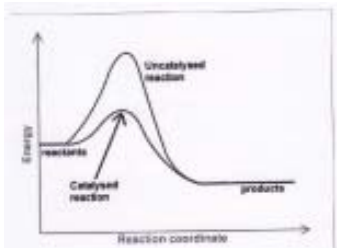


1.

experiments 1 and 2: doubling [ClO <sub>2</sub> ] quadruples the rate, so second order	1												
experiments 2 and 3: doubling [OH <sup>-</sup> ] doubles the rate, so first order	1												
rate equation = $k[\text{ClO}_2]^2[\text{OH}^-]$	1												
from experiment 2: $9.34 \times 10^{-4} = k(2.50 \times 10^{-2})^2 \times 1.30 \times 10^{-3}$ $k = 1.15 \times 10^3$	1												
units: mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>	1												
heterogeneous catalysts are in different physical state from the reactants <b>AND</b> homogeneous catalysts are in the same physical state as the reactants	1												
<table><tr><td>catalysed reaction</td><td>heterogeneous</td><td>homogeneous</td></tr><tr><td>manufacture of ammonia in the Haber process</td><td>✓</td><td></td></tr><tr><td>removal of nitrogen oxides from car exhausts</td><td>✓</td><td></td></tr><tr><td>oxidation of sulfur dioxide in the atmosphere</td><td></td><td>✓</td></tr></table>	catalysed reaction	heterogeneous	homogeneous	manufacture of ammonia in the Haber process	✓		removal of nitrogen oxides from car exhausts	✓		oxidation of sulfur dioxide in the atmosphere		✓	2
catalysed reaction	heterogeneous	homogeneous											
manufacture of ammonia in the Haber process	✓												
removal of nitrogen oxides from car exhausts	✓												
oxidation of sulfur dioxide in the atmosphere		✓											
2MnO <sub>4</sub> <sup>-</sup> + 6H <sup>+</sup> + 5(CO <sub>2</sub> H) <sub>2</sub> → 2Mn <sup>2+</sup> + 10 CO <sub>2</sub> + 8 H <sub>2</sub> O correct Mn : (CO <sub>2</sub> H) <sub>2</sub> ratio rest of equation	2 1 1												
first section: flatter second section: steeper, before flattening	2 1 1												
 <p>diagram catalyst lowers E<sub>a</sub> for both the forward and reverse reactions so the process requires less energy / can occur at a lower temperature</p>	3 1 1 1												
$K_p = (\text{pNH}_3)^2/(\text{pN}_2)(\text{pH}_2)^3$ $1.45 \times 10^{-5} = (\text{pNH}_3)^2 / 20 \times 60 \times 60 \times 60$	1												
pNH <sub>3</sub> = 7.91	1												

2.

**M1**  $\Delta H_{\text{latt}}$  and  $\Delta H_{\text{hyd}}$  decrease / both become less exothermic / less negative

3

**M2**  $\Delta H_{\text{latt}}$  decreases / changes less/becomes less exothermic by a smaller extent **OR**  $\Delta H_{\text{hyd}}$  decreases / changes more / dominant factor

**M3**  $\Delta H_{\text{sol}}$  becomes less exothermic / less negative

**OR**  $\Delta H_{\text{sol}}$  becomes (more) endothermic / (more) positive

**OR**  $\Delta H_{\text{sol}} = \Delta H_{\text{hyd}} - \Delta H_{\text{latt}}$  expression **AND** reaction becomes less exothermic

Mg: fizzing

Ba: (fizzing and) white solid/ppt forms

1

**M1** solubility of  $\text{BaSO}_4$

$$= \sqrt{1.08 \times 10^{-10}} = 1.04 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$$

$$\textbf{M2} = 1.04 \times 10^{-5} \times 233.4 / 10 = 2.43 \times 10^{-4} \text{ (g per } 100 \text{ cm}^3 \text{ of solution) min 2sf}$$

2

$$-1473 = 180 + 503 + 965 + \Delta H_{\text{f}}^{\circ} - 2469$$

$$\Delta H_{\text{f}}^{\circ} \text{ of } \text{SO}_4^{2-}(\text{g}) = -652 \text{ kJ mol}^{-1}$$

**M1** correct five values used [1]

**M2** only correct five values used [1]

**M3** correct signs and evaluation [1]

3

- $\text{BaSO}_4$  is more negative/bigger
- as  $\text{Ba}^{2+}$  is smaller **OR**  $\text{Ba}^{2+}$  has a larger charge
- stronger force of attraction between the ions

One mark for two correct

Two marks for all three correct

2

$$\textbf{M1} \Delta G^{\circ} = 0 \text{ so } T = \Delta H_{\text{f}}^{\circ} / \Delta S^{\circ}$$

**M2**

$$T = 132 / 0.616 = 214.3 \text{ K}$$

$$T = -58.7^{\circ} \text{C min 2sf}$$

2

$$\textbf{M1} \Delta S^{\circ} = (203 + (70 \times 8) + (2 \times 192)) - (427 - (2 \times 95)) = +530 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\textbf{M2} \Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

$$\textbf{M3} \Delta G^{\circ} = 133 - (298 \times 0.530) = -24.9 \text{ kJ mol}^{-1} \text{ ecf 1dp min}$$

3

3.

**M1** solubility decreases (down the Group) [1]

**M2** because lattice energy and hydration energy **decreases**

**OR** lattice energy and hydration energy become **less exothermic / more endothermic** [1]

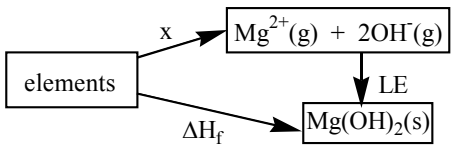
**M3** because hydration energy decreases to a **greater extent** (than does  $\Delta H_{\text{latt}}$ ) [1]

3

$$(K_{\text{w}} = ) [\text{H}^+][\text{OH}^-]$$

1

[1] or each correct tick	2												
<table><tr><td>effect of increasing temperature</td><td>decreases</td><td>stay the same</td><td>increase</td></tr><tr><td>pH</td><td>✓</td><td></td><td></td></tr><tr><td>ratio of [H<sup>+</sup>]:[OH<sup>-</sup>]</td><td></td><td>✓</td><td></td></tr></table>	effect of increasing temperature	decreases	stay the same	increase	pH	✓			ratio of [H <sup>+</sup> ]:[OH <sup>-</sup> ]		✓		
effect of increasing temperature	decreases	stay the same	increase										
pH	✓												
ratio of [H <sup>+</sup> ]:[OH <sup>-</sup> ]		✓											
[H <sup>+</sup> ] = 10 <sup>-13.25</sup> = 5.62 × 10 <sup>-14</sup> [1] [OH <sup>-</sup> ] = K <sub>w</sub> /[H <sup>+</sup> ] = 1.0 × 10 <sup>-14</sup> /5.62 × 10 <sup>-14</sup> [OH <sup>-</sup> ] = <b>0.18</b> (0.178) (mol dm <sup>-3</sup> ) [1] ecf correct answer scores [2]	2												
HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> → H <sub>2</sub> CO <sub>3</sub> <b>OR</b> HCO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> → CO <sub>2</sub> + H <sub>2</sub> O [1] H <sub>2</sub> CO <sub>3</sub> + OH <sup>-</sup> → HCO <sub>3</sub> <sup>-</sup> + H <sub>2</sub> O [1]	2												
<b>CH<sub>3</sub>COOH</b> + H <sub>2</sub> O ⇌ CH <sub>3</sub> COO <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> [1] acid + base ⇌ base + acid [1]	2												
<b>M1</b> moles NaOH = 0.15 × 20/1000 = <b>0.0030</b> <b>AND</b> initial moles CH <sub>3</sub> COOH = 0.25 × 30/1000 <b>OR 0.0075</b> [1] <b>M2</b> equilibrium moles CH <sub>3</sub> COOH = <b>0.0045</b> <b>AND</b> equilibrium moles CH <sub>3</sub> COONa = <b>0.0030</b> [1] <b>M3</b> [CH <sub>3</sub> COOH] = 0.0045/0.05 = <b>0.090</b> <b>AND</b> [CH <sub>3</sub> COONa] = 0.003/0.05 = <b>0.060</b> [H <sup>+</sup> ] = K <sub>a</sub> × [CH <sub>3</sub> COOH]/[CH <sub>3</sub> COONa] = <b>2.625 × 10<sup>-5</sup></b> [1] <b>M4</b> pH = -log[H <sup>+</sup> ] = <b>4.6</b> [1] correct answer scores [4]	4												
end point = 28 cm <sup>3</sup>	1												
<b>M1</b> reaction <b>M</b> bromothymol (blue) / bromocresol (green) <b>AND</b> reaction <b>N</b> bromothymol (blue) / thymolphthalein [1] <b>M2</b> (both indicators have) a pH range / colour change <b>within / in</b> end-point / vertical region / sharp fall of the graph [1] (pH =) -log[H <sup>+</sup> ] <b>OR</b> -lg[H <sup>+</sup> ] [1] (K <sub>w</sub> =) [H <sup>+</sup> ][OH <sup>-</sup> ] [1]	2  2												
[H <sup>+</sup> ] = 1 × 10 <sup>-14</sup> / 0.027 = 3.7037 × 10 <sup>-13</sup> pH = -log(3.7037 × 10 <sup>-13</sup> )= <b>12.4</b> [1] min 3sf	1												
[H <sup>+</sup> ] = √3.72 × 10 <sup>-8</sup> × 0.010 = 1.9287 × 10 <sup>-5</sup> pH = -log(1.9287 × 10 <sup>-5</sup> )= <b>4.7</b> [1] min 2sf	1												
K <sub>pc</sub> = (0.935 / 50) / (0.065 / 50) K <sub>pc</sub> = <b>14.4</b> (14.38) [1] min 3sf	1												
<b>M1:</b> 14.4 = ((0.935 - x) / 50) / (x / 100) [1] ecf from <b>4(c)(i)</b> <b>M2:</b> x = <b>0.114</b> g [1] min 2sf ecf from M1 <b>M1</b> ΔH <sub>latt</sub> and ΔH <sub>hyd</sub> both decrease <b>OR</b> ΔH <sub>latt</sub> and ΔH <sub>hyd</sub> both become less exothermic / more endothermic <b>M2</b> ΔH <sub>latt</sub> decreases more than ΔH <sub>hyd</sub> (as OH <sup>-</sup> being smaller than M <sup>2+</sup> ) <b>M3</b> ΔH <sub>sol</sub> becomes more exothermic / more negative	2  3												
(for MCO <sub>3</sub> ) change / decrease in ΔH <sub>hyd</sub> is larger than decrease in ΔH <sub>latt</sub>	1												
<b>M1</b> Sr and Ba could be used <b>AND</b> Mg could not be used <b>M2</b> solubility of MgCO <sub>3</sub> is more than Mg(OH) <sub>2</sub> <b>OR</b> SrCO <sub>3</sub> / BaCO <sub>3</sub> is less than Sr(OH) <sub>2</sub> / Ba(OH) <sub>2</sub>	2												

	$K_{sp} = [\text{Mg}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 \quad \text{OR} \quad K_{sp} = (2.0 \times 10^{-4})(4.0 \times 10^{-4})^2$ $= 3.2 \times 10^{-11}$	2
	<b>M1</b> (white) ppt. / solid (of $\text{BaCO}_3$ ) will appear <b>M2</b> due to the common ion effect OR the $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ equilibrium shifts to the left	2
	 <p> <math>-2993 + 148 + 736 + 1450 + 2\Delta H_f(\text{OH}^{-}(\text{g})) = -925</math>  <math>2\Delta H_f(\text{OH}^{-}(\text{g})) = -266</math>  <math>\Delta H_f(\text{OH}^{-}(\text{g})) = -133 \text{ (kJ mol}^{-1}\text{)}</math>            (solubility) increases (down the group)         </p>	3
6.	down the group: lattice energy <b>or</b> hydration energy decrease lattice energy decreases more than hydration energy enthalpy change of solution becomes more negative / exothermic	1
	$K_{sp} = [\text{Sr}^{2+}][\text{OH}^{-}]^2$	3
	$K_{sp} = (3.37 \times 10^{-2}) \times (6.74 \times 10^{-2})^2 = 1.5 \times 10^{-4}$ units: $\text{mol}^3 \text{ dm}^{-9}$	1
	$2 \text{ SrO}_2 \longrightarrow 2 \text{ SrO} + \text{O}_2$	2
	temperature will increase (down the group) charge density of cation decreases (down the group) this means less polarisation of the $\text{O}_2^{2-}$ ion <i>or</i> weakens the O-O bond less	1
	$\text{BaC}_2\text{O}_4 \longrightarrow \text{BaO} + \text{CO} + \text{CO}_2$	3
	the $\text{KMnO}_4$ would decolourise bubbles / gas evolution would be seen	1
7.	$K_{sp} = [\text{Ag}^+]^2[\text{S}^{2-}]$	2
	<ul style="list-style-type: none"> <li><math>[\text{S}^{2-}] = 1.16 \times 10^{-17}</math></li> <li><math>[\text{Ag}^+] = 2.32 \times 10^{-17}</math></li> <li><math>K_{sp} = 6.2(4) \times 10^{-51}</math> minimum 2 sig. fig.</li> </ul> <p>           correct answer scores 2 marks            Award 1 mark for two points, award 2 marks for three points         </p>	2
	<b>M1:</b> moles $\text{Ag}_2\text{S} = 1 / 247.9 = 0.00403$ moles [1] 2sf min <b>M2:</b> $1.16 \times 10^{-17} = 0.0040 / V$ so $V = 3.5 \times 10^{14} (\text{dm}^3)$ [1] 2sf min ecf on M1 correct answer scores 2 marks	2
	<b>M1:</b> $[\text{H}^+] = \sqrt{2.0 \times 10^{-9} \times 0.20}$ $[\text{H}^+] = 2.0 \times 10^{-5} (1.9976 \times 10^{-5})$ <b>M2:</b> pH = 4.7 (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	2

8.

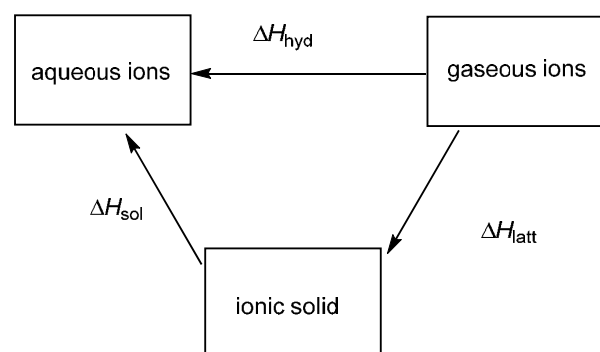
**M1:** Both equilibria correctly stated  
moles KOH =  $0.005 \times 0.2 = 1 \times 10^{-3}$   
moles HOBr(initial) =  $0.020 \times 0.2 = 4 \times 10^{-3}$   
moles HOBr(eqm) =  $4 \times 10^{-3} - 1 \times 10^{-3} = 3 \times 10^{-3}$   
moles BrO<sup>-</sup>(eqm) =  $1 \times 10^{-3}$

**M2:** ratio [OBr<sup>-</sup>]/[HOBr] = 1/3  
[H<sup>+</sup>] =  $3 \times 2.0 \times 10^{-9} = 6 \times 10^{-9}$   
pH = **8.2(2)**

correct answer scores 2 marks

$\text{Ca}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{NH}_3$   
products are Ca(OH)<sub>2</sub> and NH<sub>3</sub> [1]  
rest of the equation, balanced [1]

**M1:** solubility increases (down the Group) [1]  
**M2:** because lattice energy and hydration energy **decreases** or lattice energy and hydration energy become **less exothermic / (more) endothermic** [1]  
**M3:** because lattice energy decreases to a **greater extent** (than does  $\Delta H_{\text{hyd}}$ ) [1]



arrow label and direction correct [1] x 3

$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$  [1]  
units =  $\text{mol}^3 \text{dm}^{-9}$  [1]

$K_{\text{sp}} = 4x^3 = 3.45 \times 10^{-11}$   
 $x = 2.05 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$

$\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$

moles of  $\text{Mg}_3\text{N}_2 = 2.52 / 100.9 = 0.025 \text{ (0.0249)}$

(moles of  $\text{Mg}(\text{OH})_2 = 0.075 \text{ (0.0749)}$ )  
mass of  $\text{Mg}(\text{OH})_2 = (0.075 \times 58.3) = 4.37 \text{ g or } 4.4 \text{ g}$

solubility increases (down the group)

$\Delta H_{\text{latt}}$  and  $\Delta H_{\text{hyd}}$  both decrease / less exothermic / more endothermic

but  $\Delta H_{\text{latt}}$  decreases more (than  $\Delta H_{\text{hyd}}$  decreases)

$\Delta H_{\text{sol}}$  becomes more negative / more exothermic / less endothermic

$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$

$K_{\text{sp}} = (1.7 \times 10^{-4}) \times (2 \times 1.7 \times 10^{-4})^2 = 2.0 \times 10^{-11} \text{ (1.97} \times 10^{-11}\text{)}$

$\text{mol}^3 \text{dm}^{-9}$

cations become bigger / ionic radius increases

polarisation/distortion of anion / hydroxide ion decreases

9.

2

2

3

3

2

1

1

1

1

1

1

1

1

1

1

1

1

1

10	<b>M1:</b> using expt 2 and 3, $[\text{NH}_3] \times 2$ , rate $\times 4$ so order with respect to $[\text{NH}_3] = 2$	<b>2</b>
	<b>M2:</b> using expt 1 and 2, $[\text{ClO}^-] \times 2$ and $[\text{NH}_3] \times 2$ , as rate $\times 8 (=2^2 \times 2)$ so order with respect to $[\text{ClO}^-] = 1$	
	rate = $k[\text{NH}_3]^2[\text{ClO}^-]$	<b>1</b>
	<b>M1:</b> $k = 0.256 / (0.200 \times 0.100^2)$ $k = 128$	<b>2</b>
	<b>M2:</b> Units $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	
	curve / line showing $k$ increasing as temperature increases	<b>1</b>
	<b>M1:</b> plot a graph of $[\text{I}^-]$ against time	<b>2</b>
	<b>M2:</b> constant half-lives	
	$\text{ClO}^- + \text{I}^- \rightarrow \text{IO}^- + \text{Cl}^-$	<b>1</b>
	step 2 <b>and</b> $\text{Cl}$ is reduced / oxid no. decreases / oxid no. $+1 \rightarrow -1$ <b>or</b> step 2 <b>and</b> $\text{I}$ is oxidised / oxid no. increases / oxid no. $-1 \rightarrow +1$	<b>1</b>