

Mark Scheme (Final)

Summer 2023

Pearson Edexcel International Advanced Subsidiary Level In Chemistry (WCH14) Paper 01

Unit 4: Rates, Equilibria and Further Organic Chemistry

Section A

| Question Number | Answer | Mark |
|--------------------|---|------|
| 1 | The only correct answer is B $(K_c = \frac{[Y]^2[Z]}{[W][X]})$ | (1) |
| | A is incorrect because Y has been multiplied by 2 instead of raised to the power of its coefficient | |
| | C is incorrect because the expression has been inverted and because Y has been multiplied by 2 instead of raised to the power of its coefficient | |
| | D is incorrect because the expression has been inverted | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 2 | The only correct answer is B (homogeneous, decreases) | (1) |
| | A is incorrect because the system is homogenous at 360 $^{\circ}$ C | |
| | C is incorrect because the system is homogenous at 360 °C and K_c decreases | |
| | $m{D}$ is incorrect because K_c decreases | |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 3 | The only correct answer is C (atm ⁻²) | (1) |
| | A is incorrect because coefficients have not been taken into account | |
| | B is incorrect because coefficients have not been taken into account and the expression has been inverted | |
| | D is incorrect because these are the units for the inverted expression | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 4(a) | The only correct answer is D (time, absorption) | (1) |
| | A is incorrect because the labels are the wrong way round | |
| | $m{B}$ is incorrect because R_f is not used in HPLC | |
| | C is incorrect because R_f is not used in HPLC | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 4(b) | The only correct answer is D (G is most attracted to the stationary phase, F is the most abundant) | (1) |
| | A is incorrect because E is the least attracted to the solid phase and F is the most abundant | |
| | B is incorrect because F is the most abundant | |
| | C is incorrect because E is the least attracted to the solid phase | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 5 | The only correct answer is D (HO CH ₂ OH H ₅ C ₂ IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII | (1) |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 6 | CH3 SH | (1) |
| | The only correct answer is B $(1, H_3C-O)$ CH_3 | |
| | A is incorrect because there is only 1 chiral centre | |
| | C is incorrect because there is only 1 chiral centre | |
| | D is incorrect because there is only 1 chiral centre | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 7 | The only correct answer is A (rate = $k[H_2O_2]^2[I^-]$) | (1) |
| | B is incorrect because the concentration of hydrogen peroxide should be squared | |
| | C is incorrect because this includes an intermediate | |
| | D is incorrect because the concentration of hydrogen peroxide should be squared and includes an intermediate | |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 8 | The only correct answer is A (B is incorrect because there is an extra –OH group on the alcohol C is incorrect because a C=O on the acid has been replaced by a methyl group forming an ether linkage | (1) |
| | D is incorrect because an ester link has been replaced by an ether | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 9(a) | The only correct answer is C (6) | (1) |
| | A is incorrect because the mechanism requires 6 curly arrows | |
| | B is incorrect because the mechanism requires 6 curly arrows | |
| | D is incorrect because the mechanism requires 6 curly arrows | |
| | 6+ CH ₃ CH | |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 9(b) | The only correct answer is B (ethanamide) | (1) |
| | A is incorrect because it is not a ketone | |
| | C is incorrect because it is not an IUPAC name | |
| | D is incorrect because there are two carbon atoms in the formula | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 10 | The only correct answer is D (higher, higher) | (1) |
| | $m{A}$ is incorrect because hydrogen bonding in butanoic acid results in higher boiling temperature and solubility in water | |
| | B is incorrect because hydrogen bonding in butanoic acid results in higher boiling temperature | |
| | C is incorrect because hydrogen bonding in butanoic acid results in higher solubility in water | |

| Question Number | Answer | Mark |
|--------------------|---|------|
| 11 | The only correct answer is B (3-hydroxy-2-methylbutanoic acid) | (1) |
| | A is incorrect because the numbering of the groups is incorrect | |
| | C is incorrect because the acid does not have an additional methyl branch on the third carbon | |
| | D is incorrect because the acid is not a straight chain | |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 12 | The only correct answer is B (ethane-1,2-diol) | (1) |
| | A is incorrect because the disodium salt of the acid would be produced | |
| | C is incorrect because ethanedioic acid is not a monomer of the polyester | |
| | D is incorrect because water is used in the hydrolysis and is not a product | |

| Question Number | Answer | Mark | |
|--------------------|---|------|--|
| 13(a) | he only correct answer is B (bromothymol blue, phenol red and phenolphthalein) | | |
| | A is incorrect because bromocresol green and methyl red do not change within the vertical portion | | |
| | C is incorrect because methyl red does not change within the vertical portion | | |
| | D is incorrect because the indicators do not change within the vertical portion | | |

| Question Number | Answer | Mark |
|--------------------|--|------|
| 13(b) | The only correct answer is A (CH ₃ COOH and NaOH) | (1) |
| | B is incorrect because ammonia is not a strong base | |
| | C is incorrect because HCl is a strong acid | |
| | D is incorrect because HCl is a strong acid | |

| Question Number | Answer | |
|--------------------|---|-----|
| 14(a) | The only correct answer is A (B is incorrect because the curve is inverted C is incorrect because this is a titration curve for a monoprotic acid D is incorrect because this is a titration curve for a triprotic acid | (1) |

| Question Number | Answer | |
|--------------------|--|-----|
| 14(b) | The only correct answer is \mathbf{B} ((Z)-but-2-enedioic acid) | (1) |
| | A is incorrect because maleic acid is the Z isomer | |
| | C is incorrect because the carbon chain of maleic acid has four carbon atoms and maleic acid is the Z isomer | |
| | D is incorrect because the carbon chain of maleic acid has four carbon atoms | |

| Question Number | Answer | |
|--------------------|--|-----|
| 15 | The only correct answer is C (H ₂ CO ₃ , CO ₃ ²⁻) | (1) |
| | A is incorrect because these species are interconverted by protonation/deprotonation | |
| | B is incorrect because these species are interconverted by protonation/deprotonation | |
| | D is incorrect because these species are interconverted by protonation/deprotonation | |

| Question Number | Answer | |
|--------------------|--|-----|
| 16 | The only correct answer is D (13.1) | (1) |
| | A is incorrect because the molarity was divided by 200 instead of 0.2 | |
| | B is incorrect because the moles of barium hydroxide were used instead of the concentration of hydroxide ions | |
| | C is incorrect because the concentration of barium hydroxide is used instead of the concentration of hydroxide ions | |

TOTAL FOR SECTION A =20 MARKS

Section B

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|----------------------------------|---|------|
| 17(a) | • (+)178 (kJ mol ⁻¹) | Do not award –178 (kJ mol ⁻¹) | (1) |
| | | Ignore units even if incorrect | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|--|------|
| 17(b) | | Example of calculation: | (2) |
| | • equation or workings (1) | $\Delta_f H = \Sigma(\text{all other terms})$ $\Delta_f H = 178 + 590 + 1145 + (2 \times 122) + (2 \times -349) + (-2258)$ | |
| | • answer to 3SF with negative sign (1) | -799 (kJ mol ⁻¹) | |
| | | Correct answer scores (2) TE on incorrectly transferred values e.g. –394 Penalise omission of ×2 once only (–572 scores 1 mark) TE on one incorrect sign No TE on incorrect expression Penalise M2 for incorrect units +799 scores 1 mark | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|------|
| 17(c) | An explanation that makes reference to the following points: | | Allow reverse arguments | (4) |
| | calcium chloride is almost completely ionic | (1) | Accept CaCl ₂ is 100% ionic Allow LE is calculated assuming a pure ionic structure | |
| | calcium iodide has partially covalent character | (1) | Allow shows more covalent character Allow CaCl ₂ has less covalent character than CaI ₂ Ignore polar Do not award M2 for CaI ₂ is covalent Do not award M2 for Intermolecular forces | |
| | • iodide (ion) is larger (than chloride (ion)) | (1) | Accept iodide has a lower charge density Allow iodine ion Ignore iodine is larger Do not award molecules, Cl ₂ or I ₂ loses M3 | |
| | • (so) more (easily) polarised | (1) | Accept more (easily) distorted Allow (more) polarisable Do not award CaI ₂ is more polarised | |
| | | | If no comparison for M3 and M4 allow 1 mark, e.g., "iodide is large and is polarised" | |
| | | | Penalise iodine/chlorine or incorrect ions once only. | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|---|-----|---|------|
| 17(d)(i) | An answer that makes reference to the following points: | | An example of a completed cycle: | (2) |
| | two labelled arrows in the correct direction | (1) | $CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$ | |
| | formulae including state symbols | (1) | LE | |
| | | | $Ca^{2+}(g) + 2Cl^{-}(g)$ | |
| | | | Accept two arrows on right-hand side | |
| | | | Allow $\triangle_{\text{latt}}H/\triangle_{\text{Hlatt}}$ | |
| | | | Allow $\triangle_{hyd}H$ alone on right-hand arrow | |
| | | | Allow ΔH_{hyd} | |
| | | | Allow numerical values rather than the symbols | |
| | | | Allow missing 2 for the $\triangle_{\text{hyd}}H Cl^-$ | |
| | | | Allow left arrow going down if labelled as lattice dissociation energy or –LE | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|-----------------------------------|---|------|
| 17(d)(ii) | | Example of a calculation: | (2) |
| | • calculation (1) | $-(-2258) - 1579 - (2 \times 378)$ | |
| | • enthalpy change of solution (1) | $=-77 \text{ (kJ mol}^{-1})$ | |
| | | No TE on an incorrect cycle, but (+)77 scores 1 mark Allow TE on transcription errors from M1, and award M2 Allow ×2 omitted, answer = (+)301 (kJ mol ⁻¹) scores (1) | |

(Total for Question 17 = 11 marks)

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|---|------------|
| _ | smooth line of best-fit through all the points | An example of a graph: 1.2 1 0.8 Initial rate / mol dm ⁻³ s ⁻¹ 0.6 0.4 0.2 | (1) Expert |
| | | Ignore extrapolation at either end of the best-fit line Allow non-smooth lines, within 1 square of each point Do not award use of a ruler | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 18(a)(ii) | • graph is not a straight line (through the origin) | Accept reverse argument Accept 1st order would be a straight line Accept the relationship is not linear / directly proportional Allow 2 nd order with justification e.g., as it's a curve or rate quadruples when concentration doubles Ignore half lives Allow rate not doubling when concentration is doubled Ignore gradient not constant. Ignore exponential No TE 18(a)(i) | (1) |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|---|------------|------------------------------|------|
| 18(a)(iii) | An answer that makes reference to the following points: | | | (2) |
| | • order of reaction for NO | (1) | 2 / 2 nd / second | |
| | order of reaction for O₂ | (1) | 1 / 1 st / first | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|-------------------------|--|------|
| 18(a)(iv) | • rate = $k[NO]^2[O_2]$ | Allow TE on incorrect orders in a(iii) Allow r on LHS Do not award round brackets Must be a rate equation to gain the mark Correct answer scores 1 | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 18(a)(v) | | Example of a calculation: | (2) |
| | • substitution or rearrangement (1 | $0.040 = k (0.010)^2 (0.05)$ | |
| | | $k = \frac{0.040}{(0.010)^2(0.05)}$ | |
| | • answer and units (1 | $= 8000 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ | |
| | | Allow units in any order Allow s ⁻ Allow dm ⁶ /mol ² s but not dm ⁶ /mol ² /s | |
| | | Allow TE on a(iv) for both marks, units must match order for M2 Correct answer with units scores 2, even if expression in Q18(a)(iv) is incorrect | |
| | | in Q10(a)(1v) is incorrect | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|---|-----|--|------|
| 18(b) | An answer that makes reference to the following points: | | | (2) |
| | • the equilibrium constant is (very) large | (1) | Allow $K_p >> 1$ Allow synonyms e.g., huge, massive, etc. Allow high Ignore quite large Ignore $K_p > 1$, positive Ignore numerator is larger than the denominator Ignore references to partial pressures | |
| | the equilibrium position is (far) to the right / (heavily) favours the products | (1) | Allow goes to completion Do not award "shifts to the right" Ignore favours the forward reaction Do not award M2 for comments on rate For two marks there must be a comment on extent/magnitude | |

(Total for Question 18 = 9 marks)

| Question Number | Answer | | | Additional Guidanc | e | Mark |
|--------------------|--------------------------------|-------|---------|----------------------------------|--|------|
| 19(a)(i) | | An ex | kample | of a completed table: | | (3) |
| | • one mark per correct row (3) | | Isomer | Skeletal structure | Number of peaks on 13C NMR spectrum | |
| | | | 1 | Br | 5 | |
| | | | 2 | Br | 5 | |
| | | | 3 | Br | 3 | |
| | | If no | other n | nark is scored three correct str | ructures score 1 mark | |
| | | Accep | pt disp | layed or structural formulae | | |

| Question Number | A | nswer | Additional Guidance | Mark |
|--------------------|--|-------|--|------|
| 19(a)(ii)* | 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. Number of indicative marking Number of marks awarded for points seen in answer indicative marking points 6 4 5-4 3 3 5-2 2 11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | | 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, a response 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 were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). | (6) |
| | | | In general, it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. | |
| | Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout Answer is partially structured wit some linkages and lines of reason Answer has no linkages between and is unstructured | h 1 | 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. | |

| Indicative content: | |
|---|---|
| • IP1: 3 peaks so 3 (proton/hydrogen/H) environments | Allow "3 chemical shifts" in place of peaks |
| • IP2: the peak in the range 3.7–4.2 (δ/ppm) is the H attached to the same carbon as the bromine | Accept -CHBr- has the highest chemical shift Allow IP2 if peak is correctly labelled on the spectrum IP2 can be awarded for any of the three formulae |
| • IP3: split into 5 peaks as next to 4 hydrogens | Allow any word that implies 5 peaks e.g., pentet, quintuplet, quintet or multiplet IP3 can be awarded for any correct explanation of splitting patterns – reference to (n+1) rule |
| • IP4: the peak at 0.8 – 1.3 (δ/ppm) is the Hs in the methyl groups and the peak at 1.6 – 2.2 (δ/ppm) is the two -CH ₂ -hydrogen groups | IP4 can be awarded for an explanation of the symmetry of the molecule leading to equivalent methyl and CH ₂ groups, if the peaks are correctly identified (including on the diagram) Allow IP4 if peaks are correctly labelled on the spectrum Allow IP4 to be awarded if the correct splitting patterns are described for δ-values of both peaks. |
| • IP5: peak areas 1:4:6 | Allow numbers in any order Allow ratio alone |
| IP6: identification of 3-bromopentane by name or structural formula | Allow single values for chemical shifts throughout (within each range) |
| | I1, I2, I4, I5 and I6 can be shown on a labelled diagram with labelled spectrum |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 19(b) | An answer that makes reference to the following points lone pair on oxygen of OH⁻ dipole on C–Br curly arrow from lone pair to delta positive carbon curly arrow from C–Br bond to Br or just beyond (allow shown on transition state) | Example of a mechanism: $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ HO \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ H_5 \\ HO \\ H \end{array} $ $ \begin{array}{c} H_5C_2 \\ H_5 \\ H_7 \end{array} $ $ \begin{array}{c} H_5C_2 \\ H_7 \end{array} $ $ \begin{array}{c} H_5C_2 \\ H_7 \end{array} $ $ \begin{array}{c} H_7C_2 \\ H_7C_2$ | (4) |
| | transition state (including partial bonding) negative charge anywhere on transition state | Ignore charges for P5 Do not award OH–C connectivity for P5 TE on incorrect reactant molecule | |
| | • propan-1-ol and Br ⁻ | TE on incorrect connectivity from transition state for P7 but otherwise do not award OH–C Allow 2D representations S _N 1 mechanisms could score points 1, 2, 4 and 7 (2 marks max) All 7 points score 4 marks, 5 or 6 points scores 3 marks, 3 or 4 points scores 2 marks, 2 points scores 1 mark | |

(Total for Question 19 = 13 marks)

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|------|
| 20(a)(i) | | | Example of a calculation: | (2) |
| | expression or suitable working | (1) | $(192 + 0.5 \times 205) - (220)$ | |
| | • correct answer | (1) | $(+)74.5 (J K^{-1} mol^{-1})$ | |
| | | | Correct answer scores 2 | |
| | | | -74.5 scores 0 | |
| | | | TE on small errors in M1 e.g., miss out 0.5, as long as | |
| | | | the answer is positive | |
| | | | Penalise incorrect units once only for ai-aiii | |
| | | | Allow J K ⁻ mol ⁻ | |
| | | | Allow J/K mol but not J/K/mol | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 20(a)(ii) | • balanced equation or suitable working (1) | Example of a calculation: ΔS surroundings = $-\Delta H/T$ = $-(-82000) \div (2048)$ = $82000 \div 2048$ | (2) |
| | • correct answer (1) | (+) 40.039 (J K ⁻¹ mol ⁻¹) Correct answer scores 2 Ignore SF – 40 scores 1 mark 0.04 scores 1 mark with correct units or without units, 2 marks with kJ K ⁻¹ mol ⁻¹ | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|---|------|
| 20(a)(iii) | total entropy change | Example of a calculation: $74.5 + 40.0 = (+)114.5 \text{ (J K}^{-1} \text{ mol}^{-1})$ | (1) |
| | | TE on ai and aii, but both must be in the correct units Ignore SF except 1SF | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|-------------------------|---|------|
| 20(b) | | Example of a calculation: | (2) |
| | • gradient (1) | $\frac{(-197) - (-190)}{(0.00673) - (0.00649)} = \frac{-7}{0.00024}$ | |
| | | gradient = -29 167 (K) (allow any negative value between 28 300-30 000) | |
| | • activation energy (1) | $(-8.31 \times -29\ 167) \div 1000 = (+)242.4 \text{ (kJ mol}^{-1})$ | |
| | | (allow values between 235.1 to 249.3 for 2 marks) | |
| | | Ignore SF except 1 SF Allow TE from M1 Answers in J mol ⁻¹ score both marks if in the allowed range (235100-249300) | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|------------|--|------|
| 20(c) | An explanation that makes reference to the following points: (thermodynamically) feasible because ΔS_{total} is positive activation energy high so the reaction is very slow (at low temperatures) | (1) (1) | Ignore thermodynamically stable/unstable Allow high temperature will provide Ea so reaction will proceed Allow reaction may not happen as Ea is (very) high Allow high Ea so kinetically stable Allow high Ea so kinetically non-feasible TE on 20(a)(iii) but not on 20(b) | (2) |

(Total for Question 20 = 9 marks)

| Question Number | Answer | | A | Additional Guidance | | | |
|--------------------|---------------------------------------|-----|--|---------------------|-------------------------------------|--|--|
| 21(a) | An answer that makes reference to the | | Example of an answer: | | | | |
| | following points: | | Reagent and conditions | Reaction (√/×) | Name of organic product (if formed) | | |
| | row for oxidation correct | (1) | refluxed with excess acidified potassium dichromate(VI) | × | (N/A) | | |
| | row for reduction correct | (1) | excess lithium tetrahydrioaluminate(III) in dry ether | ✓ | hexane-2,5-diol | | |
| | | | Accept no product or be Accept 2,5-hexanediol Ignore errors with space Do not award hex-2,3- | in secon | | | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|---|------|
| 21(b) | An answer that makes reference to the following point: | | (1) |
| | • (pale) yellow crystals | Allow precipitate / ppt / ppte / solid Allow antiseptic smell Ignore formulae even if incorrect Do not award yellow-orange Use the list principle: if two answers and one correct and one wrong, no credit. | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|-------------------------------|------|
| 21(c)(i) | An answer that makes reference to the following point: | | (1) |
| | • nucleophilic addition | Do not award S_N1 or S_N2 | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|--|------|
| 21(c)(ii) | An answer that makes reference to the following point: | | (1) |
| | CH ₃ C(OH)(CN)CH ₂ CH ₂ C(OH)(CN)CH ₃ | Allow displayed / skeletal / any combination Do not award missing hydrogens or single bonds shown between C and N. If two structures are given both must be correct. | |
| | | If two structures are given both must be correct. | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|--|------|
| 21(d)(i) | An answer that makes reference to the following point: | | (1) |
| | orange precipitate | Allow yellow / red Allow crystals / solid / ppt / ppte Ignore modifiers e.g., dark/light/brick Do not award reddish-brown | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|---|---|------|
| 21(d)(ii) | A description that makes reference to the following points: | | (2) |
| | • (re)crystallise (1 | Ignore purify the product | |
| | measure the melting temperature and compare with known values | Allow refer to database, etc. Ignore NMR / mass spec. etc. | |

(Total for Question 21 = 8 marks) TOTAL FOR SECTION B = 50 MARKS

Section C

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|---|-----------------------------------|--|------|
| 22(a) | An answer that makes reference to the following points: | | An example of a sketch: (1) (1) (2) (1) (1) (1) (2) (1) (2) (hemical shift, δ/ppm | (3) |
| | three peaks peaks shown in approximately the correct height ratio (peak area 6:3:2), highest peak can't be on the right appropriate δ values for 2 or 3 peaks | (1)(1) | Allow vertical lines for peaks Do not award split peaks for M1 M2 is dependent on M1 group allowable δ values (ratio) amine 0.5-2.5 2 alcohol 2.0-4.0 3 CH2 3.0-4.0 6 If labels are given, they must be correct. Use the list principle if 4 peaks are shown, then 3 must be in the right area to score M3. 5 or more peaks score 0 | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|--------|
| 22(b)(i) | An explanation that makes reference to the following points: | | | (3) |
| | • Tris accepts (small amounts of) H ⁺ /protons | (1) | Allow increase in H ⁺ causes the equilibrium to move to the right Allow reacts with/removes Ignore mops up | Expert |
| | base and conjugate acid are present in high concentrations / (large) reservoir of both | (1) | Allow large amounts of tris and salt/acid | |
| | the ratio of [base]/[acid] only changes very slightly and pH changes only slightly | (1) | Allow pH/[H ⁺] is unchanged with ratio comment Allow ratio changes a little / changes slightly with comment on pH Ignore there is no change in concentrations / the ratio is unchanged Ignore references to base/alkali/molecules/ions | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|----------------------|---|------|
| 22(b)(ii) | • correct expression | Allow use of skeletal structure or molecular formula $K_a = \frac{[C_4H_{11}NO_3][H^+]}{[C_4H_{12}NO_3^+]}$ Do not accept round brackets $NB \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$ | (1) |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|------------|---|------|
| 22(b)(iii) | | | Example of a calculation: | (5) |
| | • $M_{\rm r}$ of C ₄ H ₁₂ NO ₃ Cl | (1) | $M_{\rm r} = 157.5$ | |
| | • concentration of C ₄ H ₁₂ NO ₃ Cl | (1) | $100 \div 157.5 = 0.6349 \text{ mol} 0.6349 \div 0.5 = 1.2698 \text{ mol dm}^{-3}$ | |
| | • substitution and rearrangement of K _a | (1) | $[H^{+}] = 8.413 \times 10^{-9} \times [1.2698]$ $[0.2]$ TE on inverted K _a expression from (b)(ii) | |
| | • H ⁺ concentration | (1) | $[H^+] = 5.342 \times 10^{-8}$ | |
| | • pH calculation | (1) | $pH = -log_{10}[H^+] = 7.27$ | |
| | | | They can also use moles rather than $conc^ns$ as the volume terms cancel out in the expression $[H^+] = K_a \times ([acid]/[salt])$ M1, M4 and M5 are the same as above. M2 – Moles base = $0.2 \times 0.5 = 0.1$ and 0.6349 mol of $C_4H_{12}NO_3Cl$ M3 – substitution and rearrangement: $[H^+] = 8.413 \times 10^{-9} \times (0.635 \div 0.1)$ | |
| | | | TE throughout, for M5 the answer must be above 7 to score Correct answer with some working scores 5 Ignore SF except 1 SF | |
| | | | 8.88 scores 4 marks with a correct expression in (b)(ii) or 5 marks if their expression was inverted in (b)(ii). | |
| | | | | |
| | | | $M4 = pH = pK_a + \log_{10} \left(\frac{[A^-]}{[HA]} \right)$ OR | |
| | | | $pH = 8.075 + \log_{10} \left(\frac{[0.2]}{[1.2698]} \right) (1)$ | |
| | | | M5 pH correct for expression and above 7 | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|--------|
| 22(c) | | | Example of a calculation: | (4) |
| | • calculation of concentration of acid | (1) | $0.0150 \div 94.5 = 0.0001587 / 1.59 \times 10^{-4}$ $0.0001587 \div 1.5 = 0.00010582 / 1.058 \times 10^{-4} (mol dm-3)$ | Expert |
| | • calculation of [H ⁺] value | (1) | $[H^+] = 10^{-3.42} = 3.802 \times 10^{-4} \text{ (mol dm}^{-3})$ | |
| | • expression or substitution into expression | (1) | $([H^+]^2 = 1.445 \times 10^{-7})$ $K_a = \frac{[H^+]^2}{[acid]} \text{ or } K_a = \frac{[1.445 \times 10^{-7}]}{[1.058 \times 10^{-4}]}$ | |
| | • evaluation of K_a | (1) | $K_a = 0.0013655 / 1.37 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ TE from M3 if answer < 1 | |
| | | | Allow 1.36 × 10 ⁻³ (mol dm ⁻³) for 4 marks Ignore SF except 1 SF Correct answer with no working scores 4 | |
| | | | Penalise incorrect units for M4 | |

| Question Number | Answer | | Additional Guidance | Mark |
|--------------------|--|-----|---|--------|
| 22(d)(i) | An explanation that makes reference to the | | | (2) |
| | following points: • over a large range from 4 to 16.4 (cm³) of acid added | (1) | Allow a range between 2 and 16.4 of acid added | Expert |
| | • there is little difference in pH | (1) | Allow no (significant) change M2 is dependent on M1 | |
| | | | Large volume of acid added before a change in pH is seen scores 1 The pH doesn't change when a large volume of acid is added scores 1 | |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--------|------------------------------------|------|
| 22(d)(ii) | • 5.8 | Allow answers in the range 5.6-6.2 | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|--------------------|--|--|--------|
| 22(d)(iii) | An answer that makes reference to one of the following points: | | (1) |
| | • pH is important for enzyme function | Allow enzymes may be denatured at high or low pH Allow enzymes may be denatured at the wrong pH NB The word denatured is not on the specification so not essential | Expert |
| | constant pH is important for living organisms pH regulates growth of bacteria and fungi | Allow to have the correct pH for metabolic processes / reactions | |
| | pH is linked to oxygen availability in water | Allow to maintain the pH of blood Allow sudden pH change can be dangerous to organs of the body Ignore "resists change to pH" | |

(Total for Question 22 = 20 marks)
TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS