Mark Scheme (SAM)

Pearson Edexcel International Advanced Level in Chemistry

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry

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.
- Mark schemes will indicate within the table where, and which strands of Quality of Written Communication, are being assessed. The strands are as follows:
    i. ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear
    ii. select and use a form and style of writing appropriate to purpose and to complex subject matter
    iii. organise information clearly and coherently, using specialist vocabulary when appropriate.

Using the Mark Scheme

Examiners should NOT give credit for incorrect or inadequate answers, but allow 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 still be creditworthy.

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.
Bold	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)(transfer error)(consequential) 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. 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 that involve the writing of continuous prose require 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 Quality of Written Communication is likely to be particularly important are indicated (Quality of Written Communication) in the mark scheme, but this does not preclude others.

Section A

Question Number	Answer	Mark
1(a)	C	(1)
1(b)	A	(1)

Question Number	Answer	Mark
2	B	(1)

Question Number	Answer	Mark
3	C	(1)

Question Number	Answer	Mark
4(a)	B	(1)
4(b)	D	(1)

Question Number	Answer	Mark
5(a)	B	(1)
5(b)	C	(1)
5(c)	B	(1)

Question Number	Answer	Mark
6	A	(1)

Question Number	Answer	Mark
7	A	(1)

Question Number	Answer	Mark
8	C	(1)

Question Number	Answer	Mark
9	A	(1)

Question Number	Answer	Mark
10	A	(1)

Question Number	Answer	Mark
11	D	(1)

Question Number	Answer	Mark
12	B	(1)

Question Number	Answer	Mark
13	B	(1)

Question Number	Answer	Mark
14	C	(1)

Question Number	Answer	Mark
15	D	(1)

Question Number	Answer	Mark
16	D	(1)

Total for Section A = 20 Marks

Section B

Question Number	Acceptable Answer	Reject	Mark
17(a)	Units are not required in (a) or (c) but if used should be correct. Penalise incorrect units in (a), (b) and (c) once only. IGNORE Case of J and K. Order of units. **First mark:** 65.3/130.6 **and** 69.9 (J mol^{-1} K^{-1}) **(1)** **Second mark:** ΔS = 69.9 - (130.6 + 102.5) **(1)** **Third mark:** ΔS = -163.2 = - 163 (J mol^{-1} K^{-1}) **(1)** Correct answer with no working scores 3 IGNORE SF except 1 SF TE at each stage. If 65.3 used instead of 130.6 penalise once (answer is then ΔS = - 97.9 (J mol^{-1} K^{-1}).	+163 or any positive answer	**(3)**

Question Number	Acceptable Answer	Reject	Mark
17(b)	$\Delta S_{surroundings}$ = - ΔH/T or just numbers **(1)** = +285800/298 = +959.06 = +959 J mol^{-1} K^{1}/ +0.959 kJ $mol^{-1}K^{-1}$ Correct value to 3SF. **(1)** Correct units and positive sign. **(1)** Correct answer with no working scores 3.	Answer with no sign	**(3)**

Question Number	Acceptable Answer	Mark
17(c)	$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ **(1)** Allow $\Delta S_{reaction}$ for ΔS_{system} ΔS_{total} = answer (a) + answer (b) = -163.2 + 959 = (+)795.8 = (+)796 (J mol^{-1} K^{-1}) If $\Delta S_{surroundings}$=+959.06 then ΔS_{total} = +795.9 **(1)** Correct answer with no working scores 2. Ignore SF except 1 SF. TE on values in (a) and (b). No TE on incorrect equation. If answer to (a) = -97.9 (J mol^{-1} K^{-1}) ΔS_{total} = (+)861.1 (J mol^{-1} K^{-1})	**(2)**

Question Number	Acceptable Answer	Reject	Mark
17(d) Quality of Written Communication	A mixture of hydrogen and oxygen is **thermodynamically** unstable **because** ΔS_{total} is positive. OR Reaction between hydrogen and oxygen is **thermodynamically** feasible **because** ΔS_{total} is positive. ALLOW ΔS for ΔS_{total} **(1)** No TE on negative ΔS_{total} from (c). The mixture is kinetically inert /stable or reaction is (very) slow **because** the activation energy is (very) high. **(1)** Mixture/reaction is **kinetically** inert/stable but **thermodynamically** unstable/feasible scores 1 mark. IGNORE References to spark/flame providing the (activation) energy for reaction.	Reference to the stability of individual elements	**(2)**

Total for Question 17 = 10 Marks

Question Number	Acceptable Answer	Mark
18(a)(i)	$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$ (or →) ALLOW $H_2O(aq)$ Equation **(1)** states **(1)** ALLOW for 1 mark. $HC_2O_4^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + H^+(aq)$ States mark is not stand-alone but can be awarded if the equation has a minor error, e.g. an incorrect charge.	**(2)**

Question Number	Acceptable Answer	Reject	Mark
18(a)(ii)	$K_a = [C_2O_4^{2-}]\,[H_3O^+]/[HC_2O_4^-]$ OR $K_a = [C_2O_4^{2-}]\,[H^+]/[HC_2O_4^-]$ No TE on incorrect equation in (a)(i). Penalise incorrect charges in (i) and (ii) once only.	$K_a = [H^+]^2/[HC_2O_4^-$ $[H^+][A^-]/[HA]$	**(1)**

Question Number	Acceptable Answer	Mark
18 (a)(iii)	No TE on (a)(ii) $K_a = 10^{-4.28}$ OR 5.24807×10^{-5} (mol dm^{-3}) **(1)** $K_a = [H^+]^2/[HC_2O_4^-]$ $K_a = [H^+]^2/0.050$ $[H^+] = \sqrt{(0.05 \times 10^{-4.28})} = 1.61988 \times 10^{-3}$ (mol dm^{-3}) **(1)** TE on incorrect K_a value. pH = -log 1.61988×10^{-3} = 2.7905 = 2.8 **(1)** For final mark TE on algebraic/arithmetical errors providing pH ≥ 1..3 Correct answer with no working scores 3. IGNORE SF except 1 SF.	**(3)**

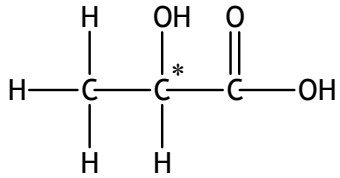
Question Number	Acceptable Answer	Reject	Mark
18(b)(i)	IGNORE explanations. **First mark:** $HC_2O_4^-$/hydrogenethanedioate ion ionization negligible. ALLOW Acid for $HC_2O_4^-$. Slight/partial/incomplete/does not dissociate for negligible. OR $[HC_2O_4^-]_{equilibrium} = [HC_2O_4^-]_{initial}/0.050$ ($mol\ dm^{-3}$) **(1)** **Second mark:** $[H^+]$ due to ionization of water negligible OR auto ionization of water negligible OR $[H^+]$ only due to ionization of $HC_2O_4^-$/acid OR $[C_2O_4^{2-}] = [H^+]$ **(1)** IGNORE references to temperature and to HA and A^-. Penalise omission of [] in discussion once only.	Use of $NaHC_2O_4$ for $HC_2O_4^-$ OR Sodium hydrogen-ethanedioate for hydrogen-ethanedioate ion throughout this item	**(2)**

Question Number	Acceptable Answer	Reject	Mark
18(b)(ii) Quality of Written Communication	**First mark:** Ethanedioic acid is a (much) stronger acid (than hydrogenethanedioate ion/sodium hydrogenethanedioate). OR Ethanedioic acid has a (much) smaller pK_a (than hydrogenethanedioate). OR Ionization/dissociation of ethanedioic acid is (much) greater (than hydrogenethanedioate). OR Reverse arguments. IGNORE $NaHC_2O_4$ ionization negligible. **Second mark:** Approximation of negligible ionization invalid/incorrect. OR $[H_2C_2O_4]_{equilibrium}$ not equal to $[H_2C_2O_4]_{initial}$ No TE on 18(a)(iii). IGNORE Second ionization occurs.	Ethanedioic acid is a strong acid/ fully dissociated Just 'approximation invalid'	**(2)**

Question Number	Acceptable Answer	Reject	Mark
18(c)(i)	Start pH at 2.8 ALLOW 2-4 **(1)** Vertical section at 25 cm^3 within pH range 6-11 and 2.5-4 units long. **(1)** End pH (approaching) value in range 12-13 (asymptotically). **(1)**	Deviation from vertical Maximum before final pH	**(3)**

Question Number	Acceptable Answer	Mark
18(c)(ii) Quality of Written Communication	**First mark:** Methyl yellow range = 2.9-4 and the phenolphthalein range = 8.2-10. ALLOW pK_{in} (methyl yellow) = 3.5 and pK_{in} (phenolphthalein) = 9.3. **(1)** **Second mark:** (The volumes are different) because ethanedioic acid is dibasic/diprotic/has two **replaceable/acidic** hydrogen atoms. ALLOW dicarboxylic (acid) (therefore there are two stages to the neutralization). OR Methyl yellow range coincides with neutralization of first proton and phenolphthalein range coincides with neutralization of second proton. **(1)**	**(2)**

Total for Question 18 = 15 Marks

Question Number	Acceptable Answer	Reject	Mark
19(a)(i)	A chiral molecule is non-superimposable on its mirror image/3D molecule with no plane of symmetry. **(1)** 2-hydroxypropanoic acid has a carbon atom which is asymmetric/has **four** different groups attached. **(1)** **Middle** carbon labelled in any clear way. **(1)** e.g.  ALLOW asymmetric C described but not labelled. IGNORE references to rotation of plane polarized light.	Just 'non-superimposable' Just 'no plane of symmetry' Molecules for groups	**(3)**

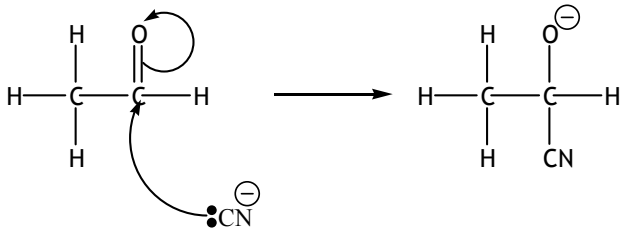
Question Number	Acceptable Answer	Reject	Mark
19(a)(ii)	2-hydroxypropanoic acid formed in muscles is a single (allow pure) enantiomer/(optical) isomer. ALLOW Unequal mixture of enantiomers/(optical) isomers. **(1)** 2-hydroxypropanoic acid formed in milk is a racemic mixture/equimolar mixture of the two enantiomers/racemate. **(1)** If milk and muscles are reversed but the rest is correct, one mark is awarded.	Just 'not a racemic mixture' Just 'a mixture of enantiomers'	**(2)**

Question Number	Acceptable Answer	Reject	Mark
19(b)(i)	**First step** NaOH(aq)/KOH(aq) or names **(1)** Second mark dependent on first being correct. **Second step** HCl(aq)/hydrochloric acid/H_2SO_4(aq)/sulfuric acid ALLOW HNO_3/nitric acid/dil HCl/(dil) H_2SO4/(dil) HNO_3 or any strong acid (name or formula) including HBr((aq)) and HI((aq)). **(1)** IGNORE Omission of (aq) and references to temperature. Ethanolic alcoholic solutions. ALLOW One mark for correct two reagents in the wrong order. One mark for 'alkali/OH^- followed by acid/H^+/H_3O^+'.	OH^-/alkali H^+/H_3O^+/acid	**(2)**

Question Number	Acceptable Answer	Reject	Mark
19(b)(ii)	**First mark:** (stand-alone) A racemic mixture is not formed. OR More of one enantiomer/(optical) isomer is formed. OR Only one enantiomer/(optical) isomer is formed. **(1)** **Second mark:** (stand-alone) (Some of the) reaction is S_N2. **(1)** **Third mark:** (stand-alone) Nucleophile/OH^- only attacks from one side of the molecule/from the opposite side to leaving group. **(1)** ALLOW Use of 'intermediate' for 'transition state' in description of S_N2. Reverse argument based on S_N1 forming a racemic mixture.	Carbocation (for molecule)	**(3)**

Question Number	Acceptable Answer	Reject	Mark
19(c)(i)	Nucleophilic **(1)** Addition **(1)**	S_N1/S_N2	**(2)**

Question Number	Acceptable Answer	Reject	Mark
19(c)(ii)	Cyanide (ion)/CN^- /$C\equiv N^-$/$:C\equiv N^-$/^-CN	HCN/ $C\equiv N$	**(1)**

Question Number	Acceptable Answer	Reject	Mark
19(c) (iii)	 Both curly arrows. **(1)** Intermediate **(1)** ALLOW Omission of lone pair. Curly arrow from anywhere on nucleophile including from charge or nitrogen. Formation of charged canonical form followed by attack of cyanide ion. IGNORE δ+/δ- even if unbalanced.	Omission of charges (penalise once only) Full charges on ethanal –C–NC in inter-mediate	**(2)**

Question Number	Acceptable Answer	Reject	Mark
19(c) (iv) Quality of Written Communication	Racemic mixture/equal amounts of the two enantiomers/racemate formed. **(1)** Stand-alone mark. CHO/aldehyde group is (trigonal) planar. **(1)** ALLOW ethanal/molecule is (trigonal) planar. Cyanide (ion)/CN^-/nucleophile attacks (equally) from above or below/either side (of the molecule). **(1)** Penalise use of intermediate/ion for aldehyde group **once** only. Third mark cannot be awarded if the reaction is described as a nucleophilic substitution.	Intermediate/ carbonyl group/CO is planar Two positions Intermediate	**(3)**

Question Number	Acceptable Answer	Reject	Mark
19(d)(i)	Any value/range within the range 3750-2500 cm^{-1} due to O–H/OH/–OH. IGNORE COOH/CO_2H/carboxylic acid.	Wavenumbers alone OH in alcohol	**(1)**

Question Number	Acceptable Answer	Reject	Mark
19(d)(ii) Quality of Written Communication	These three marks are stand-alone. Q is due to C=O. **(1)** The (C=O) aldehyde range is 1740-1720 cm^{-1} **and** (C=O) carboxylic acid range is 1725-1700 cm^{-1} **(1)** So the peaks/absorptions cannot be used to distinguish these two compounds because they overlap. OR The (broad) absorption Q covers both the aldehyde and the carboxylic acid. ranges **(1)** ALLOW 'too close'/'quite similar' for 'overlap'.	Carboxylic acid/COOH group Just 'cannot be used to distinguish the compounds'	**(3)**

<table>
<tr><th>Question Number</th><th>Acceptable Answer</th><th>Reject</th><th>Mark</th></tr>
<tr><td>19(e)</td><td>
If reagent incorrect, observation mark can only be awarded for a near miss.

Test positive for ethanol
<table>
<tr><th>Reagent (1)</th><th>Observation (1)</th></tr>
<tr><td>Tollens’</td><td>Silver mirror/black /grey ppt</td></tr>
<tr><td>Fehling’s/ Benedict’s</td><td>Red-brown ppt</td></tr>
<tr><td>2,4-DNP(H)/Brady’s reagent</td><td>Orange/red/yellow ppt
ALLOW brick-red ppt</td></tr>
</table>
Test positive for 2-hydroxypropanoic acid
<table>
<tr><th>Reagent(1)</th><th>Observation(1)</th></tr>
<tr><td>PCl_5/Phosphorus (V)chloride/ phosphorus pentachloride</td><td>Steamy fumes*
ALLOW gas evolved turns (blue) litmus/UI red</td></tr>
<tr><td>Named metal carbonate (solution)</td><td>Effervescence
ALLOW gas/CO_2 evolved turns lime water cloudy</td></tr>
<tr><td>Sodium hydrogencarbonate (solution)</td><td>Effervescence
ALLOW gas/CO_2 evolved turns lime water cloudy</td></tr>
<tr><td>Magnesium (and water)</td><td>Effervescence</td></tr>
<tr><td>Ethanol and H_2SO_4/named strong acid</td><td>Sweet/fruity/pear drops/glue smell</td></tr>
<tr><td>Ethanoic acid and H_2SO_4/named strong acid</td><td>Sweet/fruity/pear drops/glue smell</td></tr>
</table>
ALLOW
Na and effervescence/gas evolved pops with a lighted splint for2-hydroxypropanoic acid.
(2)
ALLOW fizzing/bubbling for effervescence.

IGNORE names of product.

IF two tests given for one substance both must be correct for full marks.
*misty fumes/white fumes/gas for fumes
</td><td>
Iodine in alkali/iodoform test

Acidified potassium dichromate

Smoke
Just ‘fumes’

Any indicator as sole test

Incorrect formulae of reagents
</td><td>(4)</td></tr>
</table>

Total for Question 19 = 26 Marks

Total for Section B = 51 Marks

Section C

Question Number	Acceptable Answer	Reject	Mark
20(a)(i)	(Sodium thiosulfate) (rapidly) reacts with/reduces the iodine (as it is formed) **(1)** So prevents the starch-iodine colour appearing until a fixed amount of reaction has occurred. ALLOW (for second mark) So prevents the starch-iodine colour appearing until all the thiosulfate has reacted. OR Moles of iodine reacted/thiosulfate ÷ time is (approximately) proportional to the (initial) rate of reaction. **(1)** ALLOW Use of 'thio' for thiosulfate.	Iodide/I^-	**(2)**

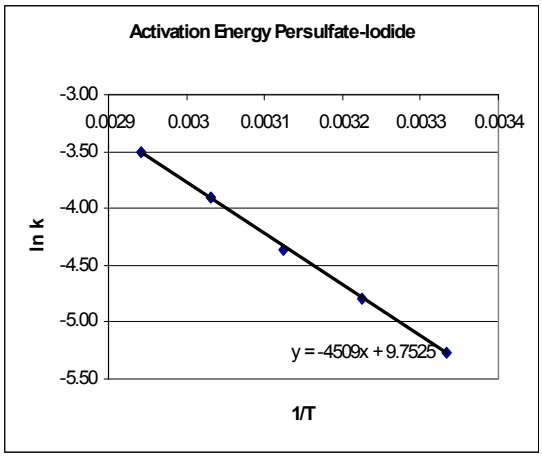
Question Number	Acceptable Answer	Reject	Mark
20(a)(ii)	(From 2 to 1) **[$S_2O_8^{2-}$]** doubles ([I^-] unchanged) and rate doubles/time halves so order wrt **$S_2O_8^{2-}$** = 1 **(1)** (From 3 to 1) **[I^-]** doubles ([**$S_2O_8^{2-}$**] unchanged) and rate doubles/time halves so order **wrt I^-** = 1 OR (if first mark awarded) (From 3 to 2) **[I^-]** doubles ([**$S_2O_8^{2-}$**] halved) and rate unchanged so order **wrt I^-** = 1 **(1)** Penalise omission of concentration/square brackets once only. Rate = $k[S_2O_8^{2-}][I^-]$ **(1)** Third mark stand-alone if no working and TE on incorrect orders. IGNORE case of k.	Rate equation =	**(3)**

Question Number	Acceptable Answer	Reject	Mark
20(b)(i)	**First mark:** Colorimetry/Use a colorimeter. **(1)** **Second mark:** Measure transmittance/absorbance (at various times). **(1)** **Third mark:** (Use a calibration curve to) convert transmittance/absorbance into concentration. OR Transmittance/absorbance proportional to concentration. ALLOW Colorimetry may be used because iodine (solution) is coloured (and other reagents are colourless)/to measure intensity of the iodine colour. **(1)** ALLOW (for the same three marks) Electrical conductivity. Measured at various times/(use a calibration curve to) convert conductivity into concentration. Conductivity reduces as reaction proceeds because 3 mol ions converted to 2 mol ions /fewer ions on right-hand side.	Sampling methods calorimeter pH meter Just conductivity changes	**(3)**

Question Number	Acceptable Answer	Reject	Mark
20(b)(ii)	$[(NH_4)_2S_2O_8]$ / $[S_2O_8^{2-}]$/[peroxodisulfate]/[persulfate] remains (approximately) unchanged during the reaction. OR $[KI]/ I^-]$ is the only variable.	$(NH_4)_2S_2O_8$ in excess. $[(NH_4)_2S_2O_8]$ etc does not affect the rate Only $[KI]/[I^-]$ affects the rate	**(1)**

Question Number	Acceptable Answer	Mark
20(b) (iii)	Plot a graph of concentration (of iodine/I_2) (on the y axis) against time. **(1)** Measure the initial gradient/gradient at t=0. **(1)** 'Plot a graph and measure the initial gradient/gradient at t=0' alone scores second mark.	**(2)**

Question Number	Acceptable Answer	Reject	Mark
20(b) (iv)	TE on 20(a)(ii) on numerical answer and appropriate units. $8.75 \times 10^{-5} = k \times 2.0 \times 0.025$ $k = 8.75 \times 10^{-5}/(2.0 \times 0.025)$ $= 1.75 \times 10^{-3}$ **(1)** $dm^3\ mol^{-1}\ s^{-1}$ **(1)** ALLOW units in any order. Correct answer including units with no working scores 2.	1 SF	**(2)**

Question Number	Acceptable Answer	Mark
20(c)(i)	 Use the overlay to mark the graph. At least 4 points within the circles on the overlay. **(1)** Best fit line on points given. **(1)**	**(2)**

Question Number	Acceptable Answer	Mark
20(c)(ii)	Gradient = -(-3.50 - -5.27)/ (0.00333 - 0.00294) = (-)4538 = (-)4500 ALLOW Values from (-)4300 to (-)4700. **(1)** Gradient value negative. **(1)** E_a = -gradient x R = - -4538 x 8.31 = (+)37700 J mol^{-1} (= (+)38 kJ mol^{-1}) **(1)** TE on value of gradient even if it is positive -4300 gives 35.7; -4700 gives 39.1 Correct units. **(1)** Correct answer from the gradient calculation with units scores final 2 marks. **BUT** correct answer with units but no gradient calculation scores units mark only.	**(4)**

Total for Section C = 19 Marks

Total for Paper = 90 Marks