Mark Scheme (Results)

January 2019

Pearson Edexcel
International Advanced Level
Chemistry (WCH04)
Paper 01 Rates, Equlibria 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.

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	**The only correct answer is B** **A** *is not correct because iodine is coloured* **C** *is not correct because the C—I absorbance increases* **D** *is not correct because iodine concentration changes*	1

Question Number	Correct Answer	Mark
2	**The only correct answer is D** **A** *is not correct because this is the factor each reactant is changed by* **B** *is not correct because this is omitting the square of the ethanedioate ion* **C** *is not correct because this is adding the factors not multiplying them*	1

Question Number	Correct Answer	Mark
3	**The only correct answer is B** **A** *is not correct because this is the gradient x R calculation* **C** *is not correct because 1/T is a variable* **D** *is not correct because 1/T is a variable*	1

Question Number	Correct Answer	Mark
4	**The only correct answer is C** **A** *is not correct because nitrogen will have a higher entropy than hydrogen as it is more complex* **B** *is not correct because the solid iron will have the lowest entropy* **D** *is not correct because the solid iron will have the lowest entropy*	1

Question Number	Correct Answer	Mark
5	**The only correct answer is A** **B** *is not correct because the forward reaction is favoured by a lower temperature* **C** *is not correct because* K_p *is affected by temperature* **D** *is not correct because this is what would happen to the rate of the backward reaction*	1

Question Number	Correct Answer	Mark
6	**The only correct answer is B** **A** *is not correct because the concentration of hydroxide should be squared not multiplied by 2* **C** *is not correct because the concentration of magnesium hydroxide should be omitted* **D** *is not correct because the concentration of magnesium hydroxide should be omitted*	1

Question Number	Correct Answer	Mark
7	**The only correct answer is A** **B** *is not correct because no ions are formed in the reaction* **C** *is not correct because no lattices are involved in the reaction* **D** *is not correct because magnesium hydroxide is not dissolved in the reaction*	1

Question Number	Correct Answer	Mark
8	**The only correct answer is D** **A** *is not correct because this is an endothermic reaction* **B** *is not correct because this reaction has fewer moles of gas on the right hand side* **C** *is not correct because this is an endothermic reaction*	1

Question Number	Correct Answer	Mark
9	**The only correct answer is C** **A** *is not correct because the solution is in 250 cm^3 not 1 dm^3* **B** *is not correct because the mass of sodium hydroxide has been used rather than the number of moles and the log has been subtracted from rather than being added to 14* **D** *is not correct because this is subtracting 0.1 moles in 250 cm^3 from 14*	1

Question Number	Correct Answer	Mark
10	**The only correct answer is A** **B** *is not correct because this is adding the acid to the wrong half of the buffer* **C** *is not correct because this is what would happen if alkali were added* **D** *is not correct because although this is true it is not a correct explanation*	1

Question Number	Correct Answer	Mark
11	**The only correct answer is D** **A** *is not correct because this is the number of moles of hydrogen and iodine reacting* ***B*** *is not correct because this is the number of moles of hydrogen and iodine reacting* **C** *is not correct because this assumes 1 mol of reactant forms 1 mol of product*	1

Question Number	Correct Answer	Mark
12	**The only correct answer is B** **A** *is not correct because there is no geometrical isomerism* **C** *is not correct because neither isomerism is present* **D** *is not correct because there is no optical isomerism*	1

Question Number	Correct Answer	Mark
13	**The only correct answer is B** **A** *is not correct because these are the correct reagents for this step* **C** *is not correct because these are the correct reagents for this step* **D** *is not correct because these are the correct reagents for this step*	1

Question Number	Correct Answer	Mark
14	**The only correct answer is B** **A** *is not correct because y is susceptible to electrophilic not nucleophilic attack* **C** *is not correct because z is also susceptible to nucleophilic attack* **D** *is not correct because x is also susceptible to nucleophilic attack*	1

Question Number	Correct Answer	Mark
15	**The only correct answer is D** **A** *is not correct because NaI is soluble and a colourless solid* **B** *is not correct because this is a product in acidic conditions* **C** *is not correct because the product has three iodine atoms*	1

Question Number	Correct Answer	Mark
16	**The only correct answer is C** **A** *is not correct because this tests for an aldehyde* **B** *is not correct because this tests for an aldehyde* **D** *is not correct because this tests for an aldehyde / alcohol*	1

Question Number	Correct Answer	Mark
17	**The only correct answer is D** **A** *is not correct because this would not give the product* **B** *is not correct because this would not give the product* **C** *is not correct because this would not give the product*	1

Question Number	Correct Answer	Mark
18	**The only correct answer is A** **B** *is not correct because this requires two steps* **C** *is not correct because this gives a diol* **D** *is not correct because this gives an amide*	1

Question Number	Correct Answer	Mark
19	**The only correct answer is A** **B** *is not correct because this is a chlorine-37 ion* **C** *is not correct because this is* CH_3CO^+ **D** *is not correct because this is one of the two molecular ion peaks*	1

Question Number	Correct Answer	Mark
20	**The only correct answer is B** **A** *is not correct because* $[CH_3CH_2CO]^+$ *has m/e = 57* **C** *is not correct because* $[CH_3\ CH_2CO]^+$ *has m/e = 57* **D** *is not correct because* $[CH_3CH_2CO]^+$ *has m/e = 57*	1

(Total for Section A = 20 marks)

Section B

Question Number	Acceptable Answers	Reject	Mark
21(a)(i)	Units, if given, must be correct. Penalise any error only once in (a)(i) – (iv) ALLOW Units with a "-" instead of "-1" super-script $\Delta H_{f(reactants)} = -394$ (kJ mol^{-1}) AND $\Delta H_{f(products)} = -201 + (-242)$ $= -443$ (kJ mol^{-1}) (1) $\Delta H_r = \Delta H_{f(products)} - \Delta H_{f(reactants)}$ $= -443 - (-394)$ $= -49$ (kJ mol^{-1}) Correct answer with no working scores (2) ALLOW 49000 **J mol^{-1}** but units must be given (1) TE on incorrect values in MP2 as long as it is clear that the correct relationship $\Delta H_r = \Delta H_{f(products)} - \Delta H_{f(reactants)}$ is being used		2

Question Number	Acceptable Answers	Reject	Mark
21(a)(ii)	$\Delta S_{(products)}$ = 238 + 189 = 427 (J K^{-1} mol^{-1}) **and** $\Delta S_{(reactants)}$ = 214 + 3(131) = 607 (J K^{-1} mol^{-1}) OR ΔS_{system} = 427 − 607 OR ΔS_{system} = 238 + 189 − 214 − 3(131) (1) ΔS_{system} = $\Delta S_{(products)} - \Delta S_{(reactants)}$ = 427 − 607 = -180 (J K^{-1} mol^{-1}) (1) Correct answer with no working scores (2) ALLOW TE on incorrect values in MP2 as long as it is clear that the relationship ΔS_{system} = $\Delta S_{(products)} - \Delta S_{(reactants)}$ is being used.		2

Question Number	Acceptable Answers	Reject	Mark
21(a)(iii)	$\Delta S_{surroundings} = -\Delta H/T$ $= -(-49000 / 298)$ (1) $= (+) 164.430$ (J K^{-1} mol^{-1}) (1) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ $= -180 + 164.43$ $= -15.570$ (J K^{-1} mol^{-1}) (1) IGNORE SF except 1 SF Correct answer with no working scores (3) Penalise $\Delta S_{surroundings} = -(-49 / 298)$ $= (+) 0.16443$ by (1) mark unless units are kJ K^{-1} mol^{-1} ALLOW TE on values from (a)(i) and (a)(ii) TE on steps subsequent to step 1 on value given in step 1		3

Question Number	Acceptable Answers	Reject	Mark
21(a)(iv)	The reaction becomes feasible when $\Delta S_{total} = 0$ OR $\Delta S_{system} = -\Delta S_{surroundings}$ OR $\Delta S_{surroundings} = -\Delta S_{system}$ OR $T = \frac{\Delta H}{\Delta S_{system}}$ (1) IGNORE $\Delta S_{surr} = -\frac{\Delta H}{T}$ or its rearrangements This may be derived using Gibbs Free Energy $T = \frac{49000}{180} = 272$ (K) ALLOW $-1^{o}C$ (1) Correct answer with no working scores (2) IGNORE SF except 1SF ALLOW TE on answer in Q21(a)(i) irrespective of value	Any answer with –ve K	2

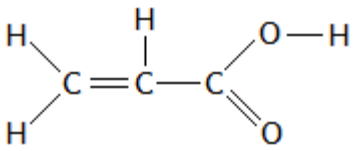
Question Number	Acceptable Answers	Reject	Mark
21(a)(v)	(At 272K, the reaction will be too slow to be economically viable) but at higher temperatures rate is increased (and becomes viable) ALLOW To make the **rate** of reaction economically viable	Just 'exothermic reaction Just 'to make it economically viable'	1

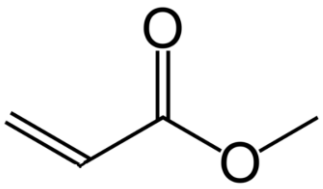
Question Number	Acceptable Answers	Reject	Mark
21(b)(i)	$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$ ALLOW Multiples or fractions IGNORE state symbols even if incorrect		1

Question Number	Acceptable Answers	Reject	Mark
*21(b)(ii)	NB All marks are independent Combustion reactions are (always) exothermic **so $\Delta S_{surroundings}$ is positive** (1) Ratio of moles in the equation is 5 to 6 / 5 reactant moles give 6 product moles **so ΔS_{system} is positive** ALLOW There are more moles of product than of reactant / more gas molecules are formed **so ΔS_{system} is positive** (1) (So) ΔS_{total} will always be positive / will be positive at all temperatures ALLOW Suggestion that ΔS_{total} is positive if reaction is feasible (1) IGNORE References to entropy change being 'higher' COMMENT Answers in terms of ΔG can score all three points If M1 and M2 are not scored, ALLOW Both $\Delta S_{surroundings}$ and ΔS_{system} are positive for (1) Both 5 moles of gas give 6 moles of gas AND combustion reactions are exothermic for (1)		3

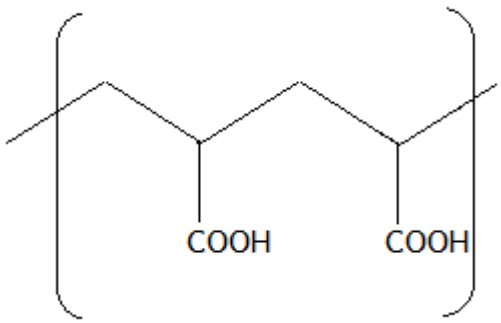
Question Number	Acceptable Answers	Reject	Mark
21(c)	Any **two** from (energy is required for / carbon dioxide is released during) Extraction of carbon dioxide (1) Manufacture of hydrogen (1) Transport of materials or products (1) Building / running cost of the plant / fuel to run the process (1)		2

(Total for Question 21 = 16 marks)

Question Number	Acceptable Answers	Reject	Mark
22(a)(i)	 ALLOW -OH but not –HO	More than one structure, unless the displayed one is indicated as the answer (underlined, boxed etc..)	1

Question Number	Acceptable Answers	Reject	Mark
22(a)(ii)	Methyl propenoate (1)  (1) IGNORE Displayed or structural formula shown as working Correct answer only for each mark – no TE for structure if name incorrect	Methyl propanoate Propene methanoate	2

Question Number	Acceptable Answers	Reject	Mark
22(a)(iii)	**Dry** ether (as a solvent) (1) ALLOW named ether e.g. ethoxyethane CH_2CHCH_2OH / $CH_2=CHCH_2OH$ (1) ALLOW Any skeletal or displayed formula IGNORE Names even if incorrect IGNORE All references to heat / temperature	Just 'no water'	2

Question Number	Acceptable Answers	Reject	Mark
22(a)(iv)	 ALLOW Displayed / skeletal or mixed formula (see example) Two units with extension bonds with or without brackets. IGNORE n after the bracket		1

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>22(b)(i)</td><td>
<table>
<tr><td>butanal</td><td>pentane</td><td>propenoic acid</td></tr>
<tr><td>76</td><td>36</td><td></td></tr>
<tr><td></td><td></td><td>38</td></tr>
</table>
All 3 correct scores (2)

Any 2 correct scores (1)

NOTE
butanal 349 / 348(.8) and pentane 309(.2) and 38 electrons scores (1)

ALLOW

Any answer for the temperatures which rounds to the given values
</td><td></td><td>2</td></tr>
</table>

Question Number	Acceptable Answers	Reject	Mark
*22(b)(ii)	All have similar numbers of electrons so similar London forces / dispersion forces / van der Waals forces / instantaneous dipole – induced dipole forces IGNORE id-id / LDF without explanation ALLOW Strength of London forces in order of number of electrons is the table (normally pentane>butanal>propenoic acid) (1) Butanal (in addition) has permanent dipole-dipole interactions which are stronger than London forces / which makes boiling temperature higher than pentane ALLOW dipole-dipole interactions IGNORE Pd-pd without explanation Butanal forms hydrogen bonds <u>with water</u> (1) Propenoic acid (in addition) has (dipole-dipole and) hydrogen bonds which are stronger than dipole-dipole forces / which are the strongest intermolecular force / which make the boiling temperature higher than butanal (1)	Any clear bond breaking in pentane Any clear bond breaking in butanal Butanal forms H bonds with itself Any clear bond breaking in propenoic acid	3

Question Number	Acceptable Answers	Reject	Mark
22(c)	IGNORE $LiAlH_4$ given as a test, followed by tests on the resulting alcohols, but allow any further tests clearly on the original liquids **For propenoic acid** Bromine water / aqueous bromine / bromine / bromine in organic solvent (1) (Brown / orange / yellow) to colourless / decolourised (1) OR (Aqueous) sodium hydrogencarbonate / sodium carbonate / metal e.g. Na, Mg (1) Effervescence (1) OR PCl_5 (1) Misty/steamy fumes (1) IGNORE white fumes OR Alcohol and acid catalyst (1) Fruity smell (1) **For butanal** Fehling's / Benedict's solution (1) (Blue to) orange / red (precipitate) (1) OR Tollens' Reagent (1) Silver mirror / black precipitate (1) OR 2,4 dinitrophenylhydrazine (solution) / 2,4 DNP(H) / Brady's Reagent (1) Yellow/orange / red precipitate (1)	$KMnO_4$ Just 'red' White smoke Do not award if 2,4-DNPH also given as test for acid	4

	OR Acidified potassium dichromate (solution) (1) Orange to green / blue (1) ALLOW name or formula for any reagent Any correct test or tests that would differentiate the three liquids, without identifying which is which scores max (2) (The third liquid is pentane)	Just 'potassium dichromate'	

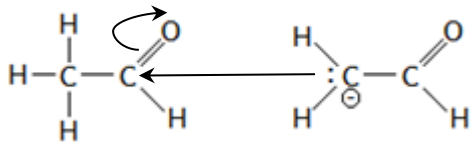
Question Number	Acceptable Answers	Reject	Mark
22(d)(i)	Pentane (1) Only two types of bond / only C-C and C-H bonds (so few different wavelengths absorbed) / only C-H vibrations present (1) ALLOW only C-H bonds ALLOW Identification of **both** sets of peaks as due to C-H vibrations e.g. by wavenumber range IGNORE Refs to functional groups present		2

Question Number	Acceptable Answers	Reject	Mark
22(d)(ii)	**M1 and M2** P is O-H (stretch) Q is C=C (stretch) R is C=O (stretch) ALLOW OH but not CO or CC All 3 correct scores (2) Any 2 correct scores (1) IF M1 and M2 NOT AWARDED ALLOW P is carboxylic acid **AND** Q is alkene **AND** R is aldehyde/carbonyl OR One correct bond and two correct groups for (1) mark **M3** (dependent on at least 1 mark being scored from **M1** and **M2**) Spectrum B is propenoic acid **AND** Spectrum C is butanal (1)	 C-O-H C=O	3

(Total for Question 22 = 20 marks)

Question Number	Acceptable Answers	Reject	Mark
23(a)	3-hydroxybutanal		1

Question Number	Acceptable Answers	Reject	Mark
23(b)(i)	Acid / proton donor		1

Question Number	Acceptable Answers	Reject	Mark
23(b)(ii)	 Arrow from lone pair to carbon (1) Arrow from double bond to, or just beyond, O (1) IGNORE Dipoles	To double bond From C	2

Question Number	Acceptable Answers	Reject	Mark
23(b)(iii)	Nucleophilic (1) Addition (1) IGNORE S_N1 / S_N2		2

Question Number	Acceptable Answers	Reject	Mark
23(b)(iv)	Catalyst (1) IGNORE Base/alkali/nucleophile **MP2** dependent on **MP1** (Is used in step 1) but is regenerated (at the end of the reaction) OR OH^- is not used up in the reaction / concentration remains unchanged / is present at the end unchanged (1) IGNORE Lowers the activation energy	Remains unchanged **throughout the process**	2

Question Number	Acceptable Answers	Reject	Mark
23(b)(v)	Attack occurs from above or below / from both sides of (the plane of) the planar carbonyl group (1) Resulting in a racemic mixture / equimolar mixture of enantiomers (1) **Marks are independent**	OH^- attacks from above or below Attacks from both sides of carbocation Planar intermediate / molecule Does not have a chiral centre	2

Question Number	Acceptable Answers	Reject	Mark
23(c)(i)	$k = \frac{8.8 \times 10^{-3}}{0.2 \times 0.04} = 1.1$ (1) $dm^3\ mol^{-1}\ s^{-1}$ (1) ALLOW Units with a "-" instead of "-1" super-script **Marks are independent**	dm^3 / mol s or units given as fractions	2

Question Number	Acceptable Answers	Reject	Mark
23(c)(ii)	Both ethanal and hydroxide present **once** in the first step / first step involves reaction of one ethanal with one OH^- ion		1

(Total for Question 23 = 13 marks)

(Total for Section B = 49 marks)

Section C

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>*24(a)(i)</td><td>
<table>
<tr><td></td><td>N_2</td><td>H_2</td><td>NH_3</td><td></td></tr>
<tr><td>Moles at equilibrium</td><td>0.80</td><td>2.4</td><td>0.40</td><td>(1)</td></tr>
<tr><td>Mole fraction</td><td>0.222</td><td>0.667</td><td>0.111</td><td>(1)</td></tr>
<tr><td>Partial pressure (atm)</td><td>0.444</td><td>1.333</td><td>0.222</td><td>(1)</td></tr>
</table>
EITHER
$K_p = \frac{0.222^2}{0.444 \times 1.333^3}$

IGNORE
any brackets – even square brackets – if numbers are substituted into K_p

OR
if no numbers are substituted

$K_p = \frac{p(NH_3)^2}{p(N_2)\,p(H_2)^3}$ (1)

$= \frac{0.049284}{0.444 \times 2.3686} = 4.686 \times 10^{-2} / 0.04686$ (1)

Units = atm^{-2} (1)

IGNORE
SF except 1 SF except moles at equilibrium where 1 SF is allowed

Use of fractions:
N_2 4/9, H_2 4/3, NH_3 2/9 gives
3/64 = 0.046875 atm^{-2} which scores full marks for the calculation

ALLOW
TE throughout
</td><td>Lack of p

Use of [ ]

0.05

Just 3/64</td><td>6</td></tr>
</table>

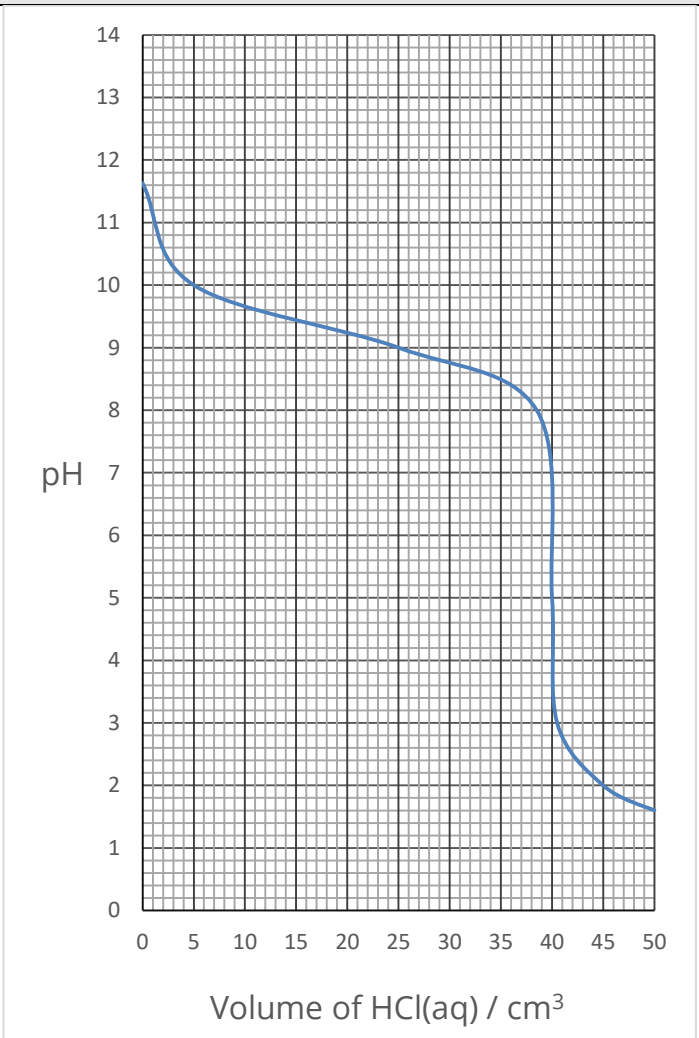
Question Number	Acceptable Answers	Reject	Mark
24(a)(ii)	$\Delta S_{total} = R\ln K_p$ / $R\ln K$ (1) ΔS_{total} = 8.31 x ln(ans (a)(i)) = -25.43351 / -25 (J K^{-1} mol^{-1}) (1) No TE on incorrect equation. Correct answer with no working scores (2) IGNORE SF except 1 SF Units even if incorrect		2

Question Number	Acceptable Answers	Reject	Mark
24(b)(i)	Moles of NH_3 = $\frac{25.0}{1000}$ x 1.00 = 0.025 (1) Volume of HCl(aq) = $\frac{0.025}{0.625}$ = 40 cm^3 / 0.04 dm^3 (1)	cm^{-3} / dm^{-3}	2

Question Number	Acceptable Answers	Reject	Mark
24(b)(ii)	NB Penalise lack of + on H_3O^+ or NH_4^+ once only in (ii) and (iii) $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$ ALLOW $NH_4^+ \rightarrow NH_3 + H^+$ ALLOW Reversible arrows IGNORE state symbols even if incorrect		1

Question Number	Acceptable Answers	Reject	Mark
24(b)(iii)	$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ OR $K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$ No TE on incorrect equation in (b)(ii)		1

Question Number	Acceptable Answers	Reject	Mark
24(b)(iv)	K_a / $5.6 \times 10^{-10} = \frac{[H^+]^2}{0.385}$ (1) $[H^+]^2 = 5.6 \times 10^{-10} \times 0.385$ $H^+ = \sqrt{5.6 \times 10^{-10} \times 0.385}$ (1) $= 1.4683 \times 10^{-5}$ $pH = -\log_{10}(1.4683 \times 10^{-5})$ $= 4.833$ (1) IGNORE SF, except 1SF		3

Question Number	Acceptable Answers	Reject	Mark
24(b)(v)	 Starts at pH 11.6 **AND** finishes below pH 3 (1) Vertical portion at 40 cm^3 starting between pH 9 and pH 7 (1) between 3 and 5 pH units in length (1) Reasonable shaped curve with no maxima or minima ALLOW Curve drawn without the initial drop (1) IF addition of alkali to acid: **M1** and **M4** cannot be scored **M2** can be scored for a vertical portion at 40 cm^3, finishing between pH 7 and pH 9 **M3** can be scored as above		4

Question Number	Acceptable Answers	Reject	Mark
24(b)(vi)	(No) because thymol blue has a pK_{in} of 8.9 (1) which does not lie on the middle of the vertical portion of the graph / outside the vertical region (1) OR (No) because thymol blue has a range of 8.0 to 9.6 (1) which does not lie (wholly) within the vertical portion of the graph (1) ALLOW For second mark: - comments about colour changing before the vertical portion is reached - use of incorrect pK_{in} or range values if different indicator used Answers TE on graph which has a suitable vertical portion of the graph to use thymol blue with answer Yes.		2

(Total for Question 24 = 21 marks)

(Total for Section C = 21 marks)

TOTAL FOR PAPER = 90 marks

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