2022 | **BORED OF STUDIES TRIAL EXAMINATION**

Chemistry

Marking Guidelines
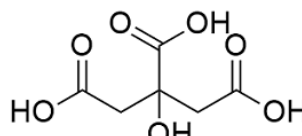
Section I

Multiple-choice answer key

1	2	3	4	5	6	7	8	9	10
C	C	D	A	B	A	D	C	B	B
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
D	A	C	B	C	D	C	C	A	B

Multiple-choice explanations

Question	Ans	Explanation
1	C	Bromine water tests for C=C bonds in alkenes by decolourising from orange-brown to colourless. Only (C) has this type of bond.
2	C	Enthalpy is negative since combustion is exothermic. Entropy is positive since in the equation $C_8H_{18}(l) + 12.5O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$ There is an increase in particle number from 13.5 to 17. $\Delta G = \Delta H - T\Delta S$ $\Delta G = (-ve) - (+ve)(+ve)$ $\Delta G = -ve - (+ve)$ $\Delta G = -ve - ve$ $\Delta G = -ve$
3	D	Since each compound has a different number of ions when dissolved in water, the molar solubility needs to be calculated based off the K_{sp} values given on the data sheet. Let x be the concentration of the salt dissolves in a 1 L saturated solution. Lead (II) chloride: $4x^3 = 1.70 \times 10^{-6}$ $x = 0.0075$ mol L^{-1} (3sf) Calcium sulfate: $x^2 = 4.93 \times 10^{-5}$ $x = 0.00702$ mol L^{-1} (3sf) Lead (II) sulfate: $x^2 = 2.53 \times 10^{-8}$ $x = 0.000159$ mol L^{-1} (3sf) Barium hydroxide: $4x^3 = 2.55 \times 10^{-4}$ $x = 0.0399$ mol L^{-1} (3sf) Therefore, barium hydroxide has the highest molar solubility

4	A	Since the pH is 2.960 then $[H_3O^+] = 10^{-2.960}$ mol L^{-1}.

	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$			
I	0.100	-	0	0
C	$-10^{-2.960}$	-	$+10^{-2.960}$	$+10^{-2.960}$
E	$0.100 - 10^{-2.960}$	-	$10^{-2.960}$	$10^{-2.960}$

$$\% \text{ unionised } = \frac{CH_3COOH_{equilibrium}}{CH_3COOH_{initlal}} = \frac{0.100 - 10^{-2.960}}{0.100} \times 100\%$$

$$= 98.9\% \ (3sf)$$

| 5 | B | The structure of citric acid is as below.

Citric acid

Due to symmetry, there are 4 carbon environments and 4 hydrogen environments. |
|---|---|---|

| 6 | A | $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$m(CaCO_3) = 12.95 \times 0.95 = 12.3025$ g

$$n(CaCO_3) = \frac{m}{MM} = \frac{12.3025}{40.08 + 12.01 + 16.00 \times 3} = 0.1229\ldots \text{mol}$$

$n(CaO) = n(CaCO_3) = 0.1229\ldots \text{mol}$
$m(CaO) = 0.1229 \times (40.08 + 16.00) = 6.89$ g (3sf) |
|---|---|---|

7	D	Ethyl propanoate has the formula $C_5H_{10}O_2$. By drawing each structure, the only one that has the formula $C_5H_{10}O_2$ is 2-methylbutanoic acid.

| 8 | C | $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$
Less oxygen is present in air from the atmosphere as it is a mixture of gases including nitrogen and carbon dioxide. Therefore, a decrease in $[O_2]$ leads to a lower reaction rate as less molecules are present which lowers the number of collisions. There is a decrease in yield as the equilibrium will shift left by Le Chatelier's Principle due to the lower $[O_2]$. |
|---|---|---|

| 9 | B | $n(HNO_3) = cv = 0.15 \times 0.450 = 0.0675$ mol
$n(Ba(OH)_2) = cv = 0.10 \times 0.250 = 0.0250$ mol

$n(H^+) = 0.0675$ mol
$n(OH^-) = 2 \times 0.0250 = 0.0500$ mol |
|---|---|---|

		Since $n(H^+) > n(OH^-)$ then H^+ is in excess. $n(H^+)$ excess $= 0.0675 - 0.0500 = 0.0175$ mol $c(H^+)$ excess $= \dfrac{n}{v} = \dfrac{0.0175}{0.700} = 0.025$ mol L^{-1} $pH = -\log_{10} 0.025 = 1.60205 \dots$ $pOH = 14 - 1.60205 \dots = 12.39794 = 12.40$
10	B	Soaps are surfactants which decreases the surface tension, thus decreasing cohesive forces. Soaps also form micelles in their cleaning action, forming emulsions.
11	D	Oxidation of the first compound gives 4-bromobutanoic acid. That is substituted with OH$^-$ to give 4-hydroxybutanoic acid. Concentrated H_2SO_4 will dehydrate it and give CH=CH-CH$_2$-COOH. There is no possibility of that to undergo condensation polymerisation. It instead undergoes addition polymerisation and so the final polymer contains all the atoms from the monomer. $MM(Z) = 4 \times 12.01 + 6 \times 1.008 + 2 \times 16.00 = 86.088$ g mol^{-1} Let N be the number of monomers that make up the polymer. $86.088 \times N = 1.03 \times 10^5$ $N = 1197.67 \dots$ Since each monomer has 4 carbon atoms, the approximate number of carbon atoms in the polymer is $4N$, which is closest to 4800.
12	A	Since HI and NaOH are a strong acid and base respectively, the net ionic reaction is: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $n(H^+) = n(HI) = cv = 0.09 \times 1.00 = 0.09$ mol $n(OH^-) = n(NaOH) = cv = 0.09 \times 1.00 = 0.09$ mol $n(H_2O) = n(H^+) = n(OH^-) = 0.09$ mol $q = mc\Delta T = (90 + 90) \times 4.18 \times 4.43 = 3333.132$ J $= 3.33132$ kJ $\Delta H_c = -\dfrac{q}{n} = -\dfrac{3.33132}{0.09} = -37.0$ kJ mol^{-1} (3sf)
13	C	Since HBr and KOH are also strong acids/bases, their net ionic reaction is the same as the reaction in Q12. Thus, the enthalpy of neutralisation is approximately the same.

14	B	For reliability of the data there needs to be at least 3 different trials that produce consistent results. Since there is only one data point for each site, none of the data is reliable for either site.
		Validity relies on the experimental setup and accuracy of assumptions in the graph. For Site A the 0.35 absorbance is within the graph's sample data points for the 5-70 ppm concentration and so it is valid to assume the line of best fit can be used to estimate the concentration in this solution.
		For Site B the 0.90 absorbance is outside the graph's data points and so it is invalid to assume that the relationship for the line of best fit will continue by extrapolation, as the trend may be different.
15	C	$A = 0.45$, so from the graph: $[Fe] = 35$ ppm $= 35$ mg L^{-1} Converting this into mol L^{-1}: $c(Fe)_{diluted} = \dfrac{0.035}{55.85} = 0.0006266 \ldots \text{mol } L^{-1}$ $n(Fe)_{diluted} = 0.0006266 \ldots \times 0.1 = 0.00006266 \ldots \text{mol}$ $c_1 v_1 = c_2 v_2$ $n(Fe)_{initial} = 0.00006266 \ldots \times \dfrac{0.2}{0.01} = 0.001253 \text{ mol}$ $m(Fe)_{initial} = n \times MM = 0.001253 \times 55.85 = 0.070 \text{ g}$ $\% \, m(Fe)_{initial} = \dfrac{70}{200} \times 100\% = 35\%$
16	D	The compounds are all salts which can form solutions that have acidic, neutral, or basic pH.
		$NaCl$ and $NaNO_3$ are neutral salts due to having a strong acid and strong base as conjugates.
		NH_4NO_3 is an acidic salt as it comes from the reaction of a weak base and strong acid. Adding NH_4NO_3 will increase $[H_3O^+]$ and so the equilibrium will shift left. This will decrease ionisation as more of the neutral acid $HOCl$ molecule will form.
		$NaCH_3COO$ is a basic salt as it comes from the reaction of a strong base and weak acid. Adding $NaCH_3COO$ will produce OH^- which reacts with H_3O^+ removing it from the solution and therefore decreasing $[H_3O^+]$. The equilibrium shifts right by Le Chatelier's Principle and so more ions are formed. This increases the degree of ionisation.

17	C	Na$_2$O is neither an acid nor a base, so (A) is incorrect.
		C$_3$H$_9$N (amine) and NaOH are both bases, not an acid and a base, so (B) is incorrect
		Glucose is neutral, so (D) is incorrect.
		C$_{17}$H$_{35}$COONa contains C$_{17}$H$_{35}$COO$^-$, which is a Bronsted-Lowry base and not an Arrhenius base. Citric acid contains 3 carboxylic acid groups, and thus is an Arrhenius acid. Hence, (C) is correct.
18	C	The number of moles of gas on either side of the equation are equal in ratio 2:2. Therefore an increase in pressure will NOT lead to a shift in the equilibrium as no side is favoured.
		However, the act of compressing the system will reduce volume and so the concentrations of each species will rise in $c = \frac{n}{v}$ and then plateau due to the lack of equilibrium shift.
19	A	Beaker A does not form a buffer and so adding a base to it will lead to pH increase. Beaker B contains a buffer solution and so adding a base will lead to a minimal pH change as the solution will resist the pH change.
20	B	Step 1: The step is correct
		Step 2: The step is correct
		Step 3: The pipette must be rinsed with the hydrochloric acid solution before being pipetted, as the distilled water in the pipette will dilute the acid.
		Step 4: The step is correct
		The actual concentration of HCl will be greater than the concentration of HCl in the pipette/conical flask.

Section II

Question 21 (a)

Criteria	Marks
• Gives TWO reasons for reflux	2
• Provides some relevant information	1

Sample answer:
Heating increases the speed of the reaction by allowing more reactants to have the required collisional energy to overcome the activation energy barrier. Cooling using a condenser is needed to prevent the loss of the reaction mixture, since all the compounds in esterification including the reactants and the ester are volatile.

Question 21 (b)

Criteria	Marks
• Provides correct calculations and a relevant reaction scheme	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:
Esters are made of alcohols and carboxylic acids. Therefore, the ester is made of propanoic acid and propanol.

Propanol may be converted to propanoic acid with acidified potassium permanganate solution. Esterification reaction between propanol and propanoic acid to form propyl propanoate using concentrated sulfuric acid catalyst.
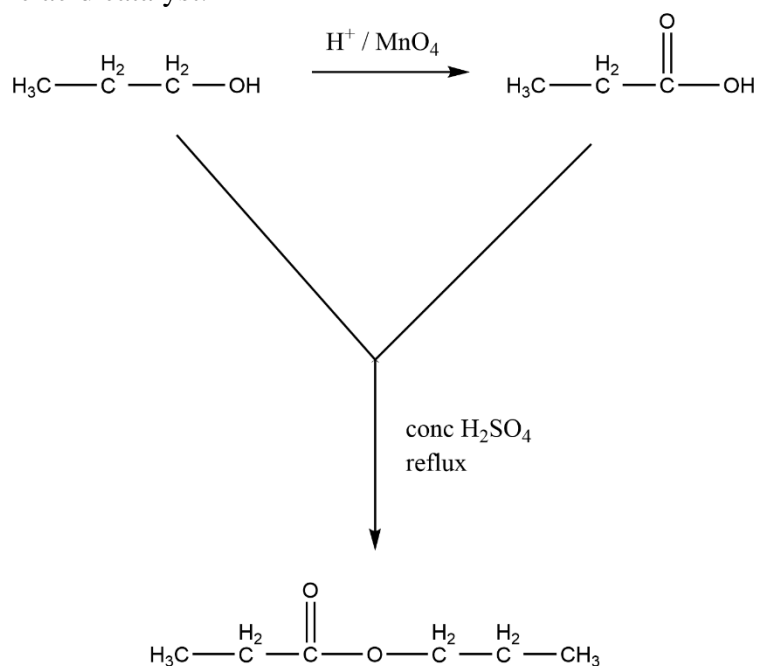
$$n(C_3H_8O) = \frac{m}{MM} = \frac{10}{3 \times 12.01 + 8 \times 1.008 + 16.00} = 0.1664 \ldots \text{ mol}$$

Mass of ester is maximised when propanoic acid and propanol react in the stoichiometric 1:1 ratio so would want to oxidise half of the propanol.

$$n(C_6H_{12}O_2) = \frac{0.1664 \ldots}{2} = 0.08321 \ldots$$

$$m(C_6H_{12}O_2) = 0.08321 \ldots \times (6 \times 12.01 + 12 \times 1.008 + 2 \times 16.00) = 9.67 \text{ g (3 sf)}$$

Question 22

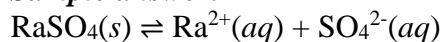| Criteria	Marks
• Explains patterns in the boiling points	3
• Explains most of the patterns in the boiling points	2
• Explains a pattern in the boiling points	1

Sample answer:
Alcohols have higher boiling points than the esters due to hydrogen bonding. The boiling points of both alcohols and esters increase with the number of carbon atoms due to increase in dispersion forces. The difference in boiling points between alcohols and esters decreases with increasing carbon atoms because dispersion forces become the predominant intermolecular force.

Question 23

Criteria	Marks
• Provides correct calculations • Provides a relevant chemical equation	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:
$RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{2-}(aq)$

First converting the solubility from grams to moles per litre:
$$[RaSO_4] = \frac{2.1 \times 10^{-3}}{322.06} = 6.521 \ldots \times 10^{-6} \text{ mol L}^{-1}$$

$$[Ra^{2+}] = [SO_4^{2-}] = 6.521 \ldots \times 10^{-6} \text{ mol L}^{-1}$$
$$K_{sp} = [Ra^{2+}][SO_4^{2-}] = 6.521 \ldots \times 10^{-6} \times 6.521 \ldots \times 10^{-6} = 4.3 \times 10^{-11} \text{ (2 sf)}$$

Question 24

Criteria	Marks
• Provides correct calculations • Provides a relevant chemical equation	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:
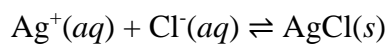
$n(BaCl_2) = cv = 0.0100 \times 0.0200 = 0.000200$ mol
$n(Cl^-) = 2 \times 0.000200 = 0.000400$ mol

$n(AgNO_3) = cv = 0.0200 \times 0.0200 = 0.000400$ mol
$n(Ag^+) = 0.00400$ mol

$[Ag^+] = \dfrac{n}{v} = \dfrac{0.000400}{0.04} = 0.0100$ mol L^{-1}

$[Cl^-] = \dfrac{n}{v} = \dfrac{0.000400}{0.04} = 0.0100$ mol L^{-1}

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

$Q = [Ag^+][Cl^-] = 0.0100 \times 0.0100 = 1.00 \times 10^{-4}$ (3 sf)

From the data sheet $K_{sp} = 1.77 \times 10^{-10}$.

Since $Q > K_{sp}$ then a precipitate forms.

Question 25 (a)

Criteria	Marks

• Provides graph with
    – correctly labelled axes including units
    – correctly plotted points
    – correct line(s) of best fit
• Correctly calculates the experimental heat of combustion
	3

• Provides a substantially correct graph and substantially correct calculations	2
• Provides some relevant information	1

Sample answer:

Temperature of water over time
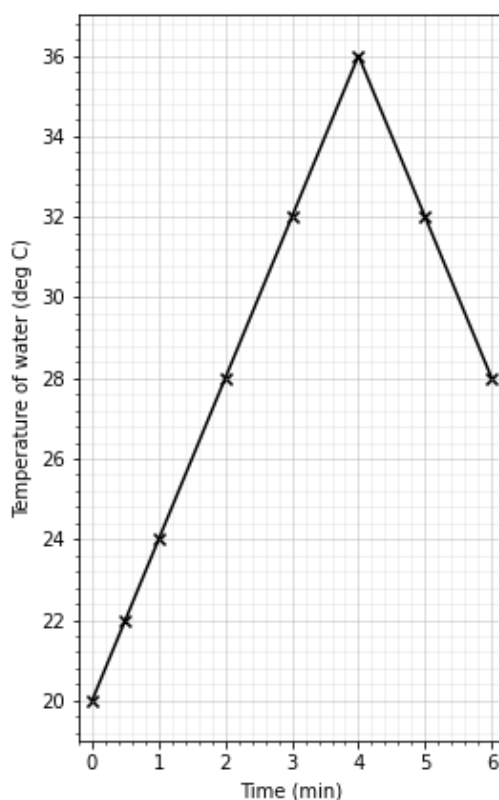
The maximum temperature is 36°C and the change in temperature is $36 - 20 = 16°C$.

The energy supplied to water is: $q = mc\Delta T = 250 \times 4.18 \times 16 = 16720 \text{ J}$

The mass of alcohol consumed is $120.00 - 119.06 = 0.94 \text{ g}$

Heat of combustion is:
$$-\frac{q}{m} = -\frac{16720}{0.94} = -177887 \text{ J g}^{-1} = -17.8 \text{ kJ g}^{-1} \text{ (3 sf)}$$

Question 25 (b)

Criteria	Marks
• Provides correct calculations • Identifies the unknown alcohol as ethanol	2
• Provides some relevant information	1

Sample answer:

The proportion of heat not lost to the surroundings is 60%.

The true heat of combustion is:

$$\frac{17.8}{0.6} = 29.7 \text{ kJ g}^{-1}$$

This is approximately equivalent to 1370 kJ mol^{-1} so:

$$MM = \frac{1370}{29.7} = 46.1 \text{ g mol}^{-1}$$

The general formula for an alcohol is $C_nH_{2n+1}OH$ which has molar mass of:
$$MM = 12.01n + (2n + 1)1.008 + 16.00 + 1.008 = 14.026n + 18.016$$

Solving for *n*:
$$14.026n + 18.016 = 46.1$$
$$n = 2.00$$

Therefore, the alcohol is ethanol (C_2H_5OH).

Question 26

Criteria	Marks
• Provides correct calculations • Provides a relevant chemical equation	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:

$pK_a = 3.16$

$K_a = 10^{-3.16}$

$K_w = K_a K_b$

$K_b = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{10^{-3.16}} = 1.445 \ldots \times 10^{-11}$

	NO₂⁻(aq) + H₂O(l) ⇌ HNO₂(aq) + OH⁻(aq)			
I	0.2	-	0	0
C	-x	-	+x	+x
E	0.2 - x	-	x	x

$K_b = \dfrac{[HNO_2][OH^-]}{[NO_2^-]} = \dfrac{x^2}{0.2 - x} = 1.445 \ldots \times 10^{-11}$

Nitrite is a weak base so $x \ll 0.2$, which means $0.2 - x \approx 0.2$.

$x = \sqrt{0.2 \times 1.445 \ldots \times 10^{-11}} = 1.700 \ldots \times 10^{-6} \text{ mol L}^{-1}$

$pOH = -\log_{10}[OH^-] = -\log_{10} x = -\log_{10} 1.700 \ldots \times 10^{-6} = 5.77 \ldots$

$pH = 14 - 5.77 \ldots = 8.23$

Question 27 (a)

Criteria	Marks
• Provides correct calculations	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:
$n(\text{HCN})_{\text{initial}} = cv = 0.10 \times 0.1 = 0.01$ mol
$n(\text{CN}^-)_{\text{initial}} = cv = 0.10 \times 0.1 = 0.01$ mol

$$c(\text{HCN})_{\text{diluted}} = \frac{n}{v} = \frac{0.01}{0.2} = 0.05 \text{ mol L}^{-1}$$

$$c(\text{CN}^-)_{\text{diluted}} = \frac{n}{v} = \frac{0.01}{0.2} = 0.05 \text{ mol L}^{-1}$$

	HCN(aq) + H$_2$O(l) $\rightleftharpoons$ CN$^-$(aq) + H$_3$O$^+$(aq)			
I	0.05	-	0.05	0
C	-x	-	+x	+x
E	0.05 - x	-	0.05 + x	x

$$K_a = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} = \frac{[\text{H}_3\text{O}^+](0.05 + x)}{0.05 - x} = 6.2 \times 10^{-10}$$
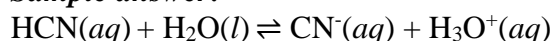
Since HCN is a weak acid then $x \ll 0.05$, which means $0.05 \pm x \approx 0.05$.
$[\text{H}_3\text{O}^+] = 6.2 \times 10^{-10}$
$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 9.21$

Question 27 (b)

Criteria	Marks
• Provides a relevant chemical equation • Explains how the buffer is able to resist a change in pH	2
• Provides some relevant information	1

Sample answer:
HCN(aq) + H$_2$O(l) $\rightleftharpoons$ CN$^-$(aq) + H$_3$O$^+$(aq)

On the addition of an acid such as HCl, the increased H$_3$O$^+$ is consumed by the reverse reaction by Le Chatelier's principle. The solution resists the pH change and can be referred to as a buffer.

Question 28 (a)

Criteria	Marks
• Provides the correct chemical equation	1

Sample answer:
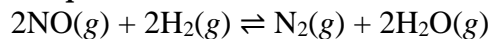
$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

Question 28 (b)

Criteria	Marks
• Provides correct calculations	3
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:

	$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$			
I	0.1	0.05	0	0.1
C	-2x	-2x	+x	+2x
E	0.1 - 2x	0.05 - 2x	x	0.1 + 2x

$0.1 - 2x = 0.062$
$x = 0.019$

$$K = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{0.019(0.1 + 2 \times 0.019)^2}{(0.1 - 2 \times 0.019)^2(0.05 - 2 \times 0.019)^2} = 6.5 \times 10^2 \text{ (2 sf)}$$

Question 29

| Criteria	Marks
• Provides a correct explanation	3
• Describes features of the acid, base and pH throughout the titration	2
• Provides some relevant information	1

Sample answer:
Ammonia and butanoic acid are weak base and weak acid respectively. The change in pH is therefore gradual throughout the titration. The indicator will change colour gradually and therefore the equivalence point cannot be accurately determined, so will need to observe the entire shape of the pH curve.

Question 30

Criteria	Marks
• Provides correct calculations of a relevant equilibrium constant • Provides a relevant chemical equation	3
• Describes some relevant steps	2
• Provides some relevant information	1

Sample answer:

The acid-base reaction between the reactants almost fully consumes the reactant material, which becomes unavailable for the desired reaction. This evidenced by the calculation below.

$$CH_3COOH(aq) + H_2NCH_3(aq) \rightleftharpoons CH_3COO^-(aq) + H_3NCH_3^+(aq)$$
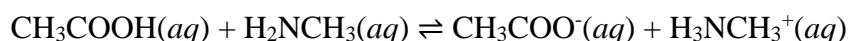
$$K = \frac{[CH_3COO^-][H_3NCH_3^+]}{[CH_3COOH][H_2NCH_3]} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \times \frac{[H_3NCH_3^+][OH^-]}{[H_2NCH_3][H^+][OH^-]}$$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \times \frac{[H_3NCH_3^+][OH^-]}{[H_2NCH_3]K_w} = \frac{K_a K_b}{K_w} = \frac{10^{-4.76} \times 10^{-3.34}}{10^{-14}} = 7.94 \times 10^5 \text{ (3 sf)}$$

Since $K \gg 1$ then the position of the equilibrium lies far away from the reactants.

Question 31

Criteria	Marks
• Explains why polymethyl methacrylate is more brittle than polycarbonate	3
• Identifies relevant features of polymethyl methacrylate	2
• Provides some relevant information	1

Sample answer:

Polymethyl methacrylate has more bulky side chains. This means that it is more difficult for the polymer chains to move into the most suitable positions and therefore instead bonds will need to stretch more than in polycarbonate. Therefore, the polymethyl methacrylate is more brittle than polycarbonate because the bonds will break earlier.

Question 32

Criteria	Marks
• Draws the correct chemical structures • Justifies the correct structures showing an understanding of the chemical tests and spectroscopic data	5
• Draws the most of the correct chemical structures • Justifies the correct structures showing an understanding of the chemical tests and spectroscopic data	3-4
• Provides some correct chemical structures	2
• Provides some relevant information	1

Sample answer:

For the compounds to be identified:

• *Unlikely* to contain an alcohol if the solution remains purple upon the addition of acidified $KMnO_4$ (an oxidant that would oxidise primary and secondary alcohols under standard conditions).

• *Likely* to contain a carboxylic acid if bubbles form upon the addition of $NaHCO_3$ (effervescence with the addition of $NaHCO_3$ to a carboxylic acid is indicative of the production of carbon dioxide gas).

Compound B:
The target product of fermentation is ethanol.

Compound C:
Using the previous lines of thought, it must be a carboxylic acid with 2 carbons and no further oxygens, so it must be ethanoic acid.
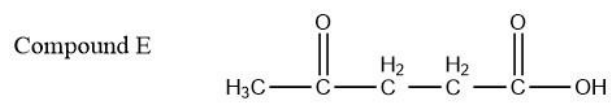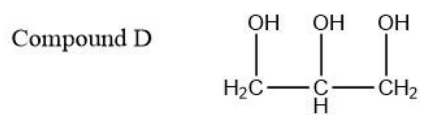
Compound E:
A carboxylic acid with 4 carbons. However, only two C^{13} NMR peaks indicate symmetry. Since there are 4 oxygens, the compound can be deduced to be butanedioic acid.
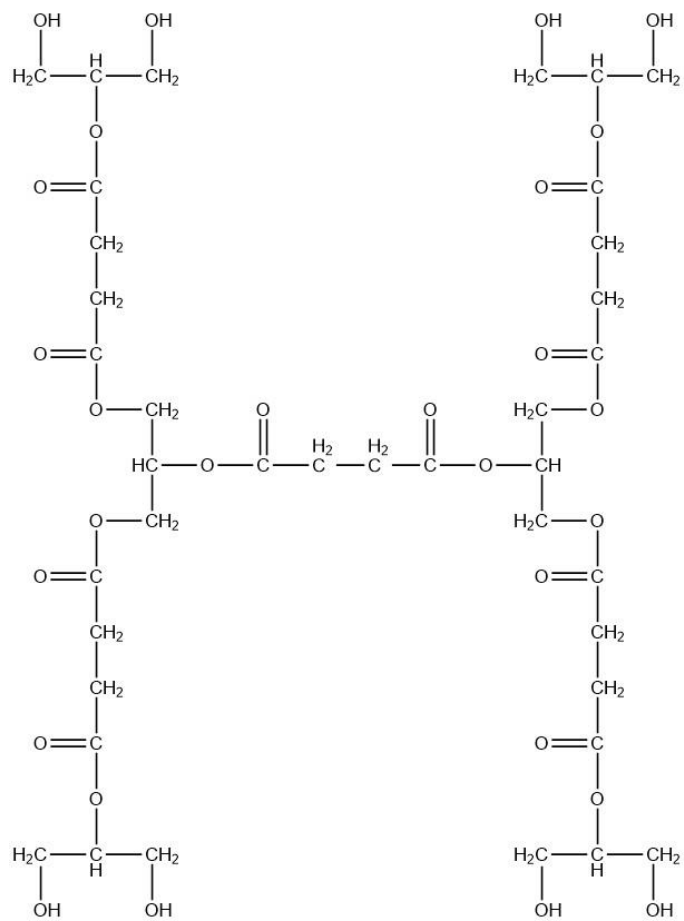
Compound D:
It is not a carboxylic acid. However, it reacts with butanedioic acid to form a polymer, which suggests that it contains an alcohol. This is further justified by the decolourisation of acidified $KMnO_4$ solution (which would decolourise upon oxidising a primary or secondary alcohol). A linear polymer is formed when reacting butanedioic acid with a diol, so 3 -OH groups must be present. Since there are two C^{13} NMR peaks, compound D must be propane-1,2,3-triol.

The structures are provided below:

Compound B

H_3C—$\overset{H_2}{C}$—OH

Compound C

H_3C—$\overset{\overset{\displaystyle O}{\|}}{C}$—$OH$

Compound D

H_2C—$\underset{H}{C}$—CH_2 with OH, OH, OH groups

Compound E

H_3C—$\overset{\overset{\displaystyle O}{\|}}{C}$—$\overset{H_2}{C}$—$\overset{H_2}{C}$—$\overset{\overset{\displaystyle O}{\|}}{C}$—$OH$

Polymer

Question 33

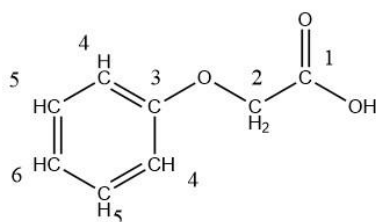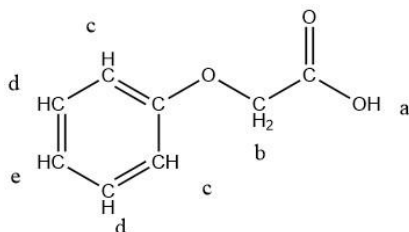| Criteria	Marks
• Writes the correct structural formula (naming not required) • Justifies the correct structure showing an extensive understanding of the interpretation of spectroscopic data • Refers explicitly to the relevant spectroscopic data	5
• Writes the correct structural formula for an isomer (naming not required) • Justifies the structure showing a thorough understanding of the interpretation of spectroscopic data • Refers to relevant spectroscopic data	4
• Shows a sound understanding of the interpretation of spectroscopic data • Uses relevant information presented in the question to justify the structure of the chemical • Provides a structural formula consistent with analysis	3
• Shows some understanding of the interpretation of spectroscopic data	2
• Provides some relevant information	1

Sample answer:
The carbon-13 peaks near 120 ppm indicate a possible structure containing a benzene ring. The carbon-13 peak near 190 indicates the likely presence of C=O. The carbon-13 peak near 66pm indicates the likely presence of a C-O-C bond.

The benzene ring is likely monosubstituted because there are 5 protons near 7 ppm. It is likely these are attached to the benzene ring. The extremely high proton NMR peak likely indicates a carboxylic acid.

Therefore, the structure and spectral assignments are:
• From lowest to highest, proton NMR: b, c, e, d, a
• From lowest to highest, carbon-13 NMR: 2, 4, 6, 5, 3, 1

The structure is provided below showing the above assignments.

Question 34

Criteria	Marks
• Provides the correct calculations of the amount of water evaporated and the amount of carbon dioxide absorbed	5
• Provides most correct steps	3-4
• Provides some relevant information	1-2

Sample answer:

The subsequent titration displays two equivalence points and there is likely the presence of a diprotic base. CO_2 absorption likely occurred according to the following reaction:

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$$
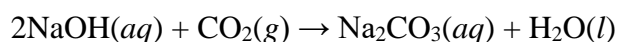
From the reaction equation it can be seen that 2NaOH is consumed to form one Na_2CO_3. The titration graph displays a greater volume addition between the first and second equivalence points. Up to the first equivalence point, clearly some other base than $Na_2CO_3(aq)$ is present. However, it could not be NaOH(aq) because then there would be three equivalence points. This base is actually $NaHCO_3$ formed from the following acid base reaction:

$$Na_2CO_3(aq) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(aq)$$
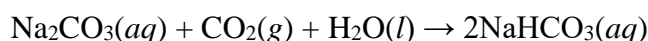
Between the start and first equivalence point, conversion of Na_2CO_3 to $NaHCO_3$ occurs. This corresponds to the amount of Na_2CO_3 present. From the graph, the volume of acid added to get to the first equivalence point is approximately 16 mL.

$$n(Na_2CO_3) = 0.0998 \times 0.016 = 0.00160 \ldots \text{ mol}$$

$$[CO_3^{2-}] = \frac{0.0016 \ldots}{0.025} = 0.0639 \ldots \text{ mol L}^{-1}$$

Between first and second equivalence point, the conversion of $NaHCO_3$ to H_2CO_3/CO_2 occurs. This corresponds to the amount of $NaHCO_3$ present *at the first equivalence point* (i.e, total $NaHCO_3$ and Na_2CO_3). From the graph, the volume of acid added to get to the second equivalence point is 43 mL. The volume of additional acid from first to second equivalence point is given by 43 – 16 = 27 mL.

$$n(Na_2CO_3) + n(NaHCO_3) = 0.0998 \times 0.027 = 0.00269 \ldots \text{ mol}$$
$$n(NaHCO_3) = 0.00269 \ldots - 0.00160 \ldots = 0.00109 \ldots \text{ mol}$$

$$[HCO_3^-] = \frac{0.00109 \ldots}{0.025} = 0.0439 \ldots \text{ mol L}^{-1}$$

Water evaporation occurred by the increase of second equivalence point. Without water evaporation, second equivalence point should not change because 2NaOH converted to Na_2CO_3 which both consumes 2 protons in titration (Na_2CO_3 is converted to $2NaHCO_3$, both of which consume two protons in titration).

Now consider the *entire* container. The $n(H^+)_{neutr}$ the container should be able to consume can be calculated from the original titration.

$$v_{titre} = \frac{26.62 + 26.65 + 26.59}{3} = 26.62 \text{ mL}$$

$$[NaOH] = 0.1006 \times \frac{0.02662}{0.025} = 0.1071 \dots \text{ mol L}^{-1}$$

$$n(H^+)_{neutr} = n(NaOH) = 0.1071 \dots \times 1.351 = 0.1447 \dots \text{ mol}$$
$$[H^+]_{neutr} = [HCO_3^-] + 2[CO_3^{2-}] = 0.0439 \dots + 2 \times 0.0639 \dots = 0.1716 \dots \text{ mol L}^{-1}$$

$$v_{final} = \frac{n(H^+)_{neutr}}{[H^+]_{neutr}} = \frac{0.1447 \dots}{0.1716 \dots} = 0.843 \dots \text{ L}$$

$$v_{evap} = 1351 - 843 \dots = 508 \text{ mL (3 sf)}$$

Amount of CO_2 absorbed is
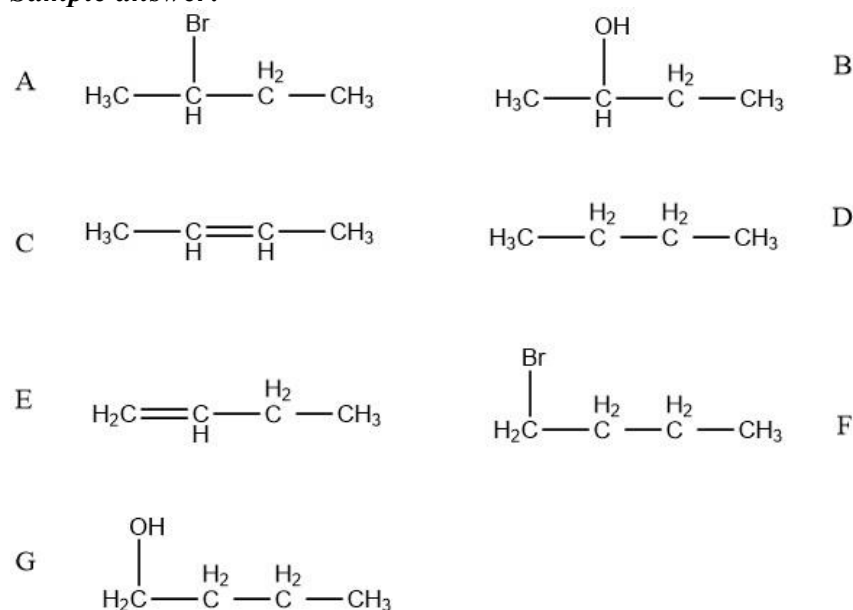$$v_{final} \times ([HCO_3^-] + [CO_3^{2-}]) = 0.843 \times (0.0439 \dots + 0.0639 \dots) = 0.0909 \text{ mol (3sf)}$$

Question 35

Criteria	Marks
• Draws correct structural formulae for all compounds	5
• Draws substantially correct structural formulae demonstrating an understanding of most reactions	3-4
• Draws structural formulae demonstrating an understanding of some different reactions	1-2

Sample answer:

Question 36 (a)

Criteria	Marks
• Provides a correct reason	1

Sample answer:

The final products consist of two species which are relatively unlikely to collide and therefore react because the concentration is low, while the complex is one species and with sufficient energy can easily decompose (no collision required).

OR

The activation energy of the reverse reaction for final product formation is much higher than the activation energy for the formation of reactants from the intermediate complex.

Question 36 (b)

Criteria	Marks
• Shows a comprehensive understanding of how pressure and temperature affect the rate of formation of CH3O gas	4
• Shows an understanding on how some aspects of pressure and temperature may affect the rate of formation of CH3O gas	2-3
• Provides some information about how pressure and/or temperature may affect the rate of formation of CH3O gas	1

Sample answer:

At high temperature (both low and high pressure), tunnelling is less important because the complex has sufficient energy to overcome the barrier to become products. Therefore, the greater the temperature, the greater the rate of product formation, because the easier it is to overcome the energy barrier.

At high pressure and low temperature, collisions reduce the energy of the complex and therefore slow the conversion back to reactants. On the other hand, conversion to products is therefore much more likely as tunnelling still operates and therefore the rate is higher than at higher (but not too much higher) temperatures.

The rate decreases with increasing temperature because conversion of complex to reactants becomes more likely than tunnelling to form products.

At low pressure and low temperature, reduction of energy of the complex by collisions is less likely. There is also not enough energy to readily overcome the activation barrier and too much energy for the complex to be more stable. Therefore, the rate at low temperature and low pressure is expected to be relatively less (or similar) to high temperatures. The rate is expected to be *much less* than at high pressures and low temperatures.

Question 37

Criteria	Marks
• Determines the identity of all unknown species • Provides correct working	7
• Determines the identity of most unknown species • Provides most correct working	5-6
• Determines the identity of some unknown species • Provides some correct working	3-4
• Provides some relevant steps	2
• Provides some relevant information	1

Sample answer:

Since the precipitate is $BaSO_4$ in the precipitometric titration (from the K_{sp}), then A is likely a sulfate, and given the 1:1 molar ratio, having formula MSO_4 for some unknown element M.

$$n(Ba^{2+}) = n(SO_4{}^{2-}) = n(M^{2+}) = 0.100 \times 0.04656 = 0.004656$$

$$MM(MSO_4) = \frac{m(MSO_4)}{n(MSO_4)} = \frac{1.000}{0.004656} = 214.8 \text{ g mol}^{-1}$$

$$MM(M) = MM(MSO_4) - MM(SO_4) = 214.8 - (32.07 + 4 \times 16.00) = 118.7 \text{ g mol}^{-1}$$

Hence, the element M is Sn and subsequently the identity of compound A is $SnSO_4$.

Note that the ratio of V_{eq} between compound B and A is $\frac{15.52}{46.56} = \frac{1}{3}$ and therefore the precipitate contains one-third of the amount of sulfate from before.

Hence, compound B has the formula Sn_3SO_4X for some unknown X. The associated ions are Sn^{2+}, $SO_4{}^{2-}$ and X^{4-}. Ammonia acts as a base (there would be too many elements were it a part of compound B) so possibilities for X include OH^- and O^{2-} and these need to add to a charge of -4.

$$n(B) = 0.100 \times 0.01552 = 0.001552$$

$$MM(B) = \frac{m(B)}{n(B)} = \frac{0.7794}{0.001552} = 502.19 \ldots \text{ g mol}^{-1}$$

$$MM(X) = MM(B) - 3MM(Sn) - MM(SO_4) = 502.19 \ldots - 3 \times 118.7 - (32.07 + 4 \times 16.00)$$
$$= 50.02 \ldots \text{ g mol}^{-1}$$
$$MM(OH^-) = 16.00 + 1.008 = 17.008 \text{ g mol}^{-1}$$
$$MM(O^{2-}) = 16.00 \text{ g mol}^{-1}$$

The logical combination is two hydroxides and one oxide to match molar mass of X as well as its charge of -4. Hence, the identity of compound B is $Sn_3(OH)_2OSO_4$.
B contains an element C does not. This is consistent with the water evaporation and that C does not have hydrogen. Hence, the identity of compound C is $Sn_3O_2SO_4$.

Question 38

| Criteria	Marks
• Provides a correct method to determine the difference in pK_a • Shows in detail how calculations can be performed to calculate the difference in pK_a	8
• Provides a correct method to determine the difference in pK_a • Shows how calculations can be performed to calculate the difference in pK_a	6-7
• Provides a portion of a correct method to determine the difference in pK_a	4-5
• Provides some relevant steps towards the determination of the difference in pK_a	2-3
• Provides some relevant information	1

Sample answer:
Represent the pK_a's of the first carboxylic acid as HA with pK_{a1} and the second carboxylic acid as HB with pK_{a2}.

Set up an equilibrium system by mixing the two acids and adjusting the pH (such as by adding an appropriate amount of NaOH) so that the amounts of HA, A⁻, HB and B⁻ are appreciable.

The following equilibrium is set up:
$HA(aq) + B^-(aq) \rightleftharpoons A^-(aq) + HB(aq)$
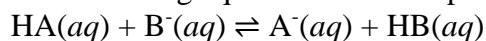
$$K = \frac{[A^-][HB]}{[HA][B^-]} = \frac{[H^+][A^-][HB]}{[HA][H^+][B^-]} = \frac{K_{a1}}{K_{a2}}$$

$$pK = -\log_{10}\left(\frac{K_{a1}}{K_{a2}}\right) = -\log_{10} K_{a1} - (-\log_{10} K_{a2}) = pK_{a1} - pK_{a2}$$

The relative amounts of protonated and deprotonated forms of each species only need to be determined. This can be done using NMR, such as ^{1}H NMR on the -C**H**-COOH, the chemical shift of which can be expected to differ based on whether the carboxylic acid is protonated or deprotonated.

For each acid, obtain the proton NMR shift for both the protonated and deprotonated forms. For the acid mixture, a single peak will be observed for each species HA/A⁻ (HA and A⁻ show up as a single peak) and HB/B⁻ (HB and B⁻ show up as a single peak). The chemical shifts in the NMR data can then be used to determine the relevant concentrations and subsequently determine the difference in pK_a.

Remark: Whilst not required in the response, the following is provided to elaborate on the actual calculation.

The peak is the weighted average, with the weights being the concentrations. Let δ_x refer to the chemical shift of species x.

With some manipulation:

$$\delta_{HA/A^-} = \frac{[HA]}{[HA] + [A^-]} \times \delta_{HA} + \frac{[A^-]}{[HA] + [A^-]} \times \delta_{A^-} = \frac{\delta_{HA} + \delta_{A^-} \frac{[A^-]}{[HA]}}{1 + \frac{[A^-]}{[HA]}}$$

$$\frac{\delta_{HA} - \delta_{HA/A^-}}{\delta_{HA/A^-} - \delta_{A^-}} = \frac{[A^-]}{[HA]}$$

Similarly

$$\frac{\delta_{HB} - \delta_{HB/B^-}}{\delta_{HB/B^-} - \delta_{B^-}} = \frac{[B^-]}{[HB]}$$

Since δ_{HA/A^-}, δ_{HA}, δ_{A^-}, δ_{HB/B^-}, δ_{HB} and δ_{B^-} can be obtained from the NMR then $\frac{[A^-]}{[HA]}$ and $\frac{[B^-]}{[HB]}$ can be calculated.

This subsequently gives the value of K and therefore the value of pK which provides the desired difference in pK_a's.

Acid/base can be added to obtain multiple values for the difference in pK_a's which can then be averaged to get an empirical value.