CHEMISTRY

Stage 3

WACE Examination 2012

Marking Key

Marking keys are an explicit statement about what the examiner expects of candidates when they respond to a question. They are essential to fair assessment because their proper construction underpins reliability and validity.

When examiners design an examination, they develop provisional marking keys that can be reviewed at a marking key ratification meeting and modified as necessary in the light of candidate responses.

Section One: Multiple-choice 25% (25 Marks)

Question No.	Answer
1	A
2	B
3	A
4	B
5	B
6	C
7	B or D
8	C
9	B
10	C
11	C
12	B
13	C
14	D
15	B
16	D
17	B or D
18	C
19	D
20	D
21	A
22	C
23	D
24	A
25	C

End of Section One

Section Two: Short answer 35% (70 Marks)

Question 26 (6 marks)

Consider the following substances, and place each in the appropriate column of the table below based on their most significant type of intermolecular force.

Dispersion	Dipole-dipole	Hydrogen bonding	Ion-dipole
F_2 C_6H_{12}	H_2S PF_3	CH_3OH HNO_3	

Description	Marks
1 mark for each correct substance in correct column.	1–6
Total	6

Question 27 (4 marks)

Examine the data in the table below. Use your knowledge of intermolecular forces to explain the differences in boiling points of the three compounds listed in the table.

Notes: The difference in boiling points is not primarily due to differences in molar masses. The differences arise due to differences in the strengths of their intermolecular forces (IMFs). Both butanol and butanoic acid have hydrogen bonding as their predominant intermolecular force which is the strongest type of IMF and hence have higher boiling points than butanal which has weaker dipole-dipole forces. Butanoic acid has a higher boiling point than butanol because it also has stronger dipole-dipole forces (as well as hydrogen bonding) associated with its carbonyl group, which is lacking in butanol.

| Description	Marks
Recognition that differences in bpts is primarily due to differences in IMFs.	1
Recognising butanol and butanoic acid have H-bonding.	1
Recognising butanal has dipole-dipole forces that are weaker than H-bonding.	1
Recognising butanoic acid has dipole-dipole associated with carbonyl group making its IMFs stronger than butanol	1
Total	4

Note: Statement 1 must be explicitly made in answer.
OR Butanoic acid has the capacity to form multiple H-bonds between its molecules (**or** dimers are formed).
Note: Reference to increasing dispersion forces due to more electrons <u>not</u> to be allocated a mark.

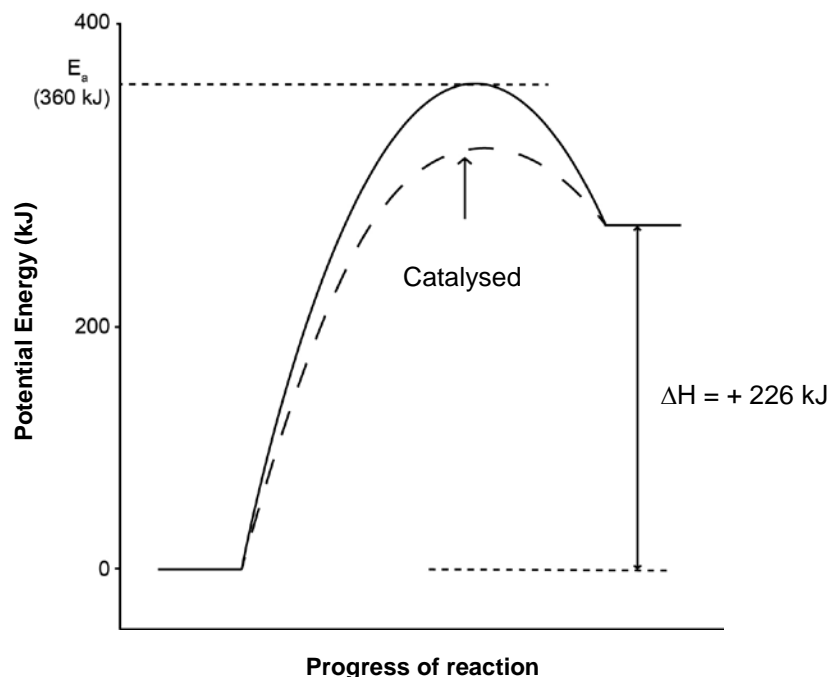**Question 28**   **(7 marks)**

Consider the following reaction.
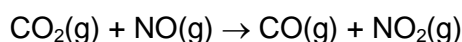
$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$ $\Delta H = + 226$ kJ, $E_a = 360$ kJ

(a)   On the axes below draw a potential energy diagram for this reaction. Label the
       activation energy (E_a) and enthalpy change (ΔH) for the reaction. Include a scale on the
       vertical axis.   (5 marks)

       On the same axes, use a dashed line to show a possible catalysed pathway.

Description	Marks
1 mark for an appropriate vertical scale (relatively accurate)	1
1 mark for shape of graph	1
1 mark for correctly labelled ΔH equal to +226 kJ (or 226 kJ)	1
1 mark for correctly labelled E_a equal to 360 kJ	1
One mark for correct possible catalysed pathway	1
Total	5

Note: Allocate 3 marks if shape incorrect but all labels are correct.

(b)   (i)   How much energy is consumed when 2.5 mol of $CO_2(g)$ is reacted with 2.5 mol
              of $NO(g)$?   (1 mark)

       (ii)   What is the activation energy when 2.5 mol of $CO_2(g)$ is reacted with 2.5 mol of
              $NO(g)$?   (1 mark)

Description	Marks
(i) +565 kJ (or 565 kJ)	1
(ii) 360 kJ	1
Total	2

Question 29 **(6 marks)**

Complete the table below by indicating the direction of the expected shift in equilibrium immediately following the changes stated in the table. Give the reason for the shift.

Test tube	Change	Direction of shift in equilibrium ('left', 'right' or 'no change')	Reason for shift
A	3 mL of water is added	**no change**	**2 moles of ions on each side of equation**
B	A few drops of concentrated nitric acid is added	**right**	**[H$^+$] is increased** Equilibrium shifts to decrease the imposed change, so favours forward reaction
C	A few drops of concentrated silver nitrate solution are added	**right**	Ag$^+$ + Cℓ^- → AgCℓ (s) **[Cℓ^-] is decreased** Equilibrium shifts to counteract the imposed change so shifts to increase the [Cℓ^-] by favouring products

If direction of shift incorrect, no mark for reason.

Description	Marks
1 mark for each correct direction of equilibrium shift	1–3
1 mark for each explanation for reason for shift direction	1–3
Total	6

Note: Minimum answers for reasons given in bold in table above (for 1 mark)
Accept arrows for direction shift.

Correct application of rates is valid for full marks.
For test-tube A: if a dash(–) is used to show direction of shift and the reason is correct, allocate 1 mark.
Reasons referring to amounts rather than concentrations in both B and C award 3 marks out of 4.

Question 30 **(6 marks)**

(a) On the axes below, draw separate curves to show how the concentrations of $NH_3(aq)$ and $[Ag(NH_3)_2]^+(aq)$ change with time as the system approaches, and finally reaches, equilibrium (Time E1). Clearly label your curve for $NH_3(aq)$ and your curve for $[Ag(NH_3)_2]^+(aq)$. Continue your curves from Time E1 to Time C. (3 marks)
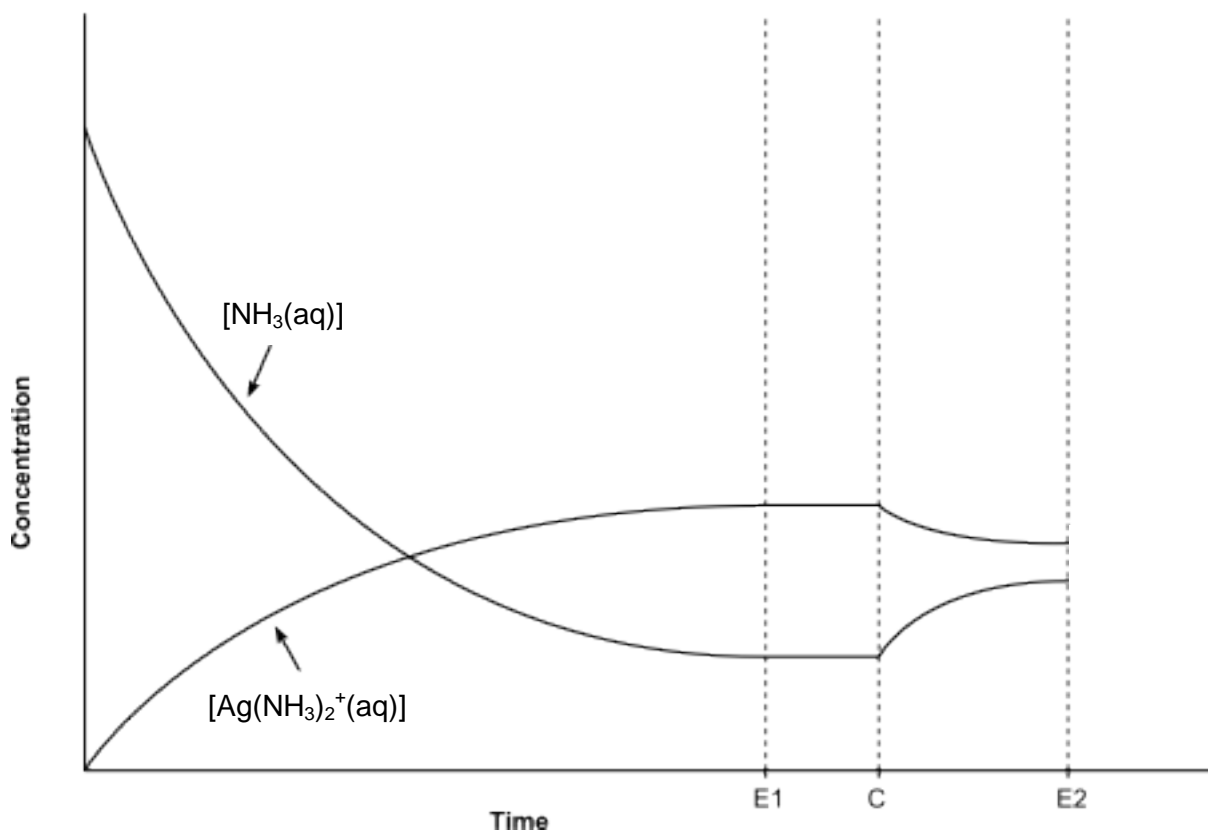
Description	Marks
Curves of correct shape for $NH_3(aq)$ **and** $[Ag(NH_3)_2]^+($ (aq)	1
Straight line (concentration constant) at E1 to C	1
Correct final position of reactant and product concentrations relative to each other at E1 (i.e. conc. (NH_3) < conc. $[Ag(NH_3)_2]^+(aq)$)	1
Total	**3**

Notes: Change in concentration shown correctly (i.e., reactant decreasing and product increasing) but shown as straight lines rather than curves), award one mark.

(b) At Time = C, as shown on the axis, a small quantity of concentrated $NaC\ell$ solution is added to the system, and the system is then again allowed to reach equilibrium at Time E2. On the same axes above, show how the concentrations of $NH_3(aq)$ and $[Ag(NH_3)_2]^+(aq)$ would change in response to the addition of $NaC\ell$ solution from Time C until equilibrium is reached at Time E2. (3 marks)

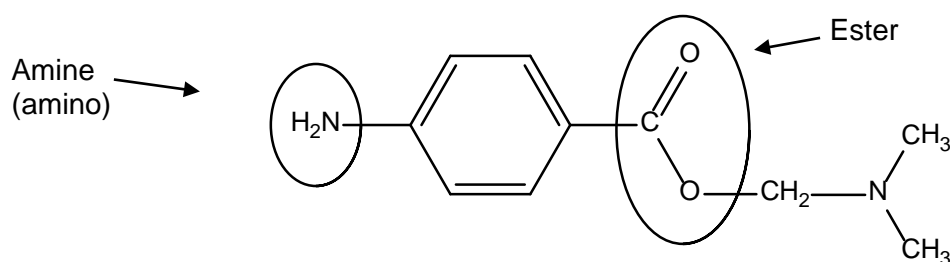| Description	Marks
Curves of correct shape for $NH_3(aq)$ **and** $[Ag(NH_3)_2]^+$ (aq)	1
Correct direction of concentration change for both $NH_3(aq)$ and $[Ag(NH_3)_2]^+$ (aq)	1
Equilibirium reached at E_2 and not before	1
Total	**3**

Question 31 **(4 marks)**

Examine the two compounds below. Compound 1 is the naturally occurring flavouring agent vanillin. Compound 2 is the local anaesthetic procaine. Name the functional groups circled in these 2 compounds.
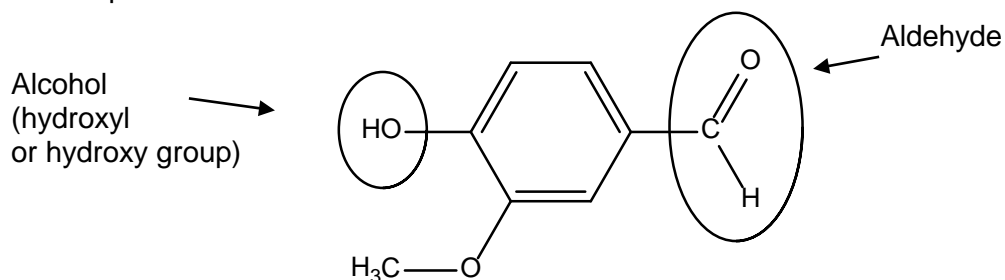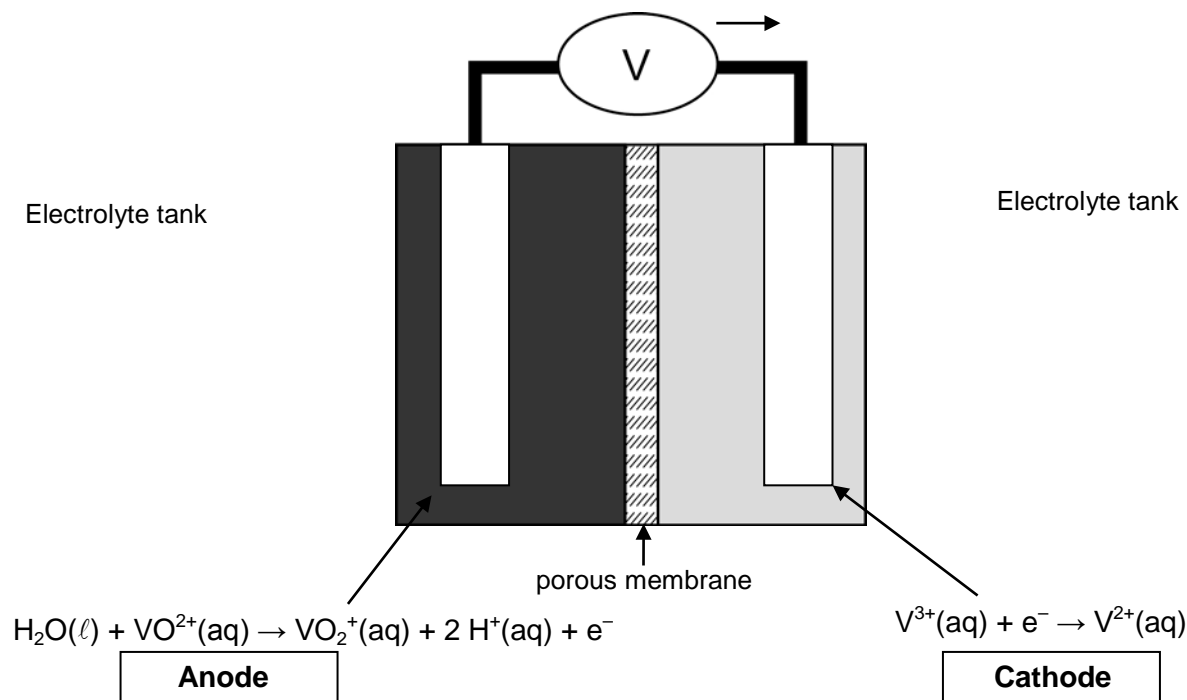

Compound 1 - vanillin

Compound 2 - procaine

Description	Marks
1 mark for each correctly named functional group	1–4
Total	4

Question 32 **(3 marks)**

The vanadium redox battery is an electrochemical cell that is being developed to store electricity produced by solar or wind on a large scale.

The general structure of the vanadium redox battery is shown below. In this battery, $VO^{2+}(aq)$ is converted to $VO_2^+(aq)$ at one electrode, while $V^{3+}(aq)$ is converted to $V^{2+}(aq)$ at the other.

Electrolyte tank   Electrolyte tank

porous membrane

$H_2O(\ell) + VO^{2+}(aq) \rightarrow VO_2^+(aq) + 2\,H^+(aq) + e^-$ $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$

Anode   **Cathode**

(a)   In the boxes above, identify and label both the anode and cathode.   (1 mark)

Description	Marks
Cathode **and** anode correctly identified and labelled	1
Total	1

Note: No mark if one electrode labelled and remaining box left blank

(b)   Draw an arrow on the diagram to indicate the direction of electron flow.   (1 mark)

Description	Marks
Appropriate arrow as shown in diagram (i.e. from anode to cathode)	1
Total	1

Note: If anode and cathode identified and labelled incorrectly but electron flow correct (based on correct identification of anode and cathode) do not award mark.

(c)   State briefly how the porous membrane functions to complete the circuit.   (1 mark)

Description	Marks
The porous membrane enables flow of ions	1
Total	1

Notes: 'To close the circuit' (or variations on this) is not acceptable. Answer must show some appreciation of the role of the membrane in allowing ion flow.

Question 33 **(7 marks)**

(a) Write the oxidation and reduction half equations, and the overall redox equation, for this reaction. (6 marks)

Oxidation half-equation: $Mn^{2+}(aq) + 4\ H_2O(\ell) \rightarrow MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$
Reduction half-equation: $BiO_3^-(aq) + 6\ H^+(aq) + 2\ e^- \rightarrow Bi^{3+}(aq) + 3\ H_2O(\ell)$
Overall redox equation: $2\ Mn^{2+}(aq) + 5\ BiO_3^-(aq) + 14\ H^+(aq) \rightarrow 2\ MnO_4^-(aq) + 5\ Bi^{3+}(aq) + 7\ H_2O(\ell)$

Description	Marks
Correct oxidation half-equation Award one mark for a correct equation (i.e. correct species) incorrectly balanced	1–2
Correct reduction half-equation Award one mark for a correct equation (i.e. correct species) incorrectly balanced	1–2
Overall redox equation correctly balanced based on provided half-equations. If H^+ and H_2O not simplified, 1 mark	1–2
Total	6

Notes:
- State symbols are not required for full marks
- If both half-equations are correct but in the wrong boxes give 3 out of 4.
- Award 2 marks if half-equation are reversed but balanced correctly i.e. products are shown as reactants

(b) In redox titrations involving permanganate or dichromate, the permanganate and dichromate must often be acidified. State why concentrated $HC\ell$ is not suitable for acidifying permanganate or dichromate solutions in redox titrations. (1 mark)

Description	Marks
$C\ell^-$ will be oxidised to $C\ell_2(g)$ or $C\ell^-$ will react with $MnO_4^-/Cr_2O_7^{2-}$	1
Total	1

Question 34   **(6 marks)**

Write the equations and observations for each of the following. Include in your equation only those species that react. In each case, describe in full what you would observe, including:

(a)   Excess sodium sulfide solution is mixed with copper(II) sulfate solution.   (3 marks)

Equation	$Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)$
Observation	Blue colour fades rapidly Black precipitate is formed

Description	Marks
Correct equation Award 1 mark for a balanced formula equation such as $CuSO_4(aq) + Na_2S(aq) \rightarrow CuS + Na_2SO_4(aq)$	1–2
Black precipitate formed and blue solution colour fades	1
Total	3

Note: State symbols not required for full marks
         Where 1 ion charge incorrect but equation correctly balanced for that ion award
         1 mark

(b)   Approximately 6 mol L^{-1} sulfuric acid is added to sodium acetate solution.   (3 marks)

Equation	$H^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq)$
Observation	Vinegar smell detected/pungent odour detected

Description	Marks
Correct equation Award 1 mark for a balanced molecular equation such as $H_2SO_4(aq) + 2\ NaCH_3COO(aq) \rightarrow Na_2SO_4(aq) + 2\ CH_3COOH(aq)$	1–2
Vinegar smell detected/pungent odour detected	1
Total	3

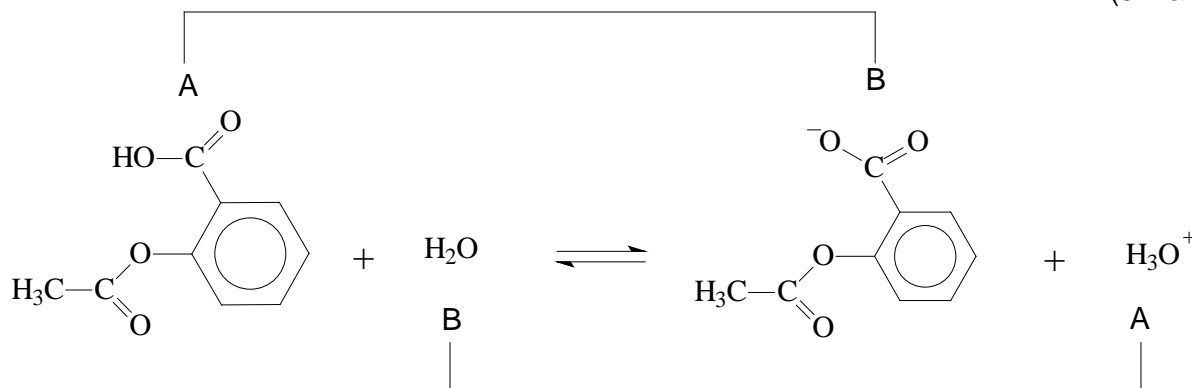Note: State symbols not required for full marks

Question 35   **(6 marks)**

(a)   Write the equation for the ionisation of acetylsalicylic acid in the space below, and identify the conjugate acid and base pairs in the reaction. Connect the acid-base pairs with a line, and label the conjugate acid in the pair 'A', and the conjugate base 'B'.

                                                          (3 marks)

Description	Marks
Correct ionisation reaction $RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$ R does not need to be correct	1
2 × connections of acid-base pairs	1
1 or both pairs correctly labelled	1
Total	3

(b)   Acetylsalicylic acid is a weak acid, and only partly ionises in water. It is poorly soluble in water, and far less soluble than a related compound, acetic acid (CH_3COOH). Explain why the water solubility of molecular acetylsalicylic acid is poor relative to that of CH_3COOH.   (3 marks)

        Notes: Although the carboxylic acid functional group may form hydrogen bonds with water, the acetylsalicylic acid molecule is composed of large non-polar functional groups that are not water-soluble. These groups compose a significant proportion of the molecule. While acetic acid also contains non-polar groups, these groups make up a smaller proportion of the molecule.

Description	Marks
Recognition of predominance of dispersion forces between acetylsalicylic acid and water	1
Recognition of predominance of H-bonding between acetic acid and water	1
Statement about solute-solvent interactions being sufficient to overcome solute-solute/solvent-solvent interactions	1
Total	3

OR

Description	Marks
Recognition of proportion of polar to non-polar	1
For acetylsalicylic acid there is only limited interaction between solute-solvent particles	1
For acetic acid, as it is a predominantly polar molecule there will be significant interactions between solute-solvent particles	1
Total	3

Question 36 **(6 marks)**

Water is able to react with itself in the process known as 'self-ionisation' or 'auto-ionisation'.

(a) Write the equation for the self-ionisation of water. (1 mark)

Description	Marks
$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ or $H_2O(\ell) \rightleftharpoons H^+(aq) + OH^-(aq)$	1
Total	1

Note: state symbols not necessary.

(b) At 25°C, K_W is approximately 1.0×10^{-14}. At 10°C, K_W is approximately 2.9×10^{-15}.
(2 marks)

What are the relative concentrations of H^+ and OH^- ions in a neutral water solution at **25°C**? Circle the correct answer.

Description	Marks
$[H^+] = [OH^-]$	1
Total	1

What are the relative concentrations of H^+ and OH^- ions in a neutral water solution at **10°C**? Circle the correct answer.

Description	Marks
$[H^+] = [OH^-]$	1
Total	1

(c) Consider the values of K_W at 10°C and 25°C, and state whether the self-ionisation of water is an endothermic or exothermic process. Give a reason to support your answer.
(3 marks)

Notes: K_W decreases as temperature is decreased. This implies that the reaction shifts to the left to produce heat, in turn implying that the forward reaction is endothermic.

Description	Marks
Endothermic	1
Identify from K_W that formation of products is favoured by increase in temperature	1
LCP predicts that endothermic direction favoured by increase in temperature	1
Total	3

Note: If candidate states 'endothermic' only, award one mark.
       If reasoning correct but exothermic, max 2 marks.
Note: Explanation may refer to increasing temperature.
       Student may refer to Le Chatelier's Principle

Question 37 **(9 marks)**

Oxalic acid dihydrate ($H_2C_2O_4•2H_2O$) is a primary standard used to standardise potassium permanganate solutions, which can be used for volumetric analysis.

(a)　List **two** properties of oxalic acid that make it a good primary standard.　(2 marks)

Description	Marks
One mark each for **any two** of: • Available in solid form • Available with high degree of purity • Not hygroscopic • High molar mass • High solubility • Readily available • Stable • Known formula	1–2
Total	2

(b)　A student was to prepare a standard solution of oxalic acid of approximate concentration 0.05 mol L^{-1}. The equipment listed below was available.

electronic balance
beakers (20 mL, 50 mL, 100 mL, 250 mL)
volumetric flasks (250 mL, 500 mL)
oxalic acid ($H_2C_2O_4•2H_2O$) (5 g)

distilled water (20 L)
stirring rod
wash bottle
weighing boats

Give a step-by-step, detailed description of a procedure for preparing the standard oxalic acid solution. Perform and include any necessary calculations.　(7 marks)

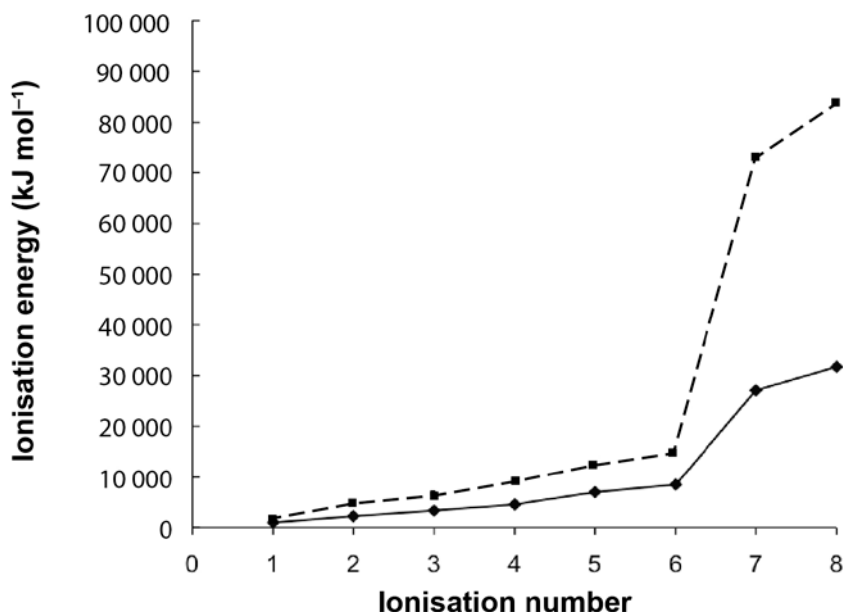| Description	Marks
Weigh out required mass into a beaker.	1
Dissolve $H_2C_2O_4•2H_2O$ in small quantity of distilled water (No mark for just 'water' throughout response)	1
(Quantitatively) transfer solution from beaker to volumetric flask, with sufficient rinsing with distilled water	1
Fill volumetric flask to the mark with distilled water	1
Thoroughly mix solution (e.g. by multiple inversions of flask)	1
Calculation of mass (Candidate may choose either the 250 mL or 500 mL volumetric flask) $M(H_2C_2O_4•2H_2O) = 126.068$ g mol^{-1} $n = cV = 0.05$ mol $L^{-1} \times 0.250$ L $= 0.0125$ mol req'd $\therefore$ $m(H_2C_2O_4.2H_2O)$ req'd $= 0.0125$ mol $\times 126.068$ g $mol^{-1} = 1.57$ g **or** $n = cV = 0.05$ mol $L^{-1} \times 0.500$ L $= 0.025$ mol req'd $\therefore$ $m(H_2C_2O_4.2H_2O)$ req'd $= 0.025$ mol $\times 126.068$ g $mol^{-1} = 3.15$ g	1–2
Total	7

End of Section Two

Section Three: Extended answer 40% (80 Marks)

Question 38 (6 marks)

A plot showing the successive ionisation energies of sulfur is given below.

(a) Define ionisation energy, and explain the gentle increase moving from the first ionisation energy to the sixth ionisation energy for sulfur. (2 marks)

Description	Marks
Ionisation energy: energy needed to remove an electron from an atom or ion (Strict definition: energy required to remove the least tightly bound electron from one mole of atoms or ions in the gaseous state) Note: strict definition not needed for 1 mark.	1
The steady increase in moving from 1st to 6th ionisation energy is accounted for by the decreasing number of electrons being held in the ion by the same nuclear charge, meaning more energy is required for removal.	1
Total	**2**

Note: Increasingly positive relative charge attracts remaining electrons is acceptable.

(b) Explain why the significant increase in moving from the sixth to the seventh ionisation energy for sulfur. (2 marks)

Description	Marks
The increase is suggestive of removal of electrons from a shell that is closer to the nucleus [consistent with electron configuration (2,8,6)].	1
More energy is required as the attraction is greater closer to the nucleus.	1
Total	**2**

(c) On the same axes above, sketch the graph you would anticipate for the first eight successive ionisation energies of oxygen. (2 marks)
See above

Description	Marks
Plot in correct position relative to sulfur (i.e. same position above the sulfur)	1
Plot of (approximate) correct shape	1
Total	**2**

Question 39 **(18 marks)**

Qualitative analysis of an organic compound showed that it contained carbon, hydrogen and oxygen only. A quantitative study of the same compound was performed, in which a 0.5096 g sample was burnt in excess oxygen to produce 0.4160 g of water and 700.7 mL of carbon dioxide, collected at 100.0°C and 102.8 kPa.

(a) Determine the empirical formula of the compound. (10 marks)

Description	Marks
$n(C) = n(CO_2) = \dfrac{PV}{RT} = \dfrac{102.8 \times 0.7007}{8.314 \times 373.15} = 2.3218 \times 10^{-2} \, mol$	1
$m(C) = 12.01 \times 2.3216 \times 10^{-2} = 0.27885$ g	1
$n(H_2O) = \dfrac{0.416}{18.016} = 2.3090586 \times 10^{-2} \, mol$	1
$n(H) = 2 \times 2.3090586 \times 10^{-2} = 4.6181 \times 10^{-2}$ mol	1
$m(H) = 1.008 \times 4.6181 \times 10^{-2} = 4.655 \times 10^{-2}$ g	1
$m(O) = 0.5096 - (0.27885 + 4.655 \times 10^{-2}) = 0.18423$ g	1
$n(O) = \dfrac{0.18423}{16.00} = 1.1514 \times 10^{-2} \, mol$	1
C H O 0.02319 0.04618 0.011514 ÷ by smallest $\dfrac{0.02319}{0.011514}$ $\dfrac{0.04618}{0.011514}$ 1.000 2.014 4.011 1.000 2 4 1 1 mark for ÷ by smallest; 1 mark for rounding	1–2
Thus EF is C_2H_4O	1
Total	**10**

Note:
If students don't multiply H × 2
     Ratio 1.79   1.79   1
     EF is C_2H_2O 8 marks
     $C_9H_9O_5$ 9 marks

If students divide H by 2
   EF is $C_7H_6O_5$ 9 marks
     $C_4H_2O_5$ 9 marks

(b) A second 0.4832 g sample of the compound was heated to 261°C. The vaporised sample was found to exert a pressure of 241 kPa in a 100.0 mL container. Use this information to determine the molecular formula of the compound. (4 marks)
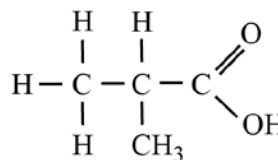
Description	Marks
$n(sample) = \dfrac{PV}{RT} = \dfrac{241 \times 0.100}{8.314 \times 534.15} = 5.4268 \times 10^{-3} mol$	1
$m(sample) = \dfrac{m}{n} = \dfrac{0.4832}{5.4268 \times 10^{-3}} = 89.04 gmol^{-1}$	1
Since Empirical formula mass = 44.052 Then MF is 2 × EF = $C_4H_8O_2$	1 1
Total	4

Note: If E.F. is incorrect max 3 marks.

(c) When the compound was reacted with acidified ethanol it produced a fruity smelling liquid. Infer the structure of the original compound, and draw its structure in the box below. Name the original compound. (2 marks)
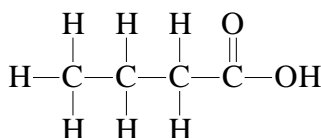
butanoic acid   **methylpropanoic acid**

Description	Marks
Correct structure	1
Correct name	1
Total	2

Note: Award one mark for correct name for incorrect structure, or incorrect name for correct structure. Must be carboxylic acid structure.

(d) Describe briefly and give observations for an additional chemical test to confirm the identity of the functional group in the original compound. (2 marks)

e.g. Test: reaction with a carbonate or Mg or Na
Observation: effervescence

Description	Marks
Any correct chemical test. e.g. react with acid suitable indicator that changes colour at appropriate pH (e.g. Universal Indicator, but not phenolphthalein)	1
Any correct observation	1
Total	2

Note: addiction of MnO_4^- and 'no reaction', is not acceptable

Question 40 **(16 marks)**

(a)   Calculate the concentration of sulfur dioxide in the wine in grams per millilitre (g mL^{-1}).
        Assume all the sulfur dioxide exists as hydrogensulfite ion in solution, and express your
        answer to the appropriate number of significant figures.   (6 marks)

Description	Marks
$V_{av}(I_2)$ = 12.82 mL (N.B. Titration 1 not included in the calculation of this value) or 12.86 if all titrations used	1
$n(I_2)$ = 0.0107 × 0.01282 = 1.3717 × 10^{-4} mol	1
In 50 mL wine, $n(SO_2) = n(HSO_3^-) = n(I_2)$ = 1.3717 × 10^{-4} mol	1
$m(SO_2)$ = 64.06 × 1.3717 × 10^{-4} = 8.7874 × 10^{-3} g	1
Concentration in g mL^{-1} = $\dfrac{8.7874 \times 10^{-3}}{50} = 1.7575 \times 10^{-4}$ g mL^{-1}	1
Concentration is 1.76 × 10^{-4} g mL^{-1} (3 s.f.)	1
Total	**6**

Note: If HSO_3^- used instead of SO_2 2.22 x 10^{-4} g mL^{-1} 5 marks

(b)   Given that the density of the wine is 0.975 g mL^{-1}, determine the concentration of sulfur
        dioxide in the wine in parts per million (ppm) and state whether the manufacturing
        process is producing wine with sulfur dioxide at the desired concentration.   (4 marks)

        Express your answer to three significant figures. Note: You must show sufficient
        working to justify your answer.

Description	Marks
m(1 mL wine) = 0.975 g = 9.75 × 10^{-4} kg	1
Concentration in ppm = $\dfrac{1.7575 \times 10^{-1}}{9.75 \times 10^{-4}} = 180.25$ ppm	1
Concentration = 180 ppm (3 s.f.) (1.80 × 10^2 ppm) 181	1
Yes, the manufacturing process is operating correctly	1
Total	**4**

1 mL of wine contains 1.7575 × 10^{-4} g of SO_2
i.e.   1 mL of wine contains 0.17575 mg of SO_2

and   1 mL of wine weighs 0.975 g i.e. 9.75 × 10^{-4} kg

thus   ppm = $\dfrac{1.7575 \times 10^{-1}}{9.75 \times 10^{-4}} = 180.25$ ppm

If HSO_3^- used   228 ppm   4 marks follow through
                     + no, the manufacturing process is not operating correctly.

(c) Draw the Lewis structures of SO_2 and SO_3 in the boxes below. You must show all valence electrons in your structure. (2 marks)

SO₂	**SO₃**

Description	Marks
1 mark for each correct structure	1–2
Correct structure but non-bonding electrons around the oxgens not shown	1
Total	**2**

(d) Compare the water solubility of these gases: that is, predict which one would be more soluble in water. Give reasoning to support your answer, and discuss briefly the relevance of their solubilities to acid rain. (4 marks)

Notes: SO_2 would be more soluble in water than SO_3. SO_2 is a bent molecule and is polar. SO_3 is a trigonal planar molecule and is non-polar. The polar SO_2 molecule and SO_2 (g) is more readily soluble in H_2O, and is likely to be a more significant contributor to acid rain than $SO_3(g)$.

Description	Marks
SO_2 is (bent and) polar	1
SO_3 is (trigonal planar) and non-polar	1
Predict that $SO_2(g)$ is more soluble in water than $SO_3(g)$	1
$SO_2(g)$ is more likely to contribute to acid rain that $SO_3(g)$ because of its water-solubility	1
Total	**4**

Note: Shape of molecule not necessary for 1 mark in first two rows

Or

Description	Marks
Both SO_2 and SO_3 react will react with H_2O	1
SO_2 is less reactive (reacts slower) than SO_3.	1
The acid formed by SO_2 is weaker than acid formed by SO_3	1
$\therefore$ SO_3 will contribute more to acid rain due to the strength of its acid.	1
Total	**4**

Question 41 **(12 marks)**

(a)   How many moles of NH_4NO_3 are produced by the reaction of one mole of CH_4? (1 mark)

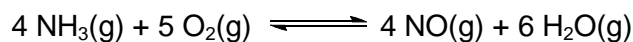| Description	Marks
2 moles of NH_4NO_3 are produced by 1 mole of CH_4	1
Total	1

(b)   Calculate the mass of CH_4 required to produce 2.50×10^5 tonnes of NH_4NO_3. Assume all reactions are 100% efficient and express your answer to three significant figures.
(6 marks)

Description	Marks
$M(NH_4NO_3) = (2 \times 14.01) + (3 \times 16) + (4 \times 1.008) = 80.052$ g	1
$n(NH_4NO_3) = \dfrac{2.5 \times 10^5 \times 10^6}{80.052} = 3.122970069 \times 10^9$ mol NH_4NO_3	1
$n(CH_4)$ req'd $= \dfrac{3.122970069}{2} \times 10^9 = 1.561485035 \times 10^9$ mol	1
$M(CH_4) = 12.01 + (4 \times 1.008) = 16.042$ g mol^{-1}	1
$\therefore$ m(CH_4) req'd $= 1.561485035 \times 10^9$ mol $\times$ 16.042 g mol^{-1} $= 2.504934293 \times 10^{10}$ g	1
i.e. m(CH_4) req'd) $= 2.50 \times 10^{10}$ g (3 s.f.)	1
Total	6

Note: other methods with fewer steps should be awarded full marks

If ratio of ½ from (a)
                          (b) 1.00×10^{11}g   6 marks

    ratio of 1 from   (a)
                          (b) 5.01×10^{10}g   6 marks

(c) The equation for Step 3 of the process is reproduced below. It is an exothermic reaction (ΔH = - 1130 kJ) and is carried out at 900°C and atmospheric pressure. Use your understanding of reaction rates and Le Chatelier's principle to explain why these conditions are employed for this reaction. (5 marks)

$$4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g)$$

Description	Marks
• The forward reaction is exothermic, so would be favoured by low temperature • Although low temperature favours the forward reaction, a high temperature is used. The high temperature increases the rate of the reaction • There are 9 moles of gas on the LHS and 10 moles of gas on the right hand side; low pressure favours the forward reaction (marginally) • The reactions will proceed reasonably well at atmospheric pressure. The difference in moles of gas on the left and right hand sides is not significant enough to justify the cost of lowering the pressure. • The high temperature used is a compromise between rate and yield. • High pressure favours high rate.	1–5
Total	5

Students to give 5 or 6 points for full marks.

Question 42 **(12 marks)**

Large public swimming pools are often chlorinated using chlorine gas. The gas is bubbled through the water forming the equilibrium reaction shown below.

$$Cl_2(aq)\ +\ H_2O(l) \rightleftharpoons HOCl\ (aq)\ +\ H^+(aq)\ +\ Cl^-(aq) \qquad \text{(Reaction 1)}$$

The equilibrium constant for this reaction, at 25°C, is 3.94×10^4.

(a) What can be said about the relative amounts of chlorine and hypochlorous acid at equilibrium at 25°C? (1 mark)

Description	Marks
The quantity of hypochlorous acid is much greater than chlorine	1
Total	1

The hypochlorous acid can dissociate as shown in the equilibrium below to give hypochlorite ion.

$$HOCl\ (aq)\ +\ H_2O(l) \rightleftharpoons H_3O^+(aq)\ +\ OCl^-(aq) \qquad \text{(Reaction 2)}$$
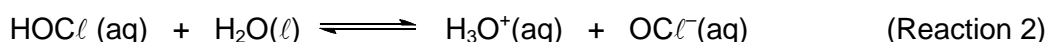
(b)   The pH of swimming pools is kept at approximately 7.5. A reason for this is to maximise the concentration of the hypochlorous acid, most effective disinfectant form of chlorine in water. Explain, using the appropriate chemistry concepts, why a pH of about 7.5 will maximise hypochlorous acid concentration. Your explanation should consider equilibrium Reactions 1 and 2.   (3 marks)

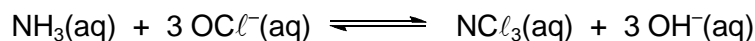| Description	Marks
At low pH (less than 7), in equilibrium (1) the reverse reaction is favoured which results in less hypochlorous acid.	1
For equilibrium (2) a pH less than 7 will favour the reverse reaction which leads to more hypochlorous acid	1
Thus as a compromise a pH slightly above 7 is used. At this pH, equilibrium (1) moves forward whilst for equilibrium (2) the forward reaction will not be strongly favoured thus maximising production of hypochlorous acid	1
Total	**3**

For equilibrium (1) at a high pH the forward reaction is favoured resulting in more hypochlorous acid. (1 mark)

(c)   If the concentration of hypochlorous acid is to be 1.50 mg L^{-1}, what volume of chlorine gas, at standard pressure and 25°C, is required for an Olympic size swimming pool with a volume of water of 2.50×10^6 L? Assume all the chlorine gas reacts to produce hypochlorous acid.   (5 marks)

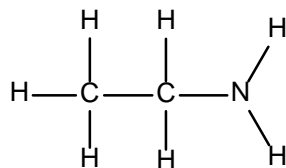| Description	Marks
$m(HOC\ell) = 1.5 \times 2.5 \times 10^6 = 3.75 \times 10^6$ mg $= 3750$ g	1
$n(HOC\ell) = \dfrac{3750}{52.458} = 71.49$ mol	1
$n(C\ell_2) = n(HOC\ell) = 71.49$ mol	1
Rearrangement of PV = nRT to $V = \dfrac{nRT}{P}$	1
$V(C\ell_2) = \dfrac{71.49 \times 8.314 \times 298}{100} = 1.77 \times 10^3 \text{L}$	1
Total	**5**

If P = 101.3   V = 1.75×10^3 L (5 marks)

(d)   Write a balanced equation showing the reaction of hypochlorite ion with ammonia to give nitrogen trichloride and hydroxide ion.   (1 mark)

$$NH_3(aq) \ + \ 3\,OC\ell^-(aq) \ \rightleftharpoons \ NC\ell_3(aq) \ + \ 3\,OH^-(aq)$$

Description	Marks
Equation as given above (state symbols not required for the mark)	1
Total	**1**

(e) Organic chloramines are produced by the reaction of an amine with hypochlorite ion. Give the structure of and name the primary amine with 2 carbon atoms. Show all atoms in your structure, and draw your structure in the box below. (2 marks)

ethanamine

Description	Marks
Structure as given above or condensed structure acceptable (no mark awarded if H atoms not shown)	1
Name as above (ethyl amine also acceptable)	1
Total	**2**

Note: ethan-1-amine; 1-ethanamine okay.
'aminoethane' is unacceptable

Question 43 **(16 marks)**

(a) The domestic water supply in Perth contains 65.0 mg L^{-1} calcium ions together with hydrogencarbonate ions. A large, tea-drinking family boils and consumes, on average, 4.2 L of water per day. Determine the mass of scale that will deposit in the household kettle during a 365-day year. Assume all calcium ions are removed from solution during boiling. (5 marks)

Description	Marks
4.2 L of water contains 4.2 L $\times$ 65 mg L^{-1} Ca^{2+} = 273 mg Ca^{2+}	1
$n(Ca^{2+}) = \dfrac{0.273}{40.08} = 6.8113 \times 10^{-3}$ mol	1
$n(CaCO_3) = n(Ca^{2+})$ $\therefore n(CaCO_3) = 6.8113 \times 10^{-3}$ mol	1
$m(CaCO_3) = 6.8113 \times 10^{-3} \times (40.08 + 12.01 + 48) = 0.68174$ g per day	1
$\therefore$ mass $CaCO_3$ per year = 0.68174 $\times$ 365 = 248.83 g = 249 g	1
If students assume scale is $Ca(HCO_3)_2$ m = 403 g **Total**	**5**

If students assume scale is $Ca(HCO_3)_2$
$m(Ca(HCO_3)_2)$ = 1.104 g per day
$\therefore$ per year $m(Ca(HCO_3)_2)$ = 403 g (5 marks)

(b) What volume of $CO_2(g)$, measured at the boiling point of water, is produced during boiling of 1.00 L of this water at standard pressure? (3 marks)

Description	Marks
1 L of water contains 65 mg Ca^{2+} = $\dfrac{0.065}{40.08}$ = 1.62176×10^{-3} mol	1
$\therefore$ $n(CO_2)$ = 1.62175×10^{-3} mol	1
PV = nRT $V = \dfrac{nRT}{P} = \dfrac{(1.62175 \times 10^{-3})(8.314)(373)}{100}$ $\quad$ = 0.050292 $\quad$ = 5.03×10^{-2} L CO_2	1
Total	**3**

If P = 101.3 used, V = 4.96×10^{-2} L (3 marks)

In the liming process, the pH of water is raised when $Ca(OH)_2(s)$ is added.

(c) Calculate the pH of a 1.05×10^3 L water solution to which 125 mg of $Ca(OH)_2$ have been added. Assume all added $Ca(OH)_2$ dissolves. (3 marks)

Description	Marks
$n(Ca(OH)_2)$ = $\dfrac{0.125}{74.096}$ = $1.687000678 \times 10^{-3}$ mol	1
$[Ca(OH)_2]$ = $\dfrac{1.687000678 \times 10^{-3} \text{ mol}}{1050 \text{ L}}$ = $1.606667284 \times 10^{-6}$ mol L^{-1} $\therefore$ $[OH^-]$ = $3.213334567 \times 10^{-6}$ mol L^{-1}	1
pOH = -log $(3.213334567 \times 10^{-6})$ = 5.49 $\therefore$ pH = 14 − 5.49 = 8.51	1
Total	**3**

don't double $[OH^-]$ pH = 8.21 (2 marks)

(d) Explain what is meant by the term 'buffering capacity'. (1 mark)

Description	Marks
The extent to which a solution can resist changes in pH or The extent to which a solution can resist the effects of added OH^- or H^+	1
Total	**1**

(e) Write two equations that demonstrate the buffering capacity of hard water containing HCO_3^-. (2 marks)

Description	Marks
$HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$	1
$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$	1
Total	**2**
Or accept as well:	
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	1
$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$	1
Total	**2**

(f)   Write equations to show how the addition of OH^- shifts the equilibria of the carbonate
       species in water.   (2 marks)

Description	Marks
$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O$	1
$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$	1
Total	**2**

End of questions