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RECOGNISING ACHIEVEMENT

GCE

Chemistry B (Salters)

Advanced GCE **F335**

Chemistry by Design

Mark Scheme for June 2010

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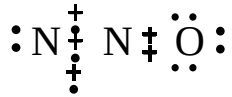
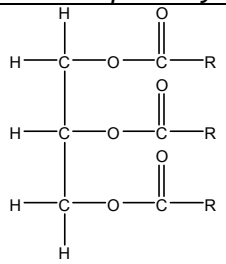
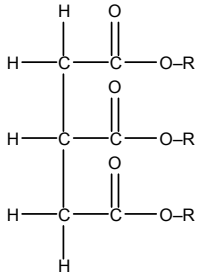
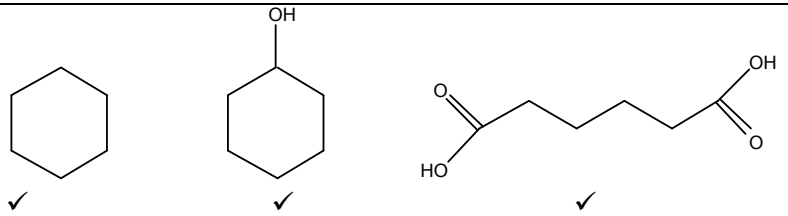
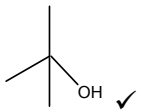
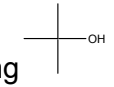
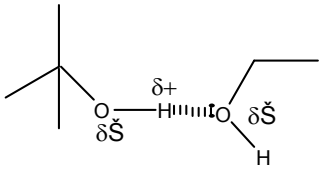
Question			Expected Answers	Marks	Additional Guidance
1	a	i	dinitrogen oxide / nitrogen(I) oxide / dinitrogen(I) oxide ✓	1	**ALLOW** dinitrogen monoxide **IGNORE** gaps
	a	ii	 dative bond ✓ completely correct ✓ shape – linear ✓ (depends on diagram – see advice)	3	To score first mark there must be (only) two electrons of the same symbol between the nitrogen and oxygen **ALLOW** (for this mark) if they are oxygen's electrons. To score the second mark there must be alternating dots and crosses for the elements' electrons as one moves from N to N to O **ALLOW** shared electron pairs horizontally (eg •+) **ALLOW** alternatives to linear, eg "straight" or 180 **IGNORE** 'planar' **IF diagram is wrong, use it to determine shape mark:** • No diagram no mark • No lone pairs on central N: linear, etc • One or two lone pairs/single electrons: bent (**NOT** triangular), allow 120±2 or 109±2 as appropriate
	b	i	+5 ✓ +1 ✓	2	5, 1 does not score. 5+, 1+ scores 1
	b	ii	**10** $H^+ + 2NO_3^- +$ **8** $e^- \rightarrow N_2O +$ **5** H_2O 10 **AND** 5 ✓ 8 ✓ *Mark separately*	2	Each piece of additional material in the equation **CON**s a mark
	b	iii	(nitrogen / nitrate) gain of electrons ✓ oxidation number / state <u>of nitrogen</u> goes down / goes from (+)5 to (+)1 (or ecf from b(i), provided this is a fall) ✓	2	**'**gain of electrons' need not be qualified but any other reagents quoted apart from nitrogen/nitrate are **CON** **IGNORE** answers in terms of oxygen lost **IGNORE** what has gained electrons Answers can both be on same line *NB – 1(b)(i) answer line is shown on the screen to allow for ecf*
	b	iv	<u>nitrogen</u> (in compounds) <u>/nitrate(s)</u>: is less available to plants / crops is needed by plants / crops is a fertliliser makes plants / crops grow (*AW*) ✓	1	For the mark, nitrate or 'nitrogen' is needed (**ALLOW** N but **NOT** N_2), **AND** an indication of its availability / need by plants **OR** fertiliser function **IGNORE** '(nitrogen) is reduced', implying less of it

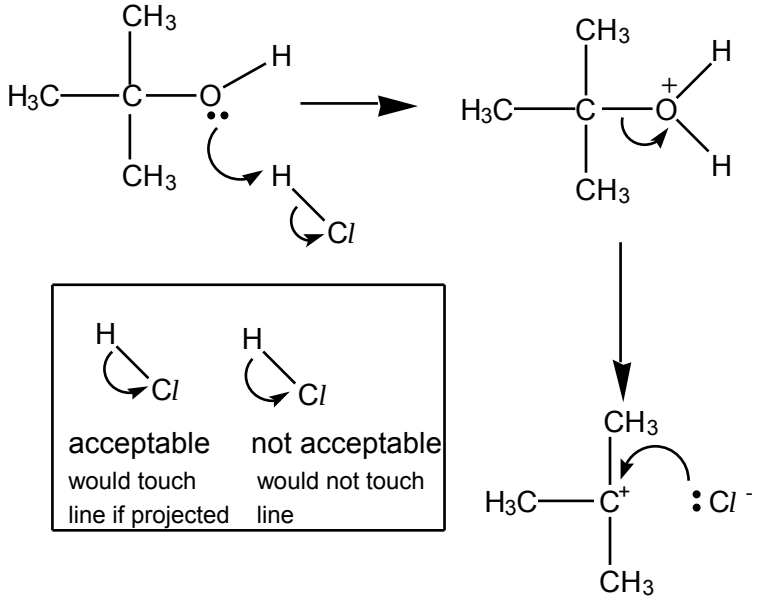
Question			Expected Answers	Marks	Additional Guidance
	c		33% N **OR** 1:2 by moles (stated or implied) **OR** two-thirds oxygen ✓ NO_2✓ *no ecf from the wrong working* *Mark separately*	2	Answer alone scores 1 (**NOT** 2) if first marking point is not scored **IGNORE** Multiples of NO_2 (eg N_2O_4) but working can score
	d	i	 backbone with O atoms attached ✓ completely correct ✓	2	**ALLOW** CH_2 etc for first mark must be full structural to score second mark **ALLOW** dashes or numbers on R, but no other representation of acid side-chain  scores 1
	d	ii	instantaneous (dipole) – induced dipole/ permanent (dipole) – permanent dipole ✓ intermolecular bonds are similar *stated or implied* **OR** imb formed are stronger than / similar to those broken ✓ *Mark separately*	2	**ALLOW** either or both types as imb for either compound or between compounds (**ALLOW** permanent dipole – induced dipole between). **Hydrogen bonds are CON**. **NOT** abbreviations of bond descriptions for *this* mark **IGNORE** references to molecules being non-polar eg 'both have....' give this mark, even if imb stated is wrong but reference to covalent bonds is **CON** to this mark

Question			Expected Answers	Marks	Additional Guidance
	e	i	 ✓ ✓ ✓	3	**ALLOW** carboxylic acid groups in any orientation Ignore 'drafting' lines, give BOD if possible no ecf for non-skeletal structures for more than one compound **CON** O–H on first appearance, then allow as ecf – including 2(a) –OH connected through the H is a **CON** only the first time it occurs OH OH acceptable unacceptable up to bar of H beyond bar of H
	e	ii	190 and 226 ✓ 190 x 100/226 = 84/84.1% ✓	2	Full marks for correct answer with no / inaccurate working shown. 64.6/65 with no working scores 1 Second mark is for writing a ratio of two numbers (including eg '100 + 2x63') and correctly evaluating the answer (but **NOT** if answer >100%) **ALLOW** 100% **ALLOW** 2 or more sig figs (allow any value between 84 and 84.1)
			Total	**22**	

Question			Expected Answers	Marks	Additional Guidance
2	a		 ✓ 2-methylpropan-2-ol / methylpropan-2-ol ✓ *Mark separately – no ecf*	2	Ignore 'drafting' lines, give BOD if possible **ALLOW** other skeletal representations, including  O of OH must be attached to carbon (see rule in 1ei) **ALLOW** ecf on O–H if it occurred in 1ei and mark was not awarded because of this **NOT** three-dimensional representations with wedges and dashes **IGNORE** dashes, commas, gaps in name **ALLOW** 'methly' but no other mis-spellings
	b	i	carbon with OH is attached to three other carbons / methyl (groups) / alkyl (groups) / R (groups) **OR** carbon with OH has no hydrogens / only carbons attached ✓	1	It must be clear that the carbon is being referred to **ALLOW** 'central carbon' instead of 'carbon with OH'
	b	ii	from: orange/yellow ✓ to: green/blue ✓ butanone ✓ *Mark separately*	3	**DO NOT ALLOW** other colours apart from mixtures or shades of those given **ALLOW** butan-2-one (ignore dashes, brackets commas and gaps) **IGNORE** formula

Question			Expected Answers	Marks	Additional Guidance
	c		 or vice-versa (from eth to t-but) the two alcohols with hydrogen bond between O and H **AND** linear O-H-O ✓ lone pair on oxygen pointing down hydrogen bond ✓ partial charges on **both** oxygens and hydrogen ✓ *Mark separately*	3	Hydrogen bond can be represented by a dashed line but **NOT** a solid line (unless labelled as 'hydrogen bond') **ALLOW** 'OH' for O–H Representation of alcohols can be in any way that indicates their structures (**ALLOW** missing Hs), provided OH groups are clear. **ALLOW** ecf from wrong alcohol structure in 2a **ALLOW** ambiguous attachment of alkyl groups (eg via Hs) but not OH (see rule in 1di) Ignore 'drafting' lines, give BOD if possible **If only an incorrectly positioned hydrogen bond is drawn (eg to alkyl H) it scores zero out of three**. *But...If there is more than one hydrogen bond*: • Incorrectly positioned hydrogen bonds **CON** the first mark • **IGNORE** any extra **correctly** positioned hydrogen bonds • Mark the best hydrogen bond • A 'square' of two hydrogen bonds can be considered for all except the first mark

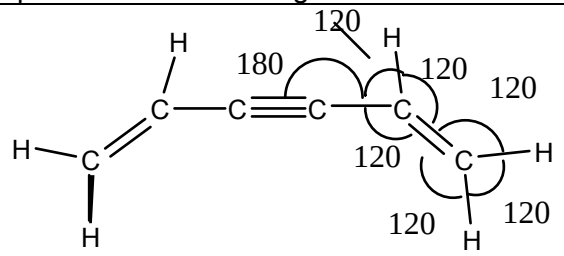
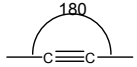
Question			Expected Answers	Marks	Additional Guidance
	d		instantaneous (dipole) – induced dipole bonds/forces ✓	3	**NOT** abbreviations for this mark **ALLOW '**Van der Waals' (ignore capitals) **other bonds accounting for the difference are CON** **ALLOW** 'it' for 't-butanol'
			(intermolecular bonds) are weaker in t-butanol / less energy (or heat) required to: break (intermolecular bonds) in t-butanol / separate molecules in t-butanol *ORA* ✓		**IGNORE** less/fewer imb or 'less likely to form' **ALLOW** second mark for any one of the following described as weaker: just 'intermolecular bonds / forces' **OR any** named intermolecular bond (including hydrogen bonds or different ones for the two alcohols) **OR** abbreviated (eg 'id-id' / imb)
			t-butanol molecules/chains **OR** t-butanol: can't get as close together / don't line up / don't pack/stack together so well/so easily / less areas of contact *ORA* ✓		*Mark third mark separately* **IGNORE** more / less branched or linear **IGNORE** atoms

Question	Expected Answers	Marks	Additional Guidance
e	 ✓✓✓✓ one for each arrow *Mark separately – no ecf*	4	**First arrow** must start at lone pair and point between O and H or at H **second arrow** must start on (or above or below) bond (**NOT** on H) and point towards Cl (see box) **third arrow** must start on bond and point towards O **fourth arrow** must start on lone pair and point between C^+ and Cl or at C^+ Any **wrong** arrows in excess of four are each **CON** to one correct arrow First and third arrows can be straight Single-headed arrows are **CON** only the first time they appear in an otherwise correct situation; accept after that

Question	Expected Answers	Marks	Additional Guidance
f	$CH_3CH_2OCH_2CH_3$ ✓	6	**Please annotate by ticking each point scored. Always look for information on page 8 and mark appropriately.** Page 8 is available as a thumbnail on the left Accept any clear structural formula of ethoxyethane, including $C_2H_5OC_2H_5$ **IGNORE** name Ignore 'drafting' lines, give BOD if possible
	IR (two marks) no peak above 3000 / 3200 / 3640 (cm^{-1}) **OR** no peak at 3600 – 3640 / 3200 – 3600 ✓ no OH / not alcohol ✓		**IGNORE** references to other peaks *Mark two IR marks separately. Can score if the structure is wrong.*
	NMR (one mark plus QWC) QWC is scored for relating NMR evidence to structure, as described below *Look first for:* (protons identified) CH_3 (–C) / methyl **AND** O(–)$CH_{(2)}$ (or in words or indicated on structure)✓ The **QWC** mark is then scored from this response if '$CH_3CH_2OCH_2CH_3$' (or more displayed) structure given. Place tick under pencil icon ✓		*Note brackets carefully*: H_3 in first and O in second are essential **- NOT** CHO for second one but CH–O and CH_2O are acceptable. **IGNORE** any shifts quoted **ALLOW** 'protons' stated or implied (eg 'methyl group')
	OR *if the above are absent, incomplete or wrong, look for:* two proton / hydrogen environments ✓ **QWC** is awarded here if there is an indication of two environments on the *correct* structure (using the formula or describing it in words) ✓ Place tick under pencil icon		For QWC here **ALLOW** references to symmetry or 'two C_2H_5'
	splitting (one mark): *general:* indication that no. of peaks is one more than the no. of protons on the **adjacent** carbon **OR** *specific:* identification of **one of** CH_3 CH_2 (ie triplet for hydrogens on C next to CH_2 **or** quartet for hydrogens on C next to CH_3) (ignore anything incorrect) ✓		Either way, the idea of number of protons / hydrogens on *adjacent* (*AW*) carbon (**IGNORE** adjacent environment) must be there to score the mark. **IGNORE** specific if general correct **Can score splitting mark if the structure is wrong** **NOT** just 'n+1 rule' without explanation
	Total	**22**	

Question			Expected Answers	Marks	Additional Guidance
3	a	i	Endothermic (forward reaction), (high / increasing temp moves) equilibrium (position) to right / towards products ✓ (high) pressure pushes equilibrium (position)* to the left ✓ more moles / molecules / particles on the right *ORA* ✓ **one** correct reference to yield related to equilibrium movement (ignore wrong references) ✓ *'position' must be mentioned *once.* Award one of these marks without 'position' but for both marks it must be mentioned once.	4	**IGNORE** references to rate **ALLOW** 'reverse reaction is exothermic' **IGNORE** 'moves in / favours endothermic direction' **NOT '**more atoms' or 'more products' (can assume *high* pressure or temperature since given in the question)
	a	ii	(the energy source must) not produce carbon dioxide / CO_2 **OR** fossil fuels produce carbon dioxide / CO_2 (*AW*) ✓	1	**ALLOW** "It" for the Sun, so allow, eg, "It does not form CO_2"
	b	i	$Kc = [CO]^2 [O_2] / [CO_2]^2$ ✓	1	Must have square brackets; **NO** mark if p symbols. In top line: may have multiplication sign, **must not** have plus sign. **IGNORE** state symbols
	b	ii	4×10^{-20} ✓ 1sf ✓ mol dm^{-3} ✓ *Mark separately*	3	***ALLOW** ecf for first and third marks from b(i) UNLESS plus sign used* *The (b)(i) answer is shown on the screen to facilitate ecf* Award sf mark if the number is to 1 sf and is the correct or incorrect result of any calculation shown. units: **ALLOW** mol/dm^3 4×10^{-20} on answer line scores 2
	c	i	+172 (number with sign) ✓✓	2	+188, 172 and –172 score one mark; nothing else does

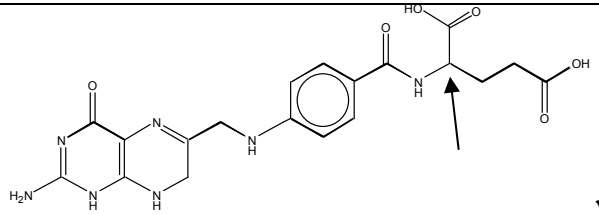
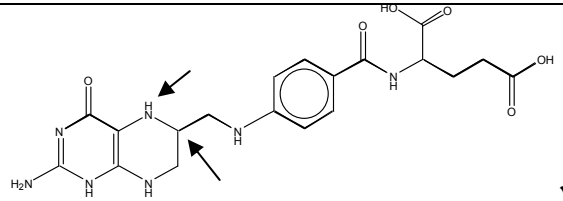
Question			Expected Answers	Marks	Additional Guidance
	c	ii	T= 566000/172 ✓ = 3290 K ✓	2	**ALLOW** ecf from c(i) negative temperatures are CON second mark is for manipulation and correct statement of unit; no ecf from errors in first mark(i.e. 3.29 K scores zero) **ALLOW '**Kelvin' and lower-case 'k' negative answers score zero allow 2 or more sf: 3300, 3291, 3290.7 etc correct answer with no working scores 2
	d	i	$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ ✓	1	**ALLOW** $Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$ **IGNORE** state symbols. Brackets in formulae must be correct Anything extra on either side is **CON**
		ii	acid-base ✓	1	**ALLOW** any unambiguous indication of the answer eg circling any others indicated are **CON**
		iii	uses a lot of $Ca(OH)_2$ / large amounts of solid (or $CaCO_3$) formed **OR** CO_2 emitted in manufacture of $Ca(OH)_2$ (*AW*)✓	1	Must have idea of 'large amount' to score in this way **IGNORE** cost, expense, damage to environment etc
			Total	**16**	

Question			Expected Answers	Marks	Additional Guidance
4	a	i	1/13 x 44 = 3.38 g Correct M_r values 44 and 13 (or 78/6) ✓ Correct manipulation of recognisable M_r values and evaluation (with ecf) ✓	2	Full marks for correct answer **ALLOW** two or more sf 0.56(4) scores 1
	a	ii	(it will be the value of the) highest <u>mass</u> / $\frac{m}{z}$ peak / molecular ion (peak) / M^+ (peak) peak furthest to the right ✓	1	**NOT** just "highest peak" **IGNORE** base peak
	b	i	 structure ✓ 180 ✓ 120±2 ✓	3	structure need not be the correct shape (eg it can be linear) **NOT** 3-dimensional structure (showing dashes and wedges) any **one** 180 angle and any **one** 120±2 angle should be illustrated NB **NOT**  **ALLOW**  (extra wrong angles are **CON** to one correct angle mark each) If there are errors in parts of this structure, bond angle marks can still be given for the correct parts. However, wrong structures (eg Kekulé benzene) score zero marks out of three.
	b	ii	Alkene / C=C groups / double bonds / unsaturated groups / alkyne **AND** react with HBr / undergo addition reactions ✓	1	**IGNORE** references back to 'structure in (i)' **IGNORE** references to decolorising / reaction with bromine 'substitution' is **CON**

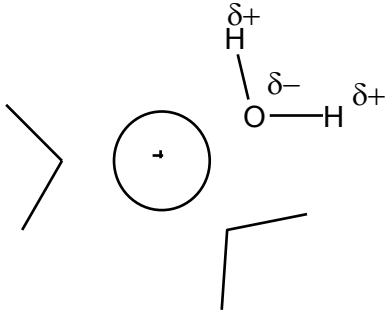
Question			Expected Answers	Marks	Additional Guidance
	c		*accounts for:* bond angle same / 120 ✓ three bonds **OR** three groups / sets of electrons around each carbon ✓ *does not account for:* bond lengths equal ✓ single bonds longer than double bonds ✓ *Mark separately*	4	ignore that it is evidence for the hexagon alone (rather than a symmetrical hexagon) **NOT** pairs of electrons
	d	**i**	delocalised (electrons) ✓ one electron from each carbon ✓ two rings ✓ above and below <u>carbon atoms / carbon ring</u> ✓ *Mark separately*	4	QWC 'delocalised' must be spelt correctly to score first mark **ALLOW** 'delocalized' or derivations such as 'delocalisation' 'Above and below' in last point will cover the 'two' in the previous point **IGNORE** 'either side of C atoms' **ALLOW** second two marking points from a diagram

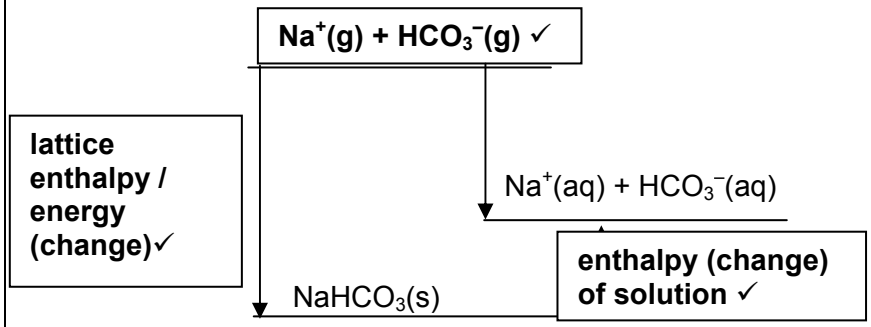
Question			Expected Answers	Marks	Additional Guidance
	d	ii	<u>electron</u> is excited / jumps up energy levels **AND** (as a result of) light / (UV) radiation / energy / photons ✓ frequency (absorbed) depends on energy change **OR** (∆)E = hv ✓ dyes / coloured compounds / 'compounds containing more benzene rings' (*AW*) <u>absorb</u> in the visible / <u>absorb</u> light ✓ QWC ✓ – see guidance ***plus two from****:* energy levels are closer / energy gap is smaller / excitation energy is smaller when there is: more delocalisation more conjugation more than one benzene ring larger chromophore ✓ frequency of uv (radiation / light) is greater than visible / light ***ORA*** ✓ (dyes) transmit / reflect (**NOT** emit) the <u>complementary</u> colour ✓	6	**Please annotate each point scored with a tick** **IGNORE** references to d-shells must be energy change, not just energy, for example: separation of energy levels / size of gap between levels / difference in energy (between levels) / the excitation energy **IGNORE** 'absorb energy' QWC scored if second marking point is made **in words** and first marking point made Place QWC tick by 'pencil' symbol or cross if not awarded **max 2 (out of six) if 'emission by dropping down energy levels (*AW*)' mentioned. Highlight in yellow the words that imply this** Must imply 'emission', otherwise **IGNORE** 'electrons dropping back' **ALLOW** wavelength smaller **ALLOW '**complimentary'
	e		one ✓ 6.4 – 8.2 (ppm) ✓ *Mark separately*	2	

Question			Expected Answers	Marks	Additional Guidance
	f	i	bromobenzene ✓	1	**ALLOW** 1 - bromobenzene with or without dash **ALLOW** 'bromo-benzene' or 'bromo benzene' no other spelling errors
		ii	$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ ✓	1	**ALLOW** skeletal formulae for aromatic compounds **IGNORE** state symbols **IGNORE** 'Fe' / '$FeBr_3$' / conditions over arrow Any other additions are **CON**
		iii	electrophile is a (partially) positively charged / electron deficient (species) ✓ (electrophile) accepts a pair of electrons / forms (covalent) bond ✓ bromine (molecule) is polarised (or diagram) / forms $Br^{\delta+}$ **AND** positive end (*AW*) attacks / forms bond / reacts / substitutes / is electrophile ✓	3	 **ALLOW** Br+ (formed) and attacks / is electrophile
			Total	**28**	

Question			Expected Answers	Marks	Additional Guidance
5	a	i	one COOH group ringed ✓	1	**ALLOW** ring to cross C-C bond anywhere but not to include next carbon away from COOH
		ii	*Any **two** from:* amine ✓ (secondary) amide ✓ imine ✓	2	**IGNORE** ketone*, carbonyl*, amino* **ALLOW** alkene **ALLOW** primary and secondary amines as two groups (but both 'primary' **and** 'secondary' must be stated to score more than one mark) *extra incorrect groups (apart from these) are each **CON** to a mark gained
		iii	 ✓	1	Any other arrows are **CON** **ALLOW** other unambiguous indications of chiral carbon **NB** lack of an arrow is 'NR'
	b		 ✓✓ one for each arrow	2	Arrows in excess of two each **CON** a correct one
	c		it fits into the <u>active/receptor</u> site ✓ blocks site / 'prevents substrate (*AW*) from binding' ✓ (trimetrexate): has arene ring / is aromatic **OR** does not have: C=N / double bond / alkene (*AW*) ✓	3	Idea of fit needed ('similar shape' **and** 'binds / bonds to active site' covers this) **IGNORE** references to methyl group

Question			Expected Answers	Marks	Additional Guidance
	d		CH_3Cl / chloromethane (**ALLOW** methyl chloride) ✓ $AlCl_3$ / aluminium chloride ✓ reflux **OR** anhydrous conditions **OR** ionic liquid (solvent) ✓	3	Max 1 for reagents if extra incorrect reagents are included (wrong name is **CON** to correct formula and vice versa) only accept 'reflux' if one other mark scored
	e	**i**	$HA \rightleftharpoons H^+ + A^-$ **OR** $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ ✓	1	must be equilibrium sign **NOT** $[H^+]$ or $[A^-]$ State symbols, apart from '(aq)' ((*l*) for water) are **CON**
	e	**ii**	$HA \rightleftharpoons H^+ + A^-$ conjugate acid conjugate base ✓	1	**ALLOW** $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ conjugate base conjugate acid **OR** $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ conjugate acid conjugate base **ALLOW** if arrow, rather than equilibrium sign
		iii	$[H^+]\ [A^-]/[HA]$ ✓	1	Must have square brackets. **ALLOW** multiplication sign (or dot) on top but NOT plus **NOT** signs outside brackets **ALLOW** $[H_3O^+]$ for $[H^+]$ but **NOT** $[H_2O]$ on bottom State symbols, apart from '(aq)' are **CON**
		iv	$(-\log 5 \times 10^{-3}) = 2.3$ ✓	1	**ALLOW** more sf than 2.3 if it rounds to 2.3
		v	$[H^+] = \sqrt{(5.0 \times 10^{-3} \times 0.1)}$ ✓ $(= 2.24 \times 10^{-2})$ pH = $-\log [H^+]$ = 1.65/1.7/1.66 (early rounding to 0.022) ✓	2	Must say '$[H^+]$ =' or 'H^+ =' to score this mark on its own or where ecf is considered Allow ecf from first mark if working or evaluation of $[H^+]$ is present and $[H^+]$ is smaller than 5×10^{-2} **ALLOW** more sf than 1.65/1.66 if it rounds to 1.65/1.66 Correct answer with no working scores 2
		vi	concentration of acid at equilibrium = concentration of acid initially (*AW*) ✓ $[H^+]$ **or** 2.24×10^{-2} compared with 0.1 **or** compared with [HA] is not negligible (*AW*) ✓	2	**IGNORE** $[H^+] = [A^-]$ *Second mark depends on first*

Question			Expected Answers	Marks	Additional Guidance
	f		$[H^+] = 3.98 / 4 / 4.0 \times 10^{-8}$ ✓ $\frac{[A^-]}{[HA]} = K_a/[H^+] = 1.25 / 1.26 / 1.3 \times 10^5$ ✓	2	must say '$[H^+] =$' or '$H^+ =$' to score this mark on its own or where ecf is considered Allow ecf from first mark if value of $[H^+]$ is present and $[H^+]$ is smaller than 5×10^{-2} **ALLOW** more sf on ratio (eg 125594/125628) Correct answer with no working scores 2
	g	**i**	hydrogencarbonate ✓	1	**ALLOW** 'hydrogen carbonate' **IGNORE** 'bicarbonate' **ALLOW** (IV) after name, but no other numbers
		ii	($[H^+]$ increases) so equilibrium (position) moves to left / equilibrium moves to form more CO_2 ✓ excess / reservoir / large concentrations / large amounts of (CO_2 and) HCO_3^- ✓ pH (virtually) unchanged (*AW*) ✓ *Mark separately*	3	Must be in terms of equilibrium **ALLOW** 'salt' or 'A^-' for HCO_3^- constancy of pH scores this mark
	h	**i**	circle (or Na (with or without '+')) surrounded by three or more bent or triangular shapes ✓ circle shown as '+' (or Na^+ shown) and H and O atoms labelled on at least one shape, with at least one H labelled $\delta+$ and one O labelled $\delta-$ and O pointing to central ion✓	2	 **IGNORE** $\delta+$ on Na
	h	**ii**	ion-dipole ✓	1	**IGNORE** anything else (eg ionic dipole)

Question			Expected Answers	Marks	Additional Guidance
	h	iii		3	**ALLOW** ΔH_{LE}, $\Delta H_{sol(n)/\ solution}$ **ALLOW** 'enthalpy change of lattice formation' but **NOT** 'enthalpy change of lattice' **ALLOW** 'solution enthalpy' **IGNORE:** • anything after correct answers in the bottom two boxes (eg 'of hydrogencarbonate') • 'sum of' before 'lattice enth' and 'enth of soln' • negative signs in lattice enthalpy box • 'gaseous ions' in top box **Please remember to check *each time* that there is no writing on pages 23 and 24. These will not show as 'Additional objects' but they show up for this question on the 'thumbnails' to the left as 'item 2' and 'item 3'. Annotations made in other questions will not show here. Please ensure that some annotation (default: cross) appears on the top left corner of pages 23 and 24.**
			Total	**32**	

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