

Chemistry B (Salters)

Advanced GCE

Unit **F335**: Chemistry by Design

Mark Scheme for June 2011

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All Examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the Report on the Examination.

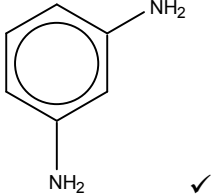
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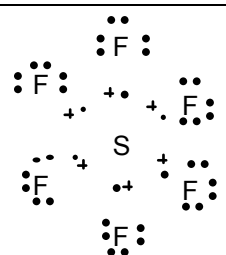
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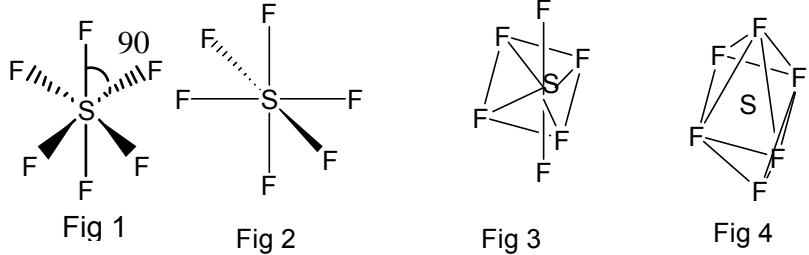
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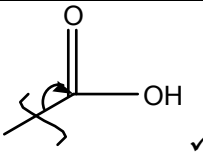
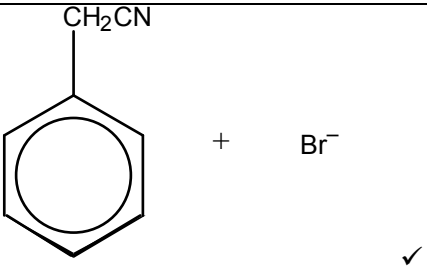
Question			Answer	Mark	Guidance
1	a	i	phenylamine/aniline ✓	1	ALLOW aminobenzene, 'phenyl amine' IGNORE formulae
1	a	ii		1	amine groups meta in any positions NH ₂ groups can be displayed any other groups or lines from benzene ring are CON
1	a	iii	below 5 °C OR a temperature between -10 and +5 °C ✓	1	IGNORE acid/alkali ALLOW 'ice cold' Anything else is CON
1	a	iv	electrophilic ✓; substitution ✓	2	any extra terms CON one awarded mark e.g. 'electrophilic addition' scores one mark, 'nucleophilic electrophilic substitution' scores one mark
1	b	i	orange / the dye colour is between brown and yellow ✓ two (amine groups) is between 1 and 3 ✓	2	IGNORE 'mixture of brown and yellow' ALLOW answers in terms of delocalisation, e.g. 'two (amine groups) have intermediate delocalisation' or in terms of chromophore size (AW) Must clearly imply 'between', not just a series. So 'more amine groups take colour from yellow to brown' does not score either mark; 'one has one more NH ₂ and the other one less' does score second mark.

Question			Answer	Mark	Guidance
1	b	ii	<p>A <u>electrons</u> are excited/move (up) ✓ B (move) to higher <u>energy level</u> ✓</p> <p>C absorption of light / absorption of colour / absorption in the visible ✓ (only award if A or B scored: QWC)</p> <p>D frequency/wavelength depends on: energy <u>gap/difference</u> OR energy needed to excite electrons OR $\Delta E = hv$ / $\Delta E = hf$ ✓</p> <p>E complementary colour <u>transmitted/reflected</u> ✓</p> <p>F different no. of amine groups / different amounts of delocalisation / different chromophores: affect ΔE / energy to excite electron / energy absorbed / frequency absorbed / wavelength absorbed ✓</p>	6	<p>Please indicate with a tick where a marking point is scored</p> <p>'electrons move up energy levels' scores A and B. Can score B without reference to electrons</p> <p>must use absorbed/absorption ALLOW absorbtion</p> <p>NOT just $E=hv$ unless 'energy gap'/'excite electrons' or similar are mentioned</p> <p>IGNORE 'emitted' in E ALLOW 'frequencies/ colours not absorbed' for 'complementary colour'</p> <p>IGNORE the direction of the effect of delocalisation/chromophore size on ΔE</p> <p>If 'light/energy is given out <u>when electron drops/moves down</u>' is stated then maximum of three.</p>
1	c		<p>A delocalisation (any mention of) ✓ B stability retained in substitution ✓</p> <p>C addition product loses delocalisation/ is less stable/ has higher energy OR energy required to break delocalisation in addition ✓</p>	3	<p>mark separately</p> <p>ALLOW 'maintain delocalisation' if stability has been linked to delocalisation ALLOW lower energy product (of substitution reactions) NOT 'increase stability'</p>
Total				16	

Question			Answer	Mark	Guidance
2	a	i	S/sulfur ✓ from 0 to +4 ✓ S/sulfur ✓ from 0 to -2 ✓	4	second mark of each pair depends on first (i.e. 'S/sulfur' not present means no mark for that line) ALLOW 'sulphur' NOT signs after numbers, but use of 4+ and 2- scores one of the oxidation state marks
2	a	ii	$3\text{SF}_4 + \text{O}_2 \rightarrow 2\text{SF}_6 + \text{SO}_2$ ✓	1	ALLOW multiples ALLOW one missing '+' ALLOW $2\text{SF}_4 + \text{O}_2 \rightarrow \text{SF}_6 + \text{F}_2 + \text{SO}_2$
2	b	i	$1s^2 2s^2 2p^6 3s^2 3p^4$ ✓	1	ALLOW [Ne] $3s^2 3p^4$ ALLOW capital letters but numbers must be superscripts
2	b	ii	 <p>6 shared pairs with F ✓ 3 lone pairs on F ✓</p>	2	shape not important ALLOW '•x' in a line between S and F ALLOW 'f' for fluorine mark separately ALLOW two fluorines with one lone pair missing but no single electrons on fluorine

Question			Answer	Mark	Guidance
2	b	iii	 <p>Fig 1 Fig 2 Fig 3 Fig 4</p> <p>shapes as above ✓ bond angle clearly indicated ✓ bond angle labelled 90 ✓</p>	3	<p>Figs 1 and 2 - ALLOW dotted line for 'retreating wedge' Do NOT allow 2 wedges or 2 dashes at 180°</p> <p>Fluorines and S must be shown for first mark, but not others ALLOW 'f' for fluorine</p> <p>between any two adjacent bonds (even if bonds are 3-dimensionally incorrect)</p>
2	c	i	<p>M_r values Li = 6.9 (or 7) and SF_6 = 146.1 (or 146) ✓ <i>stated or implied</i> ALLOW 55.2 or 56 (8 moles) for Li $297/146.1 \times 8 \times 6.9$ and evaluated (112.2) ✓ 2 or 3 sf for any calculated answer ✓</p>	3	<p>If full marks are not given please indicate with a tick where marks are awarded 110, 112 or 114 score all three marks with no reference to working ALLOW ecf for second and third mpts from wrong/rounded M_r ALLOW working or answer for second mpt DO NOT AWARD sf mark if rounding is incorrect</p>
2	c	ii	lithium sulfide ✓	1	ALLOW 'lithium(I)' and 'sulphide' NOT 'dilithium sulfide' or 'sulfide(II)'
2	c	iii	<p>metallic ✓</p> <p>covalent ✓</p> <p>ionic ✓</p>	3	<p>IGNORE 'giant' or 'network'</p> <p>IGNORE 'small' or 'molecule' or 'simple' or 'molecular' IGNORE references to intermolecular bonding NOT dative covalent</p> <p>IGNORE 'giant' or 'network'</p>

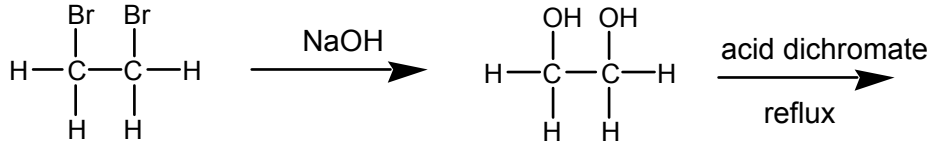
Question			Answer	Mark	Guidance
2	d	i	<p>A SF₆ has instantaneous (dipole)-induced dipole (bonds) ✓</p> <p>B hexanedioic acid has hydrogen bonds ✓</p> <p>C imb in acid stronger than imb in SF₆ ✓</p> <p>D (more) <u>energy/enthalpy</u> required to separate molecules / break (or overcome) (im) bonds* (AW)/boil/melt acid (ora) ✓</p> <p>*this can score C also (if comparison)</p>	4	<p>QWC – ‘instantaneous (dipole)-induced dipole’ must be spelled correctly first time to score</p> <p>IGNORE other imb for hexanedioic acid in B</p> <p>ALLOW C whatever imb mentioned but needs to be a comparison – though can be achieved by ‘weak’ for SF₆ and ‘strong’ for hexanedioic acid</p> <p>(not e.g. ‘hydrogen bonds are strong’, but ‘hydrogen bonds strongest’ OK)</p> <p>ALLOW ‘intermolecular forces’/imb/imf for ‘intermolecular bonds’ throughout</p> <p>ALLOW abbreviations for named imbs in B,C,D</p> <p>IGNORE references to covalent bonds</p> <p>D need not be comparison (e.g. just ‘hydrogen bonds require (a lot of) energy to break’)</p> <p>IGNORE ‘activation’ before ‘enthalpy/energy’</p> <p>must imply imb</p>
2	e	i	<p>‘products – reactants’ expressed as numbers: ([6x36] + 40 – 292 – [8x29])✓ –268 ✓ no ecf</p>	2	<p>ALLOW first mark if multiples for LiF and Li are wrong or missing or if one number is mis-copied</p> <p>Correct answer scores both marks without reference to working</p> <p>+268 scores 1 mark</p>
2	e	ii	<p>use of $\Delta S_{\text{sys}} - \Delta H/T$ ✓ (–268 + 3000000/298) = +9799 ✓</p>	2	<p>Correct answer scores 2 with no reference to working.</p> <p>ALLOW only first mark if ΔH is not converted to J (i.e. –268 + 3000/298 [= –258], scores 1 overall)</p> <p>ALLOW ecf from value in (e)(i)</p> <p>ALLOW 1 or more sf (10000, 9800, 9799(114094)) but rounding must be correct to score second mark.</p> <p>Plus sign must be present for second mark</p> <p>–10335 (to any sf) (wrong sign for $\Delta H/T$) scores 1</p>
2	f	i	KClO ₄ ✓	1	
2	f	ii	<p>((e)(ii) shows reaction is) spontaneous / likely to occur / feasible / favourable ✓</p> <p>(fuse implies) high activation enthalpy/energy/slow reaction ✓</p>	2	<p>ecf for negative ΔS values from (e)(ii): ALLOW reverse of points given for first mark</p> <p>ALLOW ‘increases rate of reaction’ mark separately</p>
Total				29	

Question			Answer	Mark	Guidance
3	a		$C_8H_8O_2$ ✓	1	ALLOW any order of atoms
3	b		$2C_8H_8O_2 + CaCO_3 \rightarrow (C_8H_7O_2)_2Ca + CO_2 + H_2O$ formation of calcium salt + CO_2 ✓ completely correct (with molecular formulae) ✓	2	salt can have Ca first ALLOW only $C_8H_8O_2Ca$ or $(C_8H_7O_2)_2Ca$ or $C_8H_7O_2Ca$ (or equivalent structural formulae) for first mark ecf for molecular formula from (a) including in salts above
3	c	i		1	arrow must start on bond (or hit bond if arrow's curve is continued) and end on C of COOH (or hit this carbon if arrow's curve is extended) (arrow can be below bond rather than above and can start either side of the bond breaking sign)
3	c	ii	they do not exist OR they are (very) unstable (AW) OR cannot be obtained OR they are theoretical ✓	1	IGNORE anything else
3	c	iii		1	ALLOW displayed or partially displayed CH_2CN but must be correct ALLOW with missing '+'
3	c	iv	$H^+(aq)/H_2O$ reflux ✓	1	ALLOW the H_2O or the (aq) missing. ALLOW 'acid' or named mineral acid for ' H^+ '
3	c	v	(equilibrium (position)) moves to left ✓ moves in endothermic direction (ora) ✓ (equilibrium constant) falls/gets smaller (AW) ✓	3	ALLOW 'in backwards direction' or 'towards reactant' or 'reverse reaction' for 'left' ALLOW anything implying 'goes towards <u>endothermic</u> ' or 'going away from <u>exothermic</u> ' mark separately – no ecf
3	d	i	ether ✓	1	ALLOW alkoxy/alkoxyl

Question			Answer	Mark	Guidance
3	d	ii	(secondary) amine ✓	1	ALLOW alkene ACCEPT indole primary amine is CON
3	d	iii	Any one pair from: C=O ✓ 1700 – 1725 (cm ⁻¹) ✓ O–H ✓ 2500 – 3200 (cm ⁻¹) ✓ C–H ✓ 2850 – 2950 (cm ⁻¹) or 3000 – 3100 (cm ⁻¹) ✓	2	IGNORE <i>descriptions</i> of bonds/groups (e.g. 'alcohol') ALLOW one mark for a correct bond with no/incorrect range or a correct range with no/incorrect bond Extra incorrect bonds and/or incorrect peaks CON ONE mark already scored (e.g. C=O and 1700-1725, followed by 'N-H and/or 3300-3500' scores ONE; C=O 1720 – 1740 followed by 'N-H and/or 3300-3500' scores zero) ALLOW 'OH' for 'O-H' and 'CH' for 'C-H' but NOT 'CO' for 'C=O' IGNORE arene absorptions (1450 – 1650)
3	d	iv	ring going around COOH group AND the CH ₂ attached ✓	1	ring does not need to be a circle! it must cut the O–C bond somewhere, not through the CH ₂ or the O
3	e	i	C ₆ H ₃ Cl ₂ OCH ₂ COO ⁻ ✓ (CH ₃) ₂ NH ₂ ⁺ / (CH ₃) ₂ N ⁺ H ₂ ✓	2	ALLOW any (correct) formula for anion and cation, e.g. as shown on left, full structural, skeletal etc. the plus charge must be on or around amine group mark separately
3	e	ii	the salt/it will be (much more) soluble ✓	1	ALLOW salt is less acidic (must be comparison)
3	f		any two from: ✓✓ <ul style="list-style-type: none"> • its usefulness/effectiveness (AW) OR nothing better to use OR no alternatives • it can be used with care (AW) / used in low concs / small amounts • greater yield of crop / greater profit / cheap / cheaper food 	2	IGNORE 'washing of crops' 'use with care' can mean 'keep away from humans/animals' or 'use responsibly'
Total				20	

Question		Answer	Mark	Guidance
4	a	1,2-dibromoethane ✓ 1-bromo-2-chloroethane ✓	2	IGNORE spaces, gaps and dashes and commas ALLOW '2-bromo-1-chloroethane', '1-chloro-2-bromoethane' and '2-chloro-1-bromoethane' watch out for 'ethene' rather than 'ethane' but give BOD. If both have 'ethene' can award one if all else correct
4	b	<p>A $C^{\delta+} - \text{hal(ogen)}^{\delta-}$ OR carbon slightly positive and halogen slightly negative (AW) ✓</p> <p>B C and halogen differ in electronegativity OR halogen is more electronegative (than carbon) ✓</p> <p>C CBr_3CBr_3 all dipoles cancel OR centre of negative charge is in same place as centre of positive charge ✓</p> <p>D $\text{CH}_2\text{BrCH}_2\text{Cl}$ – reverse of C. ✓</p> <p>E difference in electronegativity between Br and Cl OR Cl more electronegative than Br (ora) OR difference in polarities of C-Cl and C-Br OR C-Cl more polar than C-Br OR partial charges of Cl and Br different ✓</p>	5	<p>Please indicate with a tick where a marking point is scored. Beware of answers that repeat the question (e.g. 'CBr_3CBr_3 has no overall dipole')</p> <p>ALLOW references to a specific halogen for mpt A and B</p> <p>IGNORE references to symmetry ALLOW 'charges cancel out/balance' (NOT 'electrons spread evenly')</p> <p>ALLOW one end/side has more (partial) negative/positive charge than the other OR charges don't cancel OR chlorine has (partial) negative charge</p> <p>the nature of the difference in electronegativity does not need to be stated in A and E, but if it is stated it must be correct</p> <p>ALLOW '(bond)polarities' for 'dipoles' throughout</p>
4	c	gas-liquid (chromatography) ✓	1	ALLOW 'GLC'

Question		Answer	Mark	Guidance
4	d	<p>A hydrogen bonds in water ✓ B dipole - dipole bonds in/between halogenoalkanes ✓</p> <p>C similar imb are formed in the mixture as are found in the separate substances (AW) (only award C if B made: QWC) OR imb formed have similar energy/strength to those broken ✓</p> <p>D hydrogen bonds stronger than imb <u>between water - halogenoalkanes</u> OR hydrogen bonds not formed <u>between halogenoalkanes and water</u> OR energy required to break hydrogen bonds is not provided by <u>imb between halogenoalkane and water</u> (AW) ✓</p>	4	<p>Please indicate with a tick where a marking point is scored ACCEPT pd-pd or id-id or pd-id or pd for B ALLOW any sort of dipole bond in B</p> <p>ALLOW abbreviations of imb throughout ACCEPT 'imf' for 'imb'</p>
4	e	i <div style="text-align: center;"> </div> <p>for curly arrows ✓✓; dipole* ✓; intermediate ✓</p> <p>* delta plus must be nearer to alkene</p>	4	<p>curly arrows must start at bonds and end on atom* (top one may end between Br and the C it is shown (in the intermediate) as bonding to) * or start and end there if curve of arrow followed ALLOW cyclic bromonium ion as intermediate ALLOW any clear structure for intermediate (e.g. CH₂BrCH₂⁺)</p> <p>IGNORE anything formed from the intermediate or Br⁻ as a product IGNORE any extra delta pluses or minuses MAX 3 if any hydrogen atoms omitted</p> <p>Half-arrows – first one is CON to correct arrow, allow second as ecf</p>
4	e	ii <p>positive / partially positive / electron deficient reagent OR attracted to area of high electron density ✓ receives electrons/lone pair AND forms (covalent) bond ✓</p>	2	

Question			Answer	Mark	Guidance
4	e	iii	<p>Cl⁻ is not an electrophile OR Cl⁻ cannot attack OR Cl⁻ is not attracted OR no Cl⁺ present ✓ Cl⁻ attacks/reacts with/is attracted to intermediate/carbocation (once Br is there) ✓</p>	2	ALLOW Cl ⁻ is a nucleophile
4	f		 <p>NaOH ✓; intermediate ✓; acid dichromate ✓; reflux ✓ starting compound need not be shown</p> <p>no ecf, mark step 1 and intermediate separately only allow acid dichromate and reflux marks if intermediate has at least one OH group</p>	4	<p>ALLOW any type of organic formula (except molecular) ALLOW KOH or OH⁻ for NaOH IGNORE conditions for first reaction ALLOW expanded names and correct formulae for 'acid dichromate'* (e.g. 'sulfuric acid and sodium dichromate') *IGNORE oxidation state of dichromate and small spelling errors (e.g. 'dicromate') IGNORE formula if correct name given 'reflux' scores only if dichromate (or its formula) is mentioned IGNORE state symbols and formula of product IGNORE attachment of H of OH to carbon must be clear which reagent performs which step</p>
4	g		<p>Check spectrum for responses each time* (errors on spectrum can be ignored)</p> <p>A CH₃CHBr₂ OR displayed ✓ B (two peaks hence) two <u>hydrogen</u> environments ✓ C hydrogens (in ratio) 3:1 ✓</p> <p>One from: D CH₃/3H split into two by: CH OR one hydrogen on adjacent C E the CH/1H split into four by: the CH₃ OR three hydrogens on adjacent C ✓</p>	4	<p>Please indicate with a tick where a marking point is scored mark separately</p> <p>C cannot be scored <i>simply</i> from '3H' '1H' ALLOW 'proton' or H for 'hydrogen'. Use of 'H⁺' or 'hydrogen molecule' for 'hydrogen' CONS one of B C, and D the first time it is used B,C and D can be indicated by appropriate labels on a formula (*or on spectrum) NOT just 'adjacent environment' peaks can be referred to by chemical shifts</p>
Total				28	

Question			Answer	Mark	Guidance
5	a	i	hydrogenphosphate(V) ✓✓ 'hydrogenphosphate' with no (or a wrong) number scores 1 mark	2	ALLOW gap ('hydrogen phosphate') ALLOW 'monohydrogen...' ALLOW spelling errors if names sound correct IGNORE '5' or '+5'
5	a	ii	H ₃ PO ₄ ✓	1	NOT H ₂ PO ₄ H
5	b	i	[HPO ₄ ²⁻] [H ⁺] / [H ₂ PO ₄ ⁻] ✓ Please check carefully	1	
5	b	ii	[H ⁺] = √(6.2 × 10 ⁻⁸ × 0.1) = 7.87(40079) × 10 ⁻⁵ ✓ pH = -log [H ⁺] = 4.1(038) ✓	2	ALLOW 2 or more sf for 1 st mark. Working alone does NOT score. Second mark for correct manipulation of any given [H ⁺] value* (to one or more decimal place) Correct answer scores 2 without reference to working (do NOT accept '4') * must say 'H ⁺ =' at least
5	c	i	little/no change in pH OR resists change in pH ✓ when <u>acid</u> or <u>alkali</u> added ✓ in <u>small</u> quantities ✓ cell <u>enzymes</u> work at specific/optimum pH OR change in pH can stop enzymes working <i>AW</i> ✓	4	Both acid AND alkali must be mentioned depends on mention of acid or alkali for second mark ALLOW 'denatured if pH changes'
5	c	ii	(increase [H ⁺]) moves equilibrium (position) to left ✓ removes H ⁺ OR restores pH / restores [H ⁺] ✓ [HPO ₄ ²⁻] large OR large amounts of HPO ₄ ²⁻ ✓	3	must mention equilibrium ALLOW H ⁺ reacts with HPO ₄ ²⁻ for second mark ALLOW HA for H ₂ PO ₄ ⁻ and A ⁻ (or salt or conjugate base) for HPO ₄ ²⁻
5	c	iii	[H ⁺] = Ka OR pH = pKa ✓ pH = 7.2 ✓	2	Correct answer scores 2 without reference to working ALLOW 7.2076 to one or more decimal places <i>no ecf</i>

Question		Answer	Mark	Guidance	
5	d	<p>ALLOW full sodium salt formulae instead of ion formulae throughout ALLOW [acid] for $[\text{H}_2\text{PO}_4^-]$ and [salt] for $[\text{HPO}_4^{2-}]$</p> <p>$[\text{H}_2\text{PO}_4^-] / [\text{HPO}_4^{2-}] = [\text{H}^+] / K_a$ (or inverse) ✓ <i>stated or implied</i></p> <p>$[\text{H}_2\text{PO}_4^-] / [\text{HPO}_4^{2-}] = 1 \times 10^{-7} / 6.2 \times 10^{-8} = 1.61$ ✓ (or inverse 0.62)</p> <p>divide ratio by 10 (0.161) moles of NaH_2PO_4 ✓</p> <p>ans x 120 = 19.2 or 19.3 or 19.4 g ✓</p>	4	<p>If marks awarded are not as below - please indicate with a tick where a marking point is scored</p> <p>Award 4 marks for correct answer without reference to working (19, 19.2, 19.3, 19.4) 193/194 scores 3 overall; 7.44 scores 2 overall; 74 scores 1 overall ALLOW 2 or more sf</p> <p>MUST be with salt ratio or $[\text{H}_2\text{PO}_4^-]$ as subject, but can have values substituted</p> <p>ONLY scores if correctly evaluated, but expression scores first mark ALLOW 0.1 for $[\text{HPO}_4^{2-}]$</p> <p>AWARD last mark if some number is shown as multiplied by 120 and correctly evaluated (to 2 or more sf)</p>	
5	e	i	<p>indication of calculation/comparison of moles of substances ✓</p> <p>statement of 1:2 ratio ✓</p>	2	<p>e.g. moles $\text{NaH}_2\text{PO}_4 = 15 \times 0.1/1000$ moles $\text{NaOH} = 7.5 \times 0.4/1000$ first mark must have indication of at least one reagent second mark can be scored from a '2' in the right place in a calculation</p> <p>ALLOW arguments such as 'twice as many moles of NaOH needed but solution 4x more concentrated, hence half as much needed' for 2 marks</p>
5	e	ii	<p>(weak acid) ionises/dissociates: as H^+ removed OR as the acid reacts with hydroxide/base <i>AW</i> OR (a weak acid) fully reacts with sodium hydroxide/strong base <i>AW</i> ✓</p>	1	<p>NOT whole molecule reacts</p>

Question		Answer	Mark	Guidance
5	f	<p><u>Na⁺(g) (+) OH⁻(g)</u> ✓</p> <p>↓</p> <p><u>NaOH(s)</u> enthalpy change of solution* ✓</p> <p>sum ✓ of enthalpy change(s)⁺ of hydration/solvation ✓</p> <p>↓</p> <p><u>Na⁺(aq) (+) OH⁻(aq)/NaOH(aq)</u> ✓</p>	5	<p>ΔH terminology may be used instead of 'enthalpy change of' (i.e. $\Delta H_{\text{hyd(ration)/solv(ation)}}$ and $\Delta H_{\text{sol/soln/solution}}$)</p> <p>ALLOW 'enthalpy' for 'enthalpy change'</p> <p>marks for enthalpy changes include correct arrows</p> <p>* mark only scored if shown as exothermic</p> <p>+ 'sum' mark is scored if answer says 'enthalpy changes' (plural) or both ions are referred to</p> <p>mark independently</p>
Total			27	

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