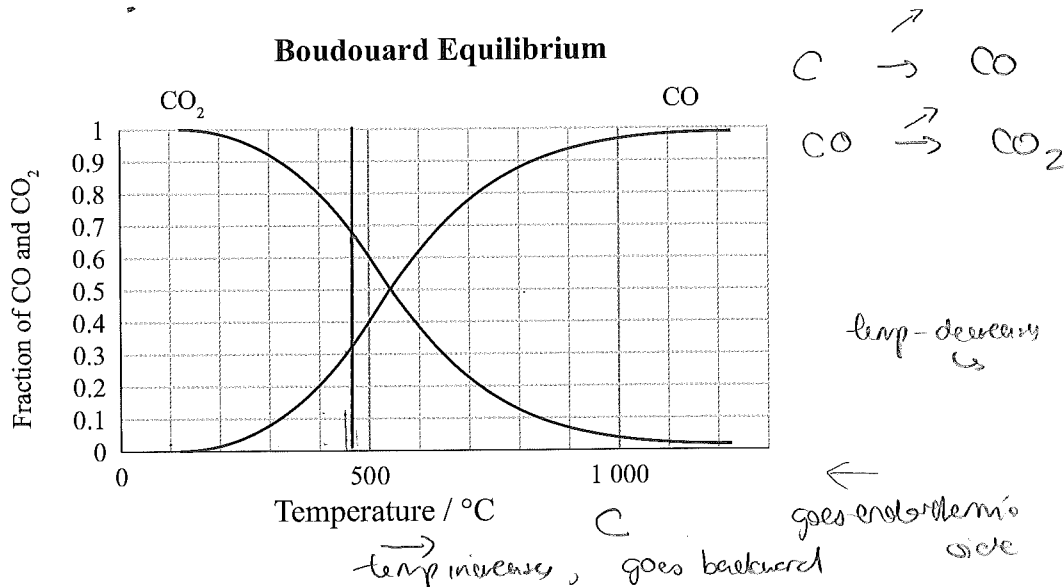
Going down the groups, the general trend in atomic radii is increasing, as ^{valence} ~~higher~~ electrons are occupying ^{higher} energy levels and thus are at a greater distance from the nucleus. Increased shielding from inner shells also reduces the effective nuclear charge, hence reducing electrostatic attractions between valence electrons and the positive nucleus. The exception to the increasing trend down the groups for atomic radii is Ga, which has an atomic radii of 122 pm (smaller than Aluminium atom's 143 pm). This is likely due to the fact that the extra energy level filled is the 3d subshell and the

4s subshell, which are comparatively close in energy levels and thus do not add significantly to the atomic radius. As the positive nuclear charge of Ga is much greater than that of Al, this thus appears to play a greater role in reducing atomic radius due to greater electrostatic attractions. In comparing ~~atomic~~ ^{ionic} radii, we can look at two separate groups of elements - the metals, and the non-metals. For the metallic elements, cations are always formed upon losing outer valence electrons. Thus, as the outer valence electrons are at a lower energy level (at a closer distance to the nucleus in the ions), all ions of metallic elements are smaller than their respective atoms. In non-metal elements, however, anions are formed upon gaining electrons to complete the outer shell. Thus, increased electron-electron repulsion between electrons in the outer shell cause the ionic radii of non-metal elements to be greater than their respective atoms. Going down all the groups, ionic radii increases as valence electrons are occupying higher energy levels. Going across the periods, ionic radii ~~increases~~ ^{decreases} for metals as ~~ions~~ in the same period are isoelectronic, yet increasingly have greater nuclear charge and thus are held more closely to the nucleus. Similarly, for non-metals ionic radii decreases across the period ~~as~~ for the same reason. However, in comparing metal ions to non-metal ions in the same period, non-metal ions are larger as the outer shells are at a greater distance from the nucleus (occupy higher energy level).



- (b) The Boudouard reaction is the name given to the oxidation-reduction reaction involving a mixture of carbon (graphite), carbon dioxide and carbon monoxide at equilibrium, at a given temperature. The reaction is an important process inside a blast furnace in the production of metals from metal oxides.

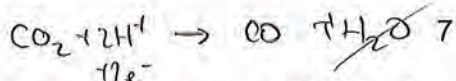
The graph below shows how the reaction mixture composition of the gases present changes with changing temperature at atmospheric pressure (101 kPa).



- (i) Identify, with justification, the product of the exothermic process in the Boudouard reaction.

Use your answer to discuss the reaction products when the hot gases from a blast furnace reach the cooler air at the top of the chimney.

As the temperature increases, the equilibrium of a reaction tends to move towards increasing the rate of the endothermic reaction. As shown in the graph, more CO is produced as temperature increases, indicating that carbon monoxide must be the product of the endothermic reaction. Thus, we can infer that the product of the exothermic process of the Boudouard reaction is CO₂, as it is present in high concentrations at low temperatures whereby equilibrium shifts towards increasing the rate of the exothermic reaction. At the cooler temperatures at the top of the chimney, ~~the opposite will occur~~ the equilibrium will thus shift towards producing more CO₂ as a product of the exothermic reaction.



- (ii) A large, heat-proof syringe with a freely moveable airtight piston initially contained 50 mL of carbon dioxide at 101 kPa and 25°C, plus 1 g of granular carbon. The apparatus was heated and maintained at a certain constant temperature until equilibrium was reached. The pressure of the system remained constant at 101 kPa throughout. The apparatus was then cooled rapidly to 25°C. (At this temperature any further change in composition was negligible.) A total of 60 mL of gas was then present.

Determine the temperature at which the reaction was carried out. $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$

Note:

- The same conditions apply to this experiment and to that represented by the graph on the previous page.
- The volume of a substance in its gas phase at a particular temperature and pressure is directly proportional to the amount in moles of the substance present.

~~$$K = \frac{[\text{CO}]}{[\text{CO}_2]}$$~~



~~$$K = \frac{[x]}{[50-x]}$$~~

~~Final volume = 60 = 50~~



I	50	0
C	-x	+2x
E		

$$(50-x) + (2x) = 60$$

$$x = 10 \text{ mL}$$

$$n(\text{CO}_2)_{\text{equi}} = 40 \text{ mL}$$

$$n(\text{CO})_{\text{equi}} = 20 \text{ mL}$$

$$\text{Fraction}(\text{CO}_2) = \frac{2}{3}$$


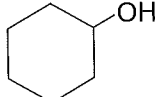
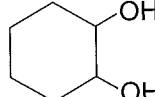
$$\text{Fraction}(\text{CO}) = \frac{1}{3}$$

→ on graph, the temp at which Fraction(CO₂) ≈ 2/3

and Fraction(CO) ≈ 1/3 is at approximately 475°C.

QUESTION TWO

(a) Account for the differences in the properties of the compounds in the table below.

Name	Structural formula	Melting Point/ $^{\circ}\text{C}$	Solubility in water at 25°C
1. Cyclohexane C_6H_{12} $M = 84 \text{ g mol}^{-1}$		7	Insoluble
2. Cyclohexanol $\text{C}_6\text{H}_{11}\text{OH}$ $M = 100 \text{ g mol}^{-1}$		25	Sparingly soluble
3. cis-cyclohexane-1,2-diol $\text{C}_6\text{H}_{10}(\text{OH})_2$ $M = 116 \text{ g mol}^{-1}$		98	Very soluble

The melting point of a substance depends directly on the sum of intermolecular attractions present between molecules. The greater the intermolecular attractions, the more energy required to separate the molecules from solid phase to liquid phase and thus the higher the temperature required at melting point.

In comparing compounds 1, 2, and 3 (numbered above), it can be noted that they progressively have larger molar masses, i.e. the molar mass for 1 is ~~smaller~~ less than 2, which are both less than 3. The molar mass of molecules in a substance directly relate to the size of the electron cloud of the molecule - both increase proportionally. Thus, as ^{size of the} electron cloud increases from 1-3, so does the instantaneous dipole attractions between molecules. Instantaneous dipole attractions are a result of temporary dipole-dipole attractions between molecules due to instantaneous disproportionate distribution of charge, thus the greater the electron cloud the greater the possibility of unequal charge distribution, thus the stronger the instantaneous dipole

attractions.

Furthermore, compound 2 and 3 are able to form hydrogen bonds between molecules due to the presence of a hydroxyl group. The highly polar O-H bond renders the hydrogen very positive, and thus free to interact with unbonded pairs of electrons on O atoms of neighbouring molecules, thus forming strong hydrogen bonds. As compound 3 has one more hydroxyl group than compound 2, it can form more hydrogen bonds ~~and~~ than compound 2. Compound 1 is not able to form hydrogen bonds as there are no hydroxyl groups.

Thus, overall compound 3 has the greatest intermolecular attractions as a result of a larger molar mass and 2 hydrogen-bonding hydroxyl groups, and hence has the highest melting point. Compound 2 can form one hydrogen bond and has a molar mass of 100 g mol^{-1} , so has the second highest melting point. Compound 1 cannot hydrogen bond and has the smallest molar mass, thus has the lowest melting point.

Solubility depends upon the ability of molecules in a compound to form hydrogen bonds with water molecules - the formation of hydrogen bonds with water molecules releases energy, and thus ~~the~~ the more hydrogen bonds formed the more energetically favourable the dissolving process, and thus the more soluble the compound. Compound 3 can form the most hydrogen bonds, and is very soluble. Compound 2 can only form a limited number of hydrogen bonds, and thus is sparingly soluble (hydration energy is not significantly greater than energy required to separate molecules in solid phase). Compound 1 cannot form any hydrogen bonds, and thus is insoluble.

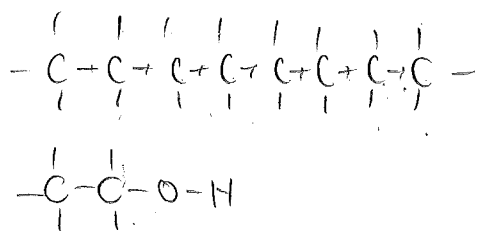
- (b) A year 11 student carried out an experiment to compare the energy released when octane and ethanol were burned as fuels. Octane was found to release considerably more energy than ethanol. The student concluded that this was because octane was a larger molecule, and so there were more chemical bonds to break, and hence more energy released in the reaction.

Discuss the misconceptions in the student's explanation and use appropriate data from the table below to provide your own answer for the observation.

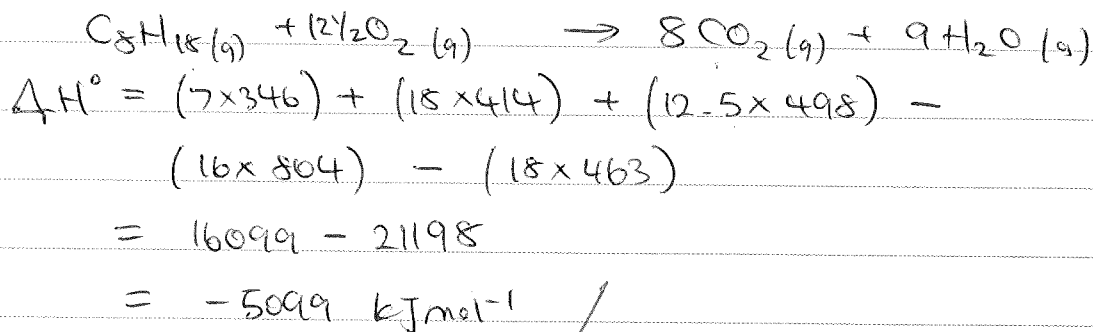
$$M(\text{octane}) = 114.0 \text{ g mol}^{-1} \quad M(\text{ethanol}) = 46.1 \text{ g mol}^{-1}$$

Bond enthalpy data / kJ mol⁻¹

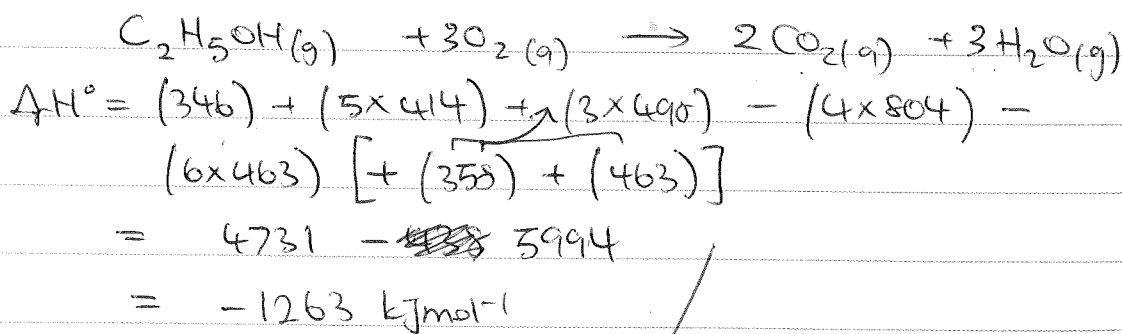
C-H	414	O-H	463
C-O	358	C=O	1076
C=O	804	H-H	436
C-C	346	O=O	498



Combustion of Octane:



Combustion of Ethanol:



Energy released per gram of octane =

$$\begin{aligned}
 E &= \left(\frac{1}{114}\right) \times -5099 \\
 &= 44.73 \text{ kJ (4s.f.)}
 \end{aligned}$$

Energy released per gram of ethanol =

$$\begin{aligned}
 E &= \left(\frac{1}{46.1}\right) \times -1263 \\
 &= 27.40 \text{ kJ (4s.f.)}
 \end{aligned}$$

In the combustion of a fuel, it is important to consider the bonds broken and the bonds formed in the reaction, and hence the student's misconception lies in failing to recognise this. The student also implies that in having to break more bonds, "more energy is released", whereas the breaking of chemical bonds is an endothermic process that requires more energy to be absorbed from the surroundings. The formation of bonds is the exothermic process that will release energy. In the combustion of octane, the total energy ~~required~~ ^{released} in the combustion of ~~to combust~~ one gram of the substance is 44.73 kJ.

This is taking into account the energy required to break bonds in the reactants (octane and oxygen), and the subsequent energy released upon forming bonds in the products (carbon dioxide and water). The molar mass of the fuel has also been taken into account, as there are less moles of octane in one gram of the substance than there are for ethanol due to its larger molar mass. Equivalent calculations using bond enthalpies have been carried out for 1 gram of ethanol, showing that less energy is released in combustion of the same mass of fuel (27.40 kJ). Hence, ^{combustion of} octane is the more exothermic process, thus more energy is released.

Note that calculations have been based on the assumption that all reactants and products are in gas phase, and that complete combustion occurs. The former assumption is unlikely, as octane and ethanol are both liquids at room temperature, and the product H_2O is usually in liquid phase. The latter assumption is also unrealistic as some carbon monoxide and soot

QUESTION THREE

- (a) A mixture contains oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, and a water soluble impurity that does not react with solutions of sodium hydroxide or potassium permanganate. To determine the composition of the mixture, 2.496 g of the mixture was dissolved in water to give 100.00 mL of solution.

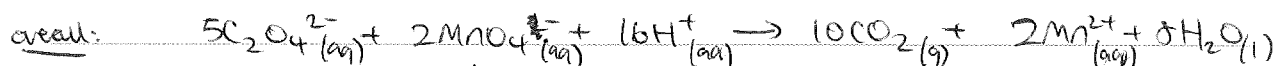
In one test, 5.00 mL of the solution was titrated with $0.01803 \text{ mol L}^{-1}$ acidified potassium permanganate solution and needed 23.35 mL to reach the equivalence point.

In another test, 10.00 mL of the solution was titrated with $0.1040 \text{ mol L}^{-1}$ sodium hydroxide solution and needed 17.30 mL to reach the equivalence point.

Determine the mass fractions of oxalic acid, oxalate ion and the impurity.

$$M(\text{H}_2\text{C}_2\text{O}_4) = 90.04 \text{ g mol}^{-1} \quad M(\text{Na}_2\text{C}_2\text{O}_4) = 134.0 \text{ g mol}^{-1}$$

→ Titration with potassium permanganate tests for $\text{C}_2\text{O}_4^{2-}$ (which is oxidised to CO_2).



$$n(\text{MnO}_4^-) = 0.01803 \times 0.02335 \\ = 4.21 \times 10^{-4} \text{ mol}$$

$$n(\text{C}_2\text{O}_4^{2-}) = \left(\frac{4.21 \times 10^{-4}}{2} \right) \times 5 \\ = 0.001053 \text{ mol (40.1)}$$

$$n(\text{C}_2\text{O}_4^{2-} \text{ in } 100\text{ml}) = \frac{0.001053}{5} \times 100 = 0.02105 \text{ mol}$$

→ Titration with sodium hydroxide tests for $\text{H}_2\text{C}_2\text{O}_4$



$$n(\text{NaOH}) = 0.104 \times 0.0173 \\ = 0.001799 \text{ mol}$$

$$n(\text{H}_2\text{C}_2\text{O}_4) = \frac{0.001799}{2} = 8.996 \times 10^{-4} \text{ mol}$$

$$n(\text{H}_2\text{C}_2\text{O}_4 \text{ in } 100\text{ml}) = 8.996 \times 10^{-4} \times 10 \\ = 8.996 \times 10^{-3} \text{ mol}$$

$$\begin{aligned}
 n(\text{Na}_2\text{C}_2\text{O}_4 \text{ original}) &= n(\text{C}_2\text{O}_4^{2-}) - n(\text{H}_2\text{C}_2\text{O}_4) \\
 &= 0.02105 - 0.008996 \\
 &= 0.01205 \text{ mol}
 \end{aligned}$$

$$\begin{aligned}
 m(\text{oxalic acid}) &= 5.996 \times 10^{-3} \times 90.04 \\
 &= \underline{0.5099 \text{ g}}
 \end{aligned}$$

$$\begin{aligned}
 \text{mass fraction (oxalic acid)} &= 0.5099 / 2.496 \\
 &= \underline{0.2045} \quad (\text{4s.f.}) \\
 &= \underline{20.45\%}
 \end{aligned}$$

$$\begin{aligned}
 m(\text{oxalate ion}) &= 0.01205 \times M(\text{C}_2\text{O}_4^{2-}) \\
 &= 0.01205 \times \text{85} \\
 &= \underline{1.061 \text{ g}}
 \end{aligned}$$

$$\begin{aligned}
 \text{mass fraction (oxalate ion)} &= 1.061 / 2.496 \\
 &= \underline{0.4250} \quad (\text{4s.f.}) \\
 &= \underline{42.50\%}
 \end{aligned}$$

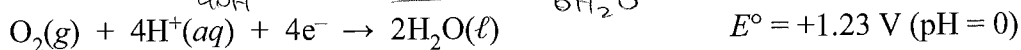
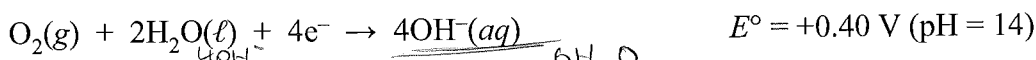
$$\begin{aligned}
 m(\text{impurity}) &= 2.496 - m(\text{H}_2\text{C}_2\text{O}_4) - m(\text{Na}_2\text{C}_2\text{O}_4) \\
 &= 2.496 - 0.5099 - (0.01205 \times 134) \\
 &= \underline{0.07076 \text{ g}}
 \end{aligned}$$

$$\begin{aligned}
 \text{mass fraction (impurity)} &= 0.07076 / 2.496 \\
 &= \underline{0.02835} \quad (\text{4s.f.}) \\
 &= \underline{2.835\%}
 \end{aligned}$$

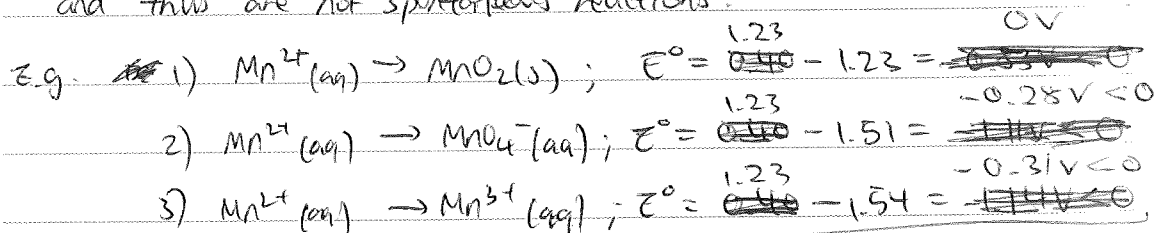
- (b) Manganese is an element that exhibits a number of different oxidation states. Half-cell reactions and potentials for the different oxidation states vary depending on the conditions. The table gives the standard reduction potentials for manganese species in aqueous solution ranging from Mn(II) to Mn(VII) at pH = 0 and at pH = 14.

Conditions	Reduction half-equation	E° / V
pH = 0	$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.19
	$MnO_4^-(aq) + H^+(aq) + e^- \rightarrow HMnO_4^-(aq)$	+0.90
	$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
	$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$	+1.54
	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$	+1.69
	$HMnO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow MnO_2(s) + 2H_2O(l)$	+2.10
	$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O(l)$	+0.95
pH = 14	$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$	+0.15
	$Mn_2O_3(s) + 3H_2O(l) + 2e^- \rightarrow 2Mn(OH)_2(s) + 2OH^-(aq)$	-0.23
	$Mn(OH)_2(s) + 2e^- \rightarrow Mn(s) + 2OH^-(aq)$	-1.19

- (i) Explain why Mn(II) is not oxidised by O_2 in solutions at pH = 0, but is oxidised by O_2 solutions in which $[OH^-]$ is 1 mol L^{-1} .



At pH=0, Mn(II) cannot be oxidised by O_2 because the E° values for redox reactions between O_2 and $Mn^{2+}(aq)$ are negative, and thus are not spontaneous reactions.



Hence none of the above reactions occur spontaneously

at pH = 0. (reaction 1 is just not spontaneous)

However, when $[OH^-]$ is 1 mol L^{-1} and pH = 14, the E° value

for the reduction of O_2 to H_2O is 0.40V, and now

a redox reaction can occur spontaneously with $Mn(OH)_2(s)$,

an Mn(II) species.



$$E^\circ = 0.40 - (-0.23) = 0.63 \text{ V} > 0 \text{ ; here spontaneous}$$

- (ii) KMnO_4 is a common oxidant, and in acidic conditions may be reduced to MnO_2 or Mn^{2+} .

Discuss why the intermediate species HMnO_4^- does not accumulate during the reduction of MnO_4^- to MnO_2 .

During the reduction of MnO_4^- to MnO_2 , it is possible for MnO_4^- to form the intermediate species HMnO_4^- . However, HMnO_4^- is itself a strong oxidant (~~itself~~ easily reduced to $\text{MnO}_2(\text{s})$), and thus undergoes subsequent energetically favourable reactions with other species in solution to form other manganese species, and ~~thus~~ due to this doesn't accumulate in the process.

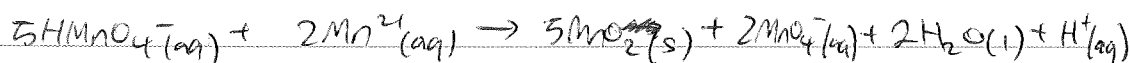
e.g. HMnO_4^- may react with Mn^{2+} species (also formed by the reduction of MnO_4^- in acidic conditions).



$$E^\circ = 2.10 - 1.23 = 0.87\text{V} > 0; \text{ hence spontaneous.}$$

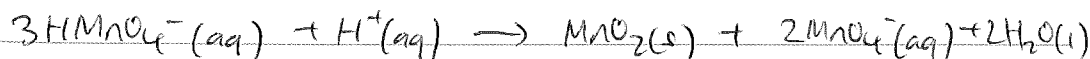
The product is $\text{MnO}_2(\text{s})$.

Alternatively, HMnO_4^- may react with Mn^{2+} to ~~not~~ regenerate MnO_4^- , which can subsequently be reduced to MnO_2 :



$$E^\circ = 2.10 - 1.51 = 0.59\text{V} > 0; \text{ hence spontaneous.}$$

HMnO_4^- can also undergo an autoxidation reaction, thus producing $\text{MnO}_4^-(\text{aq})$ and $\text{MnO}_2(\text{aq})$, leaving no HMnO_4^- present in solution.

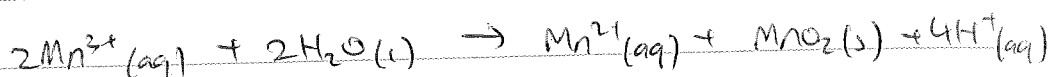


$$E^\circ = 2.10 - 0.90$$

$$= 1.2\text{V} > 0; \text{ hence spontaneous.}$$

(iii) Discuss the pH dependence of the stability of Mn(III) in aqueous solution.

At low pH i.e. in acidic conditions, ~~species~~ ~~such as~~ ~~MnO_4^-~~ ~~and~~ ~~MnO_2~~ ~~are~~ ~~favouredly~~ ~~reduced~~ ~~to~~ ~~form~~ ~~Mn^{2+}~~ ~~in~~ ~~aqueous~~ ~~solution~~, ~~and~~ ~~thus~~ Mn(III) is unstable in that it undergoes autooxidation reaction with itself to form Mn^{2+} and MnO_2 .



$$E^\circ = 1.54 - 0.95 = 0.59V > 0, \text{ hence } \leftarrow \text{spontaneous.}$$

In high pH conditions i.e. basic conditions,

Mn(III) is present as $Mn_2O_3(s)$, and this cannot undergo

similar autooxidation reaction as $E^\circ = -0.23 - 0.15$

$$= -0.38 < 0, \text{ hence } \text{not spontaneous.}$$

Thus, Mn(III) is stable in basic condition as Mn_2O_3 .

QUESTION FOUR

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- (a) (i) The normal pH in blood plasma is 7.40. The pH of body fluids is regulated by the presence of CO_3^{2-} , HCO_3^- and CO_2 dissolved in these fluids.

At 25°C , $K_a(\text{H}_2\text{CO}_3) = 4.2 \times 10^{-7}$ and $K_a(\text{HCO}_3^-) = 4.7 \times 10^{-11}$.

Identify the components from the list above that would form the best buffer at this pH and calculate their ratio.

Determine whether this buffer is more effective against added acid or base.

$$K_2(\text{H}_2\text{CO}_3) = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]}$$

$$\text{at pH} = 7.4; \quad \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = (4.2 \times 10^{-7}) \div (10^{-7.4})$$

$$= 10.55 \quad (\text{u.f.})$$

$$K_2(\text{HCO}_3^-) = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$$

$$\text{at pH} = 7.4; \quad \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = (4.7 \times 10^{-11}) \div (10^{-7.4})$$

$$= 0.00181 \quad (\text{u.f.})$$

As the ~~base:acid ratio~~ ^{conjugate base and acid} for species $(\text{HCO}_3^- \text{ (base) and } \text{H}_2\text{CO}_3 \text{ (acid)})$

are present at $\text{pH} = 7.4$ in more appreciable amounts (i.e. $\approx 10:1$ ratio

as opposed to $\approx 1:100$), these are the two components that form the best buffer at this pH. The buffer is more effective against added acid, as

- (ii) Lactic acid (HLac) is often said to be produced by the body during rapid exercise. ^{more conjugate base is present.}

Show by calculation that lactic acid is mainly present as the lactate ion (Lac^-) at $\text{pH} = 7.40$.

$$\text{p}K_a(\text{lactic acid}) = 3.86$$

$$K_2(\text{lactic acid}) = 10^{-3.86} = 1.38 \times 10^{-4}$$

$$K_2 = 1.38 \times 10^{-4} = \frac{[\text{Lac}^-][\text{H}_3\text{O}^+]}{[\text{HLac}]}$$

$$\frac{[\text{Lac}^-]}{[\text{HLac}]} = (1.38 \times 10^{-4}) \div (10^{-7.4})$$

$$= 3467.37$$

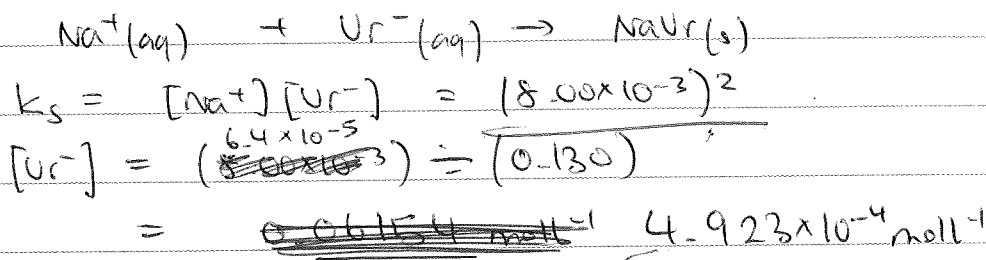
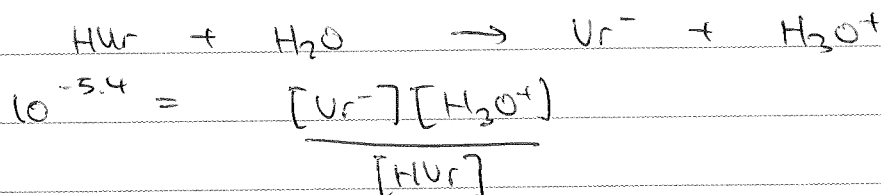
Here, as base:acid ratio is very large, this indicates that $[\text{Lac}^-]$ is present in significantly greater amounts at this pH.

- (b) Predisposition for the condition known as gout occurs when the concentration of uric acid (HUr) and urate ions (Ur^-) in the blood becomes too high. Uric acid is a weak acid. $\text{p}K_a = 5.4$ at 37°C .

At 37°C , the solubility of sodium urate is $8.00 \times 10^{-3} \text{ mol L}^{-1}$ and the solubility of uric acid is $5.00 \times 10^{-4} \text{ mol L}^{-1}$.

In blood serum, $[\text{Na}^+] = 0.130 \text{ mol L}^{-1}$ (ie at $\text{pH} = 7.4$ and temperature of 37°C).

- (i) Calculate the maximum urate concentration at which sodium urate will not precipitate, and show by calculation that uric acid will not precipitate at this concentration either.



\therefore Maximum urate concentration at which NaUr will not precipitate is $\underline{4.923 \times 10^{-4} \text{ mol L}^{-1}}$

$$[\text{HUr}] = \frac{[\text{Ur}^-][\text{H}_3\text{O}^+]}{K_a(\text{HUr})}$$

$$= \frac{4.923 \times 10^{-4} \times 10^{-7.4}}{10^{-5.4}}$$

$$= \underline{4.923 \times 10^{-6} \text{ mol L}^{-1}}$$

As $[\text{HUr}] < \text{solubility of uric acid}$, uric acid will not precipitate.

- (ii) One form of kidney stone is made of crystals of uric acid. These can form when the concentration of uric acid and urate is high, and the pH of urine drops to around 5 to 6.

Calculate the pH at which these stones can form.

Assume that the total concentration of uric acid and urate is $2.00 \times 10^{-3} \text{ mol L}^{-1}$.

$$[\text{HUr}] + [\text{Ur}^-] = 2.00 \times 10^{-3} \text{ mol L}^{-1}$$

→ $[\text{HUr}]$ is $5.00 \times 10^{-4} \text{ mol L}^{-1}$ when it crystallizes.

$$\begin{aligned} \text{Hence, } [\text{Ur}^-] &= (2.00 \times 10^{-3}) - (5.00 \times 10^{-4}) \\ &= 0.0015 \end{aligned}$$

$$\begin{aligned} 10^{-5.4} &= \frac{[\text{Ur}^-][\text{H}_3\text{O}^+]}{[\text{HUr}]} \\ &= \frac{0.0015 \times [\text{H}_3\text{O}^+]}{5.00 \times 10^{-4}} \end{aligned}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{5.00 \times 10^{-4} \times 10^{-5.4}}{0.0015} \\ &= 1.327 \times 10^{-6} \text{ mol L}^{-1} \end{aligned}$$

~~$$\text{pH} = 5.88 \quad (2 \text{ s.f.})$$~~

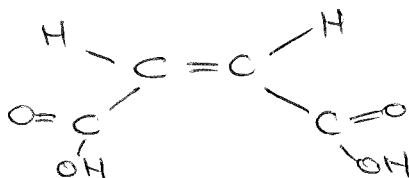
~~$$\text{pH} = 5.88 \quad (2 \text{ s.f.})$$~~

QUESTION FIVE

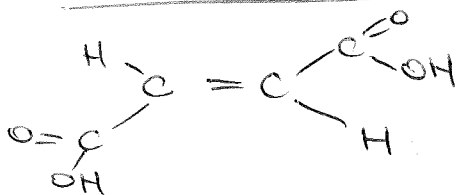
- (a) Compound A has the molecular formula $C_4H_4O_4$. Compound B is a stereoisomer of Compound A. The melting points of Compound A and Compound B are $135^\circ C$ and $287^\circ C$ respectively, due to the ability of Compound A to form an intramolecular hydrogen bond. Compound A reacts, on heating, with dilute H_2SO_4 to form Compound C, $C_4H_6O_5$. Compound C is able to exist as enantiomers. Compound A will react with potassium permanganate to form Compound D, $C_4H_6O_6$. When Compound D is oxidised by periodate ions (IO_4^-), Compound E is produced. Compound E has the molecular formula $C_2H_2O_3$ and gives a positive test with Tollens' reagent (ammoniacal silver nitrate). Each molecule of Compound D produces 2 molecules of Compound E.

- (i) Identify the structures of Compounds A–E. Justify your choice of the stereoisomers A and B and write a balanced equation for the reaction of Compound E with Tollens' reagent.

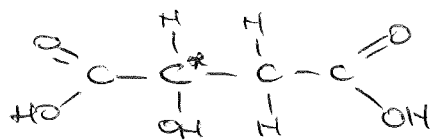
A



B

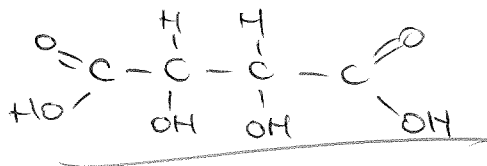


C



* marks chiral carbon; hence C is able to exhibit optical activity.

D

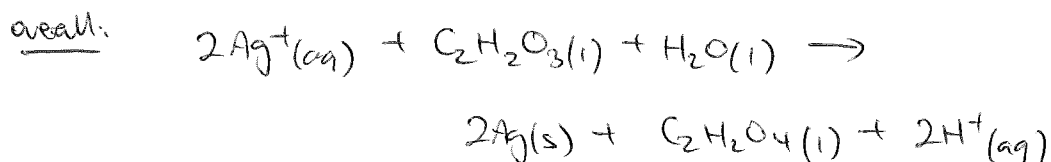
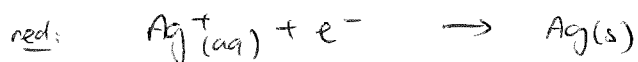


E



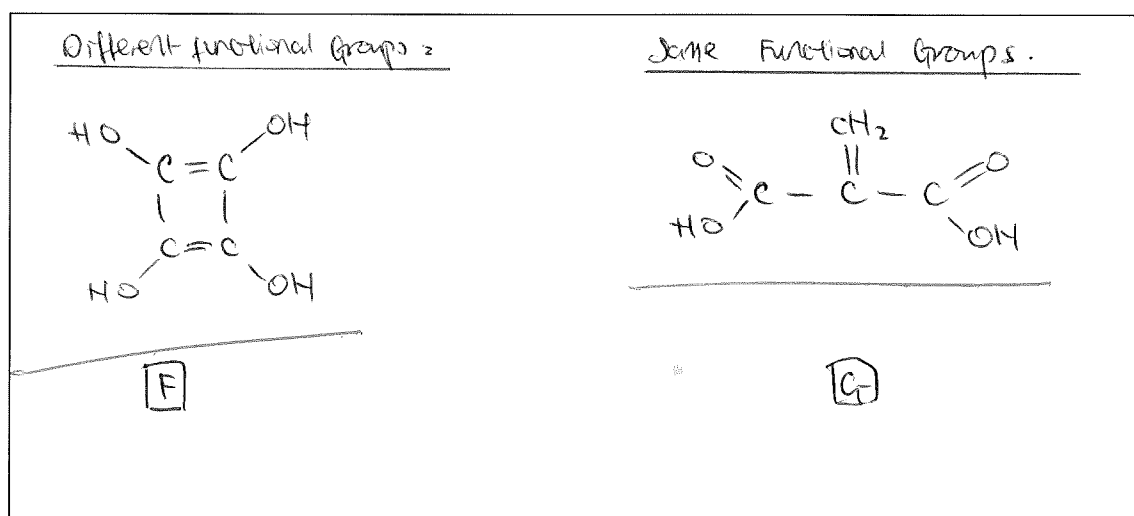
A and B are geometric isomers, and A is the cis formation of the molecule as the two carboxylic acid functional groups are on the same side of the double bond, and thus are able to form intramolecular hydrogen bonds between the two $-OH$ groups. Compound B, the trans isomer, is unable to do this as carboxylic acid functional groups are on opposite sides of the double bond. Thus, the $-OH$ groups are free to form hydrogen bonds with other molecules hence greater intermolecular attractions and greater melting point. Intramolecular hydrogen bonds in A impede its ability for intermolecular bonding, hence lower MP.

Compound Z with Tollen's reagent:



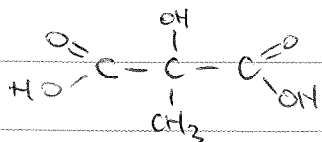
- (ii) Draw two other isomers of Compound A: one that has different functional groups from Compound A, and another that has the same functional groups as Compound A.

Explain why neither of these isomers meet the requirements to be Compound A as described in part (a).



Compound F doesn't fit described requirements because as there are two double bonds present, upon reaction with dilute H_2SO_4 a compound with formula $\text{C}_4\text{H}_8\text{O}_6$ will be produced instead (addition of 2 H_2O 's).

Compound G doesn't fit requirements because upon reaction with dilute H_2SO_4 , the following compound is produced:



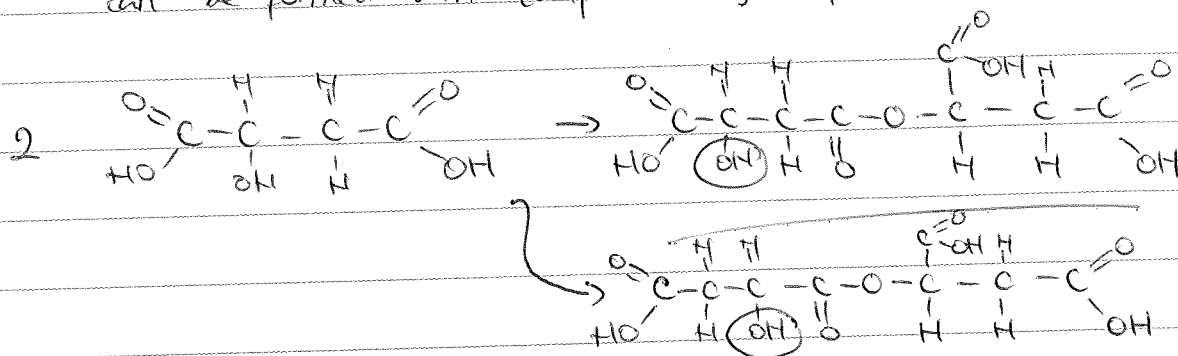
This compound cannot exhibit optical activity,

as there is no chiral carbon.

**Question Five continues
on the following page.**

(b) Discuss the potential for Compound C to form polymers.

As compound C only has one alcohol group, despite the two carboxylic acid functional groups present, (diacid) ^{straight chain} no polymer can be formed; a di-alcohol is needed to produce a polyester. However, a diester can be formed with compound C, as follows.

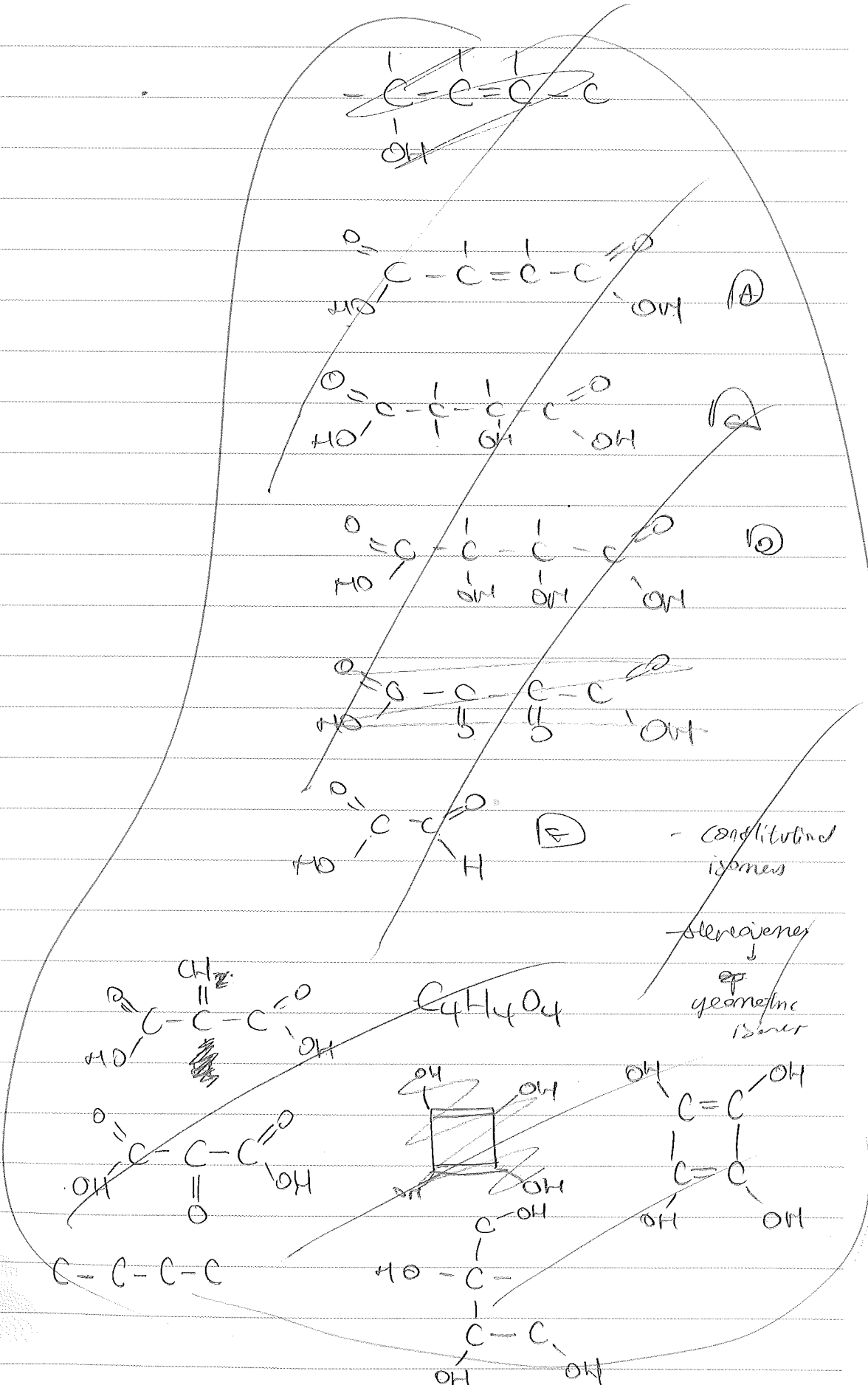


As indicated in the products drawn above, due to the -OH group still present in the diester it is thus possible for an ester linkage to be formed with another molecule of compound C. However, the polyester arising will not be a straight chain polymer, as kinks will arise due to the tetrahedral arrangement of atoms about the carbon atom to which the -OH group is attached.

Extra space if required.
Write the question number(s) if applicable.

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QUESTION
NUMBER



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Question	Mark
ONE	8 ✓ (8)
TWO	8 ✓ (8)
THREE	8 ✓ (8)
FOUR	8 ✓ (8)
FIVE	8 ✓ (8)
TOTAL	40 ✓ (40)