Suggested Answers

VCE Chemistry 2013 Year 12 Trial Exam Unit 3/4

SECTION A – Multiple Choice Answers

Q1 D The compound is an alcohol because the IR spectrum shows a distinct O-H (**alcohols**) absorption in the 3200-3550 cm^{-1} band and a separate C-H absorption in the 2850-3300 cm^{-1} band.

The ^{13}C NMR spectrum shows two peaks indicating two different carbon environments.

2-butanol, $CH_3CH_2CHOHCH_3$ has 4 different carbon environments.

1-propanol, $CH_3CH_2CH_2OH$ has 3 different carbon environments.

Ethanoic acid, CH_3COOH, has 2 different carbon environments but is **not an alcohol.**

2-methylpropan-2-ol, $(CH_3)_3COH$, has 2 different carbon environments, all the asterisked (#) C atoms in the structure shown below have the same bonding environment.
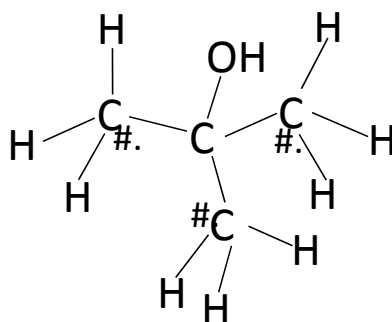
Q2 C The H_2O present in the moist sample is **not** represented in the equation for the decomposition of $NaHCO_3$.

Use the mass of solid product, Na_2CO_3, and the equation to calculate the $m(NaHCO_3)$ present in the moist sample. Then subtract the calculated $m(NaHCO_3)$ from the mass of the most sample.

$n(Na_2CO_3)$ produced $= 0.528$ g $/ 106.0$ g mol^{-1}
$= 0.00498$ mol

$n(NaHCO_3)$ reacting $= 2$ x 0.00498
$= 0.00996$

$m(NaHCO_3)$ in moist sample $= 0.00996$ mol x 84.0 g mol^{-1}
$= 0.837$ g

$m(H_2O)$ in moist sample $= m(sample) - m(NaHCO_3)$
$= 1.275 - 0.837$
$= \textbf{0.438 g}$

Q3 C 0.10 M solutions of strong monoprotic acids have pH =1 at 25°C
0.10 M solutions of weak acids have pH > 1 at 25°C
0.10 M solutions of strong bases have pH =13 at 25°C
0.10 M solutions of weak bases have pH < 13 at 25°C
Only titration curve D is for a reaction in which an acid is added to a base, but it is for a strong acid reacting with a strong base. The other three curves are for the addition of a base to an acid.
$NH_3(aq)$ is a weak base, $HCl(aq)$ is strong acid.
Titration curve C represents **the titration of 0.10 M $HCl(aq)$ by 0.10 M $NH_3(aq)$.**
The reaction occurring is **$NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$.**
At the **equivalence point,** the pH of the solution is determined by the products of the reaction. Since **$NH_4^+(aq)$ is a weak acid**, the **pH** will be **less than 7 (about 5.3)**.

Q4 A The choice of indicator is determined by the expected pH at the equivalence point. The approximate pH values at the equivalence point on the titration curves, and appropriate indicators *(Data Book Table 11)* are
Curve A: 9; **phenolphthalein**
Curve B: 7; **bromothymol blue** (phenol red, methyl red could also be effective)
Curve C: 5; **methyl red**
Curve D: 7; **bromothymol blue** (phenol red, phenolphthalein could also be effective)
Methyl orange, pH range 3.1-4.4 would be the **least suitable** choice of indicator.

Q5 A In the electrochemical series (*Data Book Table 2*) the $E°$ values for half-cells which involve a gas are
+2.87, +1.36, +1.23, +0.68, +0.40, +0.14, 0.00, -0.83.
The cell voltage of 1.22 V reflects the difference between the $E°$ values of the two half-cells.
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ 1.36 V
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$ 0.14 V
Cell half-equations
Anode (-): $H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-$
Cathode (+): $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
At the **anode**: pH decreases and a **solid** (sulfur) **is produced**.
At the cathode: gas is consumed.

Q6 D When $HClO_4$ acts as an oxidant, the oxidation number of chlorine changes. Since $HClO_4$ is the oxidant, it causes oxidation and as a consequence is itself reduced. Hence the oxidation number of Cl should decrease.
Applying the general rules of oxidation numbers, the oxidation numbers of Cl in the four alternatives are
Cl_2: 0
Cl_2O: +1
ClO_2: +4
Cl_2O_7: +7
The oxidation number of Cl in $HClO_4$ is +7.
Cl_2O_7 will not be a reduction product of $HClO_4$ because the oxidation number of Cl is +7 in both.

Q7 D $LiH(s) + H_2O(aq) \rightarrow Li^+(aq) + H_2(g) + OH^-(aq)$
Whilst the reaction is an **hydrolysis reaction** – i.e. the LiH reacts with rather than dissolves in water – this description **does not reflect all the chemistry** involved in the reaction.
Consider the oxidation numbers of H
LiH: -1, H_2O: +1; H_2: 0; OH^-: +1
The H^- (hydride) ion in LiH has been oxidised; oxidation number of H increases from -1 in LiH to 0 in H_2
H_2O has been reduced; oxidation number of H decrease from +1 in H_2O to 0 in H_2
This reaction is a **redox reaction**.
The presence of $OH^-(aq)$ as a product suggests that **water has acted as an acid** and donated H^+ (a proton) to a base. But what was the base?
The H^- which is present in LiH(s) has been converted to $H_2(g)$, i.e. H^- **has acted as the base** and accepted $H^+(aq)$ in forming $H_2(g)$.
This reaction is an **acid-base** reaction.

Q8 B The combustion of glucose is exothermic, so the temperature in the calorimeter will rise.
According to Data Book; $\Delta H_c(C_6H_{12}O_6) = -2816\ kJ\ mol^{-1}$
$n(C_6H_{12}O_6)$ $= 1.05 / 180.0$
$= 5.83\times10^{-3}$ mol
E released by 1.05 g $C_6H_{12}O_6$ $= 5.83\times10^{-3}$ mol x 2816 kJ mol^{-1}
$= 16.4$ kJ
Since $E = CF$ x ΔT then ΔT $= E / CF$
$= 16.4$ kJ / 2.35 kJ $°C^{-1}$
$= 6.99\ °C$
Final temperature $= 22.7 + 6.99 =$ **29.7°C**
This is the maximum temperature reached if there is no loss of heat to the atmosphere.

Q9 A The vanadium species with the four oxidation states are
+5 – VO_3^-
+4 – VO^{2+}
+3 – V^{3+}
+2 – V^{2+}
So the electrolytes around the electrodes contain $VO_3^-(aq)/VO^{2+}(aq)$ and $V^{3+}(aq)/V^{2+}(aq)$ respectively.
When the battery discharges, i.e. converts chemical energy to electrical energy, electrons move from the (-) electrode to the (+) electrode. Discharge involves the reaction between the strongest reductant present (V^{2+}) and the strongest oxidant present (VO_3^-).
Discharge half-equations.
 (-) electrode: $V^{2+}(aq) \rightarrow V^{3+}(aq) + e^-$
(+) electrode: $VO_3^-(aq) + 4H^+(aq) + e^- \rightarrow VO^{2+}(aq) + 2H_2O(l)$
During recharging, the half-equations at the electrodes are reversed as electrons are forced to flow from the (+) electrode to the (-) electrode.
Recharging half-equations.
(-) electrode: $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$
(+) electrode: $VO^{2+}(aq) + 2H_2O(l) \rightarrow VO_3^-(aq) + 4H^+(aq) + e^-$

Q10 D Investigations 1 and 2 showed the effect of a change in pressure at constant temperature. The data show that the yield of product is greater at higher pressure. This is also shown from the data for Investigations 3 and 4.

According to Le Chatelier's principle, an equilibrium system will partially oppose an increase in pressure by favouring the side of the equilibrium reaction with fewer particles. Since the yield of product is higher, there are **fewer particles on the right hand side**.

Investigations 2 and 3 showed the effect of a change in temperature at constant pressure. They showed that the yield decreased when the temperature was increased. An increase in temperature favours the endothermic reaction which, since the yield decreased, must be the reverse reaction. Hence the **forward reaction is exothermic**.
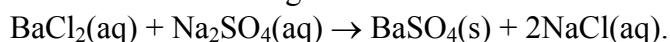
Q11 C Consider the alternatives.
    A. Fuel cells are **not 100 % efficient in the conversion of chemical energy to electrical energy**. Chemical energy is also converted to heat energy.
    B. Fuel cells utilise both acid and **alkaline electrolytes**.
    C. The **overall chemical equation for a fuel cell is the same as the equation for the combustion of the fuel** used. In direct combustion, the fuel and oxygen are in direct contact and so chemical energy is converted to thermal energy. In fuel cells the fuel and oxygen do not come in contact, and the flow of electrons from the anode (oxidation of the fuel) to the cathode (reduction of oxygen) is indicative of the conversion of chemical energy to electrical energy.
    D. Fuel cells are **not rechargeable**, they require a continuous supply of fuel and oxygen to operate.

Q12 D The reaction occurring was
$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$.
Addition of increasing volumes of $BaCl_2(aq)$ will at some point make $Na_2SO_4(aq)$ the limiting reagent, and at that point the maximum mass of $BaSO_4$ will have precipitated.
All students used 100 mL of 0.34 M $Na_2SO_4(aq)$.
$n(Na_2SO_4)$ = 0.34 mol L^{-1} x 100x10^{-3}L
                = 0.034 mol
Maximum $n(BaSO_4)$ that could be produced = 0.034 mol
Maximum $m(BaSO_4)$ = 0.034 mol x 233.4 g mol^{-1}
                            = **7.9 g**
$n(BaCl_2)$ required to produce 7.9 g $BaSO_4 = n(BaSO_4) = 0.034$ mol
$V(BaCl_2)$ required   = $n(BaCl_2) / c(BaCl_2)$
                    = 0.034 mol / 0.50 mol L^{-1}
                    = 0.068 L
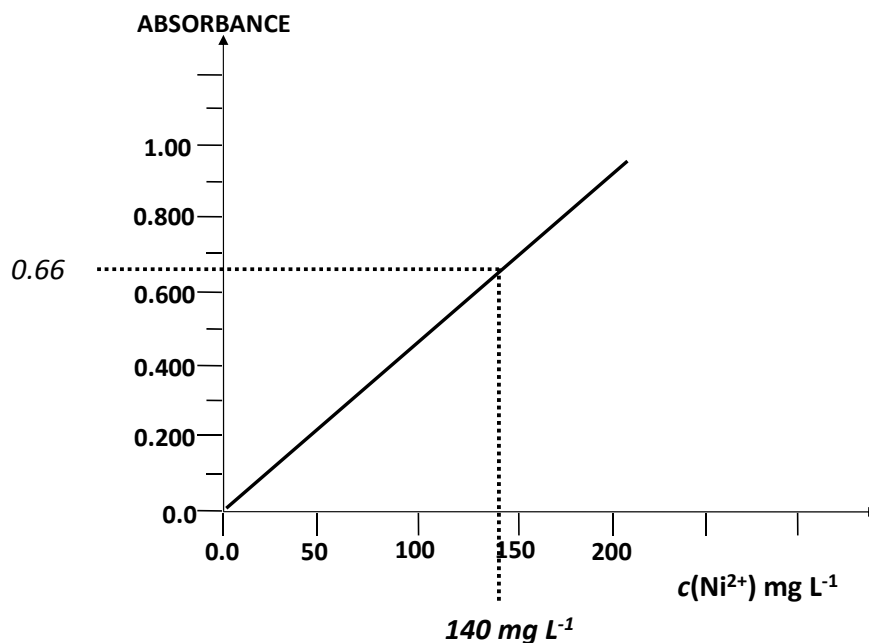   = **68 mL**
This is consistent with **Graph D**.

Q13 A Using 1.0 M $BaCl_2(aq)$, i.e. twice as concentrated as 0.50 M, means that only half as much, i.e. 34 mL, will be required to precipitate the maximum amount of $BaSO_4$.
Maximum mass $BaSO_4$ = 7.9 g
$V(BaCl_2)$ required = 34 mL
This is consistent with **Graph A.**

Q14 B Use the calibration curve to determine the $c(Ni^{2+})$ in the 25.0 mL aliquots.

140 mg L^{-1} Ni $\rightarrow$ (140 / 1000) x 25 mg Ni in 25 mL aliquot
                          $\rightarrow$ 3.5 mg Ni in 25 mL aliquot
All the Ni from 5.00 g of the ore was in the original 200 mL of solution.
m(Ni) in 5.00 g ore $= m$(Ni) in 200 mL solution
                        $= (3.5 / 25)$ x 200
                        $= 28$ mg
% Ni in ore$= (m$(Ni) g $/ m$(ore) g) x 100
        $= (28 \times 10^{-3} / 5.0)$ x 100
        $= \textbf{0.56 \%}$

Q15 B 2-methyl butanoic acid   –   semi-structural formula: $CH_3CH_2CH(CH_3)COOH$
                                    –   molecular formula: $C_5H_{10}O_2$
                                    –   alternatively, since carboxylic acids have the molecular
                                        formula $C_nH_{2n}O_2$, and 2-each methyl butanoic acid
                                        molecule has 5 C atoms, its molecular formula must be
                                        $C_5H_{10}O_2$.
$n(C_5H_{10}O_2)= N(C_5H_{10}O_2) / N_A$
          $= 1 / 6.02 \times 10^{23}$
          $= 1.66 \times 10^{-24}$ mol
n(C) $= 5$ x 1.66×10^{-24}
      $= 8.31 \times 10^{-24}$ mol
m(C) $= 8.31 \times 10^{-24}$ mol x 12.0 g mol^{-1}
      $= 9.97 \times 10^{-23}$ g
      $= 9.97 \times 10^{-23}$ x 10^{12} (1 g $= 10^{12}$ pg)
      $= \textbf{9.97} \times \textbf{10}^{\textbf{-11}}$ **pg**

Q16 **C** $n(KMnO_4)$ consumed $= 1.25 / (39.1 + 54.9 + 4\times16.0)$
$= 0.00791$ mol

$n(e^-)$ transferred $= Q / F$
$= 2290$ C $/ 96500$ C mol^{-1}
$= 0.02373$ mol

Ratio $n(e^-) / n(KMnO_4) = 0.02373 / 0.00791 = 3$
So the oxidation number of Mn has decreased by 3 as the MnO_4^- causes oxidation and is itself reduced.
Final oxidation number of Mn is +4 (decreased from +7 in $KMnO_4$).
The oxidation product in which Mn may be assigned +4 as its oxidation number is **MnO_2**. It would be produced according to the half-equation
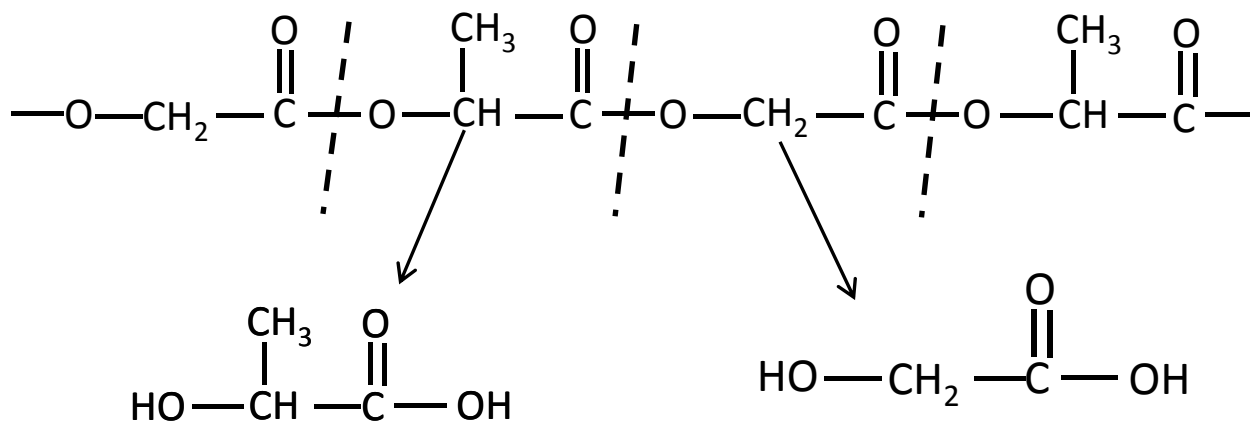$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$
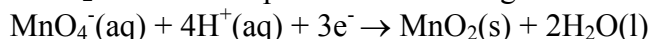
Q17 **D** The balanced equation for the reaction is
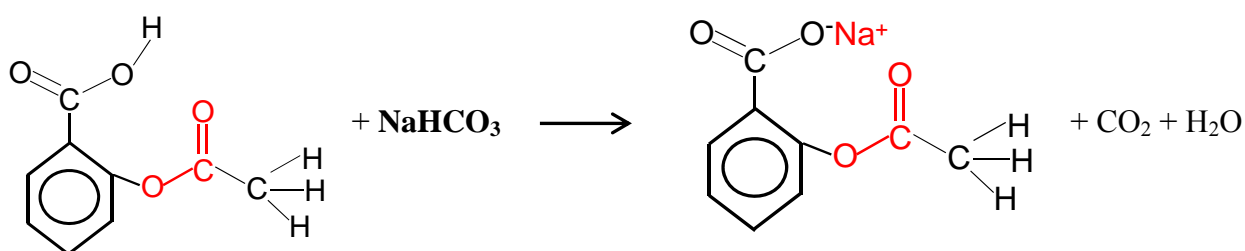
Compound X was **sodium hydrogen carbonate**
Sodium carbonate could also be used but one mol Na_2CO_3 would react with two mol of acetyl salicylic acid.

Q18 **A** PLGA is a polyester. During hydrolysis, **water reacts with the ester groups to convert them back to carboxyl, -COOH, and hydroxyl, -OH, groups**.

Q19 D At time **t,** the rates of both the forward and reverse reactions instantaneously increase. This can only happen if the concentrations of $NO_2(g)$ and $N_2O_4(g)$ both increase. This would happen if the **volume of the container was decreased** at time **t**.

The subsequent changes in the rates are consistent with this change. When the volume is decreased, the pressure increases and so the reaction producing fewer particles is favoured as the system moves to partially compensate for the pressure increase.

As the system moves to produce fewer particles the $[NO_2]$ decreases and the $[N_2O_4]$ increases, hence the rate of the forward reaction decreases and the rate of the reverse reaction continues to increase. This continues until both rates are equal when equilibrium is re-established, but the rates will be higher than initially because of the increased concentrations.

Q20 B The General equation for the ionisation of a weak acid is

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$, for which

$K_a = [H_3O^+][A^-] / [HA]$

Applying the standard weak acid assumptions:

Insignificant contribution to the $[H_3O+]$ from the self-ionisation of water

Minimal ionisation of the acid, i.e. $[HA]$equilibrium = $[HA]$initially

the equilibrium law simplifies to

$K_a = [H_3O^+]^2 / [HA]$

For 0.10 M solution

pH = 2.6 $\rightarrow [H_3O^+]$ $= 10^{-2.6}$ M (0.0025 M)

$K_a = (10^{-2.6})^2 / 0.10$

$= 6.31 \times 10^{-5}$ ….. *benzoic acid, C_6H_5COOH - Data Book Table 12*

When the solution is diluted, the same K_a applies because the temperature is still 25°C.

The original solution was diluted by a factor of 25 (10 mL to 250 mL)

After dilution $[HA]$ = 0.10 / 25

$= 0.0040$ M

$K_a = [H_3O^+]^2 / [HA]$

$6.31 \times 10^{-5} = [H_3O^+]^2 / 0.0040$

$[H_3O^+]^2 = 0.0040 \times 6.31 \times 10^{-5}$

$[H_3O^+] = \sqrt{(0.0040 \times 6.31 \times 10^{-5})}$

$= 5.02 \times 10^{-4}$

pH $= -\log_{10}(5.02 \times 10^{-4})$

$= \mathbf{3.30}$

Q21 C $n(H_2O)$ converted to steam $= 1.00 \times 10^3$ g / 18.0 g mol^{-1}

$= 55.6$ mol

Energy required to produce steam $= n(H_2O)$ x Energy per mol H_2O

$= 55.6$ mol x 44.0 kJ mol^{-1}

$= 2.44 \times 10^3$ kJ

Since 40 % of the energy released in the combustion of methane is transferred to $H_2O(l)$.

2.44×10^3 kJ $= 0.40$ x Energy released from combustion of CH_4

Energy from $CH_4 = 2.44 \times 10^3$ / 0.40

$= 6.11 \times 10^3$ kJ

$n(CH_4)$ required = Energy from CH_4 / Energy released per mol CH_4

$= 6.11 \times 10^3$ kJ / 889 kJ mol^{-1} [Data Book Table 12]

$= 6.87$ mol

$m(CH_4)$ required = 6.87 mol x 16.0 g mol^{-1}

$= 110$ g

Q22 D The major components in foods are proteins, fats and carbohydrates. These are analysed using chromatography. However the large size of the molecules and temperature sensitivity, i.e. sugars decomposing, and proteins denaturing on heating means that HPLC is a better option than GC.

Q23 D The calculations associated with this analysis would proceed along the lines of

$n(Na_2CO_3)$ in 20.0 mL aliquot

$n(HCl)$ added from burette $= 2$ x $n(Na_2CO_3)$

$c(HCl)$ in diluted brick cleaner $= n(HCl)$ / **V(titre)**

$c(HCl)$ in brick cleaner $= c(HCl)$ in diluted brick cleaner x dilution factor**.**

The only variable in this calculation sequence is the volume of diluted brick cleaner added from the burette. Since the calculations involve dividing by the titre volume, a larger volume will lead to a lower calculated $c(HCl)$ in the brick cleaner, whilst a lower volume will lead to a higher calculated concentration.

Consider the alternatives.

If the pipette used to transfer to $Na_2CO_3(aq)$ aliquot is rinsed only with water, there will be slightly less Na_2CO_3 present in the aliquot and so a smaller titre volume will be required $\rightarrow$ higher than true calculated $c(HCl)$.

If the titration flask is rinsed with diluted brick cleaner, some of the added $Na_2CO_3(aq)$ in the 20.0 mL aliquot will react with the HCl in the traces of diluted brick cleaner remaining. There will be less Na_2CO_3 to react during the titration, so a smaller titre volume will be required $\rightarrow$ higher than true calculated $c(HCl)$.

Water in the titration flask will have no effect on the titre volume used because it does not affect the $n(Na_2CO_3)$ available to react with HCl(aq) in the diluted brick cleaner.

If the burette is rinsed only with water, the traces remaining will further dilute the added dilute brick cleaner. Hence a larger titre will be required to provide the n(HCl) needed to react with the $Na_2CO_3(aq)$ $\rightarrow$ lower than true calculated c(HCl).

Q24 A The mass spectrum suggests that the parent ion has a relative mass of 74.
The IR spectrum information suggests the presence of C=O.
Both carboxylic acids and esters contain a C=O bond.
The ^{13}C NMR spectrum suggests 3 different carbon environments.
Both acids and esters have molecular formula $C_nH_{2n}O_2$, which for 3 C is $C_3H_6O_2$
$M_r(C_3H_6O_2) = 74$
Substance could be
propanoic acid, CH_3CH_2COOH *or*
ethyl methanoate, $HCOOCH_2CH_3$ *or*
methyl ethanoate, CH_3COOCH_3.
Both ethyl methanoate and propanoic have CH_3CH_2- hence will show a **quartet** (for
H on CH_2) and a **triplet** (for H on CH_3), as per the n+1 rule for splitting of signals
for H on adjacent C atoms.
However the quartet at chemical shift 4.1 *(Data Book Table 5)* suggests that the
compound has an ethyl group bonded the second O of the ester group.
Compound is **ethyl methanoate,** $HCOOCH_2CH_3$.

Q25 B The two compounds are structural isomers and have the molecular formula, $C_6H_{14}O$.
The compounds are
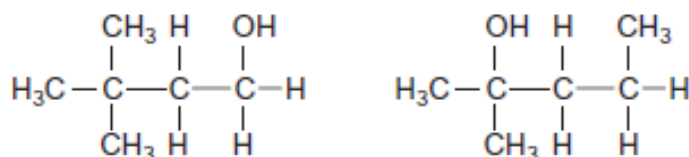
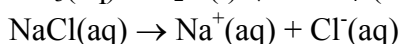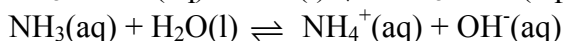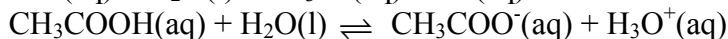3,3-dimethylbutan-2-ol   2-methyl-pentan-2-ol
A. oxidised to the acid   oxidised but NOT to the acid
B. parent ion $m/z = 102$ parent ion $m/z = 102$
C. fingerprint region   fingerprint region
D. ^{13}C NMR – 4 peaks ^{13}C NMR – 5 peaks
Only alcohols with the hydroxyl –OH group bonded to C-1, i.e. the end carbon, can
be oxidised to a carboxylic acid.
Since all compounds have unique fingerprint regions, the only one of the listed
characteristics in which they did **not differ** was the **m/z value of the parent ion
peak**.

Q26 C The nature of the aqueous solutions is represented in the equations below.
$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$
The $[OH^-]$ is most significant in $NH_3(aq)$. Doubling the volume by **adding 50 mL of
water instantaneously halves concentrations**.
However the impact is an increase in the extent of ionisation of aqueous solutions of
weak acids and weak bases. For both $CH_3COOH(aq)$ and $NH_3(aq)$, the volume
increases, and concentration decreases, causing the concentration fraction to become
less than K. As the systems move to return to equilibrium, the forward reaction is
favoured. It is in **NH₃(aq)** that this causes an **increase in [OH⁻] as the system
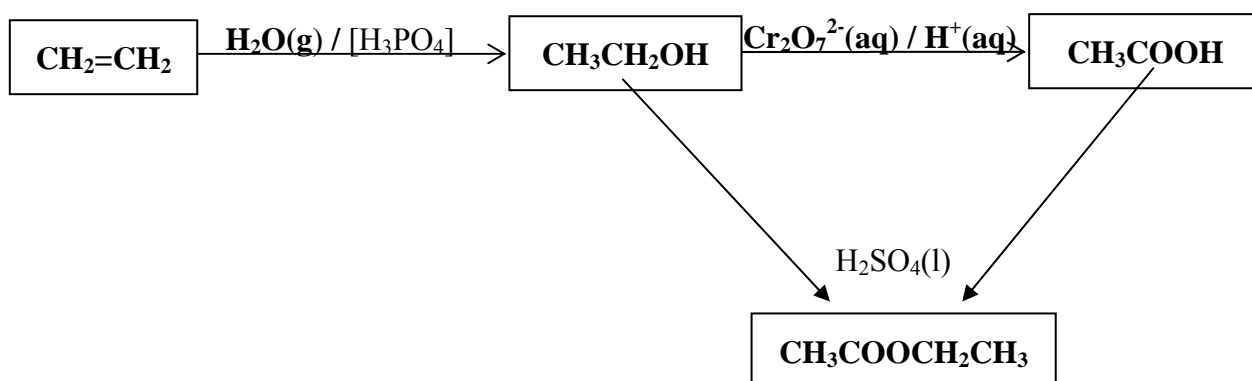returns to equilibrium**.
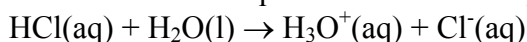
Q27 B The most **fundamental difference** between fuel cells and electrolytic cells is the **dominant energy conversion** occurring in the cells.
In all **fuel cells, chemical energy is converted to electrical energy** BUT in **electrolytic cells, electrical energy is converted to chemical energy**.
With respect to the 'supply of reactants from outside the cell', this does happen in all fuel cells but also happens in some electrolytic cells, so it is not the 'best' distinguishing feature.
Electrons leave the anode – the site of oxidation – in all electrochemical cells.
Aqueous electrolytes are present in many fuel cells and many electrolytic cells.

Q28 A **KI(l)** contains $K^+(l)$ – oxidant , and $I^-(l)$ – reductant ions
Half-equations occurring during electrolysis (*referring to Data Book – Table 2 Electrochemical series*)
Anode (+); $2I^-(l) \rightarrow$ **I_2**(s) + 2e$^-$
Cathode (-); $K^+(l) + e^- \rightarrow$ **K**(s)
$AgNO_3$(aq) contains $Ag^+(aq)$, $H_2O(l)$ – oxidants, and $H_2O(l)$ – reductants.
$NO_3^-(aq)$ is not included in the electrochemical series in the Data Book and can be ignored.
The stronger oxidant is $Ag^+(aq)$.
Half-equations occurring during electrolysis (*referring to Data Book – Table 2 Electrochemical series*)
Anode (+); $2H_2O(l) \rightarrow$ **O_2**(g) + 4H$^+$(aq) + 4e$^-$
Cathode (-); $Ag^+(aq) + e^- \rightarrow$ **Ag**(s)
Because $Ag^+(aq)$ is reduced in preference to H_2O, H_2(g) is least likely to be produced.

Q29 B KOH(aq) contains $K^+(aq)$ and $OH^-(aq)$ ions. The $K^+(aq)$ ions are not involved in the neutralisation reaction.
$KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$
Since the $K^+(aq)$ ions that were initially in 50.0 mL of 0.30 M KOH(aq) finish up in 100 mL of solution after the addition of 50.0 mL of 0.10 M HCl(aq), i.e. the volume occupied has doubled, the $[K^+]$ halves from 0.30 M to **0.15 M.**
If you did not pick up on the 'spectator ion' nature of the K^+(aq) and base your calculation on the n(KOH) in excess – incorrect because it assumes K^+ as well OH^- reacts, you would get 0.10 M or 0.20 M depending on whether you use 100 mL or 500 mL as your total volume.

Q30 C The reaction occurring is the exothermic neutralisation reaction
$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + HCl(aq)$
25.0 mL 1.0 M HNO_3(aq) reacting with 25.0 mL of 1.0 M KOH(aq) will release half as much thermal energy as 50.0 mL 1.0 M HNO_3(aq) reacting with 50.0 mL of 1.0 M KOH(aq).
However, half as much energy is being released into half the total volume, i.e. 50 mL rather than 100 mL.
So the temperature change will be the same, i.e. **6.4 °C.**

SECTION B – Short Answer (Answers)

Question 1

a. The molecular formula, deduced from the structure given, is $C_8H_{10}N_4O_2$, hence the empirical formula is $C_4H_5N_4O_2$ ❶

b. $[C_8H_{10}N_4O_2]^+$ ❶

c. The two peaks are in the absorption band 1670-1750 cm^{-1} (Data Book) and are caused by the two C=O groups ❶ in the molecule.
The peaks are centred at slightly different wavenumbers because of the different bonding environments in the caffeine molecule; one C=O is between two N atoms whilst the other C=O is between one C and one N atom. ❶

d. There are eight peaks and there are 8 'different' carbon atoms ❶ in the caffeine molecule. Each C atom has a different bonding environment (looking through the whole molecule) ❶. This means each C nucleus has different exposure to the external magnetic field and so requires a different amount of energy to change its nuclear spin state.

e.

| $CH_2=CH_2$ | →$H_2O(g)$ / $[H_3PO_4]$→ | CH_3CH_2OH | →$Cr_2O_7^{2-}(aq)$ / $H^+(aq)$→ | CH_3COOH |

CH_3CH_2OH and CH_3COOH → $H_2SO_4(l)$ → $CH_3COOCH_2CH_3$

Two marks ❶❶ for the four semi-structural formulae correct; one mark if two or three correct.
One mark ❶ for $H_2O(g)$ / [H_3PO_4]
One mark ❶ $Cr_2O_7^{2-}(aq)$ / $H^+(aq)$
One mark ❶ [$H_2SO_4(l)$]
The use of [] here is simply to remind students these substances act as catalysts in this pathway.

f. $CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ ❶
NB Correct states and equilibrium arrows necessary for the mark.

g. **i.** Because the forward reaction is endothermic, the **yield of ethyl ethanoate will be increased.** ❶
The higher temperature will **increase the rate of reaction.** ❶
ii. Ethanol is volatile and very flammable and should not be used near a naked flame. There would be a high risk of explosion. ❶
Ethanoic acid is also flammable - it has a flash point of about 44°C, (ethanol 15°C)

h. $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ ❶, ΔH = **-1364 kJ mol^{-1}** ❶
[Data Book Table 13]

Question 2

a. copper (-), platinum (+) ❶

b. (-) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ ❶
(+) $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ ❶

c. $m(Cu)$ produced during electrolysis = 14.45 – 11.27
= 3.18 g
$n(CuSO_4)$ in 100 mL solution = $n(Cu)$ produced
= 3.18 g / 63.5 g mol^{-1}
= 0.0501 mol ❶
$c(CuSO_4)$ = 0.0501 / 100x10^{-3}
= **0.501 mol L^{-1}** ❶

d. The absorbance was measured to determine when to stop the electrolysis. When the absorbance reading was zero, or constant close to zero, the all Cu^{2+} ions would have been reduced and deposited as Cu on the cathode. ❶

e. 610 nm would have been identified as a wavelength at which $Cu^{2+}(aq)$ absorb strongly but other species in the solution do not. ❶

f. Q = It; to determine Q and I are needed
Q = n(e-) x F = 2 x n(Cu) x F
= 2 x 0.0501 x 96500
= 9.70x10^3 C ❶
t = Q / I
= 9.70x10^3/ 0.500
= 1.93x104 seconds
= 322 minutes ❶

g. The time taken for the analysis, over 5 hours, is excessive given that the analysis is simply to determine the concentration of a solution. ❶ or
Predicted reactions, based on the electrochemical series are only accurate for 1 M solutions. Since the $c(Cu^{2+})$ is below 1 M initially, and decreases as the electrolysis proceeds, other reactions may be occurring *or*
maintaining a current of 0.500 A over this time period would be difficult.

h. The $c(Cu^{2+})$ would stay constant during the electrolysis. ❶
The (+) Cu electrode would be site of oxidation where Cu(s) is oxidised to $Cu^{2+}(aq)$.
The (-) Pt electrode would be the site of reduction where $Cu^{2+}(aq)$ is reduced to Cu(s).

i. Make up a set of standard $Cu^{2+}(aq)$ solutions and measure their absorbance at 610 nm. ❶
Plot a calibration curve to establish the relationship between absorbance and $c(Cu^{2+})$. ❶
Measure the absorbance of $CuSO_4(aq)$ solution being analysed at 610 nm and use the calibration curve to determine the $c(Cu^{2+})$ in the solution. ❶
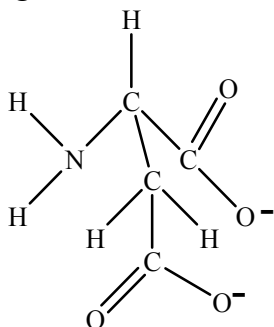
Question 3

a. ❶
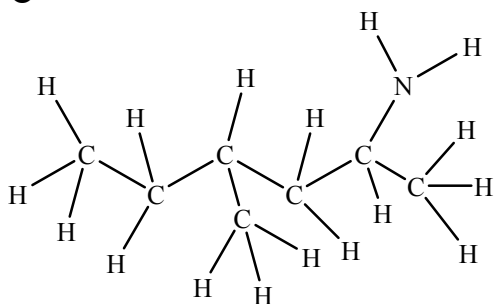
b. Amino acids contain a carboxyl –COOH functional group as well as an amino group. DMMA molecules do not have carboxyl groups. ❶

c. **2-aminopropanoic acid.** ❶

d. ❶

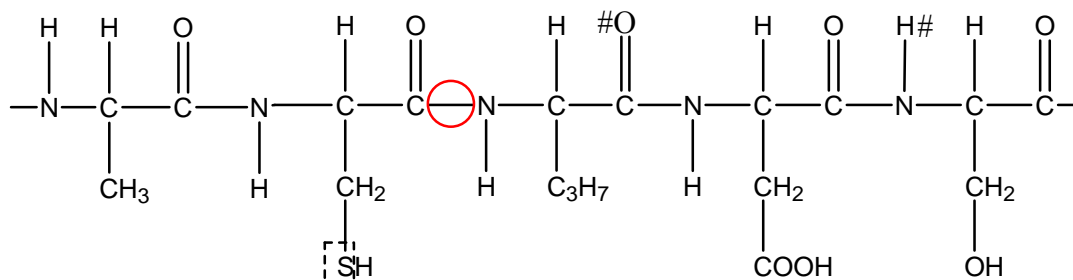**e.** A tripeptide is formed when **three amino acid molecules react together in a condensation reaction.** ❶

The **–COOH group on one amino acid reacts with the –NH₂ group, its adjacent amino acid, to form a peptide –CONH- link**. ❶ A tripeptide contains two peptide links.
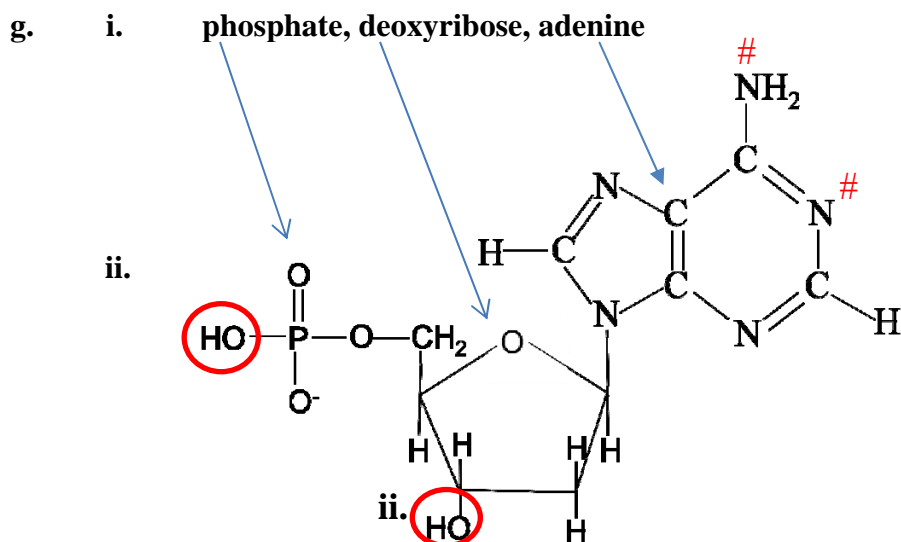
f.

i. ❶ for any C-N bond.

ii. ❶ for an 'O' on one peptide group AND an 'H' on a different peptide group.

iii. ❶ for the 'S' atom.

g.   **i.**   **phosphate, deoxyribose, adenine**

ii.

i.   ❷ for all three correct, [❶ for two correct]
ii.   ❶ for both 'OH' groups circled. Also accept POOH.
iii.   ❶ for both the N and the NH₂ on the right hand side of the nitrogen base
(adenine). No marks if the H on the C-H is asterisked.
h.   **Hydrogen bonding between complementary nitrogen bases on adjacent strands.**
Cytosine-Guanine (C-G) pairs have **three sites for hydrogen bonding,** whereas
Adenine-Thymine (A-T) pairs have only **two sites for hydrogen bonding**. ❶ The
greater the proportion of C-G (cytosine-guanine) base pairs, the stronger the attraction
between the strands.

Question 4

a. **i.** The main function and role of the catalyst is to increase the rate of reaction. ❶This then allows the use of lower temperature for the reaction which, from an equilibrium perspective, increases the yield of methanol ❶ because the forward reaction is exothermic.

NB The catalyst itself does NOT affect the yield of the reaction. The increase in yield is due to the ability to use a lower temperature because of the effect of the catalyst on reaction rate.

 ii. $$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g);$$

Initially	0.240	0.380	-	mol
Reacting	0.070	0.140 $\rightarrow$	0.070	mol
Equilibrium	**0.170**	**0.240**	**0.070**	mol ❶

At equilibrium: [CO] = 0.170 mol / 5.00 L = 0.0340 M

[H$_2$] = 0.240 / 5.00 = 0.0480 M

[CH$_3$OH] = 0.070 / 5.00 = 0.014 M ❶

$K = [CH_3OH] / [CO][H_2]^2$

$= 0.014 / \{0.034 \times 0.0480^2\}$

$= \textbf{178 ❶} (M^{-2})$

 iii. For the equilibrium constant to increase, the **forward reaction** must be **favoured**. Since the **forward reaction** is **exothermic,** the **temperature** must have **decreased. ❶**

b. **i.** **C$_3$H$_8$O$_3$ ❶** - glycerol (*Data Book Table 10*)

 ii. I$_2$ reacts in an addition reaction across the C=C double bond.

$n(I_2) = 7.61$ g /253.8 g mol^{-1}

$= 0.0300$ mol

Ratio $n(I_2)$ / n(fatty acid) = 0.0300 / 0.010

$= 3$ ❶

Hence the fatty acid molecule has 3 C=C double bonds, i.e. 6 H atoms less than the saturated fatty acid with the same number of C atoms

Acid is linolenic acid – **C$_{17}$H$_{29}$COOH ❶**

To produce the methyl ester, linolenic acid reacts with methanol according to

C$_{17}$H$_{29}$COOH(l) + CH$_3$OH(l) → C$_{17}$H$_{29}$COOCH$_3$(l) + H$_2$O(l)

❶ for correctly balanced equation, including states.

c. **i.** The ^{13}C NMR spectrum shows 2 peaks, indicating two different carbon bonding environments in the molecule, i.e. ethanoic acid, CH$_3$COOH.

CH$_3$OH(l) + CO(g) → CH$_3$COOH(l) ❶

 ii. CH$_3$CH$_2$OH

Three sets of peaks

Singlet – for the O**H** hydrogen

Triplet – for the C**H**$_3$ hydrogens

Quartet – for the C**H**$_2$ hydrogens

❶❶ for all three correct; ❶ for any two correct

d. **i.** Methanol is acting as a **reductant ❶**. It is being oxidised.

 ii. CH$_3$OH(l) is oxidised to CO$_2$(g) at the anode. The half-equation is developed by using the half-equation balancing principles.

Half-equations

Anode – **CH$_3$OH(l) + H$_2$O(l) → CO$_2$(g) + 6H$^+$(aq) + 6e$^-$ ❶**

Cathode – **O$_2$(g) + 4H$^+$(aq) + 4e$^-$ → 2H$_2$O(l) ❶** …. *from Data Book Table 2.*

Question 5

a. **i.** The oxidant in air is O_2, which is reduced at the cathode *Data Book Table 2*
$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq). \; ❶$$

ii. Mo is oxidised at the anode, O_2 is reduced at the cathode.
Oxidation: $Mo(s) + 8OH^-(aq) \rightarrow MoO_4^{2-}(aq) + 4H_2O(l) + 6e^-$ …. *from supplied information.*
Reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ ..*from (a. i.).*
Overall equation: multiply oxidation half-equation by 2 and reduction half-equation by 3, then add. Cancelling down species that appear on both sides.
$$2Mo(s) + 4OH^-(aq) + 3O_2(g) \rightarrow 2MoO_4^{2-}(aq) + 2H_2O(l) \; ❶$$

iii. $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$ $E° = +0.40$ V
$MoO_4^{2-}(aq) + 4H_2O(l) + 6e^- \rightleftharpoons Mo(s) + 8OH^-(aq)$ $E^0 = -0.91$ V
Cell voltage alkaline version = 0.40 – (-0.91)
$$= \textbf{1.31 V} \; ❶$$

b. Since the **oxidant** is supplied as needed from **air** it does **not** need to be **stored in the battery**. ❶

c. **i.** Electrical energy = $VIt = V$ x $n(e)$ x Q
Oxidation of 1 mol Zn $\rightarrow$ 2 mol e⁻
E from 1 mol Zn = 1.65 x 2 x 96500
$$= 3.18 \times 10^5 J$$
$$= \textbf{318 kJ} \; ❶$$

ii. Oxidation of 1 mol Mo $\rightarrow$ 6 mol e⁻
E from 1 mol Mo = 1.31 x 6 x 96500
$$= 7.58 \times 10^5 \text{ J}$$
$$= \textbf{758 kJ} \; ❶$$

iii. $M(Zn) = 65.4$ g mol L⁻¹
Energy per gram of **Zn** = 318 kJ mol⁻¹ / 65.4 g mol⁻¹
$$= \textbf{4.86 kJ g}^{-1} \; ❶$$
$M(Mo) = 95.9$
Energy per gram of **Mo** = 758 /95.9
$$= \textbf{7.90 kJ g}^{-1} \; ❶$$

d. The **(-) negative terminal** of the power supply (recharger) must be attached **to the (-) electrode** of the cell, and the **(+) positive terminal** of the recharger **to the (+) electrode** of the cell. ❶
The recharger must supply a **voltage greater than 3.7 V** per cell. ❶

Question 6

a. **Temperature**, **Concentration** and the use of a **Catalyst.** ❶

b. **Three** of:
HCl(aq) concentration.
Total volume of solution.
Temperature.
Diameter of reaction beaker.
❶❶ for three; ❶ for two

c. **i.** Because the total volume of the reaction mixture remains the same (50 mL), but the volume of 0.25 M $Na_2S_2O_3$(aq) used varies, the actual $c(Na_2S_2O_3)$ **at the start of the reaction is different in each investigation**. The $c(HCl)$ **is the same in all three reaction mixtures** ❶
With all three investigations at room temperature the **only variable is** $c(Na_2S_2O_3)$. ❶

    ii. **0.125 M** ❶
Total volume of solution is double that used of $Na_2S_2O_3$ (25 mL to 50 mL). Hence the concentration of $Na_2S_2O_3$ is halved at the instant before the reaction begins.

    iii. **0.20 M** ❶
Cl^- (aq) is a spectator ion so the $n(Cl^-)$ does not change. Since the volume increases by a factor of 10 (5 mL to 50 mL), the concentration decreases by a factor of 10, from 2.0 M to 0.20 M.

d. **i.** Since the equation for the reaction was not an equilibrium equation, the reaction may be assumed to go to completion, at which point the **amount of sulfur present is constant**. ❶

    ii. The initial rate of reaction in Investigation 3 is higher because the $c(Na_2S_2O_3)$ is higher.
The relative turbidity depends on the relative amounts of S(s) produced
Investigation 2. : $n(Na_2S_2O_3) = 0.25 \times 25 \times 10^{-3} = 0.00625$ mol;
$n(HCl) = 2.0 \times 5.0 \times 10^{-3} = 0.010$ mol
Since $Na_2S_2O_3$ is in excess, $n(S)$ produced $= \frac{1}{2} \times n(HCl) = $ **0.0050 mol**
Investigation 3. : $n(Na_2S_2O_3) = 0.25 \times 40 \times 10^{-3} = 0.010$ mol;
$n(HCl) = 2.0 \times 5.0 \times 10^{-3} = 0.010$ mol
Since $Na_2S_2O_3$ is in excess, $n(S)$ produced $= \frac{1}{2} \times n(HCl) = $ **0.0050 mol**
Hence the graphs for **both investigations level off at the same turbidity**.
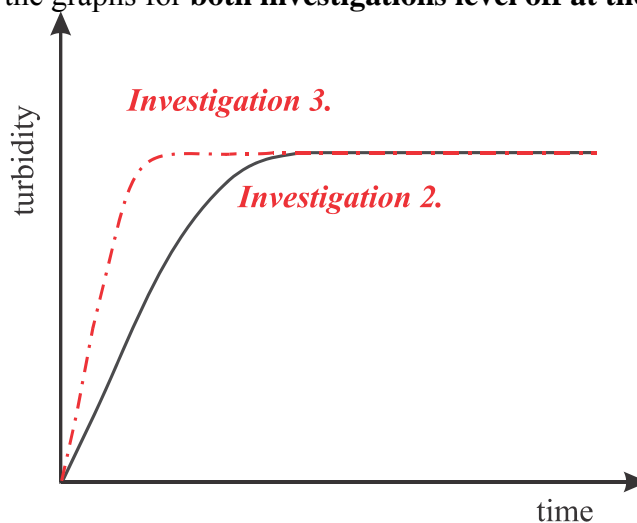
❶ for steeper gradient for Investigation 3.
❶ for graph levelling off earlier but at the same turbidity for Investigation 3.

e. **Surface area.** ❶
The **shorter reaction time (faster rate) for $Na_2S_2O_3$ powder** is consistent with the **greater surface area** allowing for more collisions between reactant particles and hence **more collisions with energy greater than the activation energy**. ❶

f. The **proportion of collisions with energy greater than the activation energy** is increased by an increase in temperature or the introduction of a catalyst.
An **increase in temperature** increases the **average kinetic energy** of the colliding particles. ❶
A **catalyst** has **no effect on the average kinetic energy** of the colliding particles but does **lower the activation energy** by providing an alternative reaction pathway. ❶

Question 7

a. Step 3: $\mathbf{NH_3(g) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)}$ ❶
      Or $NH_3(g) + H^+(aq) \rightarrow NH_4^+(aq)$
Step 4: $\mathbf{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$ ❶
      Or $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

b. $n(HCl)$ reacted with $NH_3(g)$ = $n(HCl)$ supplied − $n(HCl)$ in excess
                    = $n(HCl)$ supplied − $n(NaOH)$
                    = $\mathbf{0.100 \times 100 \times 10^{-3} - 0.200 \times 31.4 \times 10^{-3}}$ ❶
                    = $0.0100 - 0.00628$
                    = $\mathbf{0.0037\ mol}$ ❶ (0.003720)

c. $n(N)$ in sample = $n(NH_3)$ produced
                = $n(HCl)$ reacting with NH_3
                = $0.0037\ mol$
$m(N)$ in sample = 0.0037×14.0
                 = $\mathbf{0.052\ g}$ ❶

d. % N   = $[m(N) / m(\text{sample})] \times 100$
        = $(0.052 / 5.152) \times 100$
        = $\mathbf{1.01\ \%}$ ❶

e. $H_3BO_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$; $K_a = 5.8 \times 10^{-10}$ - *Data Book Table 12*
$K_a = [B(OH)_4^-][H^+] / [H_3BO_3]$
Standard weak acid assumptions may be made,
i.e. (i) negligible contribution to $[H^+]$ from self-ionisation of water so $[B(OH)_4^-] = [H^+]$
(ii) very small extent of reaction so equilibrium $[H_3BO_3]$ is the same as the initial concentration.
$5.8 \times 10^{-10} = [H^+]^2 / 0.647$
$[H^+]^2$ = $5.8 \times 10^{-10} \times 0.647$ ❶
$[H^+]$ = $\sqrt{(5.8 \times 10^{-10} \times 0.647)}$
      = 1.94×10^{-5} M ❶
pH   = $-\log_{10}(1.94 \times 10^{-5})$
      = 4.7 ❶

Question 8

a. $n(C_{12}H_{22}O_{11})$ reacting = 0.444 g / 342.0 g mol^{-1}
                                = 1.30x10^{-3} mol ❶

    Energy absorbed by water   = Heat capacity x $m(H_2O)$ x ΔT
                                = 4.18 J K^{-1} g^{-1} x 748 g x 2.06 K
                                = 6.44x10^3 J ❶

    Energy absorbed by calorimeter components = 420 J K^{-1} x 2.06 K
                                = 865 J

    Energy released in combustion of sucrose   = 6.44x10^3 + 865 J
                                = 7.31x10^3 J ❶

    Energy per mol $C_{12}H_{22}O_{11}$ = 7.31x10^3 / 1.30x10^{-3}
                                = 5.62x10^6 J mol^{-1}
                                = 5.62x10^3 kJ mol^{-1}

    $\Delta H_c(C_{12}H_{22}O_{11})$ = **-5.62x10^3 kJ mol^{-1}** ❶

b.   **$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$** ❶

c.   **i.**   **$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6H_{12}O_6(aq)$** ❶

    ii.   **$C_6H_{12}O_6(aq) \rightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$** ❶
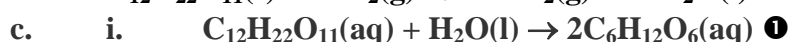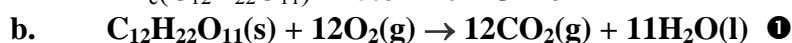
d.   **i.** $n(CH_3CH_2OH)$ reacting   = 2.0 / 46.0
                                = 0.0435 mol ❶

    Energy released = $n(CH_3CH_2OH)$ x energy available per mol CH_3CH_2OH
                                (from ΔH_c – Data Book Table 13)
                                = 0.0435 mol x 1364 kJ mol^{-1}
                                = 59.3 kJ ❶

    Maximum ΔT = Energy released / Calibration Factor
                                = 59.3 kJ / 1.32 kJ °C^{-1}
                                = **44.9 °C** ❶

    ii.   Some of the **energy** released from the ethanol may have been **lost to the surrounding environment.** ❶

End of Suggested Answers