



Mark Scheme (Results)

January 2017

Pearson Edexcel
International Advanced Subsidiary Level
in Chemistry (WCH04)
Paper 01 General Principles of Chemistry I – Rates,
Equilibria and
Further Organic Chemistry
(including synoptic assessment)

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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.

Section A (multiple choice)

Question Number	Correct Answer	Mark
1	A Unit should be $(\text{mol dm}^{-3} \text{ s}^{-1})$ divided by (mol dm^{-3}) B Correct C Unit is not $(\text{mol dm}^{-3} \text{ s}^{-1})$ divided by (mol dm^{-3}) D Unit is not $(\text{mol dm}^{-3} \text{ s}^{-1})$ divided by (mol dm^{-3})	1

Question Number	Correct Answer	Mark
2	A Rate decreases by factor of 4 when $[\text{NO}]$ is halved and increases by factor of 2 when $[\text{Br}_2]$ is doubled so overall decreases by factor of 2/ is halved B Rate is not doubled C Correct D Rate is not quartered	1

Question Number	Correct Answer	Mark
3	A k is not directly proportional to temperature B k does not decrease as temperature increases C Correct D k increases exponentially, not as shown	1

Question Number	Correct Answer	Mark
4	A The temperature drops so it is true that ΔH is positive B Correct C A gas is formed so it is true that ΔS_{system} is positive D The reaction is spontaneous so it is true that ΔS_{total} is positive	1

Question Number	Correct Answer	Mark
5	A The entropy of the system increases when more gas molecules form B The entropy of the system increases when a gas forms from a solid C Correct D The entropy of the system increases when solid turns to liquid	1

Question Number	Correct Answer	Mark
6	<p>A The enthalpy change for the equation shown is equivalent to providing the energy to form gaseous sodium and chloride ions (- Lattice energy) and then hydrating the ions (+ hydration energy) so sign of Lattice energy is incorrect</p> <p>B Sign of enthalpy change of hydration is incorrect</p> <p>C Sign of enthalpy change of hydration is incorrect</p> <p>D Correct</p>	1

Question Number	Correct Answer	Mark
7	<p>A The level of solubility is not the cause of the enthalpy change</p> <p>B The statement is true but does not explain the enthalpy change</p> <p>C The enthalpy change of hydration does not depend on the lattice energy</p> <p>D Correct</p>	1

Question Number	Correct Answer	Mark
8	<p>A The pressure of solids should not be included</p> <p>B The pressure of solids should not be included</p> <p>C Correct</p> <p>D The expression is upside down</p>	1

Question Number	Correct Answer	Mark
9	<p>A Correct</p> <p>B On warming more acid will dissociate so the pH will drop</p> <p>C On warming more acid will dissociate so [HCOOH] will decrease</p> <p>D On warming more acid will dissociate forming more methanoate ions</p>	1

Question Number	Correct Answer	Mark
10	<p>A The more concentrated NaOH will have a higher pH</p> <p>B Correct</p> <p>C Ammonia is a weaker base than NaOH so pH will be lower</p> <p>D Ammonia is a weaker base than NaOH so pH will be lower</p>	1

Question Number	Correct Answer	Mark
11	<p>A Correct</p> <p>B Weak acid/ strong base needs an indicator with a higher pH range</p> <p>C Weak acid/ weak base would not show a sharp change at pH 3.8 to 5.4</p> <p>D Not an acid/ base titration</p>	1

Question Number	Correct Answer	Mark
12	<p>A Nitric acid is a proton acceptor here</p> <p>B The HSO_4^- ion is a proton acceptor here</p> <p>C These are both proton acceptors</p> <p>D Correct</p>	1

Question Number	Correct Answer	Mark
13	<p>A $\text{S}_{\text{N}}2$ means bi-molecular, not two step</p> <p>B Correct</p> <p>C A racemic mixture would form via a planar intermediate in $\text{S}_{\text{N}}1$, not in $\text{S}_{\text{N}}2$</p> <p>D A transition state, not a planar intermediate, forms in $\text{S}_{\text{N}}2$</p>	1

Question Number	Correct Answer	Mark
14	<p>A Ammonium ethanoate would form</p> <p>B Correct</p> <p>C The product is a cyanohydrin not ethanamide</p> <p>D Ethanamide would not form</p>	1

Question Number	Correct Answer	Mark
15	<p>A The acid needed is propanoic acid and the alcohol is 3-methylbutan-2-ol</p> <p>B The alcohol needed is 3-methylbutan-2-ol</p> <p>C The acid needed is propanoic acid</p> <p>D Correct</p>	1

Question Number	Correct Answer	Mark
16	<p>A Propanone cannot be oxidised to an acid</p> <p>B Reduction of propanal would form an alcohol</p> <p>C Correct</p> <p>D The acid produced would be methanoic</p>	1

Question Number	Correct Answer	Mark
17	<p>A Correct</p> <p>B Both compounds contain C-C and C-H bonds only</p> <p>C Both compounds contain C-C ,C-H, C-O and O-H bonds only</p> <p>D Both compounds contain C-C, C-H, C-O and C=O bonds only</p>	1

Question Number	Correct Answer	Mark
18	<p>A It is carried out at temperatures where samples have been vaporised</p> <p>B It cannot be used if the samples have decomposed</p> <p>C It a cannot be used if the samples cannot be vaporised</p> <p>D Correct</p>	

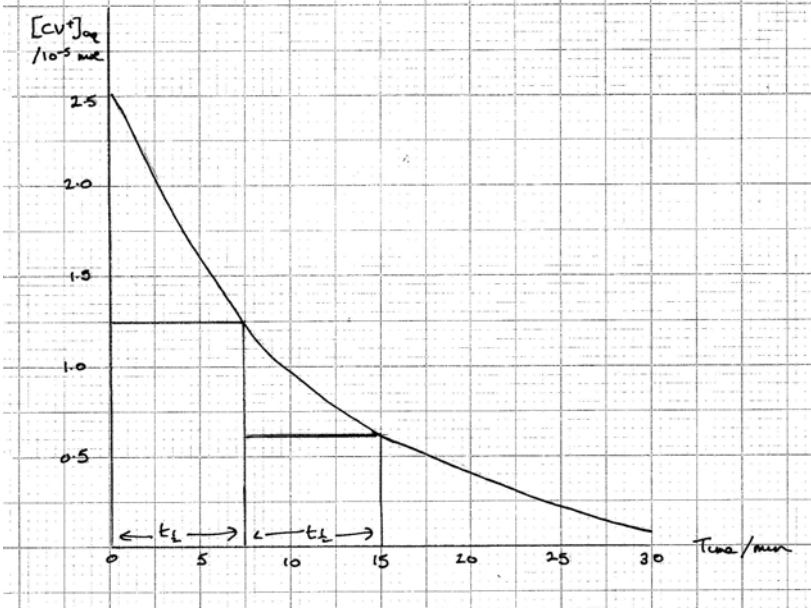
Question Number	Correct Answer	Mark
19	<p>A C₂H₂Cl would have mass 61 with these isotopes</p> <p>B C₂H₂Cl would have mass 65 with these isotopes</p> <p>C C₂H₂Cl would have mass 65 with these isotopes</p> <p>D Correct</p>	1

Question Number	Correct Answer	Mark
20	<p>A Correct</p> <p>B No peak at 1700-1680 cm⁻¹ for a ketone</p> <p>C No peak at 3750-3200 cm⁻¹ for an alcohol</p> <p>D Alkane would not have a peak at 1750 cm⁻¹</p>	1

Section B

Question Number	Acceptable Answers	Reject	Mark
21a(i)	<p>(Concentration of) NaOH / OH⁻ remains (almost) constant</p> <p>OR</p> <p>NaOH / OH⁻ is in excess, so it does not limit rate</p> <p>OR</p> <p>Only the concentration of CV⁺ changes significantly</p> <p>OR</p> <p>change in rate is dependent only on the change in CV⁺</p> <p>IGNORE references to excess / increasing reliability / ensuring rate is suitable</p>		1

Question Number	Acceptable Answers	Reject	Mark
21a(ii)	<p>Colorimetry / (use of) colorimeter</p> <p>ALLOW</p> <p>Spectrophotometry</p> <p>Measurement of light absorbed</p> <p>Recognisable but incorrect spelling</p>	<p>Calorimetry,</p> <p>pH measurement,</p> <p>conductivity,</p> <p>sampling,</p> <p>titration,</p> <p>quenching</p>	1

Question Number	Acceptable Answers	Reject	Mark
21a(iii)	 <p>One half-life (shown on graph and measured correctly) as 7.5 ± 0.5 minutes (1)</p> <p>Second half-life also 7.5 ± 0.5 minutes (1)</p> <p>Half-lives do not need to be sequential.</p> <p>ALLOW answers given on the graph</p> <p>“second half-life is the same as the first” if a correct value for the first half-life has been given</p> <p>“both half-lives are 7.5 ± 0.5 minutes” scores (2)</p>	Second half-life 15 minutes	2

Question Number	Acceptable Answers	Reject	Mark
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21a(iv)	First order As half-life is constant ALLOW As half-life is similar	(1) (1)	If zero order or second order given then (0) marks Half-life stated to be constant but with different values in (iii)	2
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Question Number	Acceptable Answers	Reject	Mark
21b(i)	$1/T = 3.37 \times 10^{-3} / 0.00337$ and $\ln k = -4.84$	$1/T = 3.36 \times 10^{-3}$ $\ln k = -4.83$ Any answer not to 3 sf	1

Question Number	Acceptable Answers	Reject	Mark
21b(ii)	<div data-bbox="252 302 1283 1086"> </div> <p data-bbox="256 1115 469 1149">Graph: 3 marks</p> <p data-bbox="256 1182 1257 1283">First mark: axes correct with sensible scales i.e points/ line covering at least half the grid (3 squares horizontally and 3 squares vertically) and $\ln k$ values becoming more negative down the axis with negative signs shown.</p> <p data-bbox="256 1285 360 1317">ALLOW</p> <p data-bbox="256 1319 673 1350">Horizontal axis at foot of graph</p> <p data-bbox="1190 1352 1225 1384">(1)</p> <p data-bbox="256 1420 1166 1489">Second mark: Both axes labelled, with units on x axis: $(1/T)/10^{-3}K^{-1}$ OR $(1/T) \times 10^3/K^{-1}$ OR 3.3×10^{-3} etc with $(1/T) / K^{-1}$ ALLOW $(1/T) \times 10^{-3}/K^{-1}$ and just $\ln k$ and no units on y axis</p> <p data-bbox="256 1592 352 1624">ALLOW</p> <p data-bbox="256 1626 775 1657">Missing brackets in expression for units</p> <p data-bbox="1225 1659 1260 1691">(1)</p> <p data-bbox="256 1727 1177 1827">Third mark: points correctly plotted and best fit straight line drawn. Allow if line covers points such that they do not show clearly but it is straight and gradient correct.</p> <p data-bbox="256 1830 794 1861">IGNORE extrapolation in either direction</p> <p data-bbox="1225 1729 1260 1760">(1)</p>	Vertical axis with ascending numbers more negative	5

	<p>Gradient: 2 marks.</p> <p>This may be shown on the graph Gradient in the range -6000 to -6400 (K) IGNORE unit</p> <p>Negative sign (as long as a value has been calculated) (1)</p> <p>Value (1)</p> <p>ALLOW Gradient calculated from data in table TE on incorrect plotting</p>	Value given as a fraction	
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Question Number	Acceptable Answers	Reject	Mark
21b(iii)	<p>$E_a = -(8.31 \times -6270 = (+) 52104)$ $= (+)52 \text{ kJ mol}^{-1} /$ $(+) 52000 \text{ J mol}^{-1} / 5.2 \times 10^4 \text{ J mol}^{-1}$</p> <p>MP1 Use of $R \times$ gradient (1)</p> <p>MP2 Value to 2sf and matching unit (1)</p> <p>TE from 21b(ii) ALLOW kJ /mol</p> <p>E_a will be from +50 to +53 for gradients of -6000 to -6400</p>	<p>kJ for kJ mol^{-1} J for J mol^{-1}</p>	2

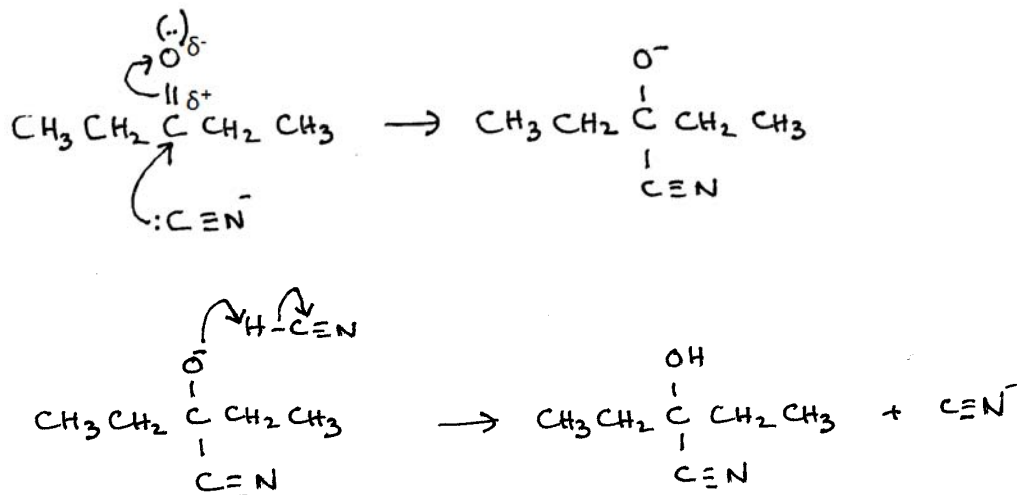
(Total for Question 21 = 14 marks)

Question Number	Acceptable Answers	Reject	Mark
22(a)	Reagent: 2,4-dinitrophenylhydrazine ALLOW Brady's reagent / 2,4-DNP(H) Formula: $C_6H_3(NO_2)_2NHNH_2$ or with ring displayed (1) Result: yellow / orange / red AND precipitate / ppt / ppte / solid / crystals (1) ALLOW combinations of these colours e.g. orange-red, but NOT red-brown No TE on incorrect reagent	Dinitrile for dinitro	2

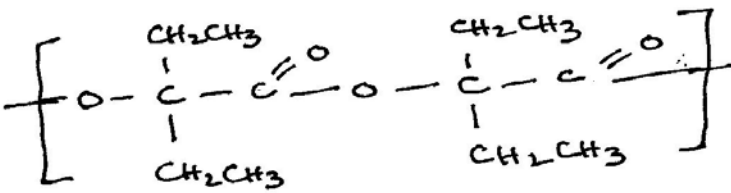
Question Number	Acceptable Answers	Reject	Mark
22(b)	Reagent: iodine and sodium hydroxide OR iodine in the presence of alkali OR iodine and hydroxide ions OR sodium chlorate(I) and potassium iodide (1) Result: (pale) yellow precipitate / solid / crystals ALLOW medicinal / antiseptic smell (with P only) (1) Identity: triiodomethane / iodoform / CHI_3 (1) ALLOW correct displayed formula IGNORE additional organic product, even if incorrect Only allow TE if "iodoform test" or "iodine" given as reagent	CH_3I	3

Question Number	Acceptable Answers	Reject	Mark
22(c)	3-methylbutan-2-ol / 3-methyl-2-butanol ALLOW 2-methylbutan-3-ol / 2-methyl-3-butanol IGNORE formula	Pentan-1-ol Pentan-2-ol	1

Question Number	Acceptable Answers				Reject	Mark
22d		P	Q			4
	Number of peaks in low resolution nmr spectrum	3	2	(1)		
	Number of H atoms producing peak with greatest area in low resolution nmr spectrum	6	6	(1)		
	Splitting pattern of peak with greatest area in high resolution nmr spectrum	Doublet (1) ALLOW Duplet 2 (lines)	Triplet (1) ALLOW 3 (lines)			

Question Number	Acceptable Answers	Reject	Mark
22e(i)	<p>  </p> <p>MP1</p> <p>Dipole on C=O (1)</p> <p>IGNORE any dipole on attacking CN⁻</p> <p>MP2</p> <p>Arrow <u>from lone pair</u> on C of CN⁻ to carbon of C=O / to space between the CN⁻ and carbon of C=O</p> <p>and arrow from C=O bond to O or just beyond O</p> <p>IGNORE Lone pairs on O (1)</p> <p>MP3</p> <p>Correct intermediate including full negative charge on O (1)</p> <p>MP4</p> <p>Arrow from oxygen to H and from H—CN bond to C of CN</p> <p>ALLOW Arrow from oxygen to H⁺</p> <p>ALLOW Arrow from (anywhere on) oxygen to H of H₂O and from H—OH bond to OH</p> <p>IGNORE Lone pairs on HCN</p> <p>IGNORE missing / incorrect CN⁻ as other product (1)</p> <p>C≡N⁻ may be written as CN⁻</p>	H ⁺ CN ⁻	4

Question Number	Acceptable Answers	Reject	Mark
22e(ii)	any named strong acid e.g. HCl / H ₂ SO ₄ Or any named strong alkali / NaOH / KOH / OH ⁻ followed by an acid IGNORE water (eg HCl/H ₂ O) IGNORE reference to dilute / concentrated IGNORE just "dilute acid" / H ⁺ / H ₃ O ⁺	Named weak acid e.g. ethanoic acid alkali and acid added at the same time	1

Question Number	Acceptable Answers	Reject	Mark
22e(iii)	 <p>Displayed COO linkage between units (1)</p> <p>Rest of structure including extension bonds</p> <p>ALLOW C₂H₅ for CH₂CH₃</p> <p>COO at one end and no O at the other (1)</p> <p>IGNORE Square brackets and subscript n</p>	<p>Bond to CH₃ of the ethyl group</p> <p>Extra O at end</p>	2

(Total for Question 22 = 17 marks)

Question Number	Acceptable Answers	Reject	Mark
23a	2-hydroxypropanoic acid	Just "2-hydroxypropanoic"	1

Question Number	Acceptable Answers	Reject	Mark
23b	<p>MP1</p> <p>Organic product with one OH substituted by Cl</p> <p>$\text{CH}_3\text{CHClCOOH}$</p> <p>OR $\text{CH}_3\text{CH}(\text{OH})\text{COCl}$</p> <p>Can be displayed. (1)</p> <p>MP2</p> <p>Second OH substituted</p> <p>$\text{CH}_3\text{CHClCOCl}$ (1)</p> <p>MP3</p> <p>POCl_3 and HCl as products in balanced equation (1)</p> <p>$\text{CH}_3\text{CH}(\text{OH})\text{COOH} + 2\text{PCl}_5 \rightarrow \text{CH}_3\text{CHClCOCl} + 2\text{POCl}_3 + 2\text{HCl}$</p> <p>OR</p> $\text{CH}_3\text{CH}(\text{OH})\text{COOH} + 2\text{PCl}_5 \rightarrow \begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{C}-\text{C}=\text{O} \\ \quad \quad \\ \text{Cl} \quad \quad \text{Cl} \end{array} + 2\text{POCl}_3 + 2\text{HCl}$ <p>MP3 available for balanced equation with any one -OH replaced by Cl</p> <p>$\text{CH}_3\text{CH}(\text{OH})\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CHClCOOH} + \text{POCl}_3 + \text{HCl}$</p> <p>OR</p> <p>$\text{CH}_3\text{CH}(\text{OH})\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COCl} + \text{POCl}_3 + \text{HCl}$</p> <p>ALLOW</p> <p>$\text{PCl}_3\text{O}$ for POCl_3</p>		3

Question Number	Acceptable Answers	Reject	Mark
23c(i)	$K_a = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$ <p>ALLOW HA and A⁻ for lactic acid and lactate if a key given</p> <p>H₃O⁺ for H⁺</p>	<p>+ symbol instead of multiply on top line</p> <p>Round brackets instead of square brackets</p> $K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$	1

Question Number	Acceptable Answers	Reject	Mark
23c(ii)	<p>Data on K_a for ethanoic acid OR pK_a for both acids must be given</p> <p>Lactic acid is stronger / ethanoic acid is weaker</p> <p>AND EITHER</p> <p>Ethanoic acid has a lower $K_a = 1.7 \times 10^{-5}$ / lactic acid has a higher K_a than 1.7×10^{-5}</p> <p>OR</p> <p>Ethanoic acid has $pK_a = 4.8$ AND lactic acid has $pK_a = 3.86$</p> <p>IGNORE comments on degree of dissociation of the acids</p>		1

Question Number	Acceptable Answers	Reject	Mark
23c(iii)	<p>Correct final answer without working scores both calculation marks.</p> <p>$[H^+]^2 = 2.07 \times 10^{-5}$</p> <p>OR</p> <p>$[H^+] = \sqrt{(0.150)(1.38 \times 10^{-4}) / (2.07 \times 10^{-5}) / 4.55 \times 10^{-3}}$ (1)</p> <p>pH = $-\log[H^+] = 2.34$</p> <p>ALLOW 2.35 from quadratic (1)</p> <p>ALLOW TE on incorrectly evaluated $[H^+]$ as long as final pH < 7 e.g final pH = 2.80, if K_a for ethanoic acid used scores 1 mark for the calculation.</p> <p>Assumption 1</p> <p>$[H^+] = [CH_3CH(OH)COO^-]$ OR H^+ is only from acid / no H^+ from ionization of water (1)</p> <p>Assumption 2</p> <p>Ionization of the (weak) acid is negligible/ very small/ insignificant</p> <p>OR $[CH_3CH(OH)COOH]_{\text{initial}} - x = [CH_3CH(OH)COOH]_{\text{eqm}}$ ALLOW i for initial</p> <p>OR $[CH_3CH(OH)COOH]_{\text{initial}} = [CH_3CH(OH)COOH]_{\text{eqm}}$</p> <p>OR $[CH_3CH(OH)COOH]_{\text{eqm}} = 0.150 \text{ (mol dm}^{-3}\text{)}$</p> <p>OR $[H^+] \ll [HA]$ (1)</p>	<p>$[H^+]$ based on $[acid] = [salt]$ (giving pH = 3.86) for both marks</p> <p>2.3</p> <p>Just “ionisation is negligible” without reference to a compound</p>	4

Question Number	Acceptable Answers	Reject	Mark
23c(iv)	<p>Correct final answer = 4 marks</p> <p>NB Rounding [lactate] to 0.21 moles gives mass = 23.52 (g), which also scores 4 marks</p> <p>Method 1</p> <p>$[H^+] \text{ in buffer} = 1 \times 10^{-4}$ (1)</p> <p>$[CH_3CH(OH)COO^-] = \frac{K_a \times [CH_3CH(OH)COOH]}{[H^+]}$</p> <p>$= \frac{(1.38 \times 10^{-4}) \times (0.150)}{1 \times 10^{-4}}$</p> <p>Rearrangement of equation to find [lactate] (1)</p> <p>[lactate] = 0.207 (mol dm⁻³) (1)</p> <p>Mass required = 0.207 x 112 = 23.184 = 23.2 (g) Ignore sf except 1 sf ALLOW TE on incorrectly calculated [lactate] (1)</p> <p>Method 2</p> <p>$pK = pH - \log[salt]/[acid]$</p> <p>OR</p> <p>$3.86 = 4.00 - \log[salt]/[acid]$ (1)</p> <p>$-\log[salt]/[acid] = 0.14$</p> <p>$[salt]/[acid] = 1.38$ OR $[acid]/[salt] = 0.72$ (1)</p> <p>$[salt] = (1.38 \times 0.15) = 0.207(\text{mol dm}^{-3})$ (1)</p> <p>Mass required = 0.207 x 112 = 23.184 = 23.2 (g) Ignore sf except 1 sf (1)</p>	<p>16.8 (g) because this is 0.15 x 112</p> <p>If clearly not [lactate] calculated, but [lactic acid], [OH⁻] or [H⁺]</p>	4

Question Number	Acceptable Answers	Reject	Mark
*23c(v)	<p>IGNORE discussion of buffer reaction with lactic acid and hydroxide ions</p> <p>(large) reservoir of lactate ions (to combine with hydrogen ions)</p> <p>ALLOW “(large) reservoir of conjugate base /salt” if lactate ions shown in equation (1)</p> <p>$\text{CH}_3\text{CH}(\text{OH})\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH}$ (1)</p> <p>Ratio of undissociated lactic acid : lactate is relatively unchanged OR Ratio of undissociated acid : (conjugate) base / salt is relatively unchanged (1)</p>	<p>“reservoir of sodium lactate”</p> <p>Equation with sodium lactate</p> <p>Reaction reversed showing lactic acid dissociation</p>	3

(Total for Question 23 =17 marks)

Question Number	Acceptable Answers	Reject	Mark
24a(i)	$K_c = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2}$ <p>IGNORE State symbols</p>	<p>Partial pressures</p> <p>Round brackets in place of square brackets</p> <p>+ symbol instead of multiply on top line</p>	1

Question Number	Acceptable Answers	Reject	Mark																				
*24a(ii)	<p>MARK CONSEQUENTIALLY ON EXPRESSION IN (i)</p> <table> <tr> <td></td> <td>NOCl</td> <td>NO(g)</td> <td>Cl₂</td> <td></td> </tr> <tr> <td>Mol at start</td> <td>2.00</td> <td>0</td> <td>0</td> <td></td> </tr> <tr> <td>Mol at eqm</td> <td>1.780</td> <td>(0.220)</td> <td>0.110</td> <td>(1)</td> </tr> <tr> <td>Concs /mol dm⁻³ (= mols at eqm ÷ 5)</td> <td>0.356</td> <td>0.044</td> <td>0.022</td> <td></td> </tr> </table> <p>This may be shown as mols at eqm ÷ 5 in K_c expression (1)</p> $K_c = \frac{((0.044)^2 \times (0.022))}{(0.356)^2} = 3.36 \times 10^{-4} \text{ mol dm}^{-3}$ <p>Value IGNORE sf except 1sf (1)</p> <p>Units (1)</p> <p>Mark independently, consistent with K_c expression in (i)</p> <p>Correct final answer without working scores 4 marks</p>		NOCl	NO(g)	Cl ₂		Mol at start	2.00	0	0		Mol at eqm	1.780	(0.220)	0.110	(1)	Concs /mol dm ⁻³ (= mols at eqm ÷ 5)	0.356	0.044	0.022			4
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Question Number	Acceptable Answers	Reject	Mark
*24a(iii)	<p>K_c is the same as ...</p> <p>EITHER</p> <p>...temperature is unchanged</p> <p>OR</p> <p>...it is unaffected by change in volume / pressure / concentration (1)</p> <p>More NO (and Cl₂) is formed because the quotient of the K_c expression decreases to keep K_c constant</p> <p>ALLOW</p> <p>More NO (and Cl₂) forms because the pressure is reduced, so the reaction goes to the side with more (gas) moles</p> <p>OR</p> <p>More NO (and Cl₂) forms because the pressure is reduced, so the reaction goes to the right (1)</p> <p>Mark independently</p>		2

Question Number	Acceptable Answers			Reject	Mark
24b(i)		ΔH_f°	S°_{298}		2
	NO	+90.2	210.7		
	Cl ₂	0	(165.0)		
	All three values (2) Any two values (1)			Blank space or a dash instead of 0	

Question Number	Acceptable Answers	Reject	Mark
24b(ii)	<p>Final answer of $\Delta H = (+) 77(.0) \text{ kJ mol}^{-1}$ scores 2</p> <p>First mark : $\Delta H = (2 \times 90.2) - (2 \times 51.7)$</p> <p>OR Hess cycle</p> <div style="text-align: center;"> $\begin{array}{ccc} 2\text{NOCl(g)} & \rightarrow & 2\text{NO(g)} + \text{Cl}_2\text{(g)} \\ (2 \times 51.7) & \nearrow & \nwarrow (2 \times 90.2) \\ & \text{N}_2\text{(g)} + \text{O}_2\text{(g)} + \text{Cl}_2\text{(g)} & \end{array}$ </div> <p style="text-align: right;">(1)</p> <p>$\Delta H = (+) 77(.0) \text{ (kJ mol}^{-1}\text{)}$ (1)</p> <p>IGNORE Units</p> <p>ALLOW Max (1) TE for using a value other than 0 for Cl_2</p>		2

Question Number	Acceptable Answers	Reject	Mark
24b(iii)	<p>$\Delta S_{\text{surroundings}} = - \Delta H / T$ ALLOW $\Delta S = - \Delta H / T$ as long as there is reference to surroundings subsequently (1)</p> <p>(As ΔH is positive), when T increases, $\Delta S_{\text{surroundings}}$ becomes less negative (so ΔS_{total} becomes less negative) IGNORE “smaller” and “decreasing” for less negative (1)</p> <p>No TE for MP2 if answer to (ii) is negative</p>		2

Question Number	Acceptable Answers	Reject	Mark
24b(iv)	<p>$\Delta S_{\text{(total)}} = R \ln K$ (1)</p> <p>IGNORE K_c / K_p</p> <p>K increases as T increases because EITHER $\Delta S_{\text{(total)}}$ increases (as T increases) OR Equilibrium moves to the right (as T increases) (1)</p>		2

Question Number	Acceptable Answers	Reject	Mark
24c(i)	<p>2nd mark dependent on 1st, for both methods.</p> <p>EITHER</p> <p>(Kinetic) energy of each particle is greater (1) ALLOW “substances” for “particles”</p> <p>So more ways of arranging particles or quanta / more disorder/ more random movement (at higher T) (1)</p> <p>IGNORE More collisions</p> <p>OR</p> <p>At the higher temperature the Maxwell- Boltzmann curve is more spread out (1)</p> <p>So there is greater randomness in the distribution of energies/ speeds (1)</p>	Answers discussing entropy change, not entropy	2

FOR 24c(ii) and 24c(iii): if mol⁻¹ is written as mol, only penalise once

Question Number	Acceptable Answers	Reject	Mark
24c(ii)	<p>+40.7 J mol⁻¹ K⁻¹ scores 2 marks</p> <p>$\Delta S_{\text{sys}} = (189.3 + 2(231.2) - 2(305.5))$ (1)</p> <p>Magnitude, sign and units (1)</p> <p>No TE on incorrect expression</p> <p>ALLOW +63 J mol⁻¹ K⁻¹ for 1 mark due to using data at 298K</p>		2

Question Number	Acceptable Answers	Reject	Mark
24c(iii)	<p>Method 1</p> <p>$\Delta S_{\text{surr}} = -\Delta H/T$ or use of expression e.g. $-53.2 \times 1000/800$ (1)</p> <p>Value of ΔS_{surr} with sign and unit (-66.5 J mol⁻¹ K⁻¹ / -0.0665 kJ mol⁻¹ K⁻¹)</p> <p>OR</p> <p>Value of ΔS_{total} with sign and unit (-66.5 + 40.7 = -25.8 J mol⁻¹ K⁻¹ / -0.0258 kJ mol⁻¹ K⁻¹) (1)</p> <p>ΔS_{total} negative so not spontaneous</p> <p>ALLOW TE on incorrect ΔS values in (ii) and (iii) If this gives a positive value for ΔS_{total}, then spontaneous (1)</p> <p>Method 2</p> <p>When $\Delta S_{\text{total}} = 0$, then $T \Delta S_{\text{system}} = \Delta H$ (1)</p> <p>$T = \Delta H / \Delta S_{\text{system}} = 53200/40.7 = 1307 \text{ K}$ (1)</p> <p>At $T < 1307 \text{ K}$ reaction is not spontaneous (1)</p> <p>Method 3</p> <p>$\Delta G = 53200 - 800 \times 40.7 /$ $= 53.2 - 800 \times (40.7/1000)$ (1)</p> <p>$= +20640 \text{ J mol}^{-1} / +20.6 \text{ kJ mol}^{-1}$ (1)</p> <p>ΔG positive so reaction is not spontaneous (1)</p>		3

(Total for Question 24 = 22 marks)

