

Unit 4 - Mark scheme

Question number	Answer	Mark
1	D butanoic acid	1

Question number	Answer	Mark
2	C hydrolysis of a nitrile by refluxing with aqueous potassium hydroxide	1

Question number	Answer	Mark
3	B ethanamide	1

Question number	Answer	Mark
4	C $\text{CH}_3\text{CH}_2\text{COCH}_3$	1

Question number	Answer	Mark
5	C an unsaturated alcohol	1

Question number	Answer	Mark
6	B the reaction is not reversible	1

Question number	Answer	Mark
7	B diprotic carboxylic acids with diols	1

Question number	Answer	Mark
8	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{Br} \\ \quad \backslash \\ \quad \text{C}_2\text{H}_5 \end{array}$ $\begin{array}{c} \text{Br} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{CH}_3 \\ \quad \backslash \\ \quad \text{C}_2\text{H}_5 \end{array}$ B	1
Question number	Answer	Mark
9	B increasing the polarity of the stationary phase	1
Question number	Answer	Mark
10(a)	$K_c = \frac{[\text{I}_2(\text{aq})]}{[\text{I}_2(\text{trichloromethane})]}$ D	1
Question number	Answer	Mark
10(b)	C iodine molecules move from the water to the trichloromethane and from the trichloromethane to the water layer	1
Question number	Answer	Mark
11(a)	C increase the temperature	1

Question number	Answer	Mark
11(b)	A $[\text{CO}_2]$	1

Question number	Answer	Mark
12	A approximately 6.5	1

Question number	Answer	Mark
13	A $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	1

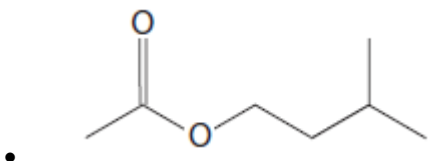
Question number	Answer	Mark
14	D titration of quenched samples	1

Question number	Answer	Mark
15	D proportion of particles with sufficient energy to react	1

Question number	Answer	Mark
16	B methyl orange	1

Question number	Answer	Mark
17	A ethane(g)	1

Question number	Answer	Mark
18	D monoclinic sulfur could change into rhombic sulfur but nothing can be deduced about the rate	1

Question number	Answer	Additional guidance	Mark
19(a)		Must be skeletal formula	1

Question number	Answer	Additional guidance	Mark
19(b)(i)	C=O peak identified and range 1750 - 1735 cm⁻¹	Allow C-O peak identified and range 1250 - 1230 cm ⁻¹	1

Question number	Answer	Additional guidance	Mark
19(b)(ii)	Absence of a peak in the range 3750 - 3200 cm⁻¹	Absence of alcoholic O-H peak	1

Question number	Answer	Additional guidance	Mark																				
19(c)	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. <table><tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr><tr><td>6</td><td>4</td></tr><tr><td>5-4</td><td>3</td></tr><tr><td>3-2</td><td>2</td></tr><tr><td>1</td><td>1</td></tr><tr><td>0</td><td>0</td></tr></table> The following table shows how the marks should be awarded for structure and lines of reasoning. <table><tr><th></th><th>Number of marks awarded for structure and sustained lines of reasoning</th></tr><tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.</td><td>2</td></tr><tr><td>Answer is partially structured with some linkages and lines of reasoning.</td><td>1</td></tr><tr><td>Answer has no linkages between points and is unstructured.</td><td>0</td></tr></table>	Number of indicative marking points seen in answer	Number of marks awarded for indicative marking points	6	4	5-4	3	3-2	2	1	1	0	0		Number of marks awarded for structure and sustained lines of reasoning	Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.	2	Answer is partially structured with some linkages and lines of reasoning.	1	Answer has no linkages between points and is unstructured.	0	Guidance on how the mark scheme should be applied. The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s). Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning. Some or all the information may be shown on a diagram of the molecule.	6
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6	4																						
5-4	3																						
3-2	2																						
1	1																						
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Question number	Answer	Additional guidance	Mark
19(c) Cont.	Indicative points: - three groups of peaks indicates three hydrogen environments - one or two shifts identified (by number) and linked to alkanes - three shifts correctly identified and linked to alkanes - two (or more) splitting patterns correctly identified - use of $n + 1$ rule to explain splitting for one (or more) group(s) of protons - areas under peaks/integration numbers linked to numbers of protons in each group.	2.1 (± 0.2) = CH₃ next to C=O 4.1 (± 0.2) = CH₂ next to C-O- 1.2 (± 0.2) = CH₃ next to CH₂ singlet, triplet, quartet ratio of areas = 3:2:3	

Question number	Answer	Additional guidance	Mark
19(d)(i)	An answer that makes reference to the following points: - HCOOCH₂CH₂CH₃ - HCOOCH(CH₃)₂ - CH₃CH₂COOCH₃ All three correct scores two marks, any two correct scores one mark	Allow displayed/skeletal formulae	2

Question number	Answer	Additional guidance	Mark
19(d)(ii)	An explanation that makes reference to the following points: • $\text{HCOOCH}(\text{CH}_3)_2$ has three carbon environments (1) whereas • $\text{HCOOCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{COOCH}_3$ both have four carbon environments. (1)		2

Question number	Answer	Additional guidance	Mark
20(a)(i)	• $\text{pH} = (0.85387) = 0.85$		1

Question number	Answer	Additional guidance	Mark
20(a)(ii)	• re-arrangement of K_a expression (1) • calculation of $[\text{H}^+]$ (1) • calculation of pH (1)	Example of calculation: $[\text{H}^+]^2 = K_a [\text{HA}]$ $[\text{H}^+]^2 = 1.76 \times 10^{-5} \times 0.14$ $= 2.464 \times 10^{-6}$ $[\text{H}^+] = \sqrt{(1.76 \times 10^{-5} \times 0.14)}$ $= 1.5697 \times 10^{-3}$ $\text{pH} = (2.8042) = 2.8(0)$ Penalise not to 2DP once only in (a)(i) and (ii) Correct answer with no working scores 3	3

Question number	Answer	Additional guidance	Mark
20(b)(i)	- at half equivalence point, $\text{pH} = \text{p}K_{\text{a}}$ (1) - reads off pH from graph (1) - calculates K_{a} (1)	Example of calculation: = 4.8 Allow 4.5 to 5.2 $K_{\text{a}} = 10^{-\text{pH}} = 10^{-4.8} = 1.6 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ Allow answers in the range 6.3×10^{-6} to 3.2×10^{-5}	3
Question number	Answer	Additional guidance	Mark
20(b)(ii)	$[\text{HA}] \gg [\text{A}^-]$ (1) - ratio $[\text{A}^-]:[\text{HA}]$ changes (significantly) in this region (1)	Allow for 1 mark 'not buffered'	2

Question number	Answer	Additional guidance	Mark
20(c)(i)	- calculation of $[HA]/[A^-] = 2/1$ (1) - correct calculation of $[H^+] = 2.6 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ (1) - correct calculation of pH (1)	Example of calculation: $[HA] = 1.0 \times 20 \div 40 = 0.50$ $[A^-] = 1.0 \times 10 \div 40 = 0.25$ or any recognition that $[HA]/[A^-] = 2/1$ $[H^+] = 2.6 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$ pH = 4.6/4.59/4.58 Correct answer with no working scores 3 marks	3

Question number	Answer	Additional guidance	Mark
20(c)(ii)	no H^+ ions come from (ionisation of) water or $[acid]_{\text{initial}} = [acid]_{\text{eqm}}$		1

Question number	Answer	Additional guidance	Mark
21(a)	$2H_2O_2 \rightarrow 2H_2O + O_2$ (1) - iodide ions act as a catalyst (as they don't appear in the overall equation) (1)	Ignore state symbols even if incorrect	2

Question number	Answer	Additional guidance	Mark
21(b)	- converts both temperatures from °C to K - correct subtraction - substitute numbers in equation correctly - correct value of E_a	Example of calculation: (1) $22.0\text{ }^{\circ}\text{C} = 295.0\text{ K}$ $47.0\text{ }^{\circ}\text{C} = 320.0\text{ K}$ (1) $\ln\left(\frac{K_1}{K_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ (1) $\ln\left(\frac{4.90 \times 10^{-4}}{1.07 \times 10^{-3}}\right) = -\frac{E_a}{8.31}\left(\frac{1}{295} - \frac{1}{320}\right)$ (1) (+)56.(0) (kJ mol⁻¹) Sign and final answer to 2 or 3 SF Incorrect units loses MP4 Correct answer with no working scores 4	4

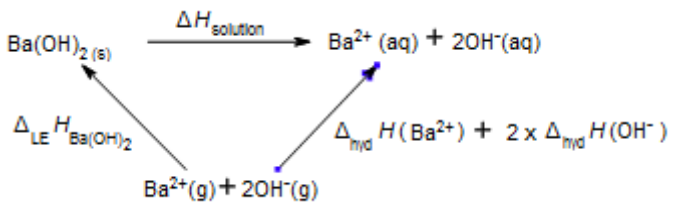
Question number	Answer	Additional guidance	Mark
21(c)(i)	An explanation that makes reference to the following points: (blue-black colour is) product of starch-iodine reaction - the iodine produced reacts (rapidly) with the thiosulfate ions (to reform iodide ions) - when all of the thiosulfate has reacted, the blue-black colour appears.	(1) (1) (1)	3

Question number	Answer	Additional guidance	Mark
21(c)(ii)	the reaction (between thiosulfate and hydrogen peroxide) is slow	Allow reaction has high E_a	1

Question number	Answer	Additional guidance	Mark
22(a)(i)	$R = O^{2-}(g)$ (1) $W =$ first electron affinity $O(g)$ (1)	Allow alternative ways to express electron affinity, e.g. EA State required Do not allow $O_2/O\cdot$	2

Question number	Answer	Additional guidance	Mark
22(a)(ii)	- correct application of cycle (1) - correct value (1) - correct sign and units (1)	Example of calculation: $\Delta_f H(\text{BaO}(s)) = \Delta_{at} H(\text{Ba}(s)) + \Delta_{at} H(\frac{1}{2}O_2(g)) + 1^{st} \text{ IE}(\text{Ba}(g)) + 2^{nd} \text{ IE}(\text{Ba}(g)) + 2^{nd} \text{ EA}(O(g)) + 1^{st} \text{ EA}(O(g)) + \Delta_{LE} H(\text{BaO}(s))$ or Correct numbers $= 180.0 + 249.2 + 503 + 965 + 798 - 141.1 - 3054$ $(-499.9 / (-)500 \text{ kJ mol}^{-1})$ Allow TE from incorrect application of cycle Allow TE for incorrect numbers Correct answer with no working scores 3	3

Question number	Answer	Additional guidance	Mark
22(a)(iii)	- ionic radius of Ba^{2+} >> ionic radius of Mg^{2+} / (have) lower charge density (1) and Ba^{2+} (ions are) less polarising / (have) lower charge density - iodide ions / I^- are large (1) and their electron clouds are easily distorted / polarised (by Group 2 cations) or oxide ions / O^{2-} are small(er) and their electron clouds are less easily distorted / polarised - more distortion / covalency leads to greater difference between theoretical and experimental values (1)	Allow reverse argument	3

Question number	Answer	Additional guidance	Mark
22(b)(i)	 - all arrows in the correct direction - correct formulae at each corner and enthalpies of hydration, and solution and LE correctly identified - correct expression or correct substitution of values - correct evaluation	Do not allow energy profile or energy level diagrams (1) Species at each corner must be approximately correct (1) Allow missing minor detail: brackets, position of subscripts, etc. but not absence of subscripts (1) Example of calculation: $\Delta_{\text{sol}}H = (\Delta_{\text{hyd}}H(\text{Ba}^{2+}) + 2\Delta_{\text{hyd}}H(\text{OH}^-)) - \text{LE}(\text{Ba}(\text{OH})_2)$ or $= (-1360 + (2 \times -460)) - (-2230)$ (1) $= -50 \text{ (kJ mol}^{-1}\text{)}$ Allow TE from their cycle if $\Delta_{\text{hyd}}H(\text{OH}^-)$ is not doubled	4

Question number	Answer	Additional guidance	Mark
22b(ii)	• entropy (change) of system/$\Delta S_{\text{system}}/\Delta S_{\text{dissolving}}$ is large and positive (and outweighs negative $\Delta S_{\text{surroundings}}$ ($-\Delta H/T$)) (1) • overall entropy change/ΔS_{total} is positive (1) - or • use of $\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$ (1) • $\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + (-\Delta H/T)$ (1)	Allow use of ΔG	2

Question number	Answer	Additional guidance	Mark
23(a)	• use of $\Delta S_{\text{system}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}}$ (1) • correct value with sign and units (1)	Example of calculation: $\Delta S_{\text{system}} = (2 \times 240.0) - 304.2$ $= +175.8 \text{ J K}^{-1} \text{ mol}^{-1}$ Correct answer with no working scores 2 Allow 3 SF	2

Question number	Answer	Additional guidance	Mark
23(b)	• use of $\Delta_r H = 2 \times \Delta_f H(\text{NO}_2) - \Delta_f H(\text{N}_2\text{O}_4)$ (1) • correct value with sign and units (1)	Example of calculation: $\Delta_r H = (2 \times 33.2) - \Delta_f H(\text{N}_2\text{O}_4) = 57.2$ $\Delta_f H(\text{N}_2\text{O}_4) = +9.2 \text{ kJ mol}^{-1}$ Correct answer with no working scores 2	2

Question number	Answer	Additional guidance	Mark
23(c)	• use of $\Delta S_{\text{surroundings}} = -\Delta H/T$ (1) • correct value (1) • answer to 3 SF with correct sign and correct units (1)	Example of calculation: $-(57.2 \times 1000/298)$ $= (-)191.(946)$ $-192 \text{ J K}^{-1} \text{ mol}^{-1}$ Allow $-0.192 \text{ kJ K}^{-1} \text{ mol}^{-1}$ for M2 and M3 Correct answer to 3 SF with no working scores 3	3

Question number	Answer	Additional guidance	Mark
23(d)(i)	• $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ • $\Delta S_{\text{total}} = +175.8 + (-191.9) = -16(.1) \text{ (J mol}^{-1} \text{ K}^{-1})$	Allow TE from 23a and 23c Allow answers in $\text{kJ mol}^{-1} \text{ K}^{-1}$	1

Question number	Answer	Additional guidance	Mark
23(d)(ii)	- correct expression - correct evaluation	Example of expression and calculation: (1) $\Delta H = T\Delta S_{\text{system}}$ or $T = \Delta H / \Delta S_{\text{system}}$ or $\Delta S_{\text{system}} = \Delta H / T$ or $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$ (1) $T = 57.2 \times 1000 / 175.8 = 325.37$ = 325 K/52 °C	2
Question number	Answer	Additional guidance	Mark
23(e)(i)	- correct expression for K_p - units of pressure	(1) $K_p = (p_{\text{NO}_2})^2 / p_{\text{N}_2\text{O}_4}$ Do not award any square brackets (1) atm	2

Question number	Answer	Additional guidance	Mark
23(e)(ii)	- moles of N_2O_4 and NO_2 at eqm - total number of moles and mole fractions calculated - converted to partial pressure - calculation of K_p	Example of calculation: $(\text{mol})\text{N}_2\text{O}_4 = 7.3$, $(\text{mol})\text{NO}_2 = 5.4$. (1) Total moles = 12.7 Mole fraction $\text{N}_2\text{O}_4 = 0.575$ Mole fraction $\text{NO}_2 = 0.425$ Allow TE from M1 (1) $P \text{ N}_2\text{O}_4 = 2.30$ (answers to $M2 \times 4$) $\text{NO}_2 = 1.70$ Allow TE from M2 (1) $K_p = 1.26$ (atm) Allow TE from M3 Ignore SF except 1 SF	4

Question number	Answer	Additional guidance	Mark
23(e)(iii)	no effect on (the value of) K_p		1

Question number	Answer	Additional guidance	Mark
23(e)(iv)	- double pressure (effect of squaring) increases numerator more than denominator (1) (but K_p must remain constant therefore) mole fraction of N_2O_4 must increase (relative to mole fraction of NO_2) (1) (therefore) % dissociation of N_2O_4 decreases (1)		3