55th INTERNATIONAL CHEMISTRY OLYMPIAD 2023

UK Round One

MARK SCHEME

Although we would encourage students to always quote answers to an appropriate number of significant figures, do not penalise students for significant figure errors. Allow where a student's answers differ slightly from the mark scheme due to the use of rounded/non-rounded data from an earlier part of the question.

In general, 'error carried forward' (referred to as ECF) can be applied. We have tried to indicate where this may happen in the mark scheme and where ECF is not allowed.

For answers with missing or incorrect units, penalise one mark for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise for subsequent occurrences in the same question.

Organic structures are shown in their skeletal form, but also accept displayed formulae as long as the representation is unambiguous.

State symbols are not required for balanced equations and students should not be penalised if they are absent.

No half marks are to be awarded. One blank tick box has been included per mark available for each part. Please mark by placing a tick in each box if mark is scored.

Question	1	2	3	4	5	**Total**
Marks Available	7	20	18	21	20	**86**

1. This question is about rocket fuel | **Mark**

(a) $H_2 + ½O_2 \rightarrow H_2O$ ☑

State symbols not required
Accept any multiple with correct stoichiometry e.g., $2H_2 + O_2 \rightarrow 2H_2O$

(b) +494 kJ mol^{-1} ☑

If the equation used is $H_2 + ½O_2 \rightarrow H_2O$:
$\Delta_r H = \sum_{\text{bonds broken(reactants)}} - \sum_{\text{bonds formed (products)}}$
$-241 \text{ kJ mol}^{-1} = [(432 + y) - (2 \times 460)] \text{ kJ mol}^{-1}$
$y = [-241 - 432 + (2 \times 460)] \text{ kJ mol}^{-1}$
$y = +247 \text{ kJ mol}^{-1}$ (for ½ mole of O_2)
1 mole of O=O is $2y = +494 \text{ kJ mol}^{-1}$

If the equation used is $2H_2 + O_2 \rightarrow 2H_2O$:
$\Delta_r H = \sum_{\text{bonds broken(reactants)}} - \sum_{\text{bonds formed (products)}}$
$[2 \times -241] \text{ kJ mol}^{-1} = [(2 \times 432) + y - (4 \times 460)] \text{ kJ mol}^{-1}$
$y = [(2 \times -241) - (2 \times 432) + (4 \times 460)] \text{ kJ mol}^{-1}$
$y = +494 \text{ kJ mol}^{-1}$

(c) (i) 35.2 mol ☑

$1 \text{ dm}^3 = 1000 \text{ cm}^3$
Density (ρ) = mass (m) / volume (v)
$m(H_2) = \rho v$
$m(H_2) = 0.071 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 = 71 \text{ g}$
$n(H_2) = m/M_r = 71 \text{ g} / 2.016 \text{ g mol}^{-1} = 35.2 \text{ mol}$

(ii) 8480 kJ ☑

Energy released = 35.2 mol × +241 kJ mol^{-1} = 8480 kJ

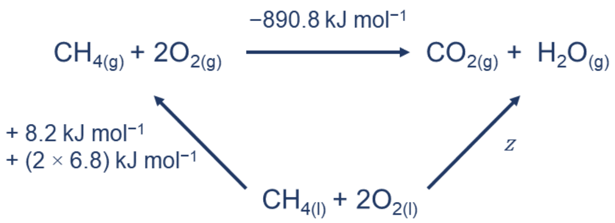
(d) (i) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ ☑

(ii) ☑

Oxidation state of H in reactant 0	Oxidation state of C in reactant +4
Oxidation state of H in product +1	Oxidation state of C in product −4

All four oxidation states must be correct for the mark. + sign is not needed.

(e) −869.0 kJ ☑



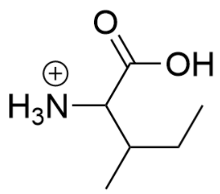
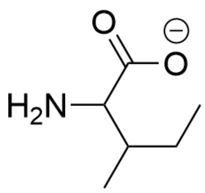
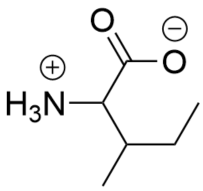
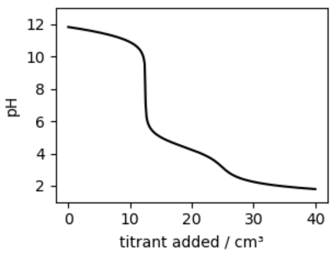
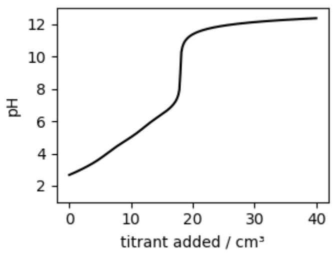
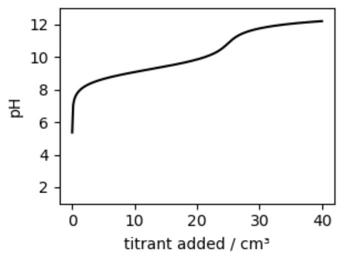
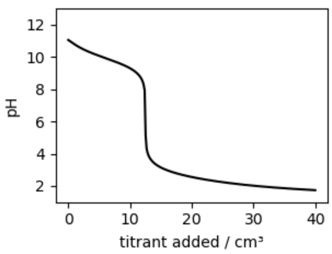
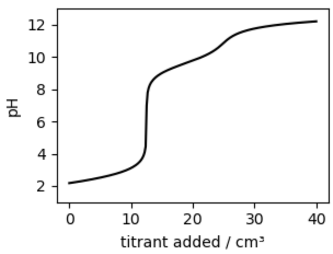
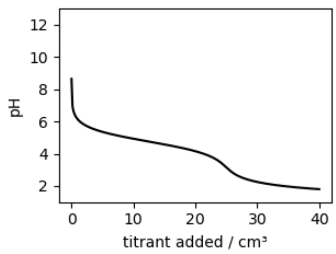
$z = [+8.2 + (2 \times 6.8) + -890.8] \text{ kJ mol}^{-1} = -869.0 \text{ kJ mol}^{-1}$, therefore −869.0 kJ.

No penalty if final answer in kJ mol^{-1}. No marks if value given in wrong units.

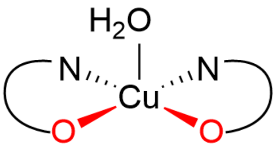
Total out of 7 **7**

2.	**This question is about electronegativity, bonding and structure**	**Mark**
(a)	0.962 $$\chi_{Cl} - \chi_H = 0.102\sqrt{427 - \frac{244 + 432}{2}}$$ $$\chi_{Cl} - \chi_H = 0.962$$ *The value should be positive, but accept if quoted as −0.962.*	☑
(b)	3.16 $$\chi_{Cl} - \chi_H = 0.962$$ $$\chi_{Cl} = 0.962 + 2.20$$ $$\chi_{Cl} = 3.16$$ *ECF can be awarded from part (a). Answer to part (b) must be 2.20 more positive than answer to part (a). No marks are to be awarded for calculation that assumes Cl is less electronegative than H.*	☑
(c)	2.96 $$\chi_N = 0.00197[\mathrm{E}_i + \mathrm{E}_{ea}] + 0.19$$ $$\chi_N = 0.00197[(14.5 \times 96.49) + 6.80] + 0.19$$ $$\chi_N = 2.96$$	☑
(d)	(i) I (ii) E (iii) L (iv) G (v) J *All five correct scores two marks. Four or three correct scores one mark. Two, one or none correct scores no marks.*	☑ ☑
(e)	AlP *Allow if they have written compound I. No ECF allowed if they have labelled one of the other five compounds in part (d) closer to the metallic corner of the triangle.*	☑
(f)	(i) B (ii) N (iii) E *One mark each*	☑ ☑ ☑
(g)	(i) $H_3BO_3 + NH_3 \rightarrow BN + 3H_2O$ *State symbols not required. Accept any multiple with correct stoichiometry.*	☑

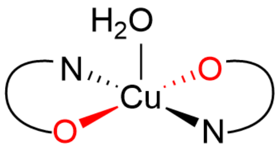
	(ii)	$B_2O_3 + 10N_2 + 3CaB_6 \rightarrow 20BN + 3CaO$ *State symbols not required. Accept any multiple with correct stoichiometry.*	☑
(h)	(i)	4.78×10^{-23} cm^3 $volume\ of\ cube = (side\ length)^3$ v = a^3 = $(3.63 \times 10^{-10}$ m$)^3$ = 4.78×10^{-29} m^3 = 4.78×10^{-23} cm^3 *No marks for answer in m^3 or Å as question asked for cm^3.*	☑
	(ii)	3.45 g cm^{-3} Unit cell has 4 B and 4 N. (4 N completely within cube. $8 \times {}^1/_8$ B on corners, $6 \times {}^1/_2$ B on faces = 4 B). Mass of unit cell is 4(10.81+14.01) g mol^{-1} / 6.02×10^{23} mol^{-1} = 1.649×10^{-22} g Density (ρ) = mass (m) / volume (v) = 1.649×10^{-22} g / 4.78×10^{-23} cm^3 = 3.45 g cm^{-3} *Correct final answer scores full marks. First mark for correct number of B and N in unit cell. Second mark for correct mass of unit cell. Third mark for final answer. Allow ECF from part (h)(i).*	☑ ☑ ☑
	(iii)	3.74×10^{-23} cm^3 $area\ of\ regular\ hexagon = \frac{3\sqrt{3}}{2} \times (side\ length)^2$ area = $\frac{3\sqrt{3}}{2} \times (1.47 \times 10^{-10}$ m$)^2$ = 5.614×10^{-20} m^2 = 5.614×10^{-16} cm^2 $volume\ of\ right\ prism = (area\ of\ base) \times (height)$ v = 5.614×10^{-16} cm^2 × 6.66×10^{-8} cm = 3.74×10^{-23} cm^3 *No marks for answer in m^3 or Å as question asked for cm^3.*	☑
	(iv)	2.20 g cm^{-3} Unit cell has 2 B and 2 N. ($6 \times {}^1/_6$ B on corners and $3 \times {}^1/_3$ B on edges, making total of 2). ($6 \times {}^1/_6$ N on corners and $3 \times {}^1/_3$ N on edges, making total of 2). Mass of unit cell is 2(10.81+14.01) g mol^{-1} / 6.02×10^{23} mol^{-1} = 8.246×10^{-23} g Density (ρ) = mass (m) / volume (v) = 8.246×10^{-23} g / 3.74×10^{-23} cm^3 = 2.20 g cm^{-3} *Correct final answer scores full marks. First mark for correct number of B and N in unit cell. Second mark for correct mass of unit cell. Third mark for final answer. Allow ECF from part (h)(iii).*	☑ ☑ ☑
	(v)	Unit cell has 2 B and 2 N. (1 B completely within unit cell, $4 \times {}^1/_{12}$ and $4 \times {}^2/_{12}$ B on corners, making total of 2). (1 N completely within unit cell, $2 \times {}^1/_6$ and $2 \times {}^2/_6$ N on edges, making total of 2). *Both must be correct for the mark.*	☑
		Total out of 20	**20**

3.	**This question is about amino acid complexes**		**Mark**
(a)	(i) 	(ii) 	☑ ☑
	One mark each. If R group not drawn out or drawn out incorrectly, then one of the two marks can be awarded if protonation states correct in both structures.		
(b)	(i)  *No marks if R group not drawn out correctly.*		☑
	(ii) 5.98 Isoelectric point = (pK_{a1} + pK_{a2}) / 2 = (2.36 + 9.60) / 2 = 5.98		☑
(c)	     ✓ 		☑
	As base is being added, pH must rise over course of titration. Expect buffer zones (line flattens out) around the pH of the two pK_a values of 2.36 and 9.60.		

(d)



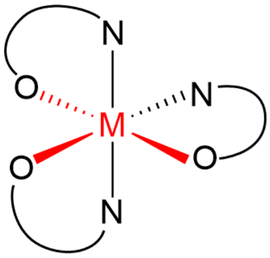
cis isomer



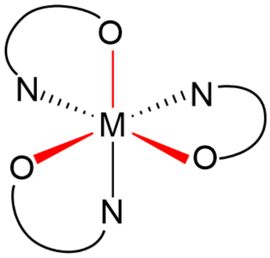
trans isomer

One mark for cis isomer, one mark for trans isomer. If three complexes are drawn maximum mark is one out of two. If four complexes are drawn no marks should be awarded. Other views are acceptable, e.g. with linking chain at front and behind.

(e)



mer isomer



fac isomer

One mark for mer isomer, this has the three O in the same meridian or plane of the metal ion. One mark for fac isomer, this has the three O on the same triangular face of the octahedron. If three complexes are drawn maximum mark is one out of two. If four complexes are drawn no marks should be awarded. Other views are acceptable, e.g. with linking chain at different positions.

(f)

$RhMt_3$

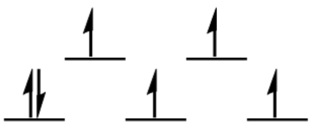
Number of d-electrons in outer shell

6

Arrangement 1

Spin magnetic moment, μ

0 BM



Arrangement 2

Spin magnetic moment, μ

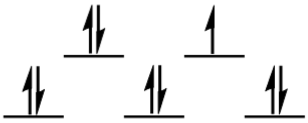
4.90 BM = $2\sqrt{6}$ BM = $\sqrt{24}$ BM

First mark for 6 d-electrons. Second mark for correct low spin arrangement. Third mark for correct high spin arrangement. Fourth mark for spin magnetic moments both correct. Student does not have to write 'low spin' or 'high spin'. Arrangements can be either way around. Do not penalise if units of BM missing. No ECF for spin magnetic moments based on incorrect orbital diagrams, or orbital diagrams based on incorrect number of d-electrons. No marks for arrangement if student draws two electrons with same spin in same orbital. All singularly filled orbitals must have parallel spins (all arrows pointing in same direction), otherwise no marks for arrangement. If singularly filled orbitals all have electrons pointing down this is also correct.

CuMt$_2$

Number of d-electrons in outer shell

9



Arrangement 1

Spin magnetic moment, μ

1.73 BM = $\sqrt{3}$ BM

Arrangement 2

Spin magnetic moment, μ

First mark for 9 d-electrons. Second and third mark for drawing the single correct spin arrangement (two marks for this). If two spin arrangements are drawn the student can get one of the two marks if at least one of these is correct. Fourth mark for spin magnetic moment correct. Student does not have to write 'low spin' or 'high spin'. Do not penalise if units of BM missing. No ECF for spin magnetic moment based on incorrect orbital diagram, or orbital diagram based on incorrect number of d-electrons. No marks for arrangement if student draws two electrons with same spin in same orbital. If singularly filled orbital has electron pointing down this is also correct.

(g)

High spin	Low spin
✓	

$$\mu = \sqrt{n(n+2)}$$

High spin n = 5, theoretical μ = 5.91 BM

Low spin n = 1, theoretical μ = 1.73 BM

Experimental data of 5.63 BM best matches high spin.

Total out of 18 **18**

4.	**This question is about vaping**	**Mark**

(a) (i)

Nitrile	Alcohol	Ester	Ketone	Ether	Carboxylic Acid
		✓		✓	

One mark each. Minus one for each incorrect answer down to zero.

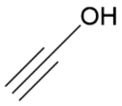
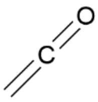
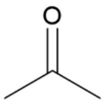
☑ ☑

(ii) 31

Full formula is $C_{31}H_{52}O_3$.

☑

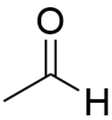
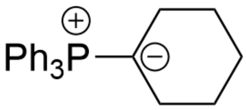
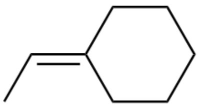
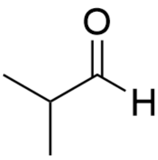
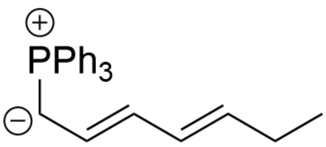
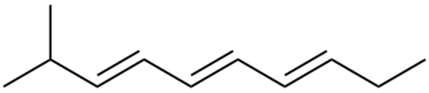
(b)

Structure	Is this structure consistent with the data from…		
	… mass spectrometry?	…^{1}H NMR?	…^{13}C NMR?
	✓	×	✓
	✓	✓	✓
	×	✓	✓
	✓	✓	×

One mark for each fully correct column.

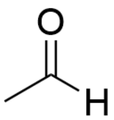
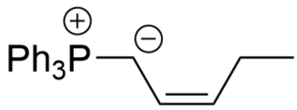
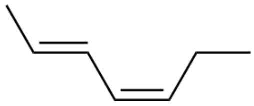
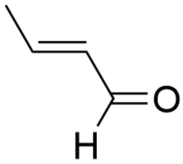
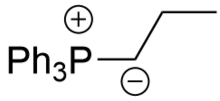
☑ ☑ ☑

(c)

aldehyde/ketone	phosphonium ylide	major alkene product
		
		

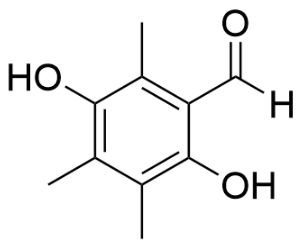
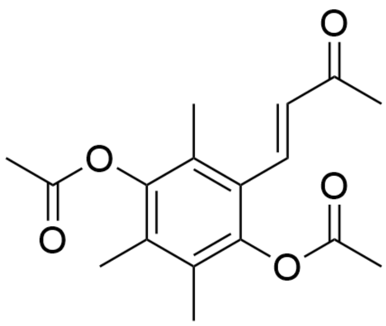
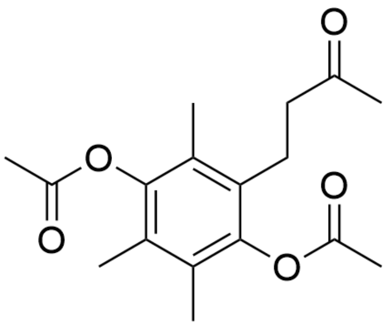
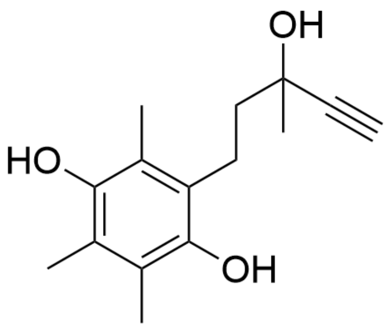
One mark each. For the first alkene product there is no difference between E and Z isomers. For the second alkene product the stereochemistry must be correctly E for all three double bonds to get the mark. The student does not have to write explicitly that the alkene is E.

☑ ☑

aldehyde/ketone	phosphonium ylide	major alkene product
		
OR		
		

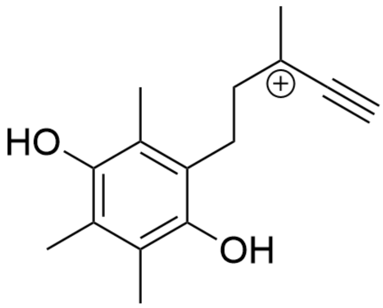
One mark each. The first row and the second row can be either way around. The two answers containing C=C bonds must have the correct stereochemistry to get the mark. The student does not have to write explicitly that the alkene is E or Z.

(d)

A	**B**
	
C	**D**
	

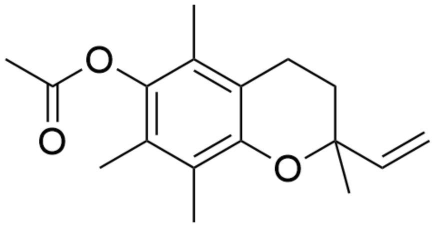
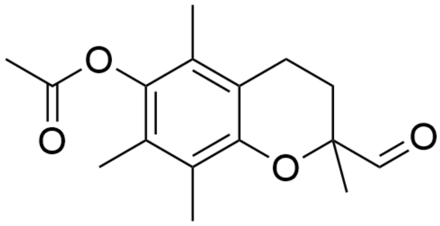
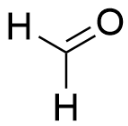
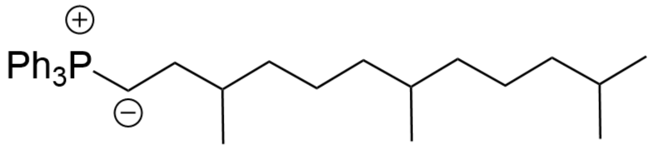
*One mark each. In **B** the alkene must be drawn with E stereochemistry for the mark. ECF can be awarded for **C** and **D** if trivial errors propagated but transformation correct.*

(e)



ECF can be awarded if trivial errors propagated but cation must be tertiary.

(f)

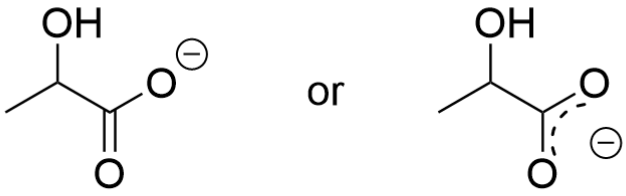
W	X
	
Y	**Z**
	

One mark each. No ECF as students have enough information to work backwards.

Total out of 21 **21**

5. **This question is about cheese** — **Mark**

(a) (i)



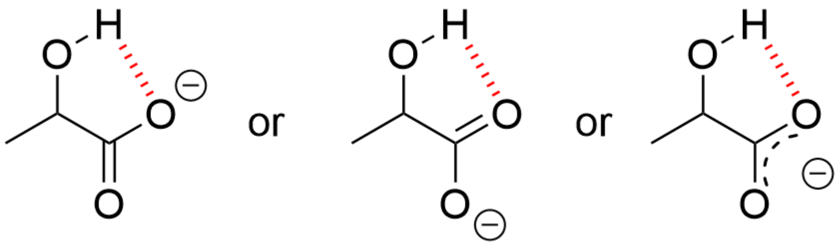
☑

(ii) 3.86

By definition, $pK_a = -log_{10}(K_a) = 3.86$

☑

(b)



It must be clearly shown that the hydrogen bond comes from the H of the hydroxyl group.

☑

(c) (i)

Oxidation	Reduction	Condensation	Hydrolysis	Isomerisation	Elimination
			✓		

No marks if more than one answer ticked.

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(ii)

A	B
glucose	galactose

One mark each.

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(d) $C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_3H_6O_3$

State symbols not required. Accept any multiple with correct stoichiometry.

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(e) $3C_3H_6O_3 \rightarrow 2C_3H_6O_2 + C_2H_4O_2 + CO_2 + H_2O$

State symbols not required. Accept any multiple with correct stoichiometry.

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(f) (i) 1.77×10^{-6} m^3

$$V = \frac{4\,\pi\,(0.5 \times 1.5 \times 10^{-2}\ m)^3}{3} = 1.77 \times 10^{-6}\ \mathrm{m^3}$$

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(ii) 1.98×10^{-2} g

$$n_{CO_2} = \frac{pV}{RT} = \frac{101325\ \mathrm{Pa} \times 1.77 \times 10^{-6}\ \mathrm{m^3}}{8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} \times (21 + 273)\ \mathrm{K}} = 7.337 \times 10^{-5}\ \mathrm{mol}$$

$$n_{C_3H_6O_3} = 3n_{CO_2} = 2.201 \times 10^{-4}\ \mathrm{mol}$$

$$M_{C_3H_6O_3} = [3 \times 12.01 + 6 \times 1.008 + 3 \times 16.00]\ \mathrm{g\ mol^{-1}} = 90.078\ \mathrm{g\ mol^{-1}}$$

$$m_{C_3H_6O_3} = n_{C_3H_6O_3} \times M_{C_3H_6O_3} = 2.201 \times 10^{-4}\ \mathrm{mol} \times 90.078\ \mathrm{g\ mol^{-1}} = 1.98 \times 10^{-2}\ \mathrm{g}$$

Allow ECF from parts (e) and (f)(i).

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(g) 3.46×10^{-2} mol dm^{-3}

Labelling the total concentration as c_{tot}, we have the two equations

$$[\mathrm{CO_{2(ch)}}] + [\mathrm{HCO^-_{3(ch)}}] = c_{tot} \qquad \text{and} \qquad \frac{[\mathrm{H^+_{(ch)}}][\mathrm{HCO^-_{3(ch)}}]}{[\mathrm{CO_{2(ch)}}]} = K$$

We use the first equation to express $[\mathrm{HCO^-_{3(ch)}}] = c_{tot} - [\mathrm{CO_{2(ch)}}]$ and substitute this into the second equation as

$$\frac{[\mathrm{H^+_{(ch)}}](c_{tot} - [\mathrm{CO_{2(ch)}}])}{[\mathrm{CO_{2(ch)}}]}$$

With $[\mathrm{H^+_{(ch)}}] = 10^{-\mathrm{pH}} = 10^{-5.20}\ \mathrm{mol\ dm^{-3}}$, this rearranges to give

$$[\mathrm{CO_{2(ch)}}] = \frac{c_{tot}}{1 + \frac{K}{[\mathrm{H^+_{(ch)}}]}} = \frac{3.70 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}}{1 + \frac{4.47\times10^{-7}\ \mathrm{mol\ dm^{-3}}}{10^{-5.20}\ \mathrm{mol\ dm^{-3}}}} = 3.46 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$$

Full credit for correct concentration of CO_2 in cheese. One mark for correctly expressing $[H^+_{(ch)}]$ in terms of pH.

(h)

	$k_H V_{ch} p_b$	$\frac{4\pi r^3 p_b}{3RT}$	$\frac{4\pi r^3 p_b}{3RT} K \cdot 10^{\mathrm{pH}}$	$K \cdot 10^{\mathrm{pH}} k_H V_{ch} p_b$	$\frac{V_{ch} p_b}{3RT}$	$K \cdot 10^{-\mathrm{pH}} k_H V_{ch} p_b$
$n_{\mathrm{CO_{2(g)}}}$		✓				
$n_{\mathrm{CO_{2(ch)}}}$	✓					
$n_{\mathrm{HCO^-_{3(ch)}}}$				✓		

One mark for every correct identification. How the expressions are derived is explained below (not required of students):

For $CO_{2(g)}$ the ideal gas law states $pV = nRT$, which rearranges to

$$n_{CO_{2(g)}} = \frac{pV}{RT} = \frac{4\pi r^3 p_b}{3RT}$$

For $CO_{2(ch)}$, $n_{CO_{2(ch)}} = [CO_{2(ch)}] \cdot V_{ch}$, which combined with Henry's law gives

$$n_{CO_{2(ch)}} = k_H V_{ch} p_b$$

For $HCO_3^-{}_{(ch)}$ rearrange the expression for the acid dissociation constant as

$$n_{HCO^-_{3(ch)}} = [HCO^-_{3(ch)}] \cdot V_{ch} = K \frac{[CO_{2(ch)}] \cdot V_{ch}}{[H^+_{(ch)}]} = K \cdot 10^{pH}\, k_H V_{ch} p_b$$

(i)

$$a = k_H V_{ch}(1 + K \cdot 10^{\mathrm{pH}}) \quad \text{and} \quad b = \frac{4\pi}{3RT}$$

One mark each for correct expression for a and b.

Working (not required of students):

$$\eta = n_{CO_{2(ch)}} + n_{HCO^-_{3(ch)}} + n_{CO_{2(g)}}$$

$$= k_H V_{ch}\left(p_{atm} + \frac{\gamma}{r}\right) + K \cdot 10^{pH} k_H V_{ch}\left(p_{atm} + \frac{\gamma}{r}\right) + \frac{4\pi r^3}{3RT}\left(p_{atm} + \frac{\gamma}{r}\right)$$

we can collect the terms as

$$\left(k_H V_{ch} + K \cdot k_H V_{ch} \cdot 10^{pH} + \frac{4\pi r^3}{3RT}\right)\left(p_{atm} + \frac{\gamma}{r}\right) = \eta$$

or

$$\left(k_H V_{ch}(1 + K \cdot 10^{pH}) + \frac{4\pi r^3}{3RT}\right)\left(p_{atm} + \frac{\gamma}{r}\right) = \eta$$

so that

$$a = k_H V_{ch}(1 + K \cdot 10^{pH}) \quad and \quad b = \frac{4\pi}{3RT}$$

(j) $r = 6.96 \times 10^{-3}$ m or $r = 1.16 \times 10^{-4}$ m

The question suggested that γr^{-1} should be small compared to p_{atm}. Only the first of these roots ($r = 6.96 \times 10^{-3}$ m) satisfies this condition and gives the correct answer.

One mark for each correct value of r that solves the equation and one mark for identifying the larger value ($r = 6.96 \times 10^{-3}$ m) as the physical solution.

$$d = \frac{2.35 \times 10^{-4}\ \text{mol}}{101325\ \text{Pa}} - 1.70 \times 10^{-9}\ \text{mol Pa}^{-1} = 6.193 \times 10^{-10}\ \text{mol Pa}^{-1}$$

$$\left(\frac{d}{b}\right)^{\frac{1}{3}} = 7.073 \times 10^{-3}\ \text{m}$$

$$\frac{\gamma\eta}{3\, p_{atm}^2 d} = \frac{9.28\ \text{Pa m} \times 2.35 \times 10^{-4}\ \text{mol}}{3 \times 101325^2\ \text{Pa}^2 \times\ 6.193 \times 10^{-10}\ \text{mol Pa}^{-1}} = 1.143 \times 10^{-4}\ \text{m}$$

The equation for r becomes

$$r = 7.073 \times 10^{-3} \times \left(1 - \ 1.143 \times 10^{-4} \cdot \frac{1}{r}\right)$$

Multiplying both side by r gives

$$r^2 = 7.073 \times 10^{-3}\, r - 8.087 \times 10^{-7} \quad \text{or} \quad r^2 - 7.073 \times 10^{-3}\, r + 8.087 \times 10^{-7} = 0$$

which is solved by

$$r = \frac{1}{2} \cdot\ 7.073 \times 10^{-3} \pm \sqrt{\left(\frac{1}{2} \cdot\ 7.073 \times 10^{-3}\right)^2 - 8.087 \times 10^{-7}}$$

giving either $r = 6.96 \times 10^{-3}$ m or $r = 1.16 \times 10^{-4}$ m.

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A note on deriving the simplified equation (non-examinable). The approximation makes use of the Taylor series $(1 + x)^\alpha = 1 + \alpha x + \cdots \approx 1 + \alpha x$, valid for $|x| \ll 1$. First write

$$a + br^3 = \eta\left(p_{atm} + \frac{\gamma}{r}\right)^{-1} = \frac{\eta}{p_{atm}}\left(1 + \frac{\gamma}{r p_{atm}}\right)^{-1} \approx \frac{\eta}{p_{atm}}\left(1 - \frac{\gamma}{r p_{atm}}\right)$$

Then subtract a and divide both sides by b

$$r^3 \approx \left(\frac{\eta}{p_{atm}} - a\right) \cdot \frac{1}{b} - \frac{\eta\gamma}{p_{atm}^2 b} \cdot \frac{1}{r} = \frac{d}{b} - \frac{\eta\gamma}{p_{atm}^2 b} \cdot \frac{1}{r}$$

and take the cube root, employing the truncated Taylor series approximation again

$$r \approx \left(\frac{d}{b} - \frac{\eta\gamma}{p_{atm}^2 b} \cdot \frac{1}{r}\right)^{\frac{1}{3}} = \left(\frac{d}{b}\right)^{\frac{1}{3}}\left(1 - \frac{\eta\gamma}{p_{atm}^2 d} \cdot \frac{1}{r}\right)^{\frac{1}{3}} \approx \left(\frac{d}{b}\right)^{\frac{1}{3}}\left(1 - \frac{\eta\gamma}{3p_{atm}^2 d} \cdot \frac{1}{r}\right)$$

Total out of 20 **20**