Pearson Edexcel

Mark Scheme (Results)

January 2023

Pearson Edexcel International Advanced Level
In Chemistry (WCH14)
Paper 01: Rates, Equilibria 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

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.

Section A (Multiple Choice)

Question number	Answer	Mark
1(a)	**The only correct answer is A** (rate = k[NO]^2[O_2]; rate = k[NO]^2[O_2]) ***B*** *is incorrect because the rate equation is not determined by the stoichiometric equation* ***C*** *is incorrect because the rate cannot depend only on the concentration of products* ***D*** *is incorrect because the rate cannot depend only on the concentration of products*	**(1)**

Question number	Answer	Mark
1(b)	**The only correct answer is B**(colorimetry; volume change) ***A*** *is incorrect because titration cannot be used for continuous monitoring of a reaction* ***C*** *is incorrect because the mass of the system does not change* ***D*** *is incorrect because the mass of the system does not change and titration cannot be used for continuous monitoring of a reaction*	**(1)**

Question number	Answer	Mark
2	**The only correct answer is C** (the time taken for the concentration of a reactant to halve) ***A*** *is incorrect because the reaction is slower and slower as it progresses* ***B*** *is incorrect because the rate constant does not change at a given temperature* ***D*** *is incorrect because time taken for the concentration of a product to double will vary*	**(1)**

Question number	Answer	Mark
3	**The only correct answer is A** (rate = k[**E**][**F**]) ***B*** *is incorrect because the rate depends on concentrations of the reacting species in the slow step and the stoichiometry of this step* ***C*** *is incorrect because the rate equation cannot include intermediate concentrations* ***D*** *is incorrect because the rate depends on concentrations of the reacting species in the slow step and the stoichiometry of this step and the rate equation cannot include intermediate concentrations*	**(1)**

Question number	Answer	Mark
4	**The only correct answer is D** (graph 4) ***A*** *is incorrect because entropy increases with temperature and the entropy change for the change from liquid to gas is greater than that for solid to liquid* ***B*** *is incorrect because entropy increases with temperature* ***C*** *is incorrect because the entropy change for the change from liquid to gas is greater than that for solid to liquid*	**(1)**

Question number	Answer	Mark
5	**The only correct answer is C** (increases; unchanged) ***A*** *is incorrect because the energy of the system does not change for an ideal gas* ***B*** *is incorrect because the entropy of the system increases and the energy of the system does not change for an ideal gas* ***D*** *is incorrect because the entropy of the system increases*	**(1)**

Question number	Answer	Mark
6	**The only correct answer is B** (kinetically stable and thermodynamically unstable) ***A*** *is incorrect because as the reaction occurs with a catalyst the reactant mixture must be thermodynamically unstable* ***C*** *is incorrect because as the reaction requires a catalyst the reactant mixture must be kinetically stable and as the reaction occurs the reactant mixture must be thermodynamically unstable* ***D*** *is incorrect because as the reaction requires a catalyst the reactant mixture must be kinetically stable*	**(1)**

Question number	Answer	Mark
7a	**The only correct answer is C** (the sum of the first and second electron affinities of oxygen) ***A*** *is incorrect because both outer electrons have been added* ***B*** *is incorrect because both outer electrons have been added* ***D*** *is incorrect because y does not include the enthalpy of atomisation*	**(1)**

Question number	Answer	Mark
7b	**The only correct answer is D**($\Delta_f H$=v + w + x + y + z) ***A*** *is incorrect because the signs of y and z are incorrect* ***B*** *is incorrect because the sign of z is incorrect* ***C*** *is incorrect because the sign of y is incorrect*	**(1)**

Question number	Answer	Mark
8	**The only correct answer is D**(anion polarised by cation;Born-Haber more exothermic) ***A*** *is incorrect because anions do not polarise cations* ***B*** *is incorrect because covalency makes the Born-Haber value more exothermic* ***C*** *is incorrect because anions do not polarise cations and covalency makes the Born-Haber value more exothermic*	**(1)**

Question number	Answer	Mark
9(a)	**The only correct answer is D**($K_c = \frac{[H_2]^4}{[H_2O]^4}$) ***A*** *is incorrect because the solids are not included in the* K_c *expression for this equilibrium* ***B*** *is incorrect because the solids are not included in the* K_c *expression for this equilibrium* ***C*** *is incorrect because the solids are not included in the* K_c *expression for this equilibrium*	**(1)**

Question number	Answer	Mark
9(b)	**The only correct answer is D**(K_c unchanged; K_c decreases) ***A*** *is incorrect because* K_c *is not affected by the state of division of the solid and* K_c *decreases for an exothermic reaction* ***B*** *is incorrect because* K_c *decreases for an exothermic reaction* ***C*** *is incorrect because* K_c *is not affected by the state of division of the solid*	**(1)**

Question number	Answer	Mark
10	**The only correct answer is A**(HCOOH, $HCOO^-$, $CH_3COOH_2^+$, CH_3COOH) ***B*** *is incorrect because methanoic acid is the stronger acid and will protonate ethanoic acid* ***C*** *is incorrect because the acids and bases have been paired incorrectly* ***D*** *is incorrect because methanoic acid is the stronger acid and the acids and bases have been paired incorrectly*	**(1)**

Question number	Answer	Mark
11	**The only correct answer is A**(increases, increases) ***B*** *is incorrect because the solution becomes less acidic with dilution so pH increases* ***C*** *is incorrect because the proportion of acid molecules dissociating increases with dilution* ***D*** *is incorrect because the proportion of acid molecules dissociating increases with dilution and the solution becomes less acidic with dilution so pH increases*	**(1)**

Question number	Answer	Mark
12(a)	**The only correct answer is C** (10.3) ***A*** *is incorrect because the concentration of OH^- ions has been obtained by halving the concentration of magnesium hydroxide rather than doubling it* ***B*** *is incorrect because the concentration of OH^- ions has been taken as equal to the concentration of magnesium hydroxide* ***D*** *is incorrect because the concentration of OH^- ions has been obtained by taking the square root of the concentration of magnesium hydroxide*	**(1)**

Question number	Answer	Mark
12(b)	**The only correct answer is B**(higher; higher) ***A*** *is incorrect because the solution at 100°C will be more alkaline* ***C*** *is incorrect because the concentration of OH^- ions at 100°C will be higher as solubility is greater* ***D*** *is incorrect because the concentration of OH^- ions at 100°C will be higher and the solution will be more alkaline*	**(1)**

Question number	Answer	Mark
13	**The only correct answer is B**(propanal forms permanent dipole-permanent dipole forces) ***A*** *is incorrect because the London forces in the two molecules will be similar* ***C*** *is incorrect because pure propanal does not form hydrogen bonds* ***D*** *is incorrect because pure propanal does not form hydrogen bonds*	**(1)**

Question number	Answer	Mark
14	**The only correct answer is B** (butanoyl chloride and 3-methylbutan-2-ol) ***A*** *is incorrect because the methyl group of the alcohol needs to be on the C3 atom* ***C*** *is incorrect because the acyl chloride needs to have four carbon atoms and the methyl group of the alcohol needs to be on the C3 atom* ***D*** *is incorrect because the acyl chloride needs to have four carbon atoms*	**(1)**

Question number	Answer	Mark
15	**The only correct answer is A (**ethanal and propanone) ***B*** *is incorrect because propanone also has the CH_3CO group that results in a positive iodoform test* ***C*** *is incorrect because ethanal also has the CH_3CO group that results in a positive iodoform test* ***D*** *is incorrect because both ethanal and propanone have the CH_3CO group that results in a positive iodoform test*	**(1)**

Question number	Answer	Mark
16	**The only correct answer is C** (0.70) ***A*** *is incorrect because the distance travelled by* ***X*** *has been measured from the solvent front* ***B*** *is incorrect because distance travelled by the solvent has been measured from the bottom of the plate* ***D*** *is incorrect because distance travelled by* ***X*** *has been measured from the bottom of the plate*	**(1)**

TOTAL FOR SECTION A = 20 MARKS

Section B

Question number	Answer	Additional guidance	Mark
17(a)(i)	An answer that makes reference to the following • sodium thiosulfate reacts with the iodine formed (1) • when (all) the sodium thiosulfate is used up has reacted the iodine reacts with the starch giving a blue-black colour (1) • the reciprocal of the time taken for the blue-black colour to appear is a measure of the rate (1)	Accept equation $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ Allow a blue-black colour forms at the end of the reaction Allow iodine reacts with the starch giving a blue-black colour Allow blue or black for blue-black Ignore reference to the colour of the solution before the starch-iodine complex forms Do not award iodide reacts with starch Allow 1/t = rate of reaction / 1/t $\propto$ rate of reaction Allow [reactant]/t $\propto$ rate of reaction Do not award thiosulfate as a reactant Allow (for M3) repeat experiment varying concentration of a reactant; plot concentration against time (for blue-black colour to appear) and measure **initial** gradient Ignore references to colorimeter	**(3)**

Question number	Answer	Additional guidance	Mark
17(a)(ii)	An answer that makes reference to the following • correct form of the rate equation (1) • values of three powers (including $[H^+]$ not shown) (2)	Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b[H^+(aq)]^c$ or Rate = $k[H_2O_2(aq)]^a[I^-(aq)]^b$ Allow any values of a, b and c for M1 provided at least one value >0. Zero order species do not need to be shown Allow K for k Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]^0$ Accept Rate = $k[H_2O_2(aq)][I^-(aq)]$ For M2 deduct a mark for each incorrect power (reactant not shown order = 0) **Overall** mark for some of these responses including M1: Rate = $k[H_2O_2(aq)][I^-(aq)][H^+(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]$ scores (2) Rate = $k[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)]^2[I^-(aq)]$ scores (2) Rate = $k[H_2O_2(aq)][H^+(aq)]$ scores (1) Rate = $k[I^-(aq)][H^+(aq)]$ scores (1) Ignore state symbols even if incorrect Correct answer with no intermediate stages scores (3) Use of round brackets deduct 1 mark	(3)

Question number	Answer	Additional guidance	Mark
17(a)(iii)	• rearrangement of rate equation (1) • calculation of value from Run 1 data (1) • units of *k* (1)	Example of calculation TE on (a)(ii) for equations in correct form. Units must match the equation used k = rate /([H_2O_2(aq)][I^-(aq)]) ignore state symbols $k = \frac{0.00181}{0.0210 \times 0.0198} = 4.3531$ Allow use of data from any run $dm^3\ mol^{-1}\ s^{-1}$ Allow units in any order Allow mol^- for mol^{-1} here and throughout paper Ignore SF except 1 SF k[I^-(aq)][H^+] gives 87.06 $dm^3\ mol^{-1}\ s^{-1}$ scores (3) if TE on (a)(ii) Correct answer with units but no working scores (3)	**(3)**

Question number	Answer	Additional guidance	Mark
17(b)	• substitution of values for both temperatures into the Arrhenius equation (1) • subtraction and rearrangement of the two equations (1) • solving equation to give value for E_a (1) • answer to 2/3 SF **and** correct units (1)	Example of calculation $\ln k_{293} = \text{constant} - \frac{E_a}{293\ xR}$ and $\ln k_{313} = \text{constant} - \frac{E_a}{313\ xR}$ $\ln\left(\frac{k_{313}}{k_{293}}\right) = \ln 4.45 = \frac{E_a}{R}\left(\frac{1}{293} - \frac{1}{313}\right)$ $E_a = (+)56887$ (+)57000 / (+)56900 J mol^{-1} Or (+)57 / (+)56.9 kJ mol^{-1} Correct answer with some working scores (4) Some attempt at a calculation using the Arrhenius equation, giving a positive value to 2 or 3 SF and correct units scores M4	**(4)**

(Total for Question 17 = 13 marks)

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>*18a</td><td>This question assesses the 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><td>Number of indicative marking points seen in answer</td><td>Number of marks awarded for indicative marking points</td></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><td></td><td>Number of marks awarded for structure of answer and sustained lines of reasoning</td></tr>
<tr><td>Answer shows a coherent 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, 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).

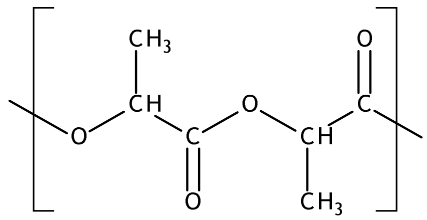
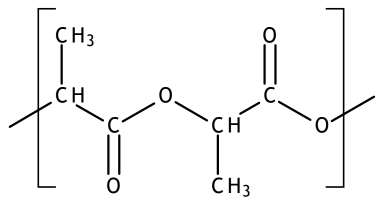
If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

In general it would be expected that
5 or 6 indicative points would get 2 reasoning marks
3 or 4 indicative points would get 1 reasoning mark
0, 1 or 2 indicative points would get 0 reasoning marks.

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</td><td></td></tr>
</table>

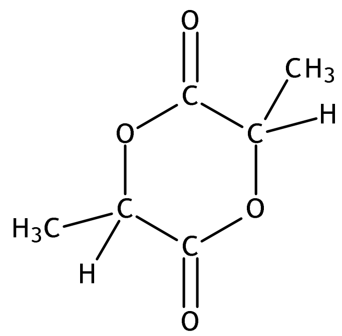
Question number	Answer	Additional guidance	Mark
*18(a)	Indicative content **IP1** ‘optically active’ means that these molecules rotate the plane of plane-polarised light **IP2** lactic acid (is optically active because its) molecules can form non-superimposable mirror images **IP3** lactic acid formed in muscles contains one type of enantiomer **and** lactic acid formed in the synthesis contains equal numbers of moles of the two enantiomers **IP4** the carbonyl group is planar **IP5 (**in the synthesis the) nucleophile / CN^- attacks (equally) from above and below the plane (of the carbonyl group) **IP6** (because) lactic acid formed in muscles involves the oxidation of an enantiomer in a way that does not involve the chiral centre	Allow rotate plane-polarised light Allow racemic mixture does not rotate (the plane of) plane-polarised light so not optically active Do not award bend / deflect / reflect / change for rotate Allow has an asymmetric carbon (atom) Allow has a chiral centre / carbon Allow has a carbon with four different groups / atoms bonded / attached to it Allow lactic acid formed in muscles contains more of one enantiomer (than the other) Allow isomers / molecule for enantiomers Allow just ‘forms a racemic mixture’ Do not award laboratory lactic acid and muscular lactic acid are different molecules Allow ethanal is planar about the carbonyl group /CHO do not award just ‘ethanal is planar’ do not award intermediate / carbocation is planar Allow nucleophile / CN^- attacks from either side / both sides / top & bottom Do not award S_N1 / S_N2 / nucleophilic substitution Allow the enzymes involved (in forming lactic acid in muscles) are stereospecific Allow enzymes react with (only) one enantiomer Allow biochemical / natural processes (often) select one particular enantiomer / (optical) isomer	**(6)**

Question number	Answer	Additional guidance	Mark
18(b)(i)	An diagram showing • ester linkage (1) • remainder of the structure including continuation bonds (1)	Example of polymer  Allow  Allow more than 2 correct repeat units Ignore omission of brackets Ignore 'n' showing repeat units Allow skeletal formula Ignore connectivity errors	**(2)**

Question number	Answer	Additional guidance	Mark
18(b)(ii)	• empirical formula mass **and** molecular formula	Example of calculation formula mass of $C_3H_4O_2$ = 72 **and** molecular formula of X = $C_6H_8O_4$ Allow just $C_6H_8O_4$	**(1)**

Question number	Answer	Additional guidance	Mark
18(b)(iii)	An answer that makes reference to the following • (two peak areas show that) there are two proton environments (1) • (relative peak area) shows 3 times as many protons in one environment compared with the other (1) • splitting shows that the two proton environments are adjacent (1)	Allow two types of proton / hydrogen / hydrogen atom Ignore just 'chemical environment' Ignore just 'two protons / hydrogens' Accept 6 protons in one environment and 2 in the other Ignore 3 protons in one environment and 1 in the other Allow the two types of proton are on neighbouring carbon atoms Allow doublet must be adjacent to one proton and quartet must be adjacent to three protons (Do not award omission of doublet and quartet) Ignore references to chemical shifts Ignore explanations of the splitting patterns even if incorrect	(3)

Question number	Answer	Additional guidance	Mark
18(b)(iv)	An answer that makes reference to the following • (three peaks show that) there are three carbon environments (1) • the carbon atoms with no hydrogen atoms must be in identical environments Or Chemical shift at about 170 ppm indicates an ester group (1)	Allow three types of carbon (atom) Ignore just 'chemical environment' Ignore reference to peak height / area Do not award three carbon atoms Accept the three environments each have two carbon atoms Allow 160−180 ppm or 'peak on LHS' Allow ester shown as structure Allow ester peak labelled on spectrum Ignore references to other chemical shifts even if incorrect Ignore references to other functional groups	(2)

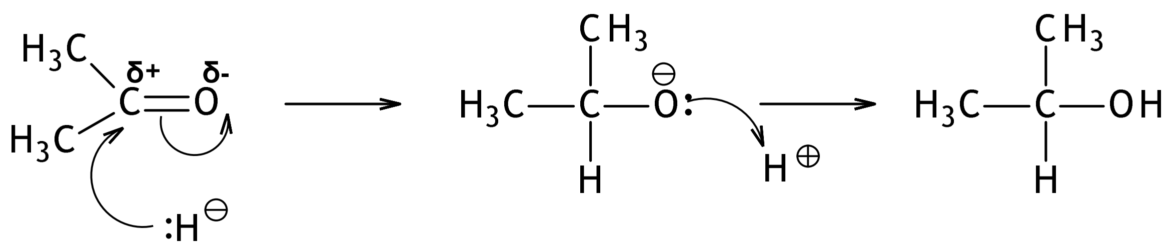
Question number	Answer	Additional guidance	Mark
18(b)(v)	An answer that makes reference to the following • structure of lactide	Example of structure  Allow skeletal or displayed formulae or any combination of these No TE on incorrect deductions in (b)(ii), (b)(iii) and (b(iv)	**(1)**

(Total for Question 18 = 15 marks)

Question number	Answer	Additional guidance	Mark
19(a)	An answer that makes reference to the following • dry **and** ether	Allow dry ethoxyethane Allow dry diethyl ether Allow 'no water' / anhydrous for 'dry' Do not award 'ester' Do not award additional reagents	**(1)**

Question number	Answer	Additional guidance	**Mark**
19(b)	An answer that makes reference to the following • dipole on C=O bond • curly arrow from C=O bond to the oxygen atom or just beyond • lone pair on hydrogen of hydride ion • curly arrow from (lone pair on) hydride to carbonyl carbon • intermediate with negative charge on O atom • lone pair on oxygen • curly arrow from (lone pair on) oxygen to hydrogen ion • final product	8 points correct scores 4 6 or7 points correct scores 3 4 or 5 points correct scores 2 2 or 3 points correct scores 1 Curly arrows should be closer to their correct origin or target than alternatives Do not award curly arrow from negative charge on hydrogen Allow curly arrow to δ+ on carbon Allow charge on bracket around intermediate Do not award intermediate with δ− Allow curly arrow to + on hydrogen Allow curly arrow to hydrogen on H─Cl with curly arrow from H─Cl bond to chlorine or just beyond Do not award curly arrow from negative charge on oxygen Ignore connectivity errors on groups	**(4)**

Example of mechanism



Question number	Answer	Additional guidance	Mark
19(c)	An explanation that makes reference to the following • the C=O bond is polarised by the (electronegative) oxygen atom (1) • H^- is are attracted to the δ+ carbon (1) • the C=C bond is non-polar OR • nucleophiles are / H^- is repelled by (π electrons of) C=C **(1)**	Allow 'the C=O bond is polar / has a permanent dipole' Ignore just 'in C=O bond C is δ+ and O is δ−' Ignore diagram of dipole shown Ignore explanations of polarity of C=O even if incorrect Ignore just 'π bond is polar' Allow nucleophiles are attracted to the δ+ carbon Allow C=C has electron density equally distributed Ignore just 'π bond / alkene is non-polar' C=C (π electrons) attract electrophiles Allow 'alkene double bond' for C=C Allow 'not attacked' for 'repelled' Ignore references to dipole-dipole interaction Ignore reference to bond strengths	**(3)**

(Total for Question 19 = 8 marks)

Question number	Answer	Additional guidance	Mark
20(a)(i)	• substitution of values into $\Delta S^{\circ}_{system} = S_{products} - S_{reactants}$ (1) • calculation of value from correct equation **and** sign and units (1)	In parts (i), (ii), (iii) and (iv) penalise omission of or incorrect units once only Allow units in any order Allow (e.g.) J/K/mol Do not award J/K mol Positive signs are not required Ignore SF except 1 SF throughout (a). Example of calculation $\Delta S^{\circ}_{system} = 229.5 + 219.5 - 310.1$ $= (+)138.9 \text{ J K}^{-1} \text{ mol}^{-1}$ TE for transcription errors on values only Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(ii)	• substitution of values into $\Delta_r H^{\circ} = \Delta_f H^{\ominus}(\text{products}) - \Delta_f H^{\ominus}(\text{reactants})$ (1) • calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta_r H^{\circ} = (-84.7 + 52.2) - (-126.5)$ $= (+)94.0 \text{ kJ mol}^{-1}$ Correct answer with no working scores (2) TE for transcription errors on values $-94.0 \text{ kJ mol}^{-1}$ scores (1) $-159.0 \text{ kJ mol}^{-1}$ scores (1) $(+)263.4 \text{ kJ mol}^{-1}$ scores (1) $-10.4 \text{ kJ mol}^{-1}$ scores (1)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iii)	• equation for $\Delta S^{o}_{surroundings}$ **and** substitution of values (1) • calculation of value from correct equation **and** sign and units (1)	Example of calculation $\Delta S^{o}_{surroundings} = -\Delta H / T$ $= -94000 \div 298$ Accept $= -94 \div 298$ $= -315.44\ J\ K^{-1}\ mol^{-1}$ / $-0.31544\ kJ\ K^{-1}\ mol^{-1}$ TE on $\Delta_r H^{o}$ from (a)(ii) Do not award use of incorrect equation Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(a)(iv)	• equation for ΔS^{o}_{total} **and** substitution of values **and** calculated value with sign and units	Example of calculation $\Delta S^{o}_{total} = \Delta S^{o}_{system} + \Delta S^{o}_{surroundings}$ $= +138.9 + -315.44$ $= -176.54\ J\ K^{-1}\ mol^{-1}$ Accept $= +0.1389 + -0.31544$ $= -0.17654\ kJ\ K^{-1}\ mol^{-1}$ TE on valuesfrom (a)(i) and (a)(iii) Do not award use of incorrect equation Do not award value obtained using mixed units Correct answer with no working scores (1)	**(1)**

Question number	Answer	Additional guidance	Mark
20(a)(v)	• equation for feasibility (1) substitution of values **and** evaluation of T (1)	Example of calculation ($\Delta S^{o}_{system} + (-\Delta H/T) = \Delta S^{o}_{total} = 0$) $\Delta S^{o}_{system} = \Delta H/T$ or $-\Delta S^{o}_{system} = -\Delta H/T$ $T = 94000 \div 138.9$ = 676.746 (K) (from unrounded values) Accept 403.746(°C) TE on valuesfrom (a)(i) and (a)(ii) Do not award use of incorrect equation (e.g. omission of negative sign in $\Delta S^{o}_{surroundings}$ expression) Do not award value obtained using mixed units Correct answer with no working scores (2)	**(2)**

Question number	Answer	Additional guidance	Mark
20(b)(i)	• equilibrium constant expression	Example of expression $K_p = \dfrac{p(C_2H_6) \text{ x } p(C_2H_4)}{p(C_4H_{10})}$ Accept p_x where x = formula or pp(X) Ignore state symbols even if incorrect Do not award square brackets	**(1)**

Question number	Answer	Additional guidance	Mark
20(b)(ii)	• moles of reactants and products (1) • mole fractions (1) • partial pressures (1) • substitution of values into K_p equation **and** evaluation (1) • units (1)	Example of calculation <table><tr><th></th><th>C_4H_{10}</th><th>C_2H_6</th><th>C_2H_4</th></tr><tr><td>mol at equil^m</td><td>5 – 4.45 = 0.55</td><td>4.45</td><td>4.45</td></tr><tr><td>mole fraction</td><td>$\frac{0.55}{9.45}$ = 0.05820</td><td>$\frac{4.45}{9.45}$ = 0.47090</td><td>$\frac{4.45}{9.45}$ = 0.47090</td></tr><tr><td>partial pressures</td><td>1.20 x 0.05820 = 0.06984</td><td>1.20 x 0.47090 = 0.56508</td><td>1.20 x 0.47090 = 0.56508</td></tr></table> $K_p = \frac{0.56508^2}{0.069841} = 4.5721$ (4.5720 with unrounded numbers) = (4.5721) atm Ignore SF except 1 SF TE on expression in (b)(i) that contains at least two species TE at each stage Correct answer with units but no working scores (5) Omission of partial pressure gives K_p = 3.8100 atm scores (4) Omission of mole fraction gives K_p = 43.21 atm scores (4)	(5)

(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

Section C

Question number	**Answer**	**Additional guidance**	**Mark**
21(a)(i)	An answer that makes reference to the following • equation for K_a	$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$ Accept H_3O^+ for H^+ Ignore $[H^+]^2$ / [RCOOH] Do not award round brackets	**(1)**

Question number	Answer	Additional guidance	Mark
21(a)(ii)	• calculation of concentration of solution (1) • substitution of values into K_a expression (1) • rearrangement to make $[H^+]$ subject of equation (1) • calculation of $[H^+]$ **and** calculation of pH (1)	Example of calculation concentration of gluconic acid solution $= \frac{4.75 \text{ x } 1000}{196 \text{ x } 250} = 0.096939 \ / \ 9.6939 \text{ x } 10^{-2} (\text{mol dm}^{-3})$ $1.38 \text{ x } 10^{-4} = \frac{[H^+]^2}{0.096939}$ $[H^+] = \sqrt{}(1.38 \text{ x } 10^{-4} \text{ x } 0.096939)$ $[H^+]^2 = 1.3378 \text{ x } 10^{-5} \ / \ 0.000013378$ $[H^+] = 3.6575 \text{ x } 10^{-3} \ / \ 0.0036575$ $\text{pH} = -\log(3.6575 \text{ x } 10^{-3}) = 2.4368 \ / \ 2.44 \ / 2.4$ Moles of acid not scaled to 1 dm^3 gives pH = 2.7378 scores (3) Omission of square root gives pH = 4.8736 scores (3) Use of g dm^{-3} gives pH = 1.2906 scores (3) Omission of square root **and** use of g dm^{-3} gives pH = 2.5814 scores (2) TE throughout but Do not award M4 unless there is some calculation to give a value for $[H^+]$ Do not award M4 if pH $\leq$ 1 or $\geq$ 7 Ignore SF except 1 SF	**(4)**

Question number	Answer	Additional guidance	Mark
21(b)(i)	An answer that makes reference to the following • the pH range of phenol red is 6.8−8.4 (1) • phenol red changes colour in the **vertical** section of the titration curve (1)	Ignore pK_{in} = 7.9 Accept the colour change of the indicator occurs over the course of the addition of a very small volume of NaOH . Allow any indication of very small volume Allow pH range covers the **vertical** section of the titration curve Allow pH range is within / at the vertical section of the titration curve Ignore 'at equivalence point' Allow steep for vertical Allow sharp rise for vertical Ignore 'straight' Ignore references to the titration involving a strong base and a weak acid	**(2)**

Question number	Answer	Additional guidance	Mark
21(b)(ii)	• calculation of the amount of gluconic acid in 25.0 cm^3 (1) • calculation of volume of NaOH needed for neutralisation (1) • calculation of excess amount of sodium hydroxide added in the titration (1) • calculation of the concentration of NaOH in the final titration mixture (1) • calculation of the pH of the final titration mixture to at least 1 decimal place (1) OR (for M2 and M3) • calculation of the amount of NaOH in 35.0 cm^3 (1) • calculation of excess amount of sodium hydroxide added in the titration (1)	Example of calculation $= \frac{25 \times 0.096939}{1000} = 2.4235 \times 10^{-3}$ / 0.0024235 (mol) Allow **any** concentration of gluconic acid used for M1 and then TE throughout volume $= \frac{1000 \times 2.4235 \times 10^{-3}}{0.105} = 23.08\ cm^3$ $\frac{(35.0-23.08) \times 0.105}{1000} = 1.2516 \times 10^{-3}$ / 0.0012516 (mol) $\frac{1000 \times 0.0012516}{(25.0 + 35.0)} = 2.086 \times 10^{-2}$ / 0.02086mol dm^{-3} Allow scaling for 60 cm^3 of any calculated concentration or amount pOH = −log(0.02086) = 1.6807 pH = pK_w –pOH = 14 – 1.6807 =12.319 / 12.32 / 12.3 or $[H^+] = 10^{-14} \div 2.086 \times 10^{-2} = 4.7939 \times 10^{-13}$ pH = $-\log(4.7939 \times 10^{-13})$ = 12.319 / 12.32 / 12.3 $35 \times 0.105 \times 10^{-3} = 3.675 \times 10^{-3}$ / 0.003675 (mol) $3.675 \times 10^{-3} - 2.4235 \times 10^{-3} = 1.2515 \times 10^{-3}$ (mol) Allow this mark even if it gives acid in excess Correct answer with some working scores (5) TE at each stage but do not award M5 if pH ≤ 7 If scaling omitted pH = 11.097 scores (4)	**(5)**

Question number	Answer	Additional guidance	Mark
21(c)(i)	An answer that makes reference to the following • gluconic acid **and** sodium gluconate present (in the buffer) in high concentration (1) • When acid is added the $RCOO^-$ / RCOONa is protonated (1) • When alkali is **added the RCOOH reacts and** removing the OH^- ion (from the solution) (1) • [RCOOH] and $[RCOO^-]$ do not change (significantly) (1)	General answer in terms of HA and A^- scores max 3 (**M2**, **M3** and **M4**). Accept names or formulae Accept RCOOH and $RCOO^-$ / RCOONa Allow large amount / large excess / form a reservoir Ignore conjugate base Allow forming RCOOH / gluconic acid for protonated Allow H^+ ion is removed from the solution Allow $RCOO^- + H^+ \rightarrow RCOOH$ Allow $RCOO^- + H^+ \rightleftharpoons RCOOH$ shifts to the right Allow alkali reacts with RCOOH forming $RCOO^-$ or $RCOO^{(-)}Na^{(+)}$ Allow OH^- reacts with H^+ **and** RCOOH dissociates to replace the H^+ Allow $RCOOH + OH^- \rightarrow RCOO^- + H_2O$ Allow $H^+ + OH^- \rightarrow H_2O$ **and** $RCOO^- + H^+ \rightleftharpoons RCOOH$ shifts to the left Accept the ratio [RCOOH] : $[RCOO^-]$ does not change (significantly) Ignore reference to pH change Allow Use of RCOOH and $RCOO^-$ OR acid and salt for [RCOOH] and $[RCOO^-]$ For **M2** and **M3**: Just 'acid reacts with $RCOO^-$ and alkali reacts with RCOOH' scores (1)	**(4)**

Question number	Answer	Additional guidance	Mark
21(c)(ii)	• calculation of $[H^+]$ (1) • rearrangement of K_a equation (1) • substitution of values **and** calculation of $[RCOO^-]$ = moles required (1) OR Use of Henderson-Hasselbalch • quotation of equation (1) • substitution of values (1) • calculation of $[RCOO^-]$ = moles required (1)	Example of calculation $[H^+] = 10^{-3.71} = 1.9498 \times 10^{-4}$ (mol dm^{-3}) $[RCOO^-] = \frac{K_a \times [RCOOH]}{[H^+]}$ $[RCOO^-] = \frac{1.55 \times 1.38 \times 10^{-4}}{1.9498 \times 10^{-4}}$ = 1.0970 / 1.10 /1.1 (mol / mol dm^{-3}) $pH = pK_a + \log \frac{[RCOO^-]}{[RCOOH]}$ Ignore round brackets or no brackets $3.71 = 3.86 + \log \frac{[RCOO^-]}{1.55}$ $[RCOO^-]$ = 1.0970 / 1.10 /1.1 (mol / mol dm^{-3}) Henderson-Hasselbalch equation with acid and salt concentration reversed gives 2.19 mol scores (2) Correct answer with some working scores (3)	**(3)**

(Total for Question 21 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS

TOTAL FORPAPER = 90 MARKS

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