

General Certificate of Education (A-level) June 2012

Chemistry

CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for standardisation each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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Question		Marking (Guidance	Mark	Additional Guidance
1(a)(i)	mol $H_2 = 0.47$ mol $I_2 = 0.17$			1	If answers reversed, ie mol $H_2 = 0.17$ mol $I_2 = 0.47$ then allow one mark (for second answer).
1(a)(ii)	$\frac{[HI]^2}{[H_2][I_2]}$	Penalise expre But mark on in	ssion containing V (a)(iv)	1	Penalise missing square brackets in this part (and not elsewhere in paper) but mark on in (a)(iv)
1(a)(iii)	equal number of moles (on each side of equation) OR equal moles (top and bottom of Kc expression)				
1(a)(iv)	$\frac{[1.94]^2}{[0.38][0.19]}$ = 52(.1)		Ignore V	1	If Kc wrong in (a)(ii) (wrong powers or upside down etc) no marks here
1(b)(i)	D			1	
1(b)(ii)	В			1	
1(b)(iii)	Α			1	
1(b)(iv)	С		-	1	

Question	Marking Guidance	Mark	Additional Guidance
2(a)	Exp 2 4.5×10^{-4} Exp 3 4.5×10^{-3} Exp 4 0.043 OR 4.3×10^{-2} OR 0.044 OR 4.4×10^{-2}	1 1 1	Min 2sf If three wrong answers, check their value of k in 2(b). They can score all 3 if they have used their (incorrect) value of k . see below.
			Exp 2 rate = $k \times (1.0125 \times 10^{-4})$ Exp 3 [Q] = $0.02/k$ Exp 4 [P] = $0.0913/\sqrt{k}$
2(b)	$k = \frac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$	1	Mark is for insertion of numbers into a correctly rearranged rate equ, $k = \text{etc}$ If upside down, score only units mark from their k AE (-1) for copying numbers wrongly or swapping two numbers
	= 4.4(4) (allow 40/9)	1	
	mol ⁻² dm ⁺⁶ s ⁻¹	1	Any order If <i>k</i> calculation wrong, allow units conseq to their <i>k</i> expression

Question		Marking Guidance	Mark	Additional Guidance
3(a)	Prot	on donor or H ⁺ donor	1	Allow donator
3(b)(i)	ВВ		1	Both need to be correct to score the mark
3(b)(ii)	A A		1	Both need to be correct to score the mark
3(b)(iii)	ВА		1	Both need to be correct to score the mark
3(c)	M1 M2 M3	[H ⁺] = $10^{-1.25}$ OR 0.05623 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ (= 2.125×10^{-3}) vol (= $\frac{2.125 \times 10^{-3}}{0.05623}$) = 0.0378 dm ³ or 37.8 cm ³ allow $0.0375 - 0.038$ dm ³ or $37.5 - 38$ cm ³	1 1 1	Mark for Working Units and answer tied Lose M3 if total given as (25+ 37.8) = 62.8 cm ³ Ignore "vol added = 12.8cm ³ " after correct answer
3(d)(i)	4.52		1	Must be 2dp
3(d)(ii)	Ka	= $\frac{[H^+][X^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in d(iii)	1	Must have all brackets but allow () Allow HA etc NO mark for 10 ^{-pKa}
3(d)(iii)	M2	$K_{a} = \frac{[H^{+}]^{2}}{[HX]} \text{ or with numbers}$ $[H^{+}] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$ $= 2.29 \times 10^{-3} - 2.3 \times 10^{-3}$ $pH = 2.64 \text{ (allow more than 2dp but not fewer)}$	1 1 1	Allow [H ⁺] = √(Ka × [HA]) for M1 Mark for <u>answer</u> Allow 1 for correct pH from their wrong [H ⁺] If square root forgotten, pH = 5.28 scores 2 for M1 and M3

3(e)	M1	mol OH ⁻ = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$	1	Mark for answer
	M2	orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{-3}$	1	Mark for answer
	M3	mol HX in buffer = orig mol HX – mol OH ⁻ = $2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$ ([HX] = $1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)	1	Mark for answer Allow conseq on their (M2 – M1) If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20) If $[H^+] = [X^-] \& \sqrt{\text{used}}$, max 3 for M1, M2 & M3 (pH = 2.89)
	M4	mol X ⁻ in buffer = mol OH ⁻ = 1.25×10^{-3} ([X ⁻] = $1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)	1	May be scored in M5 expression
	M5	$[H^{+}] \left(= \frac{\text{Ka x } [HX]}{[X^{-}]} \right)$ $= \frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}} \text{OR} \frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$ $(= 3.27 \times 10^{-5})$	1	If use $K_a = \frac{[H^+]^2}{[HX]}$ no further marks If either value of HX or X^- used wrongly or expression upside down, no further marks
	M6	pH = 4.48 or 4.49 (allow more than 2dp but not fewer)	1	Do not allow M6 for correct calculation of pH using their [H ⁺] - this only applies in 3d(iii) - apart from earlier AE

Question	Marking Guidance	Mark	Additional Guidance
4(a) 4(b)(i)	M2 (CH ₃ CH ₂) (CH ₃ CH ₂)	4 1	 M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than δ+ on C=O loses M2 If CI lost with C=O breaking, max1 for M1 M3 for correct structure with charges but Ip on O is part of M4 only allow M4 after correct/very close M3 ignore CI⁻ removing H⁺ Second 'e' and numbers needed
4(0)(1)	pentan <u>e-1,5</u> -dioi	<u>'</u>	Allow 1,5-pentanediol but this is not IUPAC name
4(b)(ii)		1	Must show ALL bonds
4(b)(iii)	All three marks are independent M1 (base or alkaline) Hydrolysis (allow close spelling) M2 <u>δ+ C</u> in polyester M3 reacts with OH ⁻ or hydroxide ion	1 1 1	Allow (nucleophilic) addition-elimination or saponification Not reacts with NaOH
4(c)(i)	СН ₃ —С ОН	1	Allow CH ₃ COOH or CH ₃ CO ₂ H

4(c)(ii)	(nucleophilic) addition-elimination OR (nucleophilic) addition followed by elimination	1	Both addition and elimination needed and in that order Do not allow electrophilic addition-elimination / esterification Ignore acylation
4(c)(iii)	any two from: ethanoic anhydride is • less corrosive • less vulnerable to hydrolysis • less dangerous to use, • less violent/exothermic/vigorous reaction OR more controllable rxn • does not produce toxic/corrosive/harmful fumes (of HCI) OR does not produce HCI • less volatile	2 max	NOT COST List principle beyond two answers
4(d)	C-OCH ₃	1	Allow COOCH ₃ or CO ₂ CH ₃ CO ₂ H
4(e)(i)	ester	1	Do not allow ether Ignore functional group/linkage/bond
4(e)(ii)	12 or twelve (peaks)	1	

4(e)(iii)	160 – 185		1	Allow a number or range within these limits Penalize extra ranges given Ignore units				
4(f)(i)	sulfuric acid sodium hydroxide $\sqrt{}$				4 correct scores 2			
	hydrochloric acid	ammonia	X or blank		3 correct scores 1			
	ethanoic acid potassium hydroxide √				2 or 1 correct scores 0			
	nitric acid	methylamine	X or blank					
4(f)(ii)	Pink to colourless				Allow 'red' OR 'purple' OR 'magenta' instead of 'pink' Do not allow 'clear' instead of 'colourless'			

Question	Marking Guidance	Mark	Additional Guidance
5(a)	nucleophilic addition M4 for lp and arrow to H ⁺ M2 CH ₃ CH ₂	4	 allow:CN⁻ M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than δ+ on C=O loses M2 M3 is for correct structure including minus sign but lone pair is part of M4 Allow C₂H₅ M1 and M4 for lp and curly arrow
5(b)	2-bromobutanenitrile	1	Allow 2-bromobutane-1-nitrile
5(c)	 M1 ammonia or NH₃ M2 excess (ammonia) excess tied to NH₃ and may score in M1 unless contradicted 	1 1 1	Ignore temp or pressure Ignore concentrated or sealed container, Acid loses conditions mark Allow close spelling
5(d)(i)	CH ₃ CH ₂ —C—H	1	Allow C ₂ H ₅ Allow –CO ₂ ⁻ Allow [†] NH ₃ – Don't penalize position of + on NH ₃
5(d)(ii)	 M1 electrostatic <u>forces between ions</u> in X QOL Marks independent M2 (stronger than) <u>hydrogen bonding</u> between CH₃CH₂CH(OH)COOH 	1	Allow ionic bonding. CE mention of molecules of X or inter molecular forces between X loses both marks

5(e)(i)	NH ₂ H—C—H COOCH ₂ CH ₃	1	Isomer of C ₄ H ₉ NO ₂ Allow NH ₂ —		
	OR CH ₃ H—N COOCH ₂ CH ₃				
5(e)(ii)	$\begin{array}{c c} CH_3 & NH_2 \\ CH_3 - C - C \\ OH \end{array}$	1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
5(e)(iii)	H ₂ N—CH ₂ CH ₂ CH ₂ —COOH or H ₂ N—(CH ₂) ₃ —COOH OR NH ₂ CH ₃ CHCH ₂ -COOH	1	Isomer of $C_4H_9NO_2$ allow NH_2- Do not allow $-C_3H_6-$ Beware – do not credit X itself		
5(f)	N(CH ₃) ₂ CH ₃ CH ₂ —C—H COOH	1	Answer has 6 carbons so NOT isomer of X Allow C_2H_5 Must have bond from C to N not to methyl group		

Question	Marking Guidance	Mark	Additional Guidance
6(a)	$CH_3COCI + AICI_3 \longrightarrow CH_3CO^+ + AICI_4^-$	1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	$AICI_4^- + H^+ \rightarrow AICI_3 + HCI$	1	
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	 M1 arrow from within hexagon to C or to + on C + must be on C of RCO in mechanism + in intermediate not too close to C1 gap in horseshoe must be centred approximately around C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H for M3 NO mark for name of mechanism
	Phenylethanone ignore 1 in name, penalise other numbers	1	Note: this is the sixth marking point in 6a
6(b)	o or co	1	+ must be on C But allow [C ₆ H ₅ CO] ⁺

6(c)	M1 about electrons	methyl group has (positive) inductive effect OR increases electron density on benzene ring OR pushes electrons OR is electron releasing		Ignore reference to delocalisation
	TIME STORY	electrophile attracted more or benzene ring better nucleophile	1	Allow intermediate ion stabilised M2 only awarded after correct or close M1

Question				Marking Guid	ance			Mark	Additional Guidance	
7(a)	If reagent is	If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br ₂ test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg AgCl ₂								
	propan-1-ol	M1	acidified potassium dichromate	sodium	Named acid + conc H ₂ SO ₄	named acyl chloride	PCI₅	1		
		M2	(orange) turns green	effervescence	Sweet smell	Sweet smell /misty fumes	Misty fumes	1		
	propanal	МЗ	add Tollens or Fehlings / Benedicts	acidified potassium dichromate	Bradys or 2,4- dnph			1	if dichromate used for alcohol cannot be used for aldehyde	
		M4	Tollens: silver mirror or Fehlings/ Benedicts: red ppt	(orange) turns green	Yellow or orange ppt			1		
	propanoic	M5	Named carbonate/ hydrogencarbonate	water and UI (paper)	Named alcohol + conc H ₂ SO ₄	sodium or magnesium	PCI ₅	1	if sodium used for alcohol cannot be used for acid	
	acid	M6	effervescence	orange/red	Sweet smell	effervescence	Misty fumes	1	if PCI₅ used for alcohol cannot be used for acid	
	1-chloro propane	M7	NaOH then acidified AgNO ₃	AgNO ₃				1	If acidification missed after NaOH, no mark here but allow mark for observation	
		M8	white ppt	white ppt				1		

7(b)	M1 oxidation (of alcohol by oxygen in air)	1	
	M2 absorption at <u>1680 -1750</u> (due to C=O)	1	Must refer to the spectrum
	M3 – comparison of polarity of molecules or correct imf statement:		
	propanone is less polar OR propan-2-ol is more polar	1	
	OR propanone has dipole-dipole forces		
	OR propan-2-ol has hydrogen bonding		
	M4 - about attraction to stationary phase or solubility in moving phase		
	Propan-2-ol has greater affinity for stationary phase or vice versa	1	
	OR propanone is more soluble in solvent/moving phase or vice versa		
	1		

Question	Marking (Guidance	Mark	Additional Guidance
8(a)	F	G		
	O_2N NO_2	NO ₂	1, 1	Penalize $-O_2N$ once Penalise missing circle once Don't penalise attempt at bonding in NO_2
8(b)	H J			
	H_3C $C=C$ CH_3 CH_3		1, 1	If both H and J correct but reversed, award one mark
A carbon in saturated ring structures should be shown as H H OR OR OR OR OR			H_2	

Question	Marking	Guidance	Mark Additional Guidano	
8(c)	К	L		
	o	O H	1, 1	
	OR O	OR		
	H ₃ C CH ₃	H ₃ C O		
	OR	H ₃ C		
	H ₃ C O			
8(d)	М	N		
	${\rm CH_3CH_2}$ ${\rm CH_2CH_3}$ ${\rm CH_2CH_3}$ ${\rm OR}$	CH ₃ CH ₃	1, 1	Allow C ₂ H ₅ but NOT allow C ₄ H ₉ or C ₃ H ₇
	CH_3 $C(CH_3)_3$	H ₃ C—C—N—C—CH ₃ H H H		

General principles applied to marking CHEM4 papers by CMI+ (June 2012)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.
- Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.

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A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip. For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (QoL) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

D. Equations

In general

- Equations must be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.

For example, **no credit** would be given for

- the cyanide ion or CN⁻ when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH⁻ when the reagent should be sodium hydroxide or NaOH;
- the Ag(NH₃)₂⁺ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

G. Marking calculations

In general

- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.

The following representations should not gain credit and will be penalised each time within a clip.

$$H_3C$$
 \longrightarrow H_3C \longrightarrow H_3C \longrightarrow Br H_3C \longrightarrow Br \longrightarrow OH

For example, the following would score zero marks

When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g. nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C C bonds in alkyl groups, given that CH₃— is considered to be interchangeable with H₃C— even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH₂— C will be allowed, although H₂N— C would be preferred.
- Poor presentation of vertical C CH₃ bonds or vertical C NH₂ bonds should **not** be penalised. For other functional groups, such as OH and CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group. By way of illustration, the following would apply.

CH ₃ -C	C CH ₃	——C—— CH ₃ CH ₂	OH—C——	С ОН
allowed	allowed	not allowed	not allowed	not allowed
NH ₂ -C	C NH ₂	NH ₂	NH ₂	NO ₂
allowed	allowed	allowed	allowed	not allowed

CN———	C	соон—с—	—С— СООН	с	
not allowed					
сно—с—	C CHO	C CHO	COCI————	c	
not allowed					

- In most cases, the use of "sticks" to represent C H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH₃COH	for	ethana
CH ₃ CH ₂ HO	for	ethanol
OHCH ₂ CH ₃	for	ethanol
C ₂ H ₆ O	for	ethanol
CH ₂ CH ₂	for	ethene
CH ₂ .CH ₂	for	ethene
CH ₂ :CH ₂	for	ethane

N.B. Exceptions may be made in the context of balancing equations

• Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
CH ₃ CHOHCH ₃	for	propan-2-ol, CH ₃ CH(OH)CH ₃

J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit. Some illustrations are given here.

but-2-ol should be **butan-2-ol**2-hydroxybutane should be **butan-2-ol**butane-2-ol should be **butan-2-ol**2-butanol should be **butan-2-ol**

ethan-1,2-diol should be **ethane-1,2-diol**

2-methpropan-2-ol should be 2-methylpropan-2-ol 2-methylbutan-3-ol should be 3-methylbutan-2-ol 3-methylpentan should be 3-methylpentane 3-mythylpentane should be 3-methylpentane should be 3-methylpentane propanitrile should be propanenitrile

aminethane should be **ethylamine** (although aminoethane can gain credit)

2-methyl-3-bromobutane should be **2-bromo-3-methylbutane** 3-bromo-2-methylbutane should be **2-bromo-3-methylbutane** should be **2-bromo-3-methylbutane**

2-methylbut-3-ene should be **3-methylbut-1-ene**

difluorodichloromethane should be dichlorodifluoromethane