General Certificate of Education (A-level) January 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.

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Question	Marking Guidance	Mark	Comments
1(a)	Exp 2 14.(4) ×10 ⁻³ OR 1.4(4) ×10 ⁻² or 0.014 Exp 3 0.1(0) Exp 4 0.3(0)	1 1 1	Allow 2sf If three wrong answers, check their value of k in 1(b). They can score all 3 if they have used their (incorrect) value of k . see below. Exp 2 rate = $0.096 \times k$ Exp 3 [Q] = $0.015/k$ Exp 4 [P] = $0.116/\sqrt{k}$
1(b)	$k = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$ = 0.15 (min 2sfs) (allow $\frac{3}{20}$) $mol^{-2} dm^{+6} s^{-1}$	1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, score only units mark AE (-1) for copying numbers wrongly or swapping two numbers Any order If k calculation wrong, allow units conseq to their k
1(c)	G	1	

Question	Marking Guidance			Mark	Commo	ents	
2(a)(i)	Mol $SO_3 = 5.2$ Mol $SO_2 = 2.8$			1 1			
2(a)(ii)	$\frac{[SO_2]^2[O_2]}{[SO_3]^2} \qquad \begin{array}{c} \text{Penalise expression containing numbers or V} \\ \text{Ignore subsequent } \underline{\text{correct}} \text{ working} \end{array}$			1	Allow () but must have all bra but otherwise correct, penalis If Kc wrong (wrong powers o only score M1 in 2(a)(iv)	e here but mark on	
2(a)(iii)	mol dm ⁻³			1	Allow conseq to their wrong	Кс	
						If Kc wrong in 2(a)(iv) (wrong etc) can only score M1	powers or upside down
2(a)(iv)	Values from (a)(1) [2.8/12] ² [1.4/12 [5.2/12] ² [0.233] ² [0.117] [0.433] ²	,	Alternative values [2.1/12] ² [1.4/12] [5.8/12] ²	M1 M2	1	For dividing all three by volumused wrongly, lose M1 & M2 I insertion of values (allow consvalues from 2a(i)) AE (-1) for copying numbers numbers	out can score M3 conseq seq use of their wrong
	= 0.0338 or 0.0 (allow 0.03376 to Min 2 sfs Ignore units in (a	0.035)	0.0153 or 0.015 (allow 0.015 to 0.017) Min 2 sfs Ignore units in (a)(iv)	M3	1	If vol missed score only M3 Values from (a)(i) 0.406 - allow values between 0.40 (if correctly rounded) and 0.41	from alternative values allow 0.18 to 0.184

2(b)(i)	Increase or more moles (of oxygen) or higher			
2(b)(ii)	No change or no effect or none or (remains) same			
2(c)	T ₁ (At Temp,T ₂ , when Kc is lower) Equm/reaction moves to left or towards reagent or towards SO ₃ OR moles SO ₃ increases This reverse reaction is exothermic, OR (forward) reaction is endothermic if Temp is increased Equm/reaction moves to right or towards product or towards SO ₂ OR moles SO ₂ increases OR (forward) reaction is endothermic	M1 M2 M3 M3 M2	1 1 1	If T ₂ CE = 0
	if Temp is decreased Equm/reaction moves to left or towards reagent or towards SO ₃ OR moles SO ₃ increases	M2		

Question	Marking Guidance		Mark	Comments
3(a)	Proton acceptor		1	
3(b)(i)	$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ + OH^-$			allow eq with or without \Longrightarrow allow $C_2H_5NH_2$ and $C_2H_5NH_3^+$ (plus can be on N or H or 3) allow RHS as $C_2H_5NH_3OH$
3(b)(ii)	Mark independently of 3b(i) reaction/equilibrium lies to left or low [OH¯] <i>OR</i> little OH¯ formed <i>OR</i> little ethylamine has reacted	brium lies to left or low [OH ⁻] OR little OH ⁻ formed		Allow Ethylamine is only partly/slightly dissociated OR Ethylamine is only partly/slightly ionized Ignore "not fully dissociated" or "not fully ionized" Ignore reference to ionisation or dissociation of water
3(c)	Ethylamine alkyl group is electron releasing/donating OR alkyl group has (positive) inductive effect increases electron density on N(H ₂) OR increased availability of Ip OR increases ability of Ip (to accept H(+))	M1 M2 M3	1 1	If wrong no marks in 3c Mark M3 is independent of M2

3(d)	CH ₃ CH ₂ NH ₃ CI allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for CI	1	Or any amine hydrochloride or a strong organic acid NOT NH ₄ CI
3(e)	Mark independently of 3(d) Extra H^+ reacts with ethylamine or $OH^ OR$ $CH_3CH_2NH_2$ + H^+ \rightarrow $CH_3CH_2NH_3^+$	1	Or makes reference to Equilibrium (in 3(b)(i)) with amine on LHS
	OR H ⁺ + OH ⁻ \rightarrow H ₂ O Equilibrium shifts to RHS OR ratio [CH ₃ CH ₂ NH ₃ ⁺]/[CH ₃ CH ₂ NH ₂] remains almost constant	1	

Question	Marking Guidance			Comments
4(a)	$[H^{+}] = 0.0170$	M1	1	
	pH = 1.77	M2	1	2 dp
				Allow M2 for correct pH calculation from their wrong [H ⁺] for this pH calculation only
4(b)(i)	$K_a = \frac{[H^+][X^-]}{[HX]}$ Ignore $K_a = \frac{[H^+]^2}{[HX]}$		1	Penalize missing [] here and not elsewhere Allow HA instead of HX
4(b)(ii)	[H ⁺] = 10 ^{-2.79} OR 1.6218 ×10 ⁻³	M1	1	If [H ⁺] wrong, can only score M2
	$K_{a} = \frac{[H^{+}]^{2}}{[HX]}$ OR $\frac{[1.62 \times 10^{-3}]^{2}}{[0.0850]}$	M2	1	Allow HA instead of HX
	$K_a = 3.09 \times 10^{-5}$ 3sfs min (allow 3.10 × 10 ⁻⁵ if 1.6218 rounded to 1.622) Ignore units	M3	1	If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$ this gives $K_a = 3.15 \times 10^{-5}$ $(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

4(c)	mol OH ⁻ (= $(38.2 \times 10^{-3}) \times 0.550$) = $2.10(1) \times 10^{-2}$ or $0.0210(1)$		M1	1	Mark for answer
	mol H ⁺ (= $(25.0 \times 10^{-3}) \times 0.620$) = 1.55×10^{-2} or 0.0155			1	Mark for answer
	excess mol OH ⁻ = $5.5(1) \times 10^{-3}$ [[OH ⁻] = $5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)] OR [OH ⁻] = $5.5 \times 10^{-3} \times \frac{10^3}{63.2}$ = $0.0870(2)$		M3	1	Allow conseq for M1 $-$ M2 If wrong method e.g. no subtraction or use of $$ can only score max of M1, M2, M3 and M4.
			M4	1	(M1 – M2) / vol in dm³ mark for dividing by volume (take use of 63.2 without 10⁻³ as AE so 9.94 scores 5) If no use or wrong use of vol lose M4 & M6 Can score M5 for showing (10⁻¹⁴/their XS alkali)
	$[H^{+}] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$ $OR \frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$ $OR POH = 1.06$		M5	1	If no use or wrong use of K _w or pOH no further marks
	pH = 12.9(4) allow 3sf		M6	1	If vol missed score max 4 for 11.7(4)
					If acid- alkali reversed max 4 for pH = 1.06 Any excess acid - max 4

Question	Marking Guidance	Mark	Comments
5(a)	H <i>OR</i> hydrogen <i>OR</i> H [·]	1	Ignore brackets ignore dot penalise + or - charge
5(b)	CH ₃ OR methyl OR CH ₃ · OR ·CH ₃	1	Ignore brackets ignore dot penalise + or - charge
5(c)	Either order C ₂ H ₅ OR ethyl OR CH ₃ CH ₂ · OR C ₂ H ₅ · CHO OR HCO OR COH OR H—C=O	1 1	Ignore brackets ignore dot penalise + or - charge
5(d)	I A II C III D IVB	1 1 1	

Question		Marking Guidance		Mark	Comments
6(a)	OH alc	<u>ohols</u>		1	
6(b)(i)	2.6	—СH ₂ -С— П О	Ignore any group on RHS On LHS, penalise H or CH or CH ₂ or CH ₃	1	Must clearly indicate relevant two H on a C next to C=O Ignore missing trailing bonds or attached R groups
6(b)(ii)	2.2	CH ₃ -C O	Ignore all groups on RHS	1	Must clearly indicate relevant three H on C next to C=O Ignore missing trailing bonds or attached R group
6(b)(iii)	1.2	CH ₃ -C-CH ₃	Or in words: two <u>equivalent</u> CH₃ groups Penalise attached H	1	Must clearly indicate two <u>equivalent</u> methyl groups. Ignore missing trailing bonds or attached R groups
6(b)(iv)	CH ₃ -C	CH ₃ 		1	

Question	Marking Guidance		Mark	Comments
7(a)	Heating speeds up (hydrolysis / breaking of peptide bonds) OR forms non-sweet (amino acids)			
7(b)	(2-)aminobutan <u>e</u> dioic acid OR (2-)aminobutan <u>e</u> (-1,4-)dioic acid			2 not necessary but penalise other numbers at start 1,4 not necessary but penalise other numbers and 1,4 must be in correct place (QoL)
7(c)	H H ₂ N-C-COO COO CH ₂ CH ₂ COO COO			allow $-CO_2^-$ allow NH_2^-
7(d)	NH ₃ -CH ₂ -C-H -COO-			allow –CO ₂ ⁻ allow ⁺ NH ₃ – don't penalize position of + on NH ₃
7(e)(i)	Compounds/molecules with same <u>structural</u> M1 formula But with <u>bonds/atoms/groups</u> arranged differently in space or in 3D M2			Not just structure Allow -with different spatial arrangement of atom/bond/group
7(e)(ii)	(Plane) polarised light Rotated in opposite directions			Not bent or turned or twisted; not different directions (QoL)

Question	Marking Guidance	Mark	Comments
8(a)(i)	(As a) soap	1	Allow washing, cleaning, degreasing, detergents
8(a)(ii)	(Bio)diesel or biofuel or fuel for cars/lorries	1	Allow to make soap
8(a)(iii)	(Cationic) surfactant /detergent /fabric softener /germicide / shampoos /(hair) conditioners /spermicidal jelly	1	Allow cleaning
8(b)(i)	(Poly)ester	1	
	Terylene <i>OR</i> PET	1	Allow polyester
8(b)(ii)	(Poly)amide	1	
	Kevlar <i>OR</i> nylons	1	Ignore numbers with nylons Allow polyamide(e)
8(b)(iii)	(Independent marks)		CE = 0
	Hydrogen bonding in b(ii)	1	
	Imfs in (b)(ii) are stronger	1	
	OR		
	H bonding stronger than dipole-dipole/van der Waals/ dispersion/London forces in b(i)		

Question	Marking Guidance	Mark	Comments
9(a)(i)	Conc HNO_3 Conc H_2SO_4 $2 H_2SO_4 + HNO_3 \rightarrow 2 HSO_4^- + NO_2^+ + H_3O^+$ OR $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$ OR via two equations $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$ $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$	1 1 1	If either or both conc missing, allow one; this one mark can be gained in equation` Allow + anywhere on NO ₂ ⁺
9(a)(ii)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	 ignore position or absence of methyl group in M1 but must be in correct position for M2 M1 arrow from within hexagon to N or + on N Allow NO₂⁺ in mechanism Bond to NO₂ must be to N horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3 + on H in intermediate loses M2 not M3
9(b)	5	1	

9(c)	2	1	
9(d)	$2C_7H_5N_3O_6 \rightarrow 5H_2O + 3N_2 + 7C + 7CO$	1	Or halved

Question	Marking Guidance	Mark	Comments
10(a)	(Nucleophilic) addition-elimination M2 M3 CH ₃ CH ₂ —CI H NH ₃ M1 M4 for 3 arrows and lp CH ₃ CH ₂ —CI NH ₂ NH ₂ Propanamide (Ignore -1-)	1 4	 Minus sign on NH₃ loses M1(but not M4 also) 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 For M4, ignore NH₃ removing H⁺ but lose M4 for CI⁻ removing H⁺ in mechanism, but ignore HCI shown as a product penalise other numbers penalise propaneamide and N-propanamide

10(b)	Nucleophilic substitution M2 CH CH CH CH CH CH CH CH CH C	1 4	 Minus sign on NH₃ loses M1 (not M4 also) + rather than δ+ on C=O loses M2 ALLOW SN1 so allow M2 for loss of Cl⁻ before attack of NH₃ on C+ for M1 only allow M4 after correct/very close M3 For M4, ignore NH₃ removing H⁺ but lose M4 for Cl⁻ removing H⁺ in mechanism, but ignore HCl shown as a product penalise other numbers allow 1-propanamine
10(c)	electron rich ring or benzene or pi cloud <u>repels</u> nucleophile/ammonia	1 max	C—CI bond is short/stronger than in haloalkane C—CI is less polar than in haloalkane resonance stabilisation between ring and CI

Question	Marking Guidance		Mark	Comments	
11	L	H 	Allow (CH ₃) ₂ CHOH or CH ₃ CH(OH)CH ₃	1	Allow name propan-2-ol Penalise contradiction of name and structure
	М	H ₃ C—C—CH ₂ H	Allow CH₃CH=CH₂	1	Allow name propene ignore -1- but penalise other numbers Penalise contradiction of name and structure
	M1	Step 1 NaBH ₄ or LiAlH ₄	Zn/HCI or Sn/HCI or H ₂ /Ni or H ₂ /Pt	1	Ignore name if formula is correct ignore solvent ignore acid (for 2nd step) but penalise acidified NaBH ₄ Apply list principle for extra reagents and catalysts.
	M2	(nucleophilic) addition	Addition (not nucleophilic)	1	Penalise electrophilic Ignore reduction
	M3	Step 2 conc H ₂ SO ₄ or cor	nc H ₃ PO ₄ or Al ₂ O ₃	1	Apply list principle for extra reagents and catalysts.
	M4	elimination		1	Independent from M3 penalise nucleophilic or electrophilic ignore dehydration
	M5	Step 3 HBr		1	Apply list principle for extra reagents and catalysts.
	M6	electrophilic addition		1	Independent from M5

General principles applied to marking CHEM4 papers by CMI+ (January 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. <u>Equations</u>

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.

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 CH_3 is considered to be interchangeable with H_3C 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—— CH₃	——C—— CH ₃ CH ₂			
allowed	allowed	not allowed			
NH ₂ -C	C NH ₂	NH ₂	NH ₂	OH—C——	—-С—- ОН
allowed	allowed	allowed	allowed	not allowed	not allowed

CN——C——	C CN	соон—с—	—С— СООН	СООН	
not allowed					
сно—с—	C CHO	C CHO	COCI	—c— coci	
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	ethanal
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 <u>may</u> 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, $H_2C = CH_2$
 $CH_3CHOHCH_3$ for propan-2-ol, $CH_3CH(OH)CH_3$

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

2-methpropan-2-ol should be 2-methylpropan-2-ol should be 3-methylbutan-2-ol should be 3-methylpentane 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**3-methyl-2-bromobutane should be **2-bromo-3-methylbutane**

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

difluorodichloromethane should be dichlorodifluoromethane