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

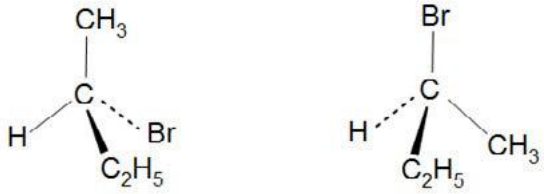
Question number	Answer	Mark
3	B ethanamide	1

Question number	Answer	Mark
4	C $CH_3CH_2COCH_3$	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	 B	1

Question number	Answer	Mark
9	B increasing the polarity of the stationary phase	1

Question number	Answer	Mark
10(a)	$K_c = \frac{[I_2(aq)]}{[I_2(trichloromethane)]}$ 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 $[CO_2]$	1

Question number	Answer	Mark
12	A approximately 6.5	1

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

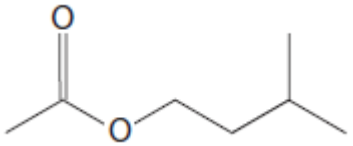
Question number	Answer	Mark
14	D titration of quenched samples	1

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

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>19(c)</td><td>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></td><td>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.</td><td>6</td></tr>
</table>

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) = CH_3 next to C=O 4.1 (±0.2) = CH_2 next to C-O- 1.2 (±0.2) = CH_3 next to CH_2 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: • $HCOOCH_2CH_2CH_3$ • $HCOOCH(CH_3)_2$ • $CH_3CH_2COOCH_3$ 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: • $HCOOCH(CH_3)_2$ has three carbon enviornments (1) whereas • $HCOOCH_2CH_2CH_3$ **and** $CH_3CH_2COOCH_3$ both have four carbon environments. (1)		**2**

Question number	Answer	Additional guidance	Mark
20(a)(i)	• pH = (0.85387) = 0.85		**1**

Question number	Answer	Additional guidance	Mark
20(a)(ii)	• re-arrangement of K_a expression (1) • calculation of $[H^+]$ (1) • calculation of pH (1)	Example of calculation: $[H^+]^2 = K_a\,[HA]$ $[H^+]^2 = 1.76 \times 10^{-5} \times 0.14$ $= 2.464 \times 10^{-6}$ $[H^+] = \sqrt{(1.76 \times 10^{-5} \times 0.14)}$ $= 1.5697 \times 10^{-3}$ 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, pH = pK_a (1) • reads off pH from graph (1) • calculates K_a (1)	Example of calculation: = 4.8 Allow 4.5 to 5.2 $K_a = 10^{-pH} = 10^{-4.8} =$ 1.6×10^{-5} (mol dm^{-3}) Allow answers in the range 6.3×10^{-6} to 3.2×10^{-5}	3

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

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

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

Question number	Answer		Additional guidance	Mark
21(b)	• converts both temperatures from °C to K	(1)	Example of calculation: 22.0 °C = 295.0 K 47.0 °C = 320.0 K	4
	• correct subtraction	(1)	$\ln\left(\frac{K_1}{K_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$	
	• substitute numbers in equation correctly	(1)	$\ln\left(\frac{4.90 \times 10^{-4}}{1.07 \times 10^{-3}}\right) = -\frac{E_a}{8.31}\left(\frac{1}{295} - \frac{1}{320}\right)$	
	• correct value of E_a	(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	

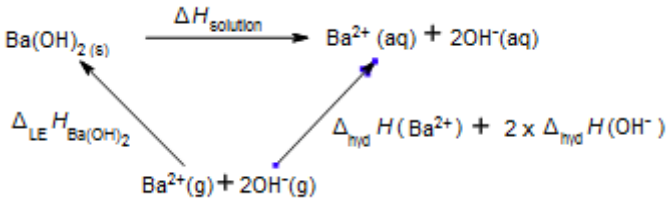
Question number	Answer		Additional guidance	Mark
21(c)(i)	An explanation that makes reference to the following points:			3
	• (blue-black colour is) product of starch-iodine reaction	(1)		
	• the iodine produced reacts (rapidly) with the thiosulfate ions (to reform iodide ions)	(1)		
	• when all of the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

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^-	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: $\Delta_f H$ (BaO(s)) = $\Delta_{at}H$(Ba(s))+$\Delta_{at}H$(½O_2(g))+ 1st IE (Ba)(g) +2nd IE (Ba(g))+2nd EA (O(g))+1st EA (O(g)) +$\Delta_{LE}H$ (BaO(s)) or Correct numbers = 180.0+249.2+503+965+798−141.1−3054 (−)499.9/(−)500 (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 **and** Ba^{2+} (ions are) less polarising/(have) lower charge density	(1)	Allow reverse argument	**3**
	• iodide ions/I^- are large **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	(1)		
	• more distortion/covalency leads to greater difference between theoretical and experimental values	(1)		

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

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

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

Question number	Answer	Additional guidance	Mark
23(b)	• use of $\Delta_r H = 2 \times \Delta_f H(NO_2) - \Delta_f H(N_2O_4)$ (1) • correct value with sign and units (1)	Example of calculation: $\Delta_r H = (2 \times 33.2) - \Delta_f H(N_2O_4) = 57.2$ $\Delta_f H(N_2O_4) = +9.2$ kJ mol^{-1} Correct answer with no working scores 2	**2**

Question number	Answer	Additional guidance	Mark
23(c)	• use of $\Delta S_{surroundings} = -\Delta H/T$ (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 J K^{-1} mol^{-1} Allow -0.192 kJ K^{-1} 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)	• $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ • $\Delta S_{total} = +175.8 + (-191.9) = -16(.1)$ (J mol^{-1} K^{-1})	Allow TE from 23a and 23c Allow answers in kJ mol^{-1} K^{-1}	**1**

Question number	Answer		Additional guidance	Mark
23(d)(ii)	• correct expression	(1)	Example of expression and calculation: $\Delta H = T\Delta S_{system}$ or $T = \Delta H/\Delta S_{system}$ or $\Delta S_{system} = \Delta H/T$ or $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$	2
	• correct evaluation	(1)	$T = 57.2 \times 1000/175.8 = 325.37$ $= 325$ K/52 °C	

Question number	Answer		Additional guidance	Mark
23(e)(i)	• correct expression for K_p	(1)	$K_p = (p_{NO_2})^2/p_{N_2O_4}$ Do not award any square brackets	2
	• units of pressure	(1)	atm	

Question number	Answer		Additional guidance	Mark
23(e)(ii)	• moles of N_2O_4 **and** NO_2 at eqm	(1)	Example of calculation: (mol)N_2O_4 = 7.3, (mol)NO_2 = 5.4.	4
	• total number of moles **and** mole fractions calculated	(1)	Total moles = 12.7 Mole fraction N_2O_4 = 0.575 Mole fraction NO_2 = 0.425 Allow TE from M1	
	• converted to partial pressure	(1)	P N_2O_4 = 2.30 (answers to M2 × 4) NO_2 = 1.70 Allow TE from M2	
	• calculation of K_p	(1)	K_p = 1.26 (atm) Allow TE from M3 Ignore SF except 1 SF	

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**