**1** This is a question about entropy changes.

Consider the reaction between the two solids, hydrated barium hydroxide and ammonium chloride. When these substances are mixed together, a white paste is formed and the temperature decreases. An equation for this process is given below.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + 10H_2O(l) + BaCl_2(s)$$

(a) (i) Identify **one** hazard associated with a named substance in this reaction.

**(1)**

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(ii) Use the standard molar entropies below to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction at 298 K. Give a sign and units with your answer.

| Compound | $S^{\ominus}$ / J mol$^{-1}$ K$^{-1}$ |
|---|---|
| $Ba(OH)_2.8H_2O(s)$ | 427 |
| $NH_4Cl(s)$ | 95 |
| $NH_3(g)$ | 192 |
| $H_2O(l)$ | 70 |
| $BaCl_2(s)$ | 124 |

**(3)**

*(iii) Give **two** reasons why the sign of your answer to (a)(ii) is as you would expect.

**(2)**

(b) The standard enthalpy change for this reaction is $\Delta H_r^{\ominus} = +162$ kJ mol$^{-1}$.

Use this value to calculate the standard entropy change of the surroundings ($\Delta S_{surroundings}^{\ominus}$) for this reaction at 298 K. Include a sign and units in your answer.

**(2)**

(c) Use your answers to (a)(ii) and (b) to calculate the total entropy change ($\Delta S_{total}^{\ominus}$) for this reaction. Include a sign and units in your answer.

**(1)**

(d) What would be the effect, if any, on the value of $\Delta S_{total}^{\ominus}$ from (c) of a small increase in temperature? Justify your answer and state any assumptions that you have made.

**(3)**

(e) The values of total entropy change and equilibrium constant of a reaction are related by the following equation.

$$\Delta S_{total} = R \ln K$$

The equation for the dissolving of barium hydroxide is

$$Ba(OH)_2(s) + aq \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq) \qquad \Delta S^{\ominus}_{total} = -44 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Calculate the value of the equilibrium constant, *K*, for this equation at 298 K.

$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

**(1)**

(ii) What does the value of the equilibrium constant suggest about the solubility of barium hydroxide?

Justify your answer.

**(1)**

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(iii) For the dissolving of calcium hydroxide, the value of the total entropy change is $-106 \text{ J mol}^{-1} \text{ K}^{-1}$

Compare the values of the total entropy changes for these two hydroxides and show that they are consistent with the trend in the solubility of Group 2 hydroxides.

**(2)**

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**(Total for Question = 16 marks)**

**2** This question is about magnesium chloride, $MgCl_2$.

It can be formed by burning magnesium in chlorine.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s) \qquad \Delta S^{\ominus}_{surroundings} = +2152 \text{ J mol}^{-1} \text{ K}^{-1}$$

Remember to include a sign and units in your answers to the calculations in this question.

(a) (i) The standard molar entropy at 298 K for 1 mol chlorine molecules, $Cl_2$, is +165 J $mol^{-1}$ $K^{-1}$. Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction.

**(2)**

*(ii) Explain fully why the sign for the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, is as you would expect.

**(2)**

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(b) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, in J $mol^{-1}$ $K^{-1}$, for this reaction, giving your answer to three significant figures.

**(2)**

(c) Use the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, to calculate the standard enthalpy change, $\Delta H^{\ominus}$, in kJ mol$^{-1}$, for the reaction at 298 K.

**(2)**

(d) 0.0300 mol of magnesium chloride, prepared by burning magnesium in chlorine, is added to 51.5 cm$^3$ of water.
50.0 cm$^3$ of 1.00 mol dm$^{-3}$ solution is formed, and the temperature rise, $\Delta$T, is 22.5°C.

(i) Calculate the energy transferred in joules for this process using:

Energy transferred in joules = volume of **solution** $\times$ 4.2 $\times$ $\Delta$T

**(1)**

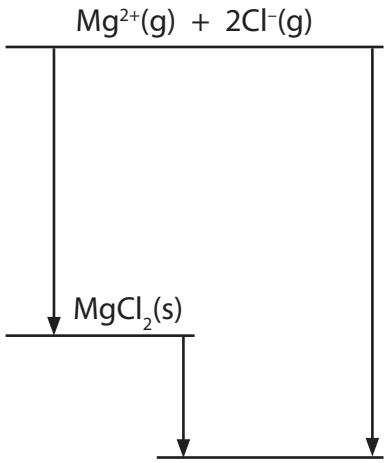
(ii) Calculate the enthalpy change of solution, $\Delta H_{\text{solution}}$, of magnesium chloride in kJ mol$^{-1}$.

**(2)**

*(iii) The enthalpy change of hydration of $Mg^{2+}(g)$ is −1920 kJ $mol^{-1}$.

Use this, your value from (d)(ii), and the experimental lattice energy from your Data Booklet, to calculate the enthalpy change of hydration of $Cl^-(g)$.

**(3)**




Answer ..... kJ $mol^{-1}$

(iv) Draw a diagram to represent a hydrated chloride ion.

**(1)**

(v) Suggest why the addition of anhydrous magnesium chloride to water results in an increase in temperature and a decrease in volume.

**(2)**

Temperature increases .....

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Volume decreases .....

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**(Total for Question = 17 marks)**

**3** This question is about calcium chloride, $CaCl_2$.

It can be formed by burning calcium in chlorine.

$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s) \qquad \Delta S^{\ominus}_{surroundings} = +2670 \text{ J mol}^{-1} \text{ K}^{-1}$$

You must include a sign and units in your answers to the calculations in this question.

(a) (i) The standard molar entropy at 298 K for 1 mole of chlorine molecules, $Cl_2$, is +165 J $mol^{-1}$ $K^{-1}$. Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change, $\Delta S^{\ominus}_{system}$, for this reaction.

**(2)**

*(ii) Explain fully why the sign for the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, is as you would expect.

**(2)**

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(b) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, in J $mol^{-1}$ $K^{-1}$, for this reaction, giving your answer to three significant figures.

**(2)**

(c) Use the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, to calculate the standard enthalpy change, $\Delta H^{\ominus}$, in kJ mol$^{-1}$, for the reaction at 298 K.

**(2)**

(d) 0.0500 mol of calcium chloride, prepared by burning calcium in chlorine, is added to 51.8 cm$^3$ of water.

50.0 cm$^3$ of a 1.00 mol dm$^{-3}$ solution is formed, and the temperature rise, $\Delta$T, is 15.0°C.

(i) Calculate the energy transferred, in joules, for this process using:

Energy transferred in joules = volume of **solution formed** $\times$ 4.2 $\times$ $\Delta$T

**(1)**

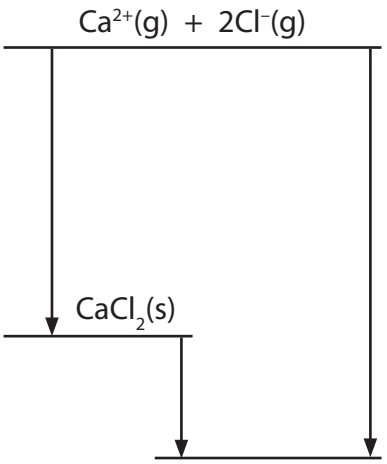
(ii) Calculate the enthalpy change of solution, $\Delta H_{\text{solution}}$, of calcium chloride in kJ mol$^{-1}$.

**(2)**

*(iii) The enthalpy change of hydration of $Ca^{2+}(g)$ is –1560 kJ $mol^{-1}$.

Use this, your value from (d)(ii) and the experimental lattice energy from your Data Booklet, to calculate the standard enthalpy change of hydration of $Cl^-(g)$.

**(3)**




Answer ..... kJ $mol^{-1}$

(iv) Draw diagrams to represent hydrated calcium ions and hydrated chloride ions.

**(2)**

(v) Suggest why the addition of anhydrous calcium chloride to water results in an increase in temperature and a decrease in volume.

**(2)**

Temperature increases .....

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Volume decreases .....

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**(Total for Question = 18 marks)**

**4** The equation for the combustion of hydrogen is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

(a) Use the standard molar entropies on page 2 and page 25 of the data booklet to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of oxygen, $S^{\ominus}[\frac{1}{2}O_2(g)] = +102.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

**(3)**

(b) The standard enthalpy change for the combustion of hydrogen is $-285.8 \text{ kJ mol}^{-1}$. Use this value to calculate the entropy change of the surroundings for the combustion of hydrogen at 298 K. Give your answer to **3** significant figures and include a sign and units.

**(3)**

(c) Use your answers to (a) and (b) to calculate the total entropy change ($\Delta S^{\ominus}_{total}$) for the combustion of 1 mol of hydrogen. Include a sign and units in your answer.

**(2)**

*(d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

**(2)**

**(Total for Question = 10 marks)**