NEW ZEALAND SCHOLARSHIP 2004

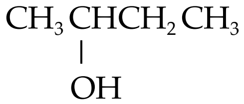
CHEMISTRY

Sample of assessed candidate work – Outstanding Performance - Performance Descriptor 1: Performance Category 1

QUESTION ONE: ORGANIC MOLECULES

(a) Determine the structures of each of the compounds **A** to **F** in the reaction scheme.

Compound A:



$CH_3\underset{\substack{|\\ OH}}{CH}CH_2CH_3$

B:

$CH_3\underset{\substack{\|\\ O}}{C}CH_2CH_2CH_3$

C:

$CH_3\underset{\substack{|\\ C1}}{CH}CH_2CH_2CH_3$

D: $CH_2 = CHCH_2CH_2CH_3$

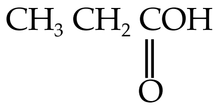
E: $CH_3CH = CH\,CH_2\,CH_3$

F: $CH_3\,CH_2\,CH\,CH_2\,CH_3$

C – Functional group sequence correct but incorrect carbon framework showing failure to <u>integrate</u> all information provided.

(b) Draw and name possible structures for the compounds **X, Y** and **Z.**

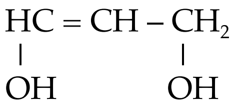
X:



$CH_3\,CH_2\,\underset{\substack{\|\\ O}}{C}OH$

propanoic acid

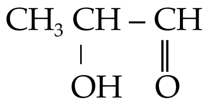
Y:



$\underset{\substack{|\\ OH}}{HC} = CH - \underset{\substack{|\\ OH}}{CH_2}$

1, 3 diol propene

Z:



$CH_3\,\underset{\substack{|\\ OH}}{CH} - \underset{\substack{\|\\ O}}{CH}$

2–hydroxypropanal

B Answer. Correctly interprets information and demonstrates understanding of principles of organic chemistry.

(c) Account for the variation in boiling points of the amines given in the table.

2-methyl – 2-propylamine and 1 – butylamine have the highest boiling points as they both can form hydrogen bonds, ad they have H bonded to the highly electronegative N. 1–butylamine has the higher b.p. of the two as it is a straight chain structure, so each molecule can be more closely packed, while 2-methyl-2-propylamine has an uneven structure, molecules cannot be packed together as closely, so force of attraction between molecules is not as strong as that of between 1-butylamine molecules, so it takes less energy to overcome these forces, so its boiling point is lower. However, both of these molecules still form hydrogen bonds, which is a stronger intermolecular force. They still form instantaneous induced dipoles as well, and these forces are equal strength to ethyldiethylamine as well, as all these three have the same molar mass, so same no. of electrons, so similar strength instantaneous induced dipoles. Diethylmethylamine, although it has a much higher M of 87.2, so stronger instantaneous induced dipoles, does not form H-bonds, which has a much great effect in determining the strength of intermolecular forces as it is much stronger. Therefore, diethylmethylamine and ethyldimethylamine both have weaker intermolecular forces than the other two, which requires less E to overcome, so they have lower boiling points.

Ethyldimethylamine and diethylmethylamine ar both polar molecules as the C-N bond is polar, and the unsymmetrical arrangement of bonds does not cancel the dipoles out, so they are polar molecules. Therefore they form permanent dipole forces, but for these two molecules, the permanent dipole forces are of similar strength, as the have the same type of polar bond (ie C-N). However, diethylmethylamine has higher molar mass, more electrons, so stronger and more often form instantaneous induced dipoles, so it takes more energy to overcome these stronger intermolecular forces, so it has higher boiling point than ethyldimethylamine.

B Answer. Correctly interprets information and demonstrates understanding of principles of organic chemistry. However, the discussion about the packing of the molecules is not in sufficient depth for an A answer

QUESTION TWO: AQUEOUS SOLUTIONS

(a) (i) Calculate the pH of the ethanolamine solution.

Equivalence point: 35 mL
half " " : 17.5 mL
At 17.5 mL, pH = 9.5 = pKa (ethanolamine)

$$\text{Ka} = 10^{-9.5} = 3.16\times10^{-10} \quad \text{Kb} = \frac{1\times10^{-14}}{3.16\times10^{-10}} = 3.16\times10^{-5}$$

$$HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3^+ + OH^-$$

Equivalence point: V(HCl) = 0.0350 L
c(HC1) = 0.0107 molL^{-1}
n (HCl) = cV = 3.75×10^{-4} mo l = n (ethanolamine)
V (ethanolamine) = 0.0250 L

$$\text{C (ethanolamine)} = \frac{\text{n}}{\text{v}} = 0.0150 \text{ molL}^{-1}$$

B Answer. Answer correct, showing ability to analyse information and apply knowledge.

$$\text{Kb} = \frac{\left[HOCH_2CH_2NH_3^+\right]\left[OH^-\right]}{\left[HOCH_2CH_2NH_2\right]}$$

$$\text{Assume:} \begin{cases} \left[HOCH_2CH_2NH_2\right] = 0.0150 \text{ molL}^{-1} \\ \left[OH^-\right] = \left[HOCH_2CH_2NH_3^+\right] \end{cases}$$

$$\left[OH^-\right]^2 = 3.16 \times 10^{-5} \times 0.0150$$

$$\left[OH^-\right] = 6.88 \times 10^{-4} \text{molL}^{-1}$$

$$\left[H_3O^+\right] = 1 \times 10^{-14} \div 6.88\times10^{-4} = 1.45\times10^{-11} \text{ molL}^{-1}$$

$$\text{pH} = -\log\left[H_3O^+\right] = 10.8$$

(ii) Show by calculation that the pH at equivalence point is 5.9

(ii) $HOCH_2NH_2 + HCl \rightarrow HOCH_2CH_2NH_3^+Cl^-$

$$HOCH_2NH_3^+ + H_2O \rightleftharpoons HOCH_2CH_2NH_2 + H_3O^+$$

$$\text{Ka} = 3.16\times10^{-10} = \frac{[HOCH_2CH_2NH_2][OH_3O^+]}{[HOCH_2CH_2NH_3^+]}$$

$$\text{Assume:} \begin{cases} \left[HOCH_2CH_2NH_3^+\right] = \dfrac{3.75\times10^{-4}}{0.0250+0.0350} = 6.24\times10^{-3}\text{molL}^{-1} \\ \left[H_3O^+\right] = \left[HOCH_2CH_2NH_2\right] \end{cases}$$

$$\left[H_3O^+\right]^2 = 3.16\times10^{-10}\times6.24\times10^{-3} \qquad \left[H_3O^+\right] = 1.40\times10^{-6}\text{molL}^{-1}$$

$$\text{ph} = 5.9$$

B Answer. Answer correct, showing ability to analyse information and apply knowledge.

(iii) Relate the change in pH and the shape of the titration curve to the change in the nature and concentration of the species in the flask as the titration is carried out.

In the beginning, when the solution of ethanolamine is untitrated, there are species H_2O, HO $CH_2CH_2NH_2$, and some $HOCH_2CH_2NH_3^+$, OH^-, and very little H_2O^+ from dissociation of H_2O. This is because ethanolamine is a weak base.
As the titration is carried out and strong acid HCl is added, $HOCH_2CH_2NH_3^+$ and Cl^- ions are formed. $HOCH_2CH_2NH_3^+$, the conjugate acid of a weak base, also dissociates in water to form H_3O^+ and $HOCH_2CH_2NH_2$. $HOCH_2CH_2NH_3^+ + H_2O \rightleftharpoons HOCH_2CH_2NH_2 + H_3O^+$. As more HCl is added, more $HOCH_2CH_2NH_3^+$ ions are formed, so as the concentration of this increases, the equilibrium shifts forward to use up the excess, so $[H_3O^+]$ increases, becomes acidic, so pH decreases. The area around half equivalence point is the buffer zone, it is relatively flat as the solution is acting as a buffer, which resists small changes to pH. This is because both the base ($HOCH_2CH_2NH_2$) and its conjugate acid are present in solution around that point, so if base was added, the acid would react it off, and vice versa for adding a base, so around this point, the solution acts as a buffer, so change in pH is not so great (but is still becoming more acidic). As the titration reaches equivalence point, there is an equal amount of HCl to ethanolamine so all of it reacts to form $HOCH_2CH_2NH_3^+$, which then dissociates forming H_3O^+. This increase in $[HOCH_2CH_2NH_3^+]$ will produce a dramatic increase in $[H_3O^+]$, therefore pH drops very sharply at equivalence point. At this point, the species present are:
$H_2O >> Cl^- \approx HOCH_2CH_2NH_3^+ > H_3O^+ = HOCH_2CH_2NH_2 >> OH^-$. There is always H_2O present (obviously …), and also a very small amount of OH^- from the dissociation of H_2O.
After equivalence point, more HCl is added but ethanolamine has been used up already, so $[H_3O^+]$ increases, pH drops. However, the HCl solution has concentration 0.0107 $molL^{-1}$ and however much is added, it is maximum that conc., so pH does not keep on dropping forever, but rather stabilises at around the HCl pH (but slightly higher as there is still other species of $HOCH_2CH_2NH_3^+$ and some $HOCH_2CH_2NH_2$ present). Hence the graph flattens out again at the end.

A Answer. Answer integrates and applies knowledge and skills from different areas of chemistry and demonstrates a depth and breadth of knowledge with insight into the application of chemical principles.

(b) Calculate the pH of a saturated solution of $Hg(OH)_2$. Justify any assumptions made in carrying out the calculation.

$Hg(OH)_2(s) \rightleftharpoons Hg^{2+}(aq) + 2OH^-(aq)$
$Ks = [Hg^{2+}][OH^-]^2 = 3.6 \times 10^{-26}$
Assume $[OH^-] = 2[Hg^{2+}]$
$4[Hg^{2+}]^3 = 3.6 \times 10^{-26}$
$[Hg^{2+}] = 2.08 \times 10^{-9}$ molL^{-1}
$[OH^-] = 4.16 \times 10^{-9}$ molL^{-1}
$[H_3O^+] = 2.40 \times 10^{-6}$ molL^{-1}
pH = 5.62

The assumptions were that $[OH^-]$ is only from dissolving $Hg(OH)_2$, and the dissociation of H_2O to form OH^- is to insignificant to effect the calculations. However, this assumption is not justified, as the Ks is very, very tiny, $[OH^-]$ is very very tiny as well, less than $[OH^-]$ from water, which is 1×10^{-7} molL^{-1}. Using the assumed $[OH^-]$ to calculate pH is not correct (giving an acidic pH), as the OH^- from water has to be taken into account, as it is much larger so has greater effect. It is the OH^- $Hg(OH)_2$ that is insignificant. So in fact, $[OH^-]$ is around 1×10^{-7}, so pH should be around 7.

B Answer. Correctly analyses and interprets information.

QUESTION THREE: ALCOHOL INVESTIGATIONS

(a) Discuss the method described above, justifying the need for each step involved.

Alcohol has to removed from the blood to be react alone, as there may be other substances in blood that react with $Cr_2O_7^{2-}$ as well. Distillation can be used as alcohol has lower bp. so it will evapourate and can be condensed off.

- $Cr_2O_7^{2-}$ acts as an oxidising agent, it oxidises the alcohol to carboxylic acid, while itself is reduced to Cr^{3+}, so colour change of orange to green. Excess is added so to measure the amount of unreacted, and as original amount is known to work out amount of alcohol. The alcohol has to be reacted with dichromate (and not in a titration), as it requires a stronger oxidising agent, such as dichromate, and also heat and time.

- $Cr_2O_7^{2-}$ is then reacted with I^- and not titrated as the colour change may not be obvious/sharp or takes time, and $Cr_2O_7^{2-}$ does not react with $S_2O_3^{2-}$, also I_2 will precipitate so then a reaction of I_2 and $S_2O_3^{2-}$ is required to determine n(I_2). Starch indicator is added as colour change of $I_2 \rightarrow I^-$, which is decolourising brown solution is not sharp, but cannot be added earlier on as it would affect the reaction.

B - This answer, along with part (c) showed a depth of knowledge of the investigation method but lacked insight on some

(b) Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80mg alcohol per 100mL of blood.

$V(S_2O_3^{2-}) = (17.94 + 17.86 + 17.84) \div 3 = 17.88 \text{ mL} = 0.0179 \text{ L}$

$n(S_2O_3^{2-}) = cV = 0.105 \times 0.0179 = 1.88 \times 10^{-3} \text{ mol}$

$$\frac{n\left(S_2O_3^{2-}\right)}{2} = n(I_2) = 9.39 \times 10^{-4} \text{mol}$$

$$\frac{n(I_2)}{3} = n\left(Cr_2O_7^{2-}\right) = 3.139 \times 10^{-4} \text{mol unreacted}$$

Original $n(Cr_2O_7^{2-}) = cV = 0.0100 \times 0.0492 = 4.92 \times 10^{-4}$ mol

Reacted $n(Cr_2O_7^{2-}) = 4.92 \times 10^{-4} - 3.13 \times 10^{-4} = 1.79 \times 10^{-4}$ mol

$$\frac{n\left(Cr_2O_7^{2-}\right)}{2} = \frac{n\left(CH_3CH_2OH\right)}{3} \quad n(CH_3CH_2OH) = \underline{2.69 \times 10^{-4} \text{mol}}$$

$M(CH_3CH_2OH) = 2 \times 12.0 + 6 \times 1.0 + 16.0 = 46.0 \text{ gmol}^{-1}$

$m(CH_3CH_2OH) = nM = 0.0124 \text{ g} = 12.4 \text{ mg}$

Sample is not above legal limit of 80 mg 100 mL.

C Answer. Answer, shows ability to analyse and interpret information and apply knowledge but there is a minor error in the calculation

(c) Explain why the procedure being used is not suitable for quantitative determination of the alcohol in the home brew and outline ways that the method could be adjusted to make it more acceptable.

There would be a high concentration of CH_3CH_2OH present in the home brew, so most of the $Cr_2O_7^{2-}$ will have reacted, so not much will react with I^- to form I_2, so not much I_2 will be present in the titration with $S_2O_3^{2-}$, therefore only a tiny amount of $S_2O_3^{2-}$ will have reacted all the I_2. Readings of 1 mL are not accurate as the percentage error would be too large.

- A lot more of excess $Cr_2O_7^{2-}$ added in the beginning would solve this problem, as then there will be enough $Cr_2O_7^{2-}$ left over to react.
- The alcohol sample can be diluted even further so there is less of it to react off the $Cr_2O_7^{2-}$.
- Use a very dilute solution of $S_2O_3^{2-}$ could also make it more acceptable, as the titre reading would be larger so more accurate.

QUESTION FOUR: COMPARING PROPERTIES

(a) Discuss, in terms of their structure, the relative sizes of the atoms and ions of the elements O, Mg and S.

The atom O is the smallest atom, as atomic radii decreases across the period and increases down a group. O has 1 less electron shell than S, so it has less shielding. Even though S has many more protons than O, so higher nucleus charge, the increase in shielding is more significant, so the force of attraction of the S nucleus to its valence electrons is less than O atom, so its electrons are held less strongly so they are further apart, so S atom is larger than O atom. The same applies for Mg atom and O atom, where Mg atom is bigger than O atom. Mg atom is also bigger than S atom. As they have the same number of electron shells, they have the same shielding. However, S has more protons than Mg, so higher nucleus charge, force of attraction on valence electrons is stronger, electrons are held closer, so the S atom is smaller than the Mg atom.

The O^{2-} ion is bigger than its O atom, as it gains electrons but is still added to the same electron shell, so shielding does not change and nucleus charge is the same as proton is same. As more electrons are added, they repel each other more, so spread further apart, electron shell is bigger, so the O^{2-} ion is larger than O atom.

A Answer. Answer correctly applies knowledge and demonstrates a depth and breadth of knowledge with insight into the application of chemical principles.

The S^{2-} ion is bigger than S atom, same reason as the O^{2-} ion and O atom.

The Mg^{2+} ion is smaller than Mg atom, as it loses it valence electrons, so it loses an electron shell, which also decreases shielding. As the protons no. so nucleus charge does not change, and shielding decreases, force of attraction from nucleus to valence electrons is stronger, so electrons are held closer, so Mg^{2+} ion is smaller than Mg atom. S^{2-} ion is the largest ion out of the three as it has 1 more electron shell than Mg^{2+} and O^{2-}, which is increased shielding so even though nucleus charge is greater, electrons are not held as closely, so it is the biggest ion.

Mg^{2+} ion is the smallest ion, as it has the same no. of electron shells as O^{2-} ions so same shielding, but Mg^{2+} has more protons/higher nucleus charge, so stronger force of attraction on valence electrons, electrons are held closer, Mg^{2+} ions is smallest.

(b) Use the data in the table to deduce which of the two compounds, ethane or ethanol, has the more negative enthalpy of combustion.

Combustion reaction:

$$CH_3CH_3(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3\,H_2O(\ell)$$

$CH_3CH_2OH(\ell)^+\ 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(\ell)$

$\Delta_cH° (CH_3CH_3) = 3 \times \Delta_fH°(H_2O) + 2 \times \Delta_fH°(CO_2) - O$
$- \Delta_fH° (CH_3CH_3)$

$\Delta_cH° (CH_3CH_2OH) = 3 \times \Delta_fH°(H_2O) + 2 \times \Delta_fH°(CO_2) - O$
$- \Delta_fH° (CH_3CH_2OH)$

as $3 \times \Delta_fH° (H_2O)$ and $2 \times \Delta_fH° (CO_2)$ change is same for both; they will not be compared.

For $\Delta_cH° (CH_3CH_3)$ is a number – (–84), and $\Delta_cH° (CH_3CH_2OH)$ is a number – (–235), this adds more, so it will be <u>less</u> negative. Also CH_3CH_2OH gives out more energy when forming, so it will require more energy to break the bonds, so overall combustion reaction energy given out will be less.

More negative $\Delta_cH°$ is CH_3CH_3.

B Answer. Answer correctly analyses and interprets information.

(c) Determine the pH of pure water at 37 °C and discuss whether this solution is neutral or not.

The solution is still neutral as the same concentration of H_3O^+ and OH^- will be present in pure water, no matter what the temperature is. The pH will have a different scale to what we normally use. Usual pH scale goes up to $-\log(1 \times 10^{-14}) = 14$, half is neutral. So the higher temperature pH scale would go up to $-\log(2.5 \times 10^{-14}) = 13.6$, at neutral, $pH = \frac{1}{2} \times 13.6 = 6.80$.

pH of pure water at 37°C is pH = 6.80.
But it is still neutral!

B Answer. Answer correctly analyses and interprets information.

(d) Calculate the standard enthalpy energy change for the combustion of sucrose ($C_{12}H_{22}O_{11}$) and determine the mass in grams of sucrose that would be needed to produce sufficient energy to evaporate exactly one litre of water.

$C_{12}H_{22}O_{11}(s) + 12\ O_2\ (g) \rightarrow 12\ CO_2\ (g) + 11\ H_2\ O\ (\ell)$

$\Delta_c H° = 12 \times \Delta_f\ (CO_2) + 11 \times \Delta_f\ (H_2O,\ \ell) - O - \Delta_f\ (G_2H_{22}O_{11})$

$= 12 \times (-393.5) + 11 \times (-285.8,) - (-2222.0)$

$\Delta_c H° = -5643.8 \approx -5640\ kJmol^{-1}$

$H_2O\ (\ell) \rightarrow H_2O\ (g)$

$\Delta_c H° = \Delta_f H°\ (H_2O,\ g) - \Delta_f H°\ (H_2O,\ \ell)$

$= -241.8 + 285.8$

$= 44.0$ kJmol–1

B Answer. Answer correctly analyses and interprets information.

$1\ L\ of\ H_2O \Rightarrow m(H_2O) = 1000\ g$ $\qquad M(H_2O) = 18.0\ gmol^{-1}$

$$n\ (H_2O) = \frac{m}{M} = \frac{1000}{18} = 55.6\ mol$$

E required to evapourate 1 L $H_2O = 55.6 \times 44.0 = 2440$ kJ

$$n(C_{12}H_{22}O_{11}) = \frac{2440}{5640} = 0.433\ mol$$

$M(C_{12}H_{22}O_{11}) = 12 \times 12 + 22 + 11 \times 16 = 342\ gmol^{-1}$

$M(C_{12}H_{22}O_{11}) = nM = 148$ g required

QUESTION FIVE: IDENTIFYING WHITE SOLIDS

Formulate a scheme for identifying the solid with reference to the data.
Provide a comprehensive justification of the steps in the scheme on the basis of the data given.

Put red litmus paper into solutions of the four. Solutions of NaOCl and $Na_2\ SO_3$ should turn it blue, the other two will remain red. This is because those two are basic.

$$NaOCl(s) \xrightarrow{H_2O} Na^+(aq) + OCl^-(aq)$$
$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-\ \text{Basic}$$
$$Na_2SO_3(s) \xrightarrow{H_2O} 2Na^+(aq) + SO_3^{2-}(aq)$$
$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-\ \text{Basic}$$

This is because OCl^- and SO_3^{2-} are conjugate bases of weak acids, so they form an equilibrium producing back the acid so it accepts an H^+ forming OH^- when in water. HOCl and HSO_3^- are weak acids as can be seen from their high pka, the higher the pka, the weaker the acid, the other two are strong acids, so their conjugate base salts do not form a basic solution.

Continued over.

Adding I^-, KIO_3 and NaOCl solution will have a reaction, I^- will be oxidised to I_2

colourless → brown solution

while those two will be reduced. I^- can only be oxidised, E°cell = E°red – E°ox = E°red – 0.62. If it E°red is greater than O, reaction will occur, so any species that is to be reduced by I^- has to have E° > 0.62. This applies to IO_3^- (which KIO_3 forms in solution), with $E°_{(IO3-/I2) = 1.20}$, IO_3^- reduced to I_2. And also to HOCl (which NaOCl forms in solution), with $E_{°(HOCl/C1-) = 1.51}$, HOCl reduced to $C1^-$.

Na_2SO_3 forms HSO_3^- in solution which then forms H_2SO_3 as HSO_3^- is amphiprotic. $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$.
H_2SO_3 reduced to S has E° = 0.45, which is less than 0.62 (E° of I^-), so it will not be reduced, and I^- will not be oxidised, ie no reaction.
NaBr forms Br^- ions in solution, and as this can only be oxidised, and so is I^-, two reductants together will produce no reaction.

A Answer. Answer integrates and applies knowledge and skills from different areas of chemistry and demonstrates a depth and breadth of knowledge with insight into the application of chemical principles.

So the reaction scheme:
Ad red litmus paper to solutions:
Turns blue → Go to (1)
Remains red → Go to (2)

1. Add acidified aqueous I^- to solutions:
   I^- oxidised to I_2, ie forms brown solution and maybe black precipitate → NaOCl
   No reaction → Na_2SO_3.

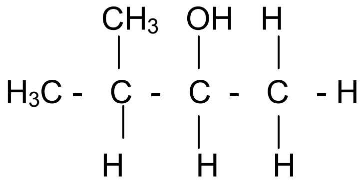
2. Add acidified aqueous I^- to solutions:
   $I^- \rightarrow I_2$, ie forms brown solution and maybe black precipitate → KIO_3
   No reaction → NaBr.

Sample of assessed candidate work – Performance Descriptor 2: Performance Category 3

QUESTION ONE: ORGANIC MOLECULES

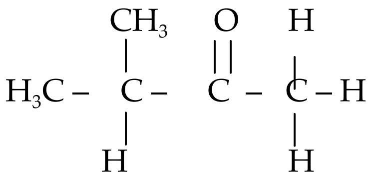
(a) Determine the structures of each of the compounds **A** to **F** in the reaction scheme.

A



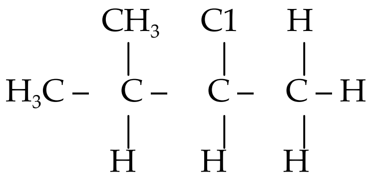
$H_3C-CH(CH_3)-CH(OH)-CH_2-H$

B



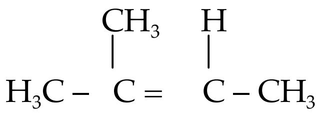
$H_3C-CH(CH_3)-C(=O)-CH_2-H$

C



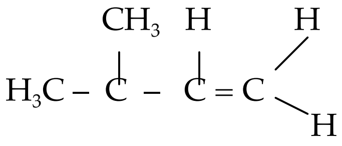
$H_3C-CH(CH_3)-CHCl-CH_2-H$

E



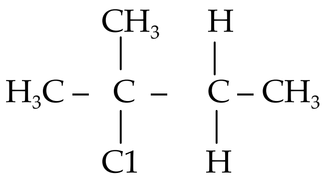
$H_3C-C(CH_3)=CH-CH_3$

D



$H_3C-CH(CH_3)-CH=CH_2$

F



$H_3C-CCl(CH_3)-CH_2-CH_3$

B Answer. Correctly interprets information and demonstrates understanding of principles of organic chemistry.

(c) Account for the variation in boiling points of the amines given in the table.

First 3 amines have some molar mass so same size electron cloud so same instaneous dipole dipole attractions.
1 does not have hydrogen bonding as there are no Ns attached to it. 1 is not as polar as others as NH_2 group in middle of molecule as shape is more symmetrical and permanent dipole is less so permanent dipole dipole attraction is less so boiling point lowest.

3. – More polar than 1 and 2 as polar NH_2 group at end of molecule so has a polar end and non polar end, this results in a larger dipole and stronger permanent dipole dipole attractions and therefore a higher boiling point. Also 3 has N-H bond. 5 – also has hydrogen bonding which is strongest intermolecular force between molecules and this also increases its boiling point.

2. – Approximately same polarity as 1 so same attractions due to permanent dipoles but prescence of N-H bond gives hydrogen bonding between molecules, this increases the intermolecular forces giving 2 a higher boiling point than 1.
Boiling point less than 3 as NH_2 group still in middle of molecule so not as polar as if on end in 3

4 – Boiling point of 4 is higher than 1 + 2 as it has a larger molar mass (because of 5 carbons) so has larger electron cloud and greater attractions between molecules due to instantaneous dipole dipole attractions. It is about the same polarity as 1 + 2 so has approximately same attractions due to permanent dipole dipole attractions. It has a lower boiling point than 3 as it does not have hydrogen bonding and is not polar. The presence of hydrogen bonding in 3 and the fact the NH_2 group is on the end of molecule so molecule is more polar and has greater permanent dipole dipole attraction and means 3 has a higher boiling point than 4 despite 4 being a larger molecule.

B Answer. Most ideas explained, however response does not demonstrate sufficient depth and breadth of understanding for an A Answer.

QUESTION TWO: AQUEOUS SOLUTIONS

(a) (i) Calculate the pH of the ethanolamine solution.

n(HCl) = 0.0107 x 0.0635 = 3.745×10^{-4} mol
ratio = 1:1 so n($HOCH_2CH_2NH_2$) at start = 3.745×10^{-4} mol
c=n/v = $3.745 \times 10^{-4}/0.025 = 0.01498$ mol L^{-1}
pKa = 9.5 from graph at half equivalence point
$10^{-9.5} = [H_30^+]^2 \times 0.01498/1 \times 10^{-14}$
$[H_3O^+] = 1.45 \times 10^{-11}$ mol L^{-1} pH = 10.84 (2dp)

B Answer. Answer correct, showing ability to analyse information and apply knowledge.

(ii) Show by calculation that the pH at equivalence point is 5.9

Weak acid solution at equivalence point

$$10^{-9.5} = \frac{[H_3O^+]\ [\text{Ethanolamine}]}{[\text{weak acid}]}$$

n weak acid = n(HCl) added = 0.0107 x 0.035 = 3.745 x 10^{-4} mol
c=n/v = 3.745 x 10^{-4}/0.06 = 0.0062 mol L^{-1} = [weak acid]
$[H_30+]$ = [ethonolamine]
$10^{-9.5} = [H_30+]^2/0.0062$
$[H_20+3 = 1.4x10^{-6}$ mol L^{-1}
plt = 5.85 = 5.9

B Answer. Answer correct, showing ability to analyse information and apply knowledge.

(iii) Relate the change in pH and the shape of the titration curve to the change in the nature and concentration of the species in the flask as the titration is carried out.

Small dip on pH of about 1 pH unit as because it is only a weak base there is not much of the conjugate acid present, buffer capacity is not high and adding acid causes an increase in $[H_30^+]$ a decrease in $[HOCH_2CH_2NH_2]$ and an increase in $[HOCH_2CH_2NH_3^+]$ $[OH^-]$ concentration decreases shape is steep here as buffer capacity not high so adding acid causes change in pH
-Then from about 10mL to 30mL flat part of curve not much decrease on pH this is because buffer capacity is high, there is lots of weak acid and weak base present so addition of acid does not cause a large change in pH
$HOCH_2CH_2NH_2+H_3O^+ \rightarrow HOCH_2CH_2NH_3+H_2O$
$[HOCH_2CH_2NH_2] \approx [HOCH_2CH_2NH_3^+]$, $[H_3O+]$ increasing slowly as pH decreases slowly, $[OH^-]$ decreases as solution is more acidic.
-Sudden drop at 35mL this is the equivalence point, the number of moles of HCl that has been added is the same as the number of moles of weak base present at start. At equivalence point solution is a weak acid so pH < 7, sudden change in pH as change from weak base solution to weak acid solution, [weak base] is small at equivalence point as weak acid does not dissociate much, $[OH^-]$ = [weak base]
$[H_3O+]$ is now larger than $[OH^-]$ so pH <7.
-After equivalence point graph flattens out and pH does not change much this is because at this point solution is a diluted strong acid. pH heads towards 1.97 (pH of 0.0107 mol L^{-1} HCl) all of weak base is converted into weak acid so [weak base] and $[OH^-]$ is small [weak acid] is higher than [weak base]. Graph is quite flat as when you add HCl you make it more acidic but also dilute solution at same time so pH does not change very much.

B Answer. An answer which demonstrates knowledge of principles of chemistry, however not an A Answer, as it makes an incorrect statement in relation to concentration of species present at the equivalence point.

(b) Calculate the pH of a saturated solution of $Hg(OH)_2$. Justify any assumptions made in carrying out the calculation.

$K_s(Hg(OH)_2) = 3.6 \times 10^{-26} = [Hg^{2+}] [OH^-]^2$
Assume no other sources of Hg^{2+} or OH^- ions in solution, assume pure water, justified as no mention of other ions in solution
Assume pH of water is neutral so $[OH^-]$ from water = 1×10^{-7} mol L^{-1}
$[Hg^{2+}] = s$
$[OH^-] = 2s + 1 \times 10^{-7}$
$3.6 \times 10^{-26} = s(2(s + 1 \times 10^{-7})^2$
assume $1 \times 10^{-7} >> s$
so $3.6 \times 10^{-26} = 1 \times 10^{-14}$ s
$s = 3.6 \times 10^{-12}$ so assumption justified
$[OH] = 2s + 1 \times 10^{-7}$
$=1.00007 \times 10^{-7}$
pH = 7.000

B Answer. Correctly analyses and interprets information.

QUESTION THREE: ALCOHOL INVESTIGATIONS

(a) Discuss the method described above, justifying the need for each step involved.

Alcohol removed from blood to purify sample, removes red colour and also any other compounds in blood which may also be oxidized by dichromate
-Distillation – way of seperating alcohol from blood as alcohol is organic and has a low boiling point
-heated with acidified potassium dichromate. Dichromate ion is an oxidant, converts alcohol into carboxylic acid. Use because there is a clear colour change from orange $Cr_2O_7^{2-}$ to green Cr^{3+}. Heated to increase reaction rate and make sure reaction goes to completion. Acid as a catalyst in reaction.
Known excess of dichromate solution so that if you know the amount of $Cr_2O_7^{2-}$ unreacted you can work out the amount that did react.
-Excess KI added, converts $Cr_2O_7^{2-}$ to Cr^{3+} and I^- to I_2. The amount of I_2 can then be found by titration. Excess KI added to make sure all of $Cr_2O_7^{2-}$ converts to Cr^{3+} so that from the amount of Iodine produced we can accurately work out how much $Cr_2O_7^{2-}$ was unreacted.
-Solution of I_2 titated with sodium thiosulfate – standard thiosulfate so you know concentration, you will get titre volume and can then work out $n(S_2O_3^{2-})$ which is needed for calculations.
Thiosulfate used as it reduces I_2 to I^- which produces a colour change with indicator and can therefore be used to find an accurate end point.
Indicator of starch used as colour change from yellow I_2 to colourless I^- has no distinct endpoint, we can not tell when all the I_2 has been reduced to I^- starch is used as it is blue black in I_2 and colourless in I^-.
Added near endpoint as starch is a big molecule and can surround the I_2 and 'lock it up' so not all of I_2 is reacted if starch is added too early giving an inaccurate titre volume. By near the end point concentration of I_2 is lower so this is less of a problem.

Combination of answer for parts (a) and (c) considered together as an A Answer. These responses demonstrate a depth and breadth of understanding of the practical procedure and experimental design.

(b) Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80mg alcohol per 100mL of blood.

Use 17.86, 17.7 and 17.84mL titre volumes as these are closest together.
Average titre volume = 0.0178L = v($S_2O_3^{2-}$)
n($S_2O_3^{2-}$) = c x v = 0.105 x 0.0178 = 0.001869 mol
Ratio $S_2O_3^{2-}$: I_2 = 2:1 so n(I_2) produced = 9.345x10^{-4} mol
Ratio I_2 : $Cr_2O_7^{2-}$ = 3:1 so n($Cr_2O_7^{2-}$) unreacted = 3.115 x 10^{-4} mol
n($Cr_2O_7^{2-}$ excess added) = 0.0492 x 0.01 = 4.92 x 10^{-4} mol
n($Cr_2O_7^{2-}$) reacted = 4.92 x 10^{-4} - 3.115 x 10^{-4}
= 1.805 x 10^{-4} mol
Ratio $Cr_2O_7^{2-}$: ethanol = 2:3
M(ethanol) = 46 n(ethanol) = 2.7075x10^{-4} mol
m(ethanol in 10mL) = 2.7075 x 10^{-4} x 46 = 0.012g in 10mL
= 12g in 100mL
=124 mg in 100mL>80mg per 100mL
so sample is above legal limit

B Answer. Correct answer, showing ability to analyse and interpret information and apply knowledge.

(c) Explain why the procedure being used is not suitable for quantitative determination of the alcohol in the home brew and outline ways that the method could be adjusted to make it more acceptable.

–Titre value less than 1 mL absolute uncertainty in titration with biurette ≈ ±0.2mL = 20% uncertainty which is too high so not suitable
-Ways to make it more acceptable
-Increase volume of $S_2O_3^{2-}$ needed by decreasing concentration of $S_2O_3^{2-}$
-Increase amount of I_2 to react with by having more unreacted $Cr_2O_7^{2-}$, do this by adding higher volume of $Cr_2O_7^{2-}$ to alcohol or using higher concentration $Cr_2O_7^{2-}$
-Use more diluted alcohol or smaller volume of alcohol

QUESTION FOUR: COMPARING PROPERTIES

(a) Discuss, in terms of their structure, the relative sizes of the atoms and ions of the elements O, Mg and S.

atoms – O is smallest atom, it is smaller than Mg and S as its valence electrons are in 2nd shell rather than 3rd shell for S and Mg. Its valence electrons are in lower energy levels so are closer into nucleus therefore its atomic radius and size is smaller than S and Mg
-S and Mg are larger as the valence electrons are in higher energy level, further from nucleus, there is increased repulsion from inner shells, atomic radius is larger and atom is larger
-S is smaller than Mg as acrros a row, electrons are added in same energy level. S has a greater atomic charge so electrostatic attraction between nucleus and electrons is greater and radius and size is smaller than Mg
ions- Mg will be smallest ion. Mg^{2+} and O^{2-} have same electron arrangement – $Is^2 2s^2 2p^6$ but because Mg^{2+} has a greater nuclear charge (12) it has a greater electrostatic attraction between the nucleus and these electrons, the electrons are held more tightly and size is smaller than for O^{2-}
-Both Mg^{2+} and O^{2-} are smaller than S^{2-} as their valence electrons are in 2nd shell as opposed to S^{2-} where they are in 3rd shell electrons in higher energy level mean they are further from the nucleus so S^{2-} has a larger atomic radius and size than Mg^{2+} and O^{2-}

B Answer. Answer correctly applies knowledge but omits the comparison between Mg and Mg^{2+}, and also between S and S^{2-}, and this omission means the response is not an A Answer.

(b) Use the data in the table to deduce which of the two compounds, ethane or ethanol, has the more negative enthalpy of combustion.

Let $2x\Delta_fCO_2 + 3x\Delta_fH_2O = a$

Combustion of $CH_3CH_3 + 3.50_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

Combustion of CH_3CH_2OH =

$CH_3CH_2OH + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

$\Delta_cH\ (CH_3CH_3) = \Delta_f$ products - Δ_f reactants
$= 2 \times \Delta_f\ CO_2 + 3 \times \Delta_f\ H_2O – (\Delta_f\ CH_3CH_3)$
$\Delta_cH(CH_3CH_2OH) = 2x\Delta_fCO_2 + 3x\ \Delta_f\ H_2O – (\Delta_f(H_3(H_2OH)$
only difference is $\Delta_f\ H\ CH_3CH_3$ or $\Delta_f\ CH_3CH_2OH$
$\Delta cH(CH_3CH_3 = a + 84$
$\Delta cH\ CH_3CH_2OH = a + 235$
both negative as combustion is exothermic
CH_3CH_3 has more negative enthalpy of combustion as it has the smaller enthalpy of formation

B Answer. Answer correctly analyses and interprets information.

(c) Determine the pH of pure water at 37 ºC and discuss whether this solution is neutral or not.

H_2O $H_3O^+ + OH^-$
$1x10^{-14} = [H_3O^+] \times [OH^-]$
K_w low reactant favoured
$2.5 \times 10^{-14} = [H_3O^+]\ [OH^-]$
increase in temperature shifts equilibrium right or left, if it shifts to the left concentration of $[H_3O^+]$ decreases as more H_2O produced so pH increases
if it shifts to the right concentration of $[H_3O^+]$ increases so pH decreases.
Reaction endothermic as it is bond breaking so shifts equilibrium to the right so $[H_3O^+]$ increases and pH decreases
$[H_3O^+]$ and $[OH^-]$ increased at same rate
so $2.5 \times 10^{-14} = [H_3O^+]^2$
$[H_3O^+] = 1.58 \times 10^{-7}$ mol L^{-1}
pH = 6.8 so solution is slightly acidic as pH is less than 7

C Answer. Answer applies knowledge but fails to integrate knowledge of chemistry, failing to recognize that when $[H_3O^+] = [OH^-]$ the solution is neutral.

(d) Calculate the standard enthalpy energy change for the combustion of sucrose ($C_{12}H_{22}O_{11}$) and determine the mass in grams of sucrose that would be needed to produce sufficient energy to evaporate exactly one litre of water.

$C_{12}H_{22}O_{11(S)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 11H_2O_{(g)}$

$\Delta_cH = 6x –393.5 + 11 \times –241.8 – (-2222$
$= -2798.8$ kJ mol^{-1}
evaporate 1L of water
$H_2O(l) \longrightarrow H_2O(g)$
$-241.8 – (-285.8) = 44$ $kJmol^{-1}$
1L of water = 1kg
$n = m/M = 1000/18 = 55.6mol$
so takes 44x55.6 = 24444kJ to evaporate 1L of water
2798.8/2444 = 1.14 mol of sucrose $M(C_{12}H_{22}O_{11}) = 342$
$m = nxM = 1.14 \times 342 = 391.6g$ of sucrose needed to provide sufficient energy

C Answer. Answer uses incorrectly balanced equation but then correctly interprets the information.

QUESTION FIVE: IDENTIFYING WHITE SOLIDS
Formulate a scheme for identifying the solid with reference to the data.
Provide a comprehensive justification of the steps in the scheme on the basis of the data given.

-Add water to each solid so you get a solution
-SO_3^{2-} weak acid so some HSO_3^- present so will turn red litmus blue if Na_2SO_3 is the solid
-OCl^- weak acid so some weak base HOCl present so will turn red litmus blue if NaOCl is the solid
-However $HOCl/Cl^- = 1.51 > 0.62$
so on addition of I^- (acidified so pH = 1) HOCl is reduced to Cl^- and I^- oxidized to I_2 so a brown solution will be observed
-if HSO^- is present some H_2SO_3 will be present HSO_4^- /H_2SO_3 and H_2SO_3/S E^o values < 0.62 so I^- not oxidised to I_2 so no colour change observed
-If red litmus does not turn blue solid must be NaBr or KIO_3
-If NaBr $Br_2/Br^- > 0.62$. Both Br^- and I^- are oxidised in these couples so no colour change so no reaction occurs as there is no oxidant
-If KIO_3 $IO_3^-/I_2 = 1.2 > 0.62$ so IO_3^- reduced to I_2 and I^- oxidised to I_2 so a colour change from colourless to yellow brown solution is observed.

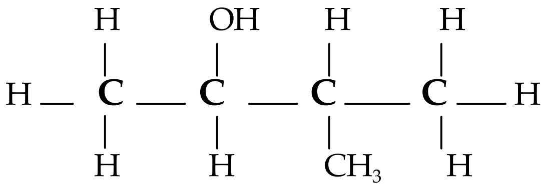
N Answer. Failed to demonstrate understanding of principles of acids and bases.
C Answer. Correctly applies knowledge of electrode potentials but answer does not clearly integrate the information.

Sample of assessed candidate work – Performance Descriptor 3: Performance Category 5

QUESTION ONE: ORGANIC MOLECULES

(a) Determine the structures of each of the compounds **A** to **F** in the reaction scheme.

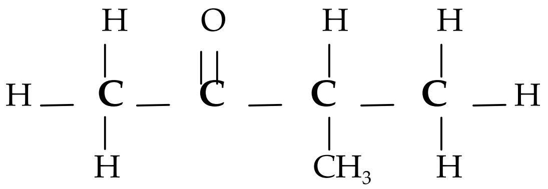
Compound A



$CH_3CH(OH)CH(CH_3)CH_3$

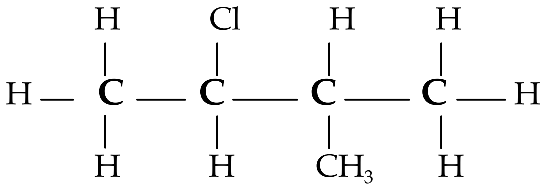
3–methyl butan-2-ol

Compound B



$CH_3COCH(CH_3)CH_3$

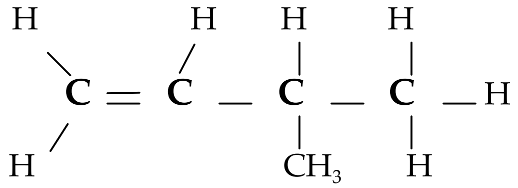
Compound C



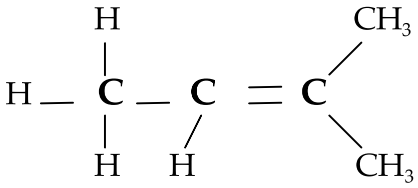
$CH_3CHClCH(CH_3)CH_3$

B – Correctly integrated and applied knowledge.

Compound D

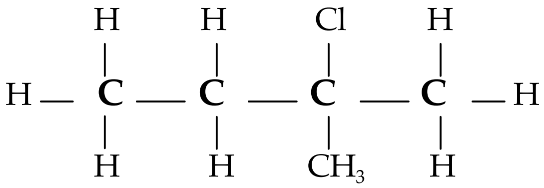


Compound E



Continued over

Compound F



$CH_3CH_2CCl(CH_3)CH_3$

(c) Account for the variation in boiling points of the amines given in the table.

Amines are held together by both hydrogen bonds from the amine group and temporary **dipole-dipole** interactions between **alkyl** chains. Hydrogen bonds between molecules form more effectively on primary amines where the nitrogen's bonds to the hydrogens make them more electronegative and therefore form stronger hydrogen bonds. These amines with longer chains have more area over which temporary dipole interactions occur and so have slightly raised boiling points, but the hydrogen bonding by the amine group raises the boiling point the most due to its strong attractive force.

N - Answer does not correctly apply knowledge of chemical principles.

QUESTION TWO: AQUEOUS SOLUTIONS

(a) (i) Calculate the pH of the ethanolamine solution.

Equivalance is at HCl = 35mL

so: $n_{HCl} = 0.0350\ L \times 0.0107\ molL^{-1}$

$= 3.75 \times 10^{-4}$ mol

so concentration of **ethanolamine** soln. = $\frac{3.75 \times 10^{-4}}{0.025} = 0.0150 molL^{-1}$

pKa = pH at 17.5mL

pKa = 9.4 therefore $Ka = 10^{-9.4} = 3.98 \times 10^{-10}$

$[H_3O^+] = \sqrt{\frac{3.98 \times 10^{-10}}{0.0150}} = 1.63 \times 10^{-11}$

pH = $-\log 1.63 \times 10^{-11} = 10.8$

(ii) Show by calculation that the pH at equivalence point is 5.9

Using p*K*a = 9.4, *K*a = 3.98×10^{-10}
equivalence volume = 60.0mL therefore conjugate $C = \frac{25.0}{60.0} \times 0.0150 = 6.25 \times 10^{-3}$

$$[H_3O^+] = \sqrt{Ka \times C_{conjugate}}$$
$$= \sqrt{3.98 \times 10^{-10} \times 6.25 \times 10^{-3}}$$
$$= 1.58 \times 10^{-6} \text{ mol L}^{-1}$$

$$pH = -\log 1.58 \times 10^{-6} = 5.8$$

B – Correctly analysed and interpreted information.

(iii) Relate the change in pH and the shape of the titration curve to the change in the nature and concentration of the species in the flask as the titration is carried out.

Initially there is 0.0150 $molL^{-1}$ of ethanolamine, a large amount of it having accepted protons, which therefore decreases the pH of the solution dramatically. When the HCl begins to be added, this neutralizes the OH^- ions in the solution which have been **deprotonated** by the **ethanolamine**. This decreases the pH but only a little at first because the removal of OH^- from the solution shifts the base's equilibrium in favour of accepting more protons, which counteracts the addition. As a consequence there are more **ethanolamine** molecules present in their protonated state and so the effect of adding more protons by adding HCl is not counteracted to such a degree because there are less molecules available to accept protons. This cause the pH to more rapidly decrease. Once all **ethanolamine** molecules are protonated then the concentration of conjugate acid/base species does not change and all that effects this pH is the addition of H_3O^+ by adding HCl. This makes the graph tend toward the pH of HCl.

N - Failed to appropriately or correctly apply knowledge to the information given in the titration curve.

(b) Calculate the pH of a saturated solution of $Hg(OH)_2$. Justify any assumptions made in carrying out the calculation.

$$K_s = 4s^3$$

$$s = \sqrt[3]{\frac{K_s}{4}} = 2.08 \times 10^{-9} \text{ mol L}^{-1}$$

Since the concentration of OH^- ions added will be below 10^{-7} $molL^{-1}$ it can be assumed that the pH of a solution is 7.0 because dissolving this will add an insignificant amount of OH^- (about 1/50 added to water's normal OH^- concentration).

B – Analysed and interpreted information correctly.

QUESTION THREE: ALCOHOL INVESTIGATIONS

(a) Discuss the method described above, justifying the need for each step involved.

The alcohol must first be removed from the blood so that the sample is colourless so that the indicator can be seen, and also because other chemicals in the blood may reduce the dichromate and give falsely high results. A known excess of dichromate is added so that the alcohol can be oxidised and the remainder of the dichromate quantified by seeing the difference between how much dichromate was added and how much was left unreacted. This difference is proportional to the alcohol level present. Excess iodide is added so that the remaining dichromate will all be reduced, and oxidise the iodide. This now means that there will be iodine present in proportion to the dichromate that was left remaining, which can be quantified by titration. A starch indicator is added which forms a black/blue complex with the iodine. **Thiosulfate** is added to reduce this iodine until there is no iodine remaining and the blue/black colour disappears.

B - This answer showed a depth of knowledge of the investigation method but lacked insight on some techniques.

(b) Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80mg alcohol per 100mL of blood.

Discarding **titre** of 17.70 mL

Average **titre** = $\frac{17.94 + 17.86 + 17.84}{3}$ = 17.88 mL = 0.01788 L (4sf)

moles of $S_2O_3^{2-}$ used = 0.01788 x 0.105 = 1.877×10^{-3} mol

therefore moles of I_2 present = 1.877×10^{-3} / 2 = 9.387×10^{-4} mol

therefore moles of $Cr_2O_7^{2-}$ present = 9.387×10^{-3} / 3 = 3.129×10^{-4} mol

total moles of $Cr_2O_7^{2-}$ put in = 0.010 x 0.0492 = 4.92×10^{-4} mol

difference in $Cr_2O_7^{2-}$ = $4.92 \times 10^{-4} - 3.129 \times 10^{-4}$

= 1.791×10^{-4} mol

therefore moles of alcohol = 1.791×10^{-4} **x** 3/2 - 2.687×10^{-4} mol

M (ethanol) = 46.0 $gmol^{-1}$

m(ethanol) = 2.687×10^{-4} x 46.0 = 0.01236 g
= 12.36 mg

Sample is 1/10 of 100mL
So concentration = 12.36 x 10
= 124 mg per 100 mL
The driver is therefore over the legal limit.

B – Correctly analysed and interpreted information.

(c) Explain why the procedure being used is not suitable for quantitative determination of the alcohol in the home brew and outline ways that the method could be adjusted to make it more acceptable.

This method is not suitable because the concentration of alcohol in home brew is about 5% by volume, whereas blood alcohol is far below this (about 0.1% for the driver above). Because of this more dichromate will be needed, either by using a higher concentration or by adding more. This will need to be done to ensure that there is excess $Cr_2O_7^{2-}$. Because of this change, the concentrations of the I^- may also need to be increased to ensure excess for the I_2 producing reaction. Alternatively, the student could consider using smaller sample sizes, but the measuring apparatus is likely to introduce more error if smaller volumes are to be measured. This volume cannot be too small either, or he may find his **titres** getting very large.

QUESTION FOUR: COMPARING PROPERTIES

(a) Discuss, in terms of their structure, the relative sizes of the atoms and ions of the elements O, Mg and S.

O is the smallest of the 3 atoms. This is because as the atomic number increases across a period, the nuclear charge increases but the electrons in the valence shell stay at about the same energies so they are pulled in more. S is the next smallest because although Mg has a large nuclear charge, it has one extra electron shell and so is larger than S because this extra shell is further out. Mg is the largest because it has more electron shells than the other 2.
Mg forms the smallest ion because it loses 2 electrons to become an ion. Less valence electrons means that there is less mutual repulsion of valence electrons and so they are not drawn outward as much, giving a small ion. O^{2-} is the next smallest ion, it is bigger than Mg^{2+} because when it forms an ion it gains 2 electrons. More electrons mutually repel each other more and make the ion larger than the atom, but also make it larger than Mg^{2+}. This is because more repulsion of electrons draws the valence shell out more.
S^{2-} is the largest because it has more electron shells than O^{2-} and has more valence electrons in it's outer shell than Mg because it forms an ion with 2 extra electrons. The extra electrons in the ion repel each other more and draw out the radius of the outer electron shell, which is further out from the nucleus than those of O^{2-}.

N - Answer does not show the necessary knowledge of the chemical principles involved.

(b) Use the data in the table to deduce which of the two compounds, ethane or ethanol, has the more negative enthalpy of combustion.

CH_3CH_3 has more negative $\Delta_C H^0$.
Since it required the most energy (it is the most positive with respect to $\Delta_f H^0$) to form, then it is expected that it will release the most energy when combusted.

N – Failed to interpret information.

(c) Determine the pH of pure water at 37 °C and discuss whether this solution is neutral or not.

pH = -log $\sqrt{2.5 \times 10^{-14}}$
= 6.8

The solution is still neutral. This is because K_W is the product of $[H_3O^+]$ x $[OH^-]$ and so by experiment it was found that at 25ºC this product was always 10^{-14} in H_2O. But this K_W value only holds for standard conditions (25 ºC, 1 atm) and so K_W for 37 ºC is 2.5×10^{-14}. If a solution is to be defined as neutral then $[H_3O^+] = [OH^-]$ and therefore $[H_3O^+]^2 = K_W$

$$\text{pH} = -\log \sqrt{K_W}$$

In this case I have assumed that the solution is neutral by using $[H_3O^+] = [OH^-]$ and have come up with the answer of pH = 6.8 so pH = 6.8 is neutral at 37ºC.

B – Correctly analysed and interpreted information.

(d) Calculate the standard enthalpy energy change for the combustion of sucrose ($C_{12}H_{22}O_{11}$) and determine the mass in grams of sucrose that would be needed to produce sufficient energy to evaporate exactly one litre of water.

Combustion

$C_{12}H_{22}O_{11} + 12O_2(g) \rightarrow 11H_2O(l) + 12CO_2(g)$

$\Delta_C H^0(C_{12}H_{22}O_{11}) = 11 \times 285.8 + 12 \times -393.5 - {}^{-}222.0$
$= -5643.8 \quad = -5644 \text{ kJ mol}^{-1}$ (4sf)

$\Delta_{Vap} H^0_{H2O} = -241.8 + 285.8$
$= +44.00 \text{ kJ mol}^{-1}$
$M(C_{12}H_{22}O_{11}) = 342 \text{ g mol}^{-1}$

1L of water in moles = $^{1000}/_{18}$ = 55.6 mol
Energy required for 55.6 mol to evaporate = 55.6 x +44.00
= + 2444 KJ
Moles of $C_{12}H_{22}O_{11}$ required = $^{2444}/_{5643}$ = 0.433 mol
Mass required = 0.433 x 342 gmol^{-1} = 148.1g (4sf)

B – Correctly analysed and interpreted information.

QUESTION FIVE: IDENTIFYING WHITE SOLIDS
Formulate a scheme for identifying the solid with reference to the data.
Provide a comprehensive justification of the steps in the scheme on the basis of the data given.

Add red litmus paper to a saturated solution of the solid. NaOCl & Na_2SO_3 are both basic in a solution and will turn red litmus paper blue. NaOCl hydrolyses are dissolved to Na^+ and HOCl, accepting a proton. Na_2SO_3 hydrolyses when in a solution to Na^+ and HSO_3^-, accepting a proton. They are therefore both basic, because they have a p*K*a above 7.
Add about 10mL of acidified aqueous I^- to a 1g sample of the solid. If the litmus paper had previously turned blue, and the sample takes on a brown colour from the iodine produced then the solid was NaOCl. If the litmus paper had previously turned blue and the solution didn't turn brown from the formation of I_2 then the solid was Na_2SO_3. If the litmus paper had not previously turned blue and a brown I_2 solution forms then the solid was KIO_3. If the litmus

N – Answer includes some application of knowledge but shows misunderstanding of principle of pK_a values.

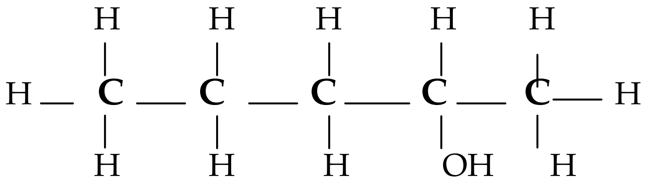
C – Correct application of principles of oxidation-reduction reactions, but insufficient justification in terms of reduction potentials.

Sample of assessed candidate work – Performance Descriptor 3: Performance Category 7

QUESTION ONE: ORGANIC MOLECULES

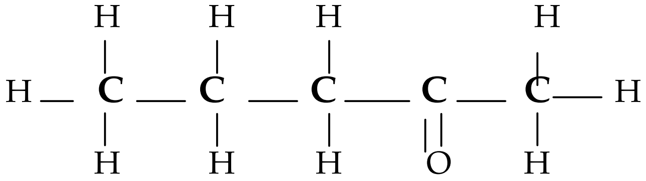
(a) Determine the structures of each of the compounds **A** to **F** in the reaction scheme.

A. $C_5H_{12}O$ alcohol



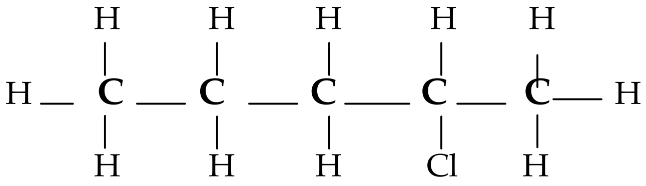
$CH_3CH_2CH_2CH(OH)CH_3$

B. $C_5H_{10}O$ ketone



$CH_3CH_2CH_2COCH_3$

C $C_5H_{11}Cl$ **haloalkane**

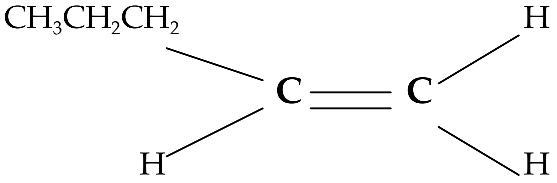


$CH_3CH_2CH_2CHClCH_3$

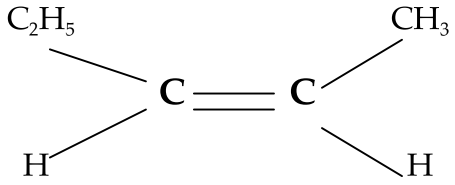
C – Functional group sequence correct but incorrect carbon framework showing failure to integrate all information provided.

Continued over

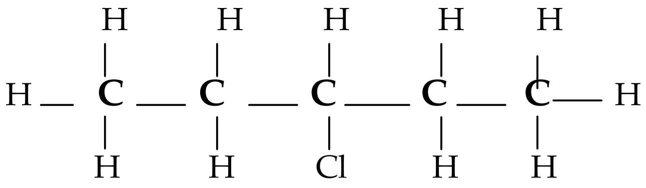
D. C_5H_{10} Alkene



E. C_5H_{10} Alkene

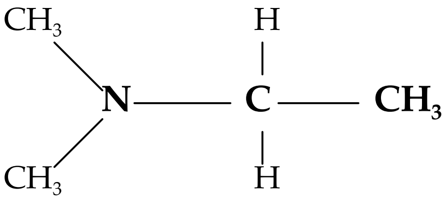


F. **Haloalkane**

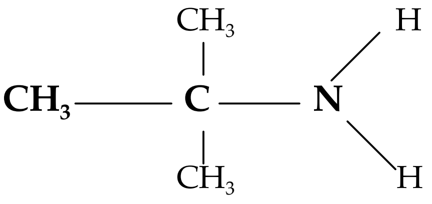


(c) Account for the variation in boiling points of the amines given in the table.

1.



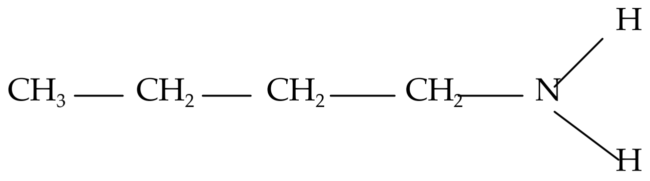
2.



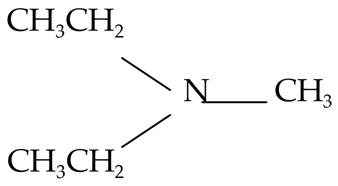
N - Answer does not show evidence of interpreting information and applying knowledge.

Continued over

3.



4.



QUESTION TWO: AQUEOUS SOLUTIONS

(a) (i) Calculate the pH of the ethanolamine solution.

pH (ethanolamine) = ?

v (HCl to reach equivalence) = 35mL

$HOCH_2CH_2NH_2 + HCl \rightarrow HOCH_2CH_2NH_3^+Cl^-$

$$n(\text{HCl @ equivalence point}) = 0.0107\ \text{molL}^{-1} \times 0.035 = 3.745 \times 10^{-4}\ \text{mol}$$

$n(HOCH_2CH_2NH_2) = 3.745 \times 10^{-4}$ mol

$$n(HOCH_2CH_2NH_2) = \frac{3.745 \times 10^{-4}}{0.025} = 0.01498\text{molL}^{-1}$$

$pK_a\ (HOCH_2CH_2NH_3^+) = 9.5$

$$[H^+] = \sqrt{\frac{K_W \times Ka}{c(\text{base})}}$$

$$= \sqrt{\frac{1\times10^{-14} \times 1\times10^{-9.5}}{0.01498}}$$

$$= 1.452928 \times 10^{-11}$$

$$pH = -\log 1.4529 \times 10^{-11}$$

$$= 10.8\ \ (3sf)$$

(ii) Show by calculation that the pH at equivalence point if 5.9

pH (at equivalence point) = 5.9

At equivalence point: $HOCH_2CH_2NH_3^+ + H_2O \rightleftharpoons HOCH_2CH_2NH_2 + H_3O^+$

At equivalence point n(HCl) = n($HOCH_2CH_2NH_3^+$)

n($HOCH_2CH_2NH_3^+$) = 3.745×10^{-4}mol

$$c(HOCH_2CH_2NH_3^+) = \frac{3.745 \times 10^{-4}\text{mol}}{(0.035 + 0.025)}$$

$$= 6.2416 \times 10^{-3}$$

$[H^+]$ (@ equivalence point) = $\sqrt{Ka \times [HA]}$

$= \sqrt{10^{-9.5} \times 6.2416 \times 10^{-3}}$

$= 1.404915\ldots \times 10^{-6}$ molL^{-1}

pH $= -\log(1.404915\ldots \times 10^{-6}$

$= 5.8523$

$= 5.9$ (2sf)

B – Both calculations correct.

(iii) Relate the change in pH and the shape of the titration curve to the change in the nature and concentration of the species in the flask as the titration is carried out.

At the beginning the pH is 10.8 as the solution in the conical flask is a weak base. As soon as a few drops of strong acid is added the pH dramatically decreases.

At mid-bufferpoint there is an equal concentration of the weak base $HOCH_2CH_2NH_2$ and its conjugate weak acid $HOCH_2CH_2NH_3^+$. In the buffer zone around the mid-buffer point the pH does not decrease dramatically because as the H^+ (from HCl) is added to the weak base it is converted into a weak acid of which only few of the acid particles donate protons, so the pH only decreases slightly:

$HOCH_2CH_2NH_2 + H^+ \rightarrow HOCH_2CH_2NH_3^+$ conjugate weak acid

so at this point as the $[HOCH_2CH_2NH_2] = [HOCH_2CH_2NH_3^+]$ the pH equals the p*K*a of the weak conjugate acid.

However as soon as all the weak base present has reacted with H^+ (ie converting it to the weak conjugate acid) the additional H^+ cause the pH to drop dramatically (steep curve). As the graph levels out the pH approaches that of the strong acid but it never reaches it due to dilution factors.

B – Discussion is incomplete so does not show sufficient depth and breadth of knowledge for higher grade.

(b) Calculate the pH of a saturated solution of $Hg(OH)_2$. Justify any assumptions made in carrying out the calculation.

$Hg(OH)_2 \rightarrow Hg^+ + 2OH^-$

$K_S = [Hg^+][OH^-]^2$

$[OH^-] = 2[Hg^+]$

$= [Hg^+][2Hg^+]^2$

$3.6 \times 10^{-26} = 4X^3$

$9.0 \times 10^{-27} = X^3$

$\sqrt{9.0 \times 10^{-27}} = X$

$X = 2.080083823 \times 10^{-9}$

$[OH^-]$ (in solution) $= 2 \times X$

$= 4.1601676\ldots \times 10^{-9}$

$[H^+] = \frac{K_W}{[OH^-]}$ assume the reaction is taking place at room temperature

$= \frac{1 \times 10^{-14}}{4.1601676 \times 10^{-9}}$

$= 2.403 \times 10^{-6}$

$pH = -\log 2.903 \times 10^{-6}$

$= 5.6$

C – Applied knowledge of solubility equilibria but did not integrate knowledge of pH of a basic solution to the situation.

QUESTION THREE: ALCOHOL INVESTIGATIONS

(a) Discuss the method described above, justifying the need for each step involved.

The first step of removing alcohol from the blood is necessary because no colour change will be able to be seen due to the red blood if the alcohol is not removed. Also there may be other chemicals in the blood which could affect the results of the titration. The alcohol is then heated (heat need to oxidise alcohol completely) with a known amount of acidified dichromate solution to convert it into ethanoic acid. An excess is used so the ethanol is completely converted to ethanoic acid and the rest used to oxidize I^- ions. If excess was not added it would not be known how much of the acidified dichromate was being used to oxidize ethanol and how much used to oxidize iodide ions. Excess potassium iodide is used so it can be converted into iodine which will give a colour change in the titration. Iodine is titrated with standard sodium thiosulfate. Starch is added near the equivalence point as this makes the equivalence point easier to detect.

B – integrated knowledge of oxidation -reduction and titration skills but in answer 3(c) did not demonstrate sufficient depth and breadth of knowledge,

(b) Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80mg alcohol per 100mL. of blood.

$$\text{Average titre} = \frac{17.84 + 17.86}{2}$$

$$= 17.85\text{mL}$$
$$= 0.01785\text{L}$$

$$n(Na_2S_2O_3) = c \times v$$
$$= 0.105 \times 0.01788$$
$$= 1.87425 \times 10^{-3} \text{ mol}$$

N-Calculation shows no recognition of process being a back-titration (failure to interpret information appropriately).

$Na_2S_2O_3$	CH_2CH_2OH
6	$^3/_2$
1	$^3/_2 \times {}^1/_6$ $= {}^3/_{12}$ $= {}^1/_4$

$$n(CH_3CH_2OH) = {}^1/_4 \times 1.87425 \times 10^{-3}$$

$$= 4.685625 \times 10^{-4} \text{ mol}$$

$$c(CH_3CH_2OH) = \frac{4.685625 \times 10^{-4}}{0.01}$$

$$= 0.04685625 \text{ molL}^{-1}$$

$$M(CH_3CH_2OH) = 2\text{x}C + 6\text{x}H + O$$
$$= 2 \times 12.0 + 6 \times 1.0 + 16.0$$
$$= 0.01685625 \text{ molL}^{-1}$$

$$m(CH_3CH_2OH) = 0.04685625 \times 46$$
$$= 2.1553875 \text{ gL}^{-1}$$
$$= 0.21553875\text{g/100mL}$$
$$= 215 \text{ mg/100mL}$$

215mg/100mL > 80mg/100mL. The sample is above the legal limit.

(c) Explain why the procedure being used is not suitable for quantitative determination of the alcohol in the home brew and outline ways that the method could be adjusted to make it more acceptable.

The procedure is not suitable because the amount of alcohol present in home brew is too high – much higher than that in a blood sample.
A small volume of ethanol would need to be taken then diluted by a large factor. The known excess of acidified dichromate solution would need to be increased and also the amount of I^- added.

QUESTION FOUR: COMPARING PROPERTIES

(a) Discuss, in terms of their structure, the relative sizes of the atoms and ions of the elements O, Mg and S.

In terms of structure relative sizes of the atoms O, Mg and S.

O<S<Mg

The oxygen atom is a smaller size then the S atom because despite increases in proton number, S has an added energy level, meaning its valance electrons are further from the positive pull of the nucleus compared to O. S also has increased shielding from inner electrons on the valence electrons, repelling them further from the positive pull of the nucleus. As the valence electrons in S are found further from the nucleus than in O, S has a larger atomic size. S is a smaller molecule than O because as the no. of protons increase, the increasing effective nuclear attraction outweighs the repulsion effect of adding more electrons to the same shell. The valence electrons in S are closer to the nucleus than in Mg => S is smaller in atomic size.

N-Insufficient application of knowledge to the question asked.

(b) Use the data in the table to deduce which of the two compounds, ethane or ethanol, has the more negative enthalpy of combustion.

$CH_3CH_3 + {}^7/_2O_2 \rightarrow 3H_2O + 2CO_2$ (1)
$CH_3CH_2OH + 3O_2 \rightarrow 3H_2O + 2CO_2$ (2)
$\Delta_cH_1 = \Delta_fH\,(H_2O) \times 3 + 2 \times \Delta_fH\,(CO_2) - \Delta_fH\,(CH_3CH_3)$
$\Delta_cH_2 = \Delta_fH\,(H_2O) \times 3 + 2 \times \Delta_fH\,(CO_2) - \Delta_fH\,(CH_3CH_2OH)$
$\Delta_fH\,(CH_3CH_2OH) < \Delta_fH\,(CH_3CH_3)$
$\Delta_cH_2 > \Delta_cH_1$
.'. (1) would release more energy
and .'. Δ_cH_1 (Δ_cH^0 for CH_3CH_3), ethane is more negative.

B-Analysed and interpreted information correctly.

(c) Determine the pH of pure water at 37 °C and discuss whether this solution is neutral or not.

$K_W = [OH^-][H_3O^+]$
$2.5 \times 10^{-14} = x^2$
$\sqrt{2.5} \times 10^{-14} = x$
$1.58113883 \times 10^{-7} = x$
$1.58113883 \times 10^{-7} = [H^+]$

$pH = -\log 1.5811388 \times 10^{-7}$
$= 6.80$ (3sf)

The solution is neutral because there is still an equal concentration of OH- and H_3O^+

B-Analysed and interpreted information correctly.

(d) Calculate the standard enthalpy energy change for the combustion of sucrose ($C_{12}H_{22}O_{11}$) and determine the mass in grams of sucrose that would be needed to produce sufficient energy to evaporate exactly one litre of water.

$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$

$\Delta_rH^0 = \sum(\Delta_fH^0 \text{ products}) - \sum(\Delta_fH^0 \text{ reactants})$
$= (12 \times 393.5 + 11 \times -285.8) – (-2222.0)$
$= 5643.8 \text{ kJ mol}^{-1}$

1 litre contains 55.55…mol of H_2O

$CH_3CH_2OH + 3O_2 \rightarrow CO_2 + 3H_2O$

(1)	$H_2 + ½ O_2 \rightarrow H_2O$	-285.8
(2)	$C + O_2 \rightarrow CO_2$	-393.5
(3)	$2C + 3H_2 + ½ O_2 \rightarrow CH_3CH_2OH$	-235

(1) x 3 $3H_2 + {}^3/_2 O_2 \rightarrow 3H_2O = -857.1$

(2) x 2 $2C + 2O_2 \rightarrow 2CO_2 = -787$

(3) reversed $CH_3CH_2OH \rightarrow 2C + 3H_2 + ½ O_2$ 235

$\Delta_{vap}H^0 = -241.8 - -285.8$
$= 44 \text{ kJ mol}^{-1}$
Heat required to evaporate exactly 1 L of H_2O = 55.55 x 44
= 2444.44 kJ

$\frac{5643.8}{2444.44}$ = 2.30882 mol of $C_{12}H_{22}O_{11}$ required

m($C_{12}H_{22}O_{11}$) required = n*M*
= 2.30882 x 342.0
= 789.6189273
= 790g of sucrose needed.

M($C_{12}H_{22}O_{11}$) = 12 x 12.0 + 22 x 1.0 + 11 x 16.0
=342 g mol^{-1}

C – Interpreted information to complete most calculations correctly.

QUESTION FIVE: IDENTIFYING WHITE SOLIDS

Formulate a scheme for identifying the solid with reference to the data.
Provide a comprehensive justification of the steps in the scheme on the basis of the data given.

NaOCl
NaBr $H^+ + Br^- \rightarrow HBr$

KCO_3
Na_2SO_3

Br_2/Br^- 1.09 .'. stronger oxidising agent
I_2/I^- 62

IO_3^-/I_2 1.2 stronger oxidising agent
$2Br^- + 2e^- \rightarrow Br_2$
$I_2 \rightarrow 2I^-$ no reaction will occur

$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

$HOCl + 2H^+ + 1e^- \rightarrow Cl^- + H_2O$
$2I^- \rightarrow I_2$ reaction will occur

$HSO_4^-\ 2H^+ + e^- \rightarrow H_2SO_3 + H_2O$
$I^- \rightarrow I_2$

C – Correctly applies knowledge of acid/base nature of species but fails to make appropriate link with pKa.

Method
1.
Dissolve each solid in acidified aqueous solution I^-. If the solution turns yellow/brown then the white solid is either NaOCl or . The H^+ in the solution will first acidifies the salt
$Na^+ + OCl^- + H^+ \rightarrow HOCl^- + Na^+$
Then and $HOCl^-$ will oxidise I^- to form I_2 which is yellow/brown.

N – Failed to demonstrate adequate knowledge of principles of oxidation reduction; answer frequently used incorrect formulae for species.

$HOCl^-$ is a stronger oxidising agent then I^-.
$HOCl + 2H^+ + 3e^-. \rightarrow Cl^- + H_2O$
$2I^- + 2I^- \rightarrow I_2$

If a yellow solid forms the salt is $Na_2SO_3^{2-}$
$H_2SO_3 + 6H^+ + 6e^-. \rightarrow S + 3H_2O$
The H^{3+} in the solution first
$2IO_3^-. + 6H^+\ 4e^-. \rightarrow I_2 + 3H_2O$
$2I^-. \rightarrow I_2 + e^-.$

2.
If the solution turns yellow/brown the white solid could also be KIO_3^- IO_3^- is a stronger oxidising agent so will oxidise I_2^- to form I_2. IO_3^- will first be acidified to HIO_3 – a stronger acid $IO_3^- + H^+ \rightarrow HIO_3$

Continued over

3.
The difference between KIO_3 and NaOCl can be determined using litmus paper. NaOCl solution will turn the litmus paper blue whereas the KIO_3 solution will not change the colour of the litmus paper as it is a strong acid.

4.
The other two salts will only be acidified by H^+ - no oxidation – reduction will take place To differentiate between them NaBr will not change the colour of the litmus paper whereas Na_2SO_3 will change the litmus paper blue.