

Assessment Schedule – 2011**Scholarship Chemistry (93102)****Evidence Statement**

Q	Evidence
<p>ONE</p> <p>(a)(i)</p> <p>(ii)</p>	<p>Electrons are negatively charged and attracted to the positively charged protons in the nucleus. The force of attraction is proportional to the size of the charge on the electrons (always -1) and the charge on the nucleus, which increases with an increasing number of protons. The force of attraction also depends on the distance between the electron and the nucleus – the greater the distance the weaker the attraction. As the valence electrons are found in energy levels further from the nucleus, the force of attraction will decrease. Electron–electron repulsions cause electrons to maximise the distance between them. Electron–electron repulsions between valence electrons and core or inner electrons reduce the effective force of attraction between an electron and the nucleus. This is commonly known as shielding or screening.</p> <p>When a cation is formed, the outer layer of electrons is lost, so the valence electron is closer to the nucleus increasing the force of attraction and decreasing the radius. When an anion is formed an extra electron is added and in order to minimize the repulsion between the electrons they move further apart, increasing the atom size.</p> <p>Size of atoms: Across a period – electrons are being added to the same energy level and the nuclear charge is increasing. The increased nuclear charge causes the electrons to be attracted more strongly so the size of the atoms decreases. Down a group the electron are in energy levels further from the nucleus with increased shielding from inner shell electrons which means that the size of the atoms increases.</p> <p>Sizes of ions: Across a period – the size of the ions initially decrease in size. Although the cations are isoelectronic the increased nuclear charge across the period attracts the valence electrons more strongly so the size of the cations decreases. Ions on the right are anions. These will be larger than the cations to the left of the period as the added electrons means that they have an extra energy level. The ions from N^{3-} to Al^{3+} are isoelectronic and the trend in size reflects the increasing nuclear charge. A similar trend is seen from S^{2-} to Ca^{2+} and Se^{2-} to Sr^{2+}. Down a group the trend in the size of the ions is similar to that for the atoms.</p> <p>Relationship of the size of anions and atoms is caused by the repulsion of the added electrons. Relationship of the size of cations and atoms is caused by the removal of an energy level, the reduced distance between the valence electrons and the nucleus and the reduced effect of shielding.</p>
<p>(b)(i)</p> <p>(ii)</p>	<p>Reaction is $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$</p> <p>Lower temperatures favour CO_2. As temperature increases, more CO is formed, so exothermic reaction favours the formation of C and CO_2. When gases reach the top of the smokestack, they will cool down and so the equilibrium reaction will move to the left to generate more heat. This favours the formation of carbon and CO_2. The carbon will form a solid.</p> <p>At equilibrium $2x$ CO formed. Volume of $\text{CO}_2 = (50 - x)$ $60 \text{ mL} = 2x + (50 - x)$ $x = 10 \text{ mL}$. So 20 mL CO and 40 mL of CO_2. This is $1/3 \text{ CO}$ to $2/3 \text{ CO}_2$. From graph, this occurs at 475°C.</p>

Marker Allocation**7–8 marks**

Shows understanding of the principles of chemistry by

- providing a coherent, correct discussion of the forces of attraction and repulsion within atoms and ions that contribute to their size and using these ideas to explain all aspects of the data provided

AND

- uses equilibrium principles to identify and justify the reactions in the chimney stack and correctly calculate the temperature of the given reaction.

5–6 marks

Shows understanding of the principles of chemistry by

- discussing the forces of attraction and repulsion within atoms and ions that contribute to their size and linking these to most of the data provided

AND

- correctly identifies the reaction products and links this to the related equilibrium.

1–4 marks

Answers include:

- attractive and repulsive forces within an atom identified
- trends in atomic size explained
- trends in ion sizes explained
- reaction products identified
- correct procedure for calculating the temperature.

<p>TWO (a)</p>	<p>Cyclohexane is a non-polar molecule. The forces of attraction between the molecules are induced dipole forces, which will be dependent on the size of the electron cloud. Cyclohexane is not soluble in water, since there is little interaction between the water and the hydrocarbon molecules, so the hydrogen-bonded network in water remains unbroken.</p> <p>Cyclohexanol has an –OH group, which allows the molecules to hydrogen bond to each other. These bonds are stronger than the forces between the hexane molecules, so the melting and boiling points are higher. The solubility of cyclohexanol is greater than for cyclohexane since the cyclohexanol molecules can hydrogen bond to water molecules. However the hydrogen bonds between the water molecules and between the cyclohexanol molecules are stronger than those between cyclohexanol and water and hence it is only sparingly soluble.</p> <p><i>cis</i>-cyclohexane-1,2-diol has 2 –OH groups on the hydrocarbon ring. This provides two places for it to hydrogen bond to other cyclohexane-diol molecules so this increases the forces of attraction between the molecules increasing the melting and boiling points. <i>cis</i>-cyclohexane-1,2-diol is very water soluble because of the increased hydrogen bonding between the diol and water molecules.</p>
<p>(b)</p>	<p>The amount of energy released in a reaction depends on the difference in the energy of the bonds in reactants and products. Breaking the bonds in reactants requires energy. Making bonds in products releases energy. If more energy is released than used, the overall reaction will be exothermic.</p> <p>For the combustion of octane: $\text{CH}_3(\text{CH}_2)_6\text{CH}_3 + 12\frac{1}{2} \text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$ Breaking – $18 \times \text{C-H}$ (18×414) + $7 \times \text{C-C}$ (7×346) + $12 \frac{1}{2} \text{O=O}$ ($12 \frac{1}{2} \times 498$) Making – $16 \times \text{C=O}$ (16×804) + $18 \times \text{O-H}$ (18×463) Overall $\Delta_c H = -5099 \text{ kJ mol}^{-1}$ or 44.7 kJ g^{-1}</p> <p>For the combustion of ethanol $\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$ Breaking – $5 \times \text{C-H}$ (5×414) + $1 \times \text{C-C}$ (1×346) + $3 \times \text{O=O}$ (3×498) + $1 \times \text{C-O}$ (1×358) + $1 \times \text{O-H}$ (463) Making – $4 \times \text{C=O}$ (4×804) + $6 \times \text{O-H}$ (6×463) Overall $\Delta_c H = -1263 \text{ kJ mol}^{-1}$ or 24.5 kJ g^{-1}</p> <p>So the net bond-breaking and bond-making for octane releases the larger amount of energy.</p>

Marker Allocation**7–8 marks**

Shows understanding of the principles of chemistry by

- providing a coherent, correct discussion linking the differences in the physical properties to the differences in forces of attraction between the molecules

AND

- correctly identifying and explaining the misconception and calculating the actual values for the combustion reactions using the data given.

5–6 marks

Shows understanding of the principles of chemistry by

- discussing the forces of attraction between the molecules and linking these to the physical properties

AND

- identifying the misconception and providing a correct answer using the data given.

1–4 marks

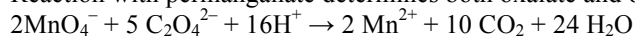
Answers include:

- forces between the molecules recognised
- forces between molecules linked to physical properties
- misconception identified
- correct procedure used for calculations.

THREE

(a)

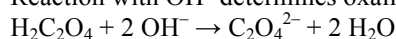
Reaction with permanganate determines both oxalate and oxalic acid



$$n(\text{MnO}_4^-) = 0.01803 \text{ mol L}^{-1} \times 0.02335 \text{ L} = 4.210 \times 10^{-4} \text{ mol}$$

$$n(\text{C}_2\text{O}_4^{2-}) = 5/2 n(\text{MnO}_4^-) = 0.001053 \text{ mol}$$

$$\text{Total } n(\text{C}_2\text{O}_4^{2-}) = 20 \times 0.001053 = 0.02106 \text{ mol}$$

Reaction with OH^- determines oxalic acid

$$n(\text{OH}^-) = 0.1040 \text{ mol L}^{-1} \times 0.01730 \text{ L} = 0.001799 \text{ mol}$$

$$n(\text{H}_2\text{C}_2\text{O}_4) = 1/2 n(\text{OH}^-) = 8.996 \times 10^{-4} \text{ mol}$$

$$\text{Total } n(\text{H}_2\text{C}_2\text{O}_4) = 10 \times 8.996 \times 10^{-4} = 0.008996 \text{ mol}$$

$$m(\text{oxalic acid}) = 0.008996 \times 90.04 = 0.810 \text{ g}$$

$$n(\text{oxalate}) = 0.02105 - 0.008996 = 0.01205 \text{ mol}$$

$$m(\text{sodium oxalate}) = 0.01205 \times 134.02 = 1.615 \text{ g} \quad \text{OR } m(\text{oxalate ion}) = 0.01205 \times 88 = 1.060 \text{ g}$$

$$\text{mass fraction oxalic acid} = 0.810 \text{ g} / 2.496 \text{ g} = 0.325$$

$$\text{mass fraction sodium oxalate} = 1.615 \text{ g} / 2.496 \text{ g} = 0.647 \quad \text{OR } \text{mass fraction oxalate ion} = 1.060 / 2.496 = 0.425$$

$$\text{mass fraction impurity} = 0.028$$

(b)(i)	<p>At pH = 0, combining equations (13) and (5)</p> $\text{Mn}^{2+}(\text{aq}) \rightarrow \text{Mn}^{3+}(\text{aq}) + \text{e}^{-} \quad E^{\circ} = +1.54 \text{ V} \quad (5)$ $\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}(\ell) \quad E^{\circ} = +1.23 \text{ V} \quad (13)$ <hr/> $4\text{Mn}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) \rightarrow \text{H}_2\text{O}(\ell) + \text{Mn}^{3+} \quad E^{\circ}_{\text{cell}} = 1.23 - 1.54 < 0$ <p>Since $E^{\circ} < 0$, reaction is not spontaneous</p> <p>At pH = 14 ($[\text{OH}^{-}] = 1 \text{ mol L}^{-1}$) Combining equations (12) and (10)</p> $2\text{Mn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-} \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\ell) + 2\text{e}^{-} \quad E^{\circ} = -0.23 \text{ V} \quad (10)$ $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 4\text{e}^{-} \rightarrow 4\text{OH}^{-} \quad E^{\circ} = +0.40 \text{ V} \quad (12)$ <hr/> $4\text{Mn}(\text{OH})_2(\text{aq}) + \text{O}_2(\text{g}) + \rightarrow 2\text{Mn}_2\text{O}_3(\text{s}) + 4\text{H}_2\text{O}(\ell) \quad E^{\circ}_{\text{cell}} = 0.40 - (-0.23) > 0$ <p>Since $E^{\circ} > 0$ reaction is spontaneous</p> <p>Hence at high pH, the species present ($\text{Mn}(\text{OH})_2(\text{s})$) will be oxidised by O_2 gas in solution to Mn_2O_3, but at low pH the species present ($\text{Mn}^{2+}(\text{aq})$) is stable to O_2.</p> <p><i>Note:</i> (Alternative answers could have MnO_2 as product.)</p>
(ii)	<p>Combining equations (2) and (7), it can be seen that HMnO_4^{-} disproportionates in acidic solution. This means that it is unstable under these conditions.</p> $2\text{HMnO}_4^{-}(\text{aq}) \rightarrow 2\text{MnO}_4^{-}(\text{aq}) + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \quad E^{\circ} = +0.90 \text{ V} \quad (2)$ $\text{HMnO}_4^{-}(\text{aq}) + 3\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\ell) \quad E^{\circ} = +2.10 \text{ V} \quad (7)$ <hr/> $3\text{HMnO}_4^{-}(\text{aq}) + \text{H}^{+} \rightarrow 2\text{MnO}_4^{-}(\text{aq}) + \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O} \quad E^{\circ} = +1.20 \text{ V}$ <p>Since $E^{\circ} > 0$, reaction is spontaneous</p>
(iii)	<p>At pH = 0 Combining equations (8) and (5)</p> $\text{Mn}^{3+} + 2\text{H}_2\text{O}(\ell) \rightarrow \text{MnO}_2 + 4\text{H}^{+} + \text{e}^{-} \quad E^{\circ} = +0.95 \text{ V} \quad (8)$ $\text{Mn}^{3+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) \quad E^{\circ} = +1.54 \text{ V} \quad (5)$ <hr/> $2\text{Mn}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\ell) \rightarrow \text{MnO}_2 + \text{Mn}^{2+} + 4\text{H}^{+} \quad E^{\circ}_{\text{cell}} = 1.54 - 0.95 > 0$ <p>Since $E^{\circ} > 0$, reaction is spontaneous</p> <p>At pH = 14 Combining equations (9) and (10)</p> $\text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^{-} \rightarrow 2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\ell) + 2\text{e}^{-} \quad E^{\circ} = +0.15 \text{ V}$ $\text{Mn}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\ell) + 2\text{e}^{-} \rightarrow 2\text{Mn}(\text{OH})_2(\text{s}) + 2\text{OH}^{-} \quad E^{\circ} = -0.23 \text{ V}$ <hr/> $2\text{Mn}_2\text{O}_3(\text{s}) + 2\text{H}_2\text{O}(\ell) \rightarrow 2\text{MnO}_2(\text{s}) + 2\text{Mn}(\text{OH})_2(\text{s}) \quad E^{\circ}_{\text{cell}} = -0.23 - 0.15 < 0$ <p>Since $E^{\circ} < 0$, reaction is not spontaneous</p> <p>At low pH, Mn^{3+} disproportionates into MnO_2 and Mn^{2+}, so is unstable, but at high pH, it is stable to disproportionation.</p>

7–8 marks

Shows understanding of the principles of chemistry by

- correctly calculating mass fractions

AND

- uses the data given to correctly discuss all the reactions given.

5–6 marks

Shows understanding of the principles of chemistry by

- using the correct procedures to calculate the mass fraction of either the oxalic acid or the sodium oxalate or oxalate ion

AND

- explaining the oxidation of Mn(II) at different pH and either discussing the intermediate species or pH dependence of Mn(III).

1–4 marks

Answers include:

- some of the correct procedure for the titration calculations
- correctly balanced redox equations
- correct choice and use of E° data
- correct procedure used for calculations.

<p>FOUR (a)(i)</p> <p>(ii)</p>	<p>When $[\text{H}_2\text{CO}_3] = [\text{HCO}_3^-]$; $K_1 = [\text{H}^+] = 4.2 \times 10^{-7}$; pH = 6.38 When $[\text{HCO}_3^-] = [\text{CO}_3^{2-}]$; $K_2 = [\text{H}^+] = 4.7 \times 10^{-11}$; pH = 10.33 For pH = 7.40, $[\text{H}^+] = 4.0 \times 10^{-8}$ so components of the best buffer are H_2CO_3 and HCO_3^- And $4.2 \times 10^{-7} = 4.0 \times 10^{-8} \times \text{HCO}_3^- / \text{H}_2\text{CO}_3 = 10.5$ More effective against acid because proportion of conjugate base present is higher.</p> <p>$K_a = 1.38 \times 10^{-4} = [\text{H}^+][\text{Lac}^-] / [\text{HLac}]$; $[\text{H}^+] = 3.98 \times 10^{-8}$ $[\text{Lac}^-] / [\text{HLac}] = 1.38 \times 10^{-4} / 3.98 \times 10^{-8} = 3467$ So $[\text{Lac}^-]$ is significantly larger than $[\text{HLac}]$.</p>
<p>(b)(i)</p> <p>(ii)</p>	<p>$K_s(\text{NaUr}) = (8.00 \times 10^{-3})^2 = 6.40 \times 10^{-5}$ When $[\text{Na}^+] = 0.130 \text{ mol L}^{-1}$, $[\text{Ur}^-] = 4.9 \times 10^{-4}$ At pH = 7.4 and $[\text{Ur}^-] = 4.9 \times 10^{-4}$ To calculate $[\text{HUr}]$ $K_a = 3.98 \times 10^{-6} = [\text{H}_3\text{O}^+][\text{Ur}^-] / [\text{HUr}]$ $[\text{HUr}] = 3.98 \times 10^{-6} \times 4.9 \times 10^{-4} / 3.98 \times 10^{-6}$ $[\text{HUr}] = 4.9 \times 10^{-6} \text{ mol L}^{-1}$ Since this is less than the solubility of HUr, there will be no precipitate.</p> <p>For precipitation $[\text{HUr}] > 0.0005 \text{ mol L}^{-1}$, $[\text{Ur}^-] < 1.5 \times 10^{-3}$ $K_a = 3.98 \times 10^{-6} = [\text{H}_3\text{O}^+][\text{Ur}^-] / [\text{HUr}]$ $3.98 \times 10^{-6} = [\text{H}_3\text{O}^+] \times 1.5 \times 10^{-3} / 5 \times 10^{-4}$ $[\text{H}_3\text{O}^+] = 1.32 \times 10^{-6} \text{ mol L}^{-1}$, pH = 5.9 OR calculation using $\text{pH} = \text{p}K_a + \log \frac{[\text{Ur}^-]}{[\text{HUr}]} = 5.4 + \log \frac{1.5 \times 10^{-3}}{5 \times 10^{-4}} = 5.9$</p>

7–8 marks

Shows understanding of the principles of chemistry by

- determining the best buffer and its effectiveness (with reasons) and showing the predominance of lactate ion at the given pH

AND

- correctly calculating the $[\text{Ur}^-]$ and showing that uric acid does not precipitate AND calculating the pH for the formation of kidney stones.

5–6 marks

Shows understanding of the principles of chemistry by

- Using data provided to determine a buffer ratio and / or to identify the most effective buffer

AND

- Using the correct procedure to determine $[\text{Ur}^-]$ and / OR $[\text{HUr}]$

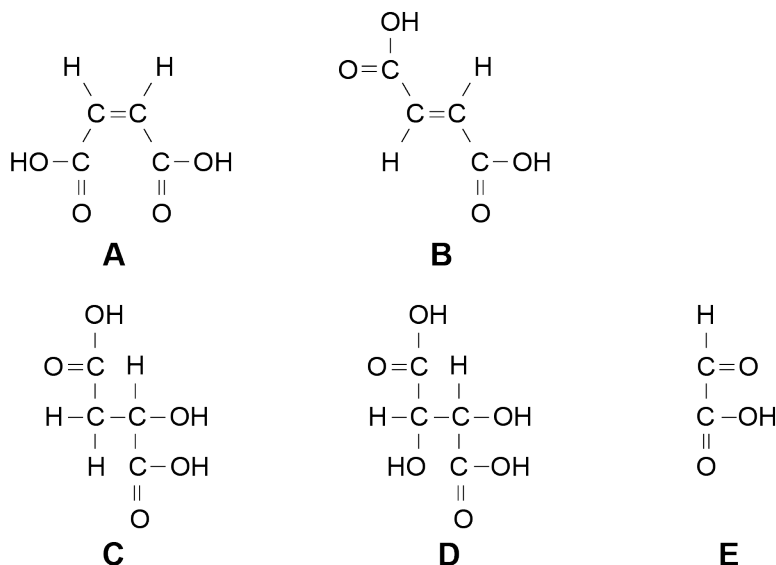
1–4 marks

Answers include:

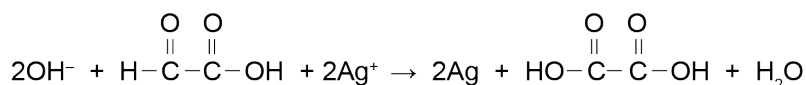
- determines the best buffer
- recognises the effectiveness of the buffer
- correct procedure used for calculations.

FIVE
(a)(i)

Compound A and Compound B are stereoisomers, so have a different arrangement about the double bond. Although Compound A is a polar molecule, it has a lower boiling point because the formation of the intramolecular hydrogen bond means that there is only one intermolecular hydrogen bond possible between the molecules. However, Compound B is able to form hydrogen bonds with the acid groups on each side of the molecule, 2 bonds per molecule, thus increasing the strength of the intermolecular attractions. Also the packing of the molecules in Compound B is more regular, allowing the molecules to get closer to each other, increasing the instantaneous dipole attractions between the molecules.

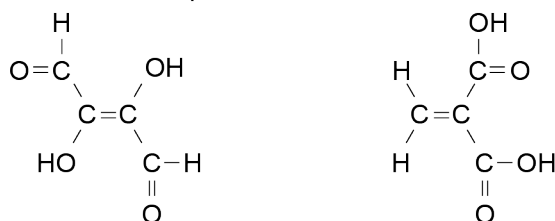


Equation for reaction of Compound E with Tollens' reagent



(ii)

other possible structures of **A**

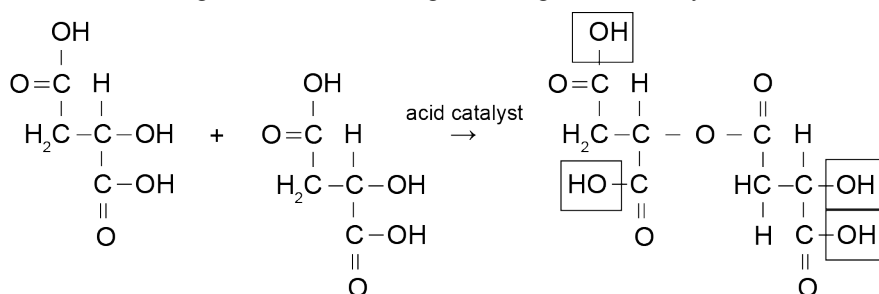


Reasons these structures not selected:

- Has alcohol and aldehyde functional groups so would give a product with 4 acid groups when reacted with KMnO_4 – so will not match the formula given for Compound D.
- Has a double bond at the end of the chain so when reacted with H_2SO_4 to form a compound the resulting product will not have enantiomers.

(b)

Compound C has two functional groups (alcohol and acid) in the same molecule. This means that under the right conditions it can form ester linkages with other molecules. There are several places in each molecule where these linkages can form, allowing for a long chain to be synthesised.



7–8 marks

Shows understanding of the principles of chemistry by identifying all the isomers A to E with justification as required AND explanations regarding isomers of A not selected AND discussion of the formation of polymers of Compound C.

5–6 marks

Shows understanding of the principles of chemistry by drawing valid structures for at least four of the Structures A to E with some justification AND either explains why other isomers for A are not selected OR discusses polymer formation using C.

1–4 marks

Answers include:

- identifying the functional groups in the unknowns
- writes balanced equation for reaction with Tollens' reagent
- draws valid structures for A to E
- recognises the requirements for polymer formation from compound C
- shows valid reaction of functional group with reagent stated.