



Mark Scheme (Results)

Summer 2019

Pearson International Advanced Level
In Chemistry (WCH04) Paper 01 General
Principles of Chemistry I - Rates, Equilibria and
Further Organic Chemistry

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. The strands are as follows:
 - i) ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
 - ii) select and use a form and style of writing appropriate to purpose and to complex subject matter
 - iii) organise information clearly and coherently, using specialist vocabulary when appropriate

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:

- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.

() means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.

Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.

ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:

- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.

Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

| Question Number | Answer | Mark |
|-----------------|---|------|
| 1 | <p>The only correct answer is C</p> <p>A is not correct because a primary halogenoalkane reacts by an S_N2 mechanism so would be second order.</p> <p>B is not correct because a primary halogenoalkane reacts by an S_N2 mechanism so would be second order.</p> <p>D is not correct because a secondary halogenoalkane reacts by a mixture of mechanisms.</p> | (1) |

| Question Number | Answer | Mark |
|-----------------|---|------|
| 2 | <p>The only correct answer is C</p> <p>A is not correct because the formation of HI and/or nitric acid would not increase the pH.</p> <p>B is not correct because there is no change in mass.</p> <p>D is not correct because iodine is not formed.</p> | (1) |

| Question Number | Answer | Mark |
|-----------------|--|------|
| 3 | <p>The only correct answer is B</p> <p>A is not correct because the rate is independent of iodine concentration.</p> <p>C is not correct because iodine concentration decreases with time.</p> <p>D is not correct because iodine concentration decreases with time.</p> | (1) |

| Question Number | Answer | Mark |
|-----------------|---|------|
| 4 | <p>The only correct answer is C</p> <p><i>A is not correct because this plot would make the gradient $-R/E_a$.</i></p> <p><i>B is not correct because this plot would make the gradient $+R/E_a$.</i></p> <p><i>D is not correct because this plot would make the gradient $+E_a/R$</i></p> | (1) |

| Question Number | Answer | Mark |
|-----------------|--|------|
| 5 | <p>The only correct answer is A</p> <p><i>B is not correct because ice is less disordered than water, and the change is exothermic so the entropy change of the surroundings is positive</i></p> <p><i>C is not correct because the change is exothermic so the entropy change of the surroundings is positive</i></p> <p><i>D is not correct because ice is less disordered than water</i></p> | (1) |

| Question Number | Answer | Mark |
|-----------------|---|------|
| 6 | <p>The only correct answer is B</p> <p><i>A is not correct because C_2H_5COOH is not acting as a proton donor.</i></p> <p><i>C is not correct because neither species is acting as a proton donor.</i></p> <p><i>D is not correct because CH_3COO^- is not acting as a proton donor.</i></p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 7 | <p>The only correct answer is B</p> <p>A is not correct because litmus does not give a sharp colour change at the end point in a titration</p> <p>C is not correct because the pK_a of phenolphthalein is above the range pH 4-7</p> <p>D is not correct because the pK_a of alizarin yellow R is above the range pH 4-7</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|---|------|
| 8 | <p>The only correct answer is D</p> <p>A is not correct because this is $-\log 0.2$ whereas $[H^+]$ is 10^{-3}</p> <p>B is not correct because this would be the pH if $[H^+] = 10^{-1}$</p> <p>C is not correct because this is $2+(-\log 0.2)$</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 9 | <p>The only correct answer is B</p> <p>A is not correct because CH_3COCl produces a strong acid with water</p> <p>C is not correct because CH_3COCl produces a strong acid with water and sodium ethanoate has a higher pH than equimolar ethanoic acid</p> <p>D is not correct because ethanoic acid has a lower pH than equimolar sodium ethanoate</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 10 | <p>The only correct answer is B</p> <p>A is not correct because the units are inverted.</p> <p>C is not correct because there is 1 mol of product in solution and 2 mol of reactant in solution.</p> <p>D is not correct because the number of moles in solution is not the same on each side of the equation.</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|---|------|
| 11 | <p>The only correct answer is A</p> <p>B is not correct because the yield increases as pressure increases.</p> <p>C is not correct because the yield increases as the temperature decreases.</p> <p>D is not correct because the yield increases as pressure increases and the temperature decreases.</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 12 | <p>The only correct answer is A</p> <p>B is not correct because $\Delta S_{\text{surroundings}}$ does not equal $+\Delta H/T$.</p> <p>C is not correct because $\Delta S_{\text{surroundings}}$ does not equal $-T\Delta H$.</p> <p>D is not correct because $\Delta S_{\text{surroundings}}$ does not equal $+T\Delta H$.</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 13 | <p>The only correct answer is C</p> <p><i>A is not correct because halogenoalkanes are insoluble in water</i></p> <p><i>B is not correct because halogenoalkanes are insoluble in water</i></p> <p><i>D is not correct because the ester is much less soluble than the acid</i></p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|---|------|
| 14 | <p>The only correct answer is D</p> <p><i>A is not correct because aldehydes do not react with PCl_5 to form acyl chlorides.</i></p> <p><i>B is not correct because the reaction would form chloroethane.</i></p> <p><i>C is not correct because ketones do not react with PCl_5 to form acyl chlorides.</i></p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 15 | <p>The only correct answer is C</p> <p><i>A is not correct because propanoyl chloride is needed</i></p> <p><i>B is not correct because propanoyl chloride is needed</i></p> <p><i>D is not correct because ethylamine is needed</i></p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 16 | <p>The only correct answer is B</p> <p>A is not correct because carboxylic acids do not form ester linkages with halogenoalkanes</p> <p>C is not correct because acyl chlorides do not form ester linkages with carboxylic acids</p> <p>D is not correct because esters do not form ester linkages with acyl chlorides</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|---|------|
| 17 | <p>The only correct answer is D</p> <p>A is not correct because hexane is less polar than pentan-1-ol</p> <p>B is not correct because hex-1-ene is less polar than pentan-1-ol</p> <p>C is not correct because pentane is less polar than pentan-1-ol</p> | (1) |

| Question Number | Answer | Mark |
|-----------------|---|------|
| 18 | <p>The only correct answer is D</p> <p>A is not correct because the two H atoms are on the same side of the double bond.</p> <p>B is not correct because the double bond is on C9.</p> <p>C is not correct because the two H atoms are on the same side of the double bond.</p> | (1) |

| Question Number | Answer | Mark |
|-----------------|--|------|
| 19 | <p>The only correct answer is A</p> <p>B is not correct because this fatty acid would not form in transesterification</p> <p>C is not correct because this ester would not form in transesterification</p> <p>D is not correct because propane-1,2,3-triol is not used as a fuel</p> | (1) |

| Question Number | Correct Answer | Mark |
|-----------------|--|------|
| 20 | <p>The only correct answer is C</p> <p>A is not correct because infrared is not used</p> <p>B is not correct because microwaves are not used</p> <p>D is not correct because ultraviolet radiation is not used</p> | (1) |

Total for Section A = 20 marks

Section B

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|-----------------------|------------|
| 21(a) | $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ALLOW multiples, including $\text{NO} + \text{H}_2 \rightarrow \frac{1}{2} \text{N}_2 + \text{H}_2\text{O}$ reversible reactions IGNORE state symbols even if incorrect conditions even if incorrect Comment: Allow suspiciously large subscripts after elements | Equations including N | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--------|------------|
| 21(b)(i) | Order wrt NO = 2 and Order wrt H ₂ = 1 (1) (Comparing Experiments 1 and 3:) when [NO] is increased ×4 (keeping [H ₂] constant) rate increases ×16 (1) (Comparing experiments 1 and 2:) when [NO] is doubled rate would increase ×4; rate actually increases ×8, so doubling [H ₂] must also double rate OWTE (1) Marks are independent, M2 and M3 can be given even if M1 is incorrect ALLOW arrows and annotations on tables showing which results have been used | | (3) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------|
| 21(b)(ii) | <p>rate = $k[\text{NO}]^2[\text{H}_2]$⁽¹⁾</p> <p>TE on incorrect orders in (b)(i)</p> <p>IGNORE state symbols even if incorrect capital k in expression</p> | | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--------|------|
| 21(b)(iii) | <p>$k = \frac{(5.5 \times 10^{-3})}{(0.0020)^2(0.020)}$</p> <p>$= 6.875 \times 10^4 / 6.9 \times 10^4 / 68750 / 69000 / 70000$ (1)</p> <p>$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ (1)</p> <p>TE on rate equation in (b)(ii)</p> <p>IGNORE SF Units in any order</p> | | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|---|------|
| 21(c)(i) | <p>The possibility of three molecules / species / particles (of gas) colliding (in the right orientation) is low</p> <p>ALLOW There are three molecules / species / particles in the rate equation OR Third order reaction is unlikely (in a single step)</p> <p>ALLOW TE on incorrect rate equation e.g. "Hydrogen is not involved in the rate determining step"</p> | <p>Three compounds Three elements</p> | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------------|
| 21(c)(ii) | <p> $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2$ OR $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{O}\cdot$ OR $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ </p> <p> ALLOW $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{N}_2\text{O}_2$ Any balanced equation with one mole of each of N_2O_2 and H_2 on LHS (1) </p> <p> The rate equation must include all the species up to and including the rate determining step (1) </p> <p> ALLOW TE on rate equation </p> | | (2) |

(Total for Question 21 =10 marks)

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|---|------|
| 22(a)(i) | $K_a = \frac{[\text{C}_2\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_2\text{H}_5\text{COOH}]}$ <p>OR</p> $K_a = \frac{[\text{C}_2\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_2\text{H}_5\text{COOH}]}$ <p>ALLOW $\text{C}_2\text{H}_5\text{CO}_2^-$</p> $K_a = \frac{[\text{propanoate}][\text{H}^+]}{[\text{propanoic acid}]}$ <p>IGNORE state symbols even if incorrect balanced equations as working</p> | <p>Round brackets</p> <p>Just expressions including HA, A⁻ and H⁺</p> <p>CH₃COOH/ CH₃COO⁻</p> $K_a = \frac{[\text{H}^+]^2}{[\text{C}_2\text{H}_5\text{COOH}]}$ | (1) |

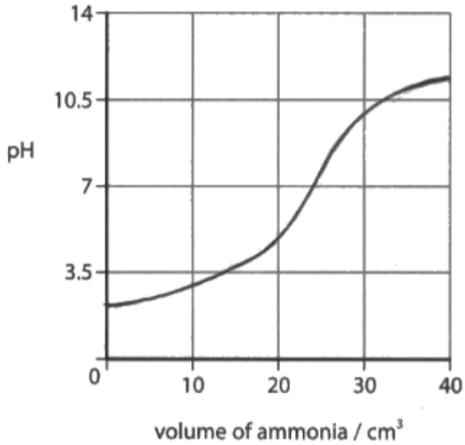
| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------|
| 22(a)(ii) | $[H^+]^2 = (K_a \times [C_2H_5COOH])$ OR $[H^+] = \sqrt{(1.30 \times 10^{-5} \times 0.120)}$ OR $[H^+] = \sqrt{(1.56 \times 10^{-6})}$ (1) $= 1.249 \times 10^{-3}$ (1) $pH = (-\log[H^+] = 2.9034)$ $= 2.90 / 2.9$ (1) Correct answer with no workings scores 3 Hydrogen ion concentration with no workings scores 2 ALLOW (Un)rearranged expression with substituted numbers for M1 TE on $[H^+]$ for M3 from M2 unless pH > 7 or pH < -1 IGNORE SF except 1 SF | | (3) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--------|------|
| 22(b)(i) | $[C_2H_5COOH] = [C_2H_5COO^-]$ $[H^+] = K_a$ ALLOW $pH = pK_a$ (1) (So $pH = -\log 1.30 \times 10^{-5}$) $= 4.8861 / 4.89 / 4.9$ (1) Correct answer without working scores 2 IGNORE SF except 1 SF | | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--|------------|
| *22(b)(ii) | <p>The mixture contains a (large) reservoir of propanoic acid and (sodium) propanoate</p> <p>ALLOW large amounts of weak acid/ conjugate base</p> <p>ALLOW "roughly equal amounts" (1)</p> <p>When OH⁻ / base is added it reacts with propanoic acid</p> <p>OR</p> <p>Equilibrium shifts to the right to produce more acid as H⁺ reacts with OH⁻</p> <p>OR</p> $\text{OH}^- + \text{C}_2\text{H}_5\text{COOH} \rightarrow \text{C}_2\text{H}_5\text{COO}^- + \text{H}_2\text{O}$ <p>OR</p> <p>When OH⁻ added, [C₂H₅COOH] falls slightly and [C₂H₅COO⁻] rises slightly (1)</p> <p>(pH depends on) ratio of propanoic acid to propanoate ions is almost unchanged / changes by a small amount (1)</p> <p>IGNORE discussion on effect of adding acid /H⁺</p> <p>ALLOW for 1 mark (if no other mark is scored) the buffer region resists a change in pH</p> <p>ALLOW Incorrect formula for propanoic acid Use of HA / A⁻</p> | <p>Equal amounts</p> <p>Just "H⁺ reacts with OH⁻ "</p> <p>remains constant</p> | (3) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------------|
| 22b(iii) | <p>Mol propanoic acid = $(25 \times 0.120/1000)$</p> <p>= 3.00×10^{-3} (mol) (1)</p> <p>Volume NaOH = $(3.00 \times 10^{-3} / 0.150)$</p> <p>= $0.02(0) \text{ dm}^3 / 20.(0) \text{ cm}^3$ (1)</p> <p>MUST have units for M2 IGNORE SF</p> <p>ALLOW TE from M1 to M2</p> | | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|----------|------|
| 22b(iv) | <p>(Excess NaOH = 20.0 cm³ in total volume of 65 cm³)</p> $[\text{OH}^-] = \frac{20.0 \times 0.15}{65} = 0.046154$ <p>ACCEPT Denominator that is 45 more than the volume (× concentration) e.g. $\frac{10 \times 0.15}{55} = 0.027$ (1)</p> <p>EITHER</p> $[\text{H}^+] = \frac{1 \times 10^{-14}}{0.046154} = 2.1667 \times 10^{-13}$ (1) <p>pH = (-log 2.1667 × 10⁻¹³)</p> <p>= 12.6642/12.7 (1)</p> <p>OR</p> <p>pOH = -log 0.046154 = 1.3358 (1)</p> <p>pH = 14 - 1.3358 = 12.6642/12.7 (1)</p> <p>Answer must be to at least 1 decimal place</p> <p>ALLOW TE on incorrect calculated moles of NaOH in M1 for M2 TE on incorrect H⁺ concⁿ for M3 if calculated pH is >7</p> <p>Correct answer with no working scores 3</p> | 12 or 13 | (3) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--|------------|
| 22(c)(i) | <p>Curve starting at pH 1.75–3.5 and finishing at pH 8.75–12.25 (<i>the half way point in each box</i>) (1)</p> <p>Gradual upward (or downward if plotted backwards) slope at pH 6–8 (with point of inflection – midpoint of the S – at pH7 and about 25 cm³ (22.5–27.5cm³) (1)</p> <p>e.g.</p>  | <p>Curve for di- or triprotic acids for M1 and M2</p> <p>Obvious vertical for M2</p> | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|----------------------------------|------------|
| 22(c)(ii) | <p>Both the acid and the base are weak so no sharp change in pH / colour of indicator occurs (when acid has completely reacted)</p> <p>OR</p> <p>pH/ colour of indicator changes gradually (throughout).</p> <p>OR</p> <p>there will not be a rapid change of pH/ colour of indicator around the end point</p> <p>Must refer to change in pH/colour of indicator</p> <p>No TE from graph</p> | <p>Just “no vertical region”</p> | (1) |

(Total for Question 22 = 17 marks)

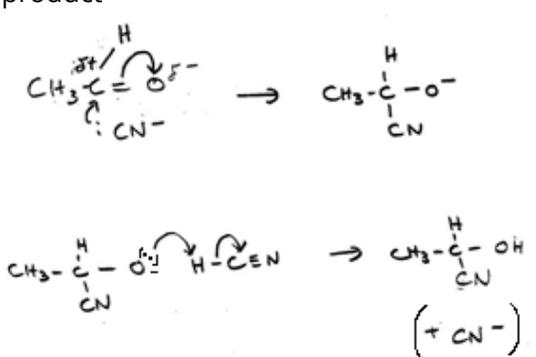
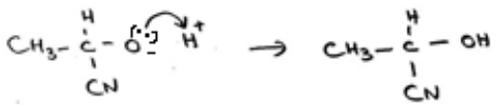
| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|---|------------|
| 23(a) | <p>Add Brady's reagent / 2,4-dinitrophenylhydrazine (1)</p> <p>ALLOW 2,4-DNP(H)</p> <p>Yellow/ orange/ red and precipitate (1)</p> <p>ALLOW crystals / ppt / solid for precipitate</p> <p>ALLOW (if no other marks awarded) Add Fehling's/ Benedict's/ Tollens' solution with correct observation for 1 mark Fehling's/ Benedict's – Red/brown ppt Tollens – silver mirror</p> <p>IGNORE Heat H₂SO₄ antiseptic smell</p> | <p>Use of acidified dichromate</p> <p>Brown</p> | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|-------------------------|------------|
| 23(b) | <p>Lithium aluminium hydride/ lithium tetrahydridoaluminate(III)/ LiAlH₄</p> <p>IGNORE Lithal (In dry ether/ ethoxyethane)</p> <p>OR</p> <p>Sodium borohydride/ sodium tetrahydridoborate/ NaBH₄ (in ethanol or water)</p> <p>Note: Allow phonetic spellings</p> | Reject aqueous solution | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------|
| 23(c)(i) | <p>CHI₃ / triiodomethane (1)</p> <p>ALLOW</p> <p>Iodoform / Cl₃I / structural formulae</p> <p>HCOONa / Sodium methanoate (1)</p> <p>ALLOW</p> <p>Methanoic acid</p> <p>If both name and formula are given, both must be correct</p> | | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------|
| 23(c)(ii) | <p>(Pale) yellow precipitate</p> <p>ALLOW</p> <p>crystals / solid / ppt</p> <p>IGNORE</p> <p>Medicinal smell</p> | | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--|------|
| 23(d)(i) | <p>Nucleophilic addition</p> <p>ALLOW</p> <p>Nucleophile addition and phonetic spellings</p> <p>IGNORE</p> <p>Heterolytic</p> | <p>Homolytic</p> <p>S_N1</p> | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--|------|
| 23(d)(ii) | <p>Partial charges shown on C=O and lone pair on carbon of CN⁻ (1)</p> <p>Arrow from lone pair on CN⁽⁻⁾ to carbonyl C and arrow from C=O bond to O or just beyond (1)</p> <p>Correct intermediate with O⁻ (1)</p> <p>IGNORE vertical connectivity of CN</p> <p>Arrow from (lone pair on) O⁻ to H of HCN and arrow from H-C bond to CN and structure of product</p>  <p>IGNORE H^{δ+} and CN^{δ-} on HCN</p> <p>OR</p> <p>Arrow from (lone pair on) O⁻ to H⁺ and structure of product (1)</p>  | <p>missing charge on CN⁻</p> <p>curly arrow from N</p> <p>bond from N to C of C-O⁻ in intermediate</p> <p>H⁺ on HCN</p> | (4) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--------|------|
| 23(d)(iii) | <p>A mixture containing equal amounts of (the two) enantiomers/ optical isomers</p> <p>ALLOW 50:50 or 1:1 as equal equimolar concentration for amounts D & L isomers (or lowercase) + & – isomers</p> <p>IGNORE</p> <p>References to plane polarised light</p> | | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--|------|
| 23(d)(iv) | <p>The aldehyde group / carbonyl group / reaction site is planar (1)</p> <p>ALLOW '(trigonal) planar about the C=O bond' OR carbonyl carbon is (trigonal) planar</p> <p>So CN⁻ can attack (equally) from above or below / from either side (1)</p> <p>ALLOW nucleophile for CN⁻ top / bottom for M2 'can attack from both sides' for M2</p> <p>Mark independently</p> | <p>"Ethanal is a planar molecule"</p> <p>"The intermediate is planar"</p> <p>carbocation</p> | (2) |

(Total for Question 23 = 14 marks)

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|---|------|
| 24(a)(iii) | <p>Minimum temperature is when $\Delta S_{\text{total}} = 0$, which is where $\Delta S^{\circ}_{\text{system}} = \Delta H/T$</p> <p>ALLOW</p> <p>This principle stated or used</p> <p>OR</p> <p>$\Delta G = \Delta H - T\Delta S_{\text{system}} = 0$ (1)</p> <p>$T = (\Delta H / \Delta S^{\circ}_{\text{system}})$ $= (173.5 \times 1000 / 262.3)$ $= 661.456$ $= 661.5 \text{ (K) / } 662 \text{ (K)}$ (1)</p> <p>Less than 4SF must be rounded up</p> <p>ALLOW TE on (a)(i) and (a)(ii) values ALLOW 388(°C)</p> <p>Correct answer without working scores 2</p> <p>IGNORE SF other than 1SF Rounding of more than 3SF</p> | <p>661 (as this would give a negative ΔS_{total} or a positive ΔG)</p> <p>Incorrect units</p> <p>Negative values</p> | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--|------|
| 24(a)(iv) | <p>The activation energy is high</p> <p>ALLOW</p> <p>Not enough energy to overcome E_a</p> <p>Reaction is kinetically stable / kinetically unfavourable / inert</p> <p>Energy needed to break the bond on LHS is too high</p> <p>IGNORE</p> <p>Reference to catalyst</p> | <p>Because conditions are not standard</p> <p>Just "Reactants are kinetically stable"</p> <p>Just "Temperature is not high enough"</p> | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|-------------|------|
| 24(b)(i) | <p>Lattice energy =</p> $\Delta H_{\text{hydration}} \text{K}^+ + \Delta H_{\text{hydration}} \text{I}^- - \Delta H_{\text{solution}}$ <p>OR</p> $\Delta H_{\text{solution}} = -\text{Lattice energy} + \Delta H_{\text{hydration}} \text{K}^+ + \Delta H_{\text{hydration}} \text{I}^-$ <p>OR</p> $\Delta H_{\text{hydration}} \text{K}^+ + \Delta H_{\text{hydration}} \text{I}^- = \text{Lattice energy} + \Delta H_{\text{solution}}$ <p>Note: Take "$\Delta H_{\text{hydration}}$" to mean sum of hydration energies</p> <p>ALLOW</p> <p>Labelled cycle for M1 (1)</p> $= (-320 -308 -20.3)$ $= -648.3 / -650 \text{ (kJ mol}^{-1}\text{)} \quad (1)$ <p>Correct answer without working scores 2</p> <p>IGNORE</p> <p>SF except 1 SF</p> <p>incorrect units</p> <p>ALLOW if no other mark awarded $-607.7 / -608$ or $(+) 648.3 / (+) 650$ for 1 mark</p> | <p>+608</p> | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--|------|
| 24(b)(ii) | <p>Radius of Na⁺ / sodium ion < radius of K⁺ / potassium ion (1)</p> <p>Charge density of Na⁺ greater than K⁺</p> <p>OR</p> <p>ions in NaI lattice are closer together than in KI lattice</p> <p>OR</p> <p>so more energy is released on formation of the lattice from the gaseous ions</p> <p>OR</p> <p>so (electrostatic) forces between ions are stronger (1)</p> | <p>Atomic radius</p> <p>References to covalency loses M2</p> | (2) |

Total for Question 24 = 11 marks)

Total for Section B = 52 marks

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|-----------------|------------|
| 25(a)(i) | $K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}} \times (p_{\text{H}_2})^2}$ <p>ALLOW Curved brackets (or no brackets) around any species P as subscript, superscript, lower or upper case or pp</p> | Square brackets | (1) |

| Question Number | Acceptable Answers | Reject | Mark | | | | | | | | | | | | | | | | |
|-----------------|---|---|---|----------------|--------------------|--------------|------|------|---|------------|------|-----|-----|----|--|---|---|--|------------|
| 25(a)(ii) | <p>Mol CO = 13 and Mol H₂ = 2.5 (1)</p> <p>(Total mol at eqm = 21) and partial pressures (can be in fractions or calculated) (1) e.g.</p> <table border="1" data-bbox="469 556 1094 934"> <thead> <tr> <th></th> <th>CO</th> <th>H₂</th> <th>CH₃OH</th> </tr> </thead> <tbody> <tr> <td>Mol at start</td> <td>18.5</td> <td>13.5</td> <td>0</td> </tr> <tr> <td>Mol at eqm</td> <td>13.0</td> <td>2.5</td> <td>5.5</td> </tr> <tr> <td>pp</td> <td>$\frac{13 \times 60}{21} =$ 37.143</td> <td>$\frac{2.5 \times 60}{21} =$ 7.1429</td> <td>$\frac{5.5 \times 60}{21} =$ 15.714</td> </tr> </tbody> </table> <p>$K_p = \frac{(15.714)}{(37.143)(7.1429)^2}$ (1)</p> <p>= 8.2923 x 10⁻³</p> <p>= 8.29 x 10⁻³ / 0.00829 atm⁻²</p> <p>Value to 3 SF ALLOW 8.30 x 10⁻³ (1)</p> <p>Units (1) ALLOW TE from (i)</p> <p>Correct final answer with units but no working scores 5 marks</p> <p>IGNORE SF on intermediate steps except 1SF</p> | | CO | H ₂ | CH ₃ OH | Mol at start | 18.5 | 13.5 | 0 | Mol at eqm | 13.0 | 2.5 | 5.5 | pp | $\frac{13 \times 60}{21} =$ 37.143 | $\frac{2.5 \times 60}{21} =$ 7.1429 | $\frac{5.5 \times 60}{21} =$ 15.714 | | (5) |
| | CO | H ₂ | CH ₃ OH | | | | | | | | | | | | | | | | |
| Mol at start | 18.5 | 13.5 | 0 | | | | | | | | | | | | | | | | |
| Mol at eqm | 13.0 | 2.5 | 5.5 | | | | | | | | | | | | | | | | |
| pp | $\frac{13 \times 60}{21} =$ 37.143 | $\frac{2.5 \times 60}{21} =$ 7.1429 | $\frac{5.5 \times 60}{21} =$ 15.714 | | | | | | | | | | | | | | | | |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|--------|------|
| 25(a)(iii) | <p>ΔH must be negative / exothermic (as K_p is greater) /as reaction proceeds further at lower temperature (1)</p> <p>$\Delta S_{\text{surroundings}} = -\Delta H/T$ so must be positive (1)</p> <p>ALLOW $\Delta S_{\text{surroundings}}$ must be positive / >0</p> <p>Marks are independent</p> <p>ALLOW if no other mark is awarded: "$\Delta S_{\text{surroundings}}$ must be negative as ΔH is positive" for 1 mark</p> | | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|---|------|
| 25(b)(i) | <p>Contains (-)COOH/ carboxylic acid (1)</p> <p>ALLOW carboxyl</p> <p>Contains a ketone / $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$ (1)</p> | <p>tertiary alcohol ether carbonyl Just C=O</p> | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|--|---|------|
| 25(b)(ii) | <p>CH_3CO^+</p> <p>ALLOW $\text{CH}_3\text{CH}_2\text{CH}_2^+$ Displayed or skeletal formula</p> | <p>CH_2COH $\text{C}_2\text{H}_3\text{O}^+$</p> <p>Negative ions</p> <p>C_3H_7^+</p> <p>displayed formula with hydrogens missing</p> | (1) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------------|
| 25(b)(iii) | <p>There are 4 hydrogen environments (in ratio 3:2:2:3) (1)</p> <p>ALLOW hydrogen environments clearly shown on the diagram</p> <p>The (two) triplets are due to $-\text{CH}_2\text{CH}_2-$ OR The (two) triplets are due to 2H atoms next to a $-\text{CH}_2$ (1)</p> <p>The (two) singlet(s) are due to 3H atoms with no adjacent H atoms OR The (two) singlets are due to 3H atoms in $\text{H}_3\text{C}-\text{C}=\text{O}$ (shift 2.2 ppm) and $\text{H}_3\text{C}-\text{O}$ (3.7 ppm) (1)</p> <p>ALLOW suitable groups of hydrogens clearly identified and labelled as singlets/triplets on the structure for 3 marks</p> <p>Identity of Q: $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOCH}_3$ (1)</p> | | (4) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------------------|------|
| 25(b)(iv) | $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COCH}_2\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$ <p>Structure of carboxylic acid P</p> <p>ALLOW TE on incorrect formula in (b)(iii) (1)</p> <p>Products of balanced equation</p> <p>ALLOW Formation of any methyl ester (1)</p> <p>ALLOW displayed and skeletal formulae → for reversible arrow</p> <p>IGNORE Catalysts Reaction conditions</p> <p>NOTE: Correct structure seen here can be awarded for (b)(iii)</p> | molecular formulae | (2) |

| Question Number | Acceptable Answers | Reject | Mark |
|-----------------|---|--------|------|
| 25(b)(v) | $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCl}$ <p>ALLOW</p> <p>Any acyl chloride Names of acyl chlorides Displayed or skeletal formulae RCOCl</p> <p>IGNORE Molecular formula</p> | C-O-Cl | (1) |

(Total for Question 25 = 18 marks)
Total for Section C = 18 marks

