
s-Block chemistry

Answers to worked examples

WE 26.1 Estimating the enthalpy change of formation of lithium nitride (Li₃N) (on p. 1178 in *Chemistry*³)

Estimate a value for the enthalpy change of formation of Na₃N and comment on the stability of this compound with respect to the elements. Use the data in Tables 26.2 (p.1171), 3.6 (p.155) and 6.4 (p.286).

Strategy

Construct a Born–Haber cycle for the formation of Na₃N from the elements. Use the Kapustinskii equation (Equation 6.11, p.297) to estimate the lattice enthalpy.

Solution

The calculation is analogous to the one for Li₃N. From the Born–Haber cycle,

$$\Delta_f H^\circ(\text{Na}_3\text{N}) = 3\Delta_a H^\circ(\text{Na}) + 3\Delta_i H(1)^\circ(\text{Na}) + \Delta_a H^\circ(\text{N}) + \Delta_{\text{eg}} H(1)^\circ(\text{N}) + \Delta_{\text{eg}} H(2)^\circ(\text{N}) + \Delta_{\text{eg}} H(3)^\circ(\text{N}) - \Delta_{\text{latt}} H^\circ(\text{Na}_3\text{N})$$

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$

$$\Delta_{\text{latt}} H^\circ(\text{Li}_3\text{N}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 4 \cdot 1 \cdot 3}{(102 + 171) \text{ pm}} = +4740 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_f H^\circ(\text{Na}_3\text{N}) &= (3 \times +107 \text{ kJ mol}^{-1}) + (3 \times +496 \text{ kJ mol}^{-1}) + (+473 \text{ kJ mol}^{-1}) + (+2565 \\ &\quad \text{kJ mol}^{-1}) - (+4740 \text{ kJ mol}^{-1}) \\ &= +107 \text{ kJ mol}^{-1} \end{aligned}$$

The formation of Na_3N is endothermic. This helps explain why, in contrast to Li_3N , Na_3N is unknown.

WE 26.2 Why doesn't MgCl exist? (on p. 1188 in *Chemistry*³)

Calculate the enthalpy change for the disproportionation of CaF to CaF_2 and Ca . Use your answer to comment on whether calcium(I) fluoride is known.

$$\begin{aligned}\Delta_a H^\circ(\text{Ca}) &= +178 \text{ kJ mol}^{-1} & \Delta_a H^\circ(\text{F}) &= +79 \text{ kJ mol}^{-1} \\ \Delta_i H(1)^\circ(\text{Ca}) &= +590 \text{ kJ mol}^{-1} & \Delta_{\text{eg}} H(1)^\circ(\text{F}) &= -328 \text{ kJ mol}^{-1} \\ \Delta_i H(2)^\circ(\text{Ca}) &= +1145 \text{ kJ mol}^{-1}\end{aligned}$$

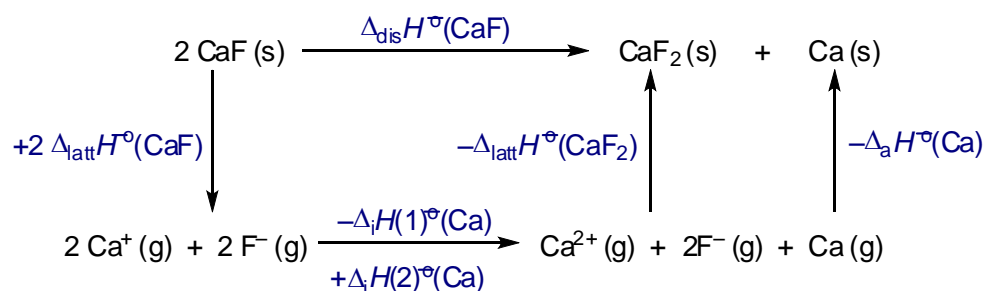
The ionic radii for Ca^{2+} , K^+ and F^- are 100 pm, 138 pm and 133 pm respectively.

Strategy

First draw an enthalpy cycle for the formation of CaF from CaF_2 and Ca . This process generates three unknown terms in the cycle, two of which are lattice enthalpies which can be calculated using the Kapustinskii equation (Equation 6.11, p.297). This means the remaining term can now be calculated,

Solution

Enthalpy cycle for the disproportionation of CaF :



Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$ to estimate the

lattice enthalpies of CaF_2 and CaF :

$$\Delta_{\text{latt}} H^\circ(\text{CaF}_2) \approx \Delta_{\text{latt}} U^\circ(\text{CaF}_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 2 \cdot 1}{(100 + 133) \text{ pm}} = +2780 \text{ kJ mol}^{-1}$$

Assuming the ionic radius of Ca^+ is equal to that of K^+ :

$$\Delta_{\text{latt}}H^\circ(\text{CaF}) \approx \Delta_{\text{latt}}U^\circ(\text{CaF}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 1 \cdot 1}{(138 + 133) \text{ pm}} = +796 \text{ kJ mol}^{-1}$$

From the enthalpy cycle:

$$\begin{aligned} 2\Delta_{\text{dis}}H^\circ(\text{CaF}) &= 2\Delta_{\text{latt}}H^\circ(\text{CaF}) + \Delta_{\text{i}}H(2)^\circ(\text{Ca}) - \Delta_{\text{i}}H(1)^\circ(\text{Ca}) - \Delta_{\text{latt}}H^\circ(\text{CaF}_2) - \Delta_{\text{a}}H^\circ(\text{Ca}) \\ &= (2 \times 796 \text{ kJ mol}^{-1}) + (+1145 \text{ kJ mol}^{-1}) - (+590 \text{ kJ mol}^{-1}) - (+2780 \text{ kJ mol}^{-1}) \\ &\quad - (+178 \text{ kJ mol}^{-1}) \\ &= -811 \text{ kJ mol}^{-1}, \text{ so} \end{aligned}$$

$$\Delta_{\text{dis}}H(\text{CaF}) = -406 \text{ kJ mol}^{-1}$$

Therefore, CaF will disproportionate to CaF₂ and Ca, and will not exist.

Answers to boxes

Box 26.1 Why is sodium peroxide more stable to heating than lithium peroxide? (on p. 1174 in *Chemistry*³)

Estimate $\Delta_{\text{r}}H^\circ$ for the decomposition of K₂O₂ to K₂O. The ionic radius of K⁺ is 138 pm.

Strategy

As both are ionic compounds, a thermochemical cycle can be constructed for this decomposition. However, it is necessary to calculate the lattice enthalpies for the two compounds using the Kapustinskii equations (Equation 6.11, p.297) before the cycle can be used to calculate $\Delta_{\text{r}}H^\circ$.

Solution

From the enthalpy cycle in Box 26.1 (p.1174),

$$\Delta_{\text{r}}H^\circ = \Delta_{\text{latt}}H^\circ(\text{K}_2\text{O}_2) + \Delta_{\text{x}}H^\circ - \Delta_{\text{latt}}H^\circ(\text{K}_2\text{O})$$

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}}U = \frac{kvz_+z_-}{r_+ + r_-}$ for the lattice enthalpies of K₂O and K₂O₂,

$$\Delta_{\text{latt}}H^\circ(\text{K}_2\text{O}) \approx \Delta_{\text{latt}}U^\circ(\text{K}_2\text{O}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 1 \cdot 2}{(138 + 140) \text{ pm}} = +2330 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}}H^\circ(\text{K}_2\text{O}_2) \approx \Delta_{\text{latt}}U^\circ(\text{K}_2\text{O}_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 1 \cdot 2}{(138 + 167) \text{ pm}} = +2120 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_r H^\circ &= \Delta_{\text{latt}}H^\circ(\text{K}_2\text{O}_2) + \Delta_x H^\circ - \Delta_{\text{latt}}H^\circ(\text{K}_2\text{O}) \\ &= (+2120 \text{ kJ mol}^{-1}) + (+845 \text{ kJ mol}^{-1}) - (+2330 \text{ kJ mol}^{-1}) \\ &= +635 \text{ kJ mol}^{-1} \end{aligned}$$

Box 26.3 Building materials (on p. 1185 in *Chemistry*³)

What advantages do hydraulic cements have over those based on calcium hydroxide?

Strategy

Calcium hydroxide based cements require carbon dioxide to harden. The final cement is based on the material, CaCO_3 (limestone). This reaction requires exposure to air for the hardening reaction to occur. Hydraulic cements use water rather than carbon dioxide to form the hard cement material. Consider why using water as the hardening agent is an advantage.

Solution

Hydraulic cements harden in air and water, whereas those based on calcium hydroxide harden only in air. Hydraulic cements are more durable, and less soluble in water so do not deteriorate in wet environments.

Box 26.4 Hard water (on p. 1191 in *Chemistry*³)

Many limescale removers contain citric acid. Suggest how this work.

Strategy

Limescale is comprised of Group 2 metal carbonates (mostly calcium carbonate) which precipitate from solutions containing carbonate and Group 2 metal cations. Limescale removers break down the Group 2 carbonates by forming soluble species.

Consider what soluble species can form from the reaction of limescale with citric acid.

Solution

Citric acid is a weak acid, and it reacts with the insoluble CaCO_3 to form soluble calcium citrate in addition to CO_2 and water. Citrate is also a chelating ligand (see Section 28.3, p.1267).

Box 26.5 Chlorophylls (on p. 1192 in *Chemistry*³)

Suggest why the leaves on deciduous trees change colour and are lost in autumn.

Strategy

The key to this question is to consider the purpose of generating green leaves during the sunny summer months which are lost when the sunlight begins to wane.

Solution

Deciduous trees produce leaves during the spring which contain the pigment, chlorophyll. While this process costs the tree some energy, the purpose of growing these leaves is to use carbon dioxide and water to produce glucose. The energy for this reaction, known as photosynthesis, is provided by absorbing red and violet light from the sun. This is why leaves appear green as the chlorophyll in the leaves absorbs the red and violet light and reflect the green light back to our eyes (see Section 10.6, p.491). During the summer the chlorophyll in leaves is constantly replenished until the light begins to fade as summer turns into autumn. Trees then stop producing the chlorophyll just before shedding the leaves as keeping the leaves alive when there is little light to use to produce energy would be pointless. As the green colour disappears, other colours are revealed. The compounds giving rise to these were present in the summer, but the colours were masked by the intense green of the chlorophyll.

Answers to end of chapter questions

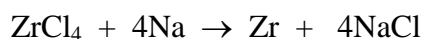
1. Sodium can be used to prepare zirconium from ZrCl_4 . What mass of sodium is required to yield 1 kg of zirconium?

Strategy

First write a balanced equation for the reaction of sodium with zirconium(IV) chloride to discover the molar ratio of Na:Zr required. Next calculate the number of moles of zirconium in 1 kg of Zr. Multiply the number of moles of zirconium by the ratio determined in the equation to calculate the moles of sodium required. Finally, multiply the number of moles of sodium by the molecular mass of sodium to determine the mass of sodium required.

Solution

The reaction between sodium and zirconium is:



so 4 mol sodium are required to give 1 mol zirconium

$$A_r(\text{Zr}) = 91.22, \text{ so } 1 \text{ kg zirconium contains } \frac{1000 \text{ g}}{91.22 \text{ g mol}^{-1}} = 10.96 \text{ mol}$$

Moles of sodium = $4 \times 10.96 \text{ mol} = 43.84 \text{ mol}$ sodium required.

$A_r(\text{Na}) = 22.99$, so the mass of sodium required is $43.84 \text{ mol} \times 22.99 \text{ g mol}^{-1} = 1010 \text{ g}$
(to 3 s.f.) = 1.01 kg

2. Identify the products and write balanced equations for the following reactions:

- adding caesium to water;
- burning rubidium in an excess of air;
- heating lithium nitrate;

Strategy

Consider the strongest bonds that can be formed in each case. Remember to take into account the relative sizes of cations and anions (remembering that large cations favour large anions).

Solution

- (a) $2 \text{Cs (s)} + 2 \text{H}_2\text{O (l)} \rightarrow 2 \text{CsOH (aq)} + \text{H}_2 \text{(g)}$
 (b) $\text{Rb (s)} + \text{O}_2 \text{(g)} \rightarrow \text{RbO}_2 \text{(s)}$
 (c) $4 \text{LiNO}_3 \text{(s)} \rightarrow 2 \text{Li}_2\text{O (s)} + 4 \text{NO (g)} + 3 \text{O}_2 \text{(g)}$

3. Use a Born–Haber cycle and the data below to explain why NaCl_2 doesn't exist. Assume the ionic radius of Na^{2+} is the same as that for Mg^{2+} .

Ionic radii: Mg^{2+} , 72 pm; Cl^- , 181 pm

$$\Delta_a H^\ominus(\text{Na}) = +108 \text{ kJ mol}^{-1}$$

$$\Delta_a H^\ominus(\text{Cl}) = +121 \text{ kJ mol}^{-1}$$

$$\Delta_i H(1)^\ominus(\text{Na}) = +496 \text{ kJ mol}^{-1}$$

$$\Delta_i H(2)^\ominus(\text{Na}) = +4562 \text{ kJ mol}^{-1}$$

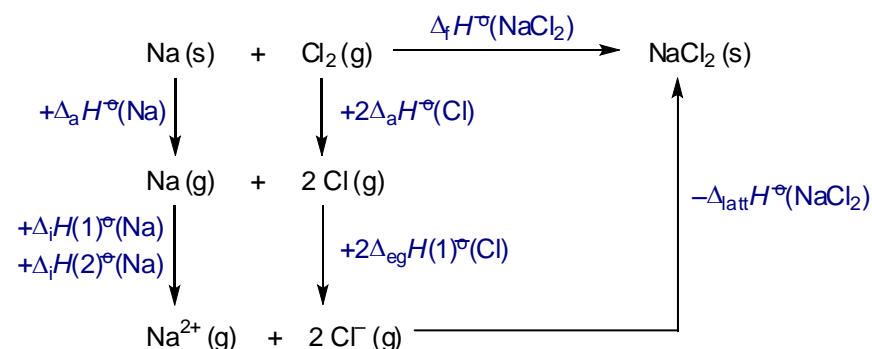
$$\Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) = -349 \text{ kJ mol}^{-1}$$

Strategy

First draw an enthalpy cycle for the formation of NaCl_2 . While the lattice enthalpy for NaCl_2 is not known, it can be calculated using the Kapustinskii equation (Equation 6.11, p.297) by assuming the radius of Na^{2+} is the same as Mg^{2+} .

Solution

Firstly, construct the Born-Haber cycle for $\Delta_f H^\ominus(\text{NaCl}_2)$,



From this, $\Delta_f H^\circ(\text{NaCl}_2) = \Delta_a H^\circ(\text{Na}) + 2\Delta_a H^\circ(\text{Cl}) + \Delta_i H(1)^\circ(\text{Na}) + \Delta_i H(2)^\circ(\text{Na}) + 2\Delta_{\text{eg}} H(1)^\circ(\text{Cl}) - \Delta_{\text{latt}} H^\circ(\text{NaCl}_2)$.

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$ to estimate

$\Delta_{\text{latt}} H^\circ(\text{NaCl}_2)$.

$$\Delta_{\text{latt}} H^\circ(\text{NaCl}_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 2 \cdot 1}{(72 + 181) \text{ pm}} = +2560 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_f H^\circ(\text{NaCl}_2) &= (+108 \text{ kJ mol}^{-1}) + (2 \times +121 \text{ kJ mol}^{-1}) + (+496 \text{ kJ mol}^{-1}) + (+4562 \text{ kJ mol}^{-1}) \\ &\quad + (2 \times -349 \text{ kJ mol}^{-1}) - (+2560 \text{ kJ mol}^{-1}) \\ &= +2150 \text{ kJ mol}^{-1} \text{ (3 s.f.)} \end{aligned}$$

The enthalpy change of formation of NaCl_2 is strongly endothermic, so it is unstable with respect to the elements. The most important factor is the very large positive value of $\Delta_i H(2)^\circ(\text{Na})$.

4. Predict which compound in each of the following pairs has the higher decomposition temperature. (a) NaNO_3 and KNO_3 ; (b) LiH and KH ; (c) Li_2CO_3 and SrCO_3 . Give reasons for your answer.

Strategy

The decomposition temperature will depend on the lattice enthalpy of the both the starting material and the product. Therefore consider what factors affect the lattice enthalpy in each case

Solution

- (a) KNO_3 has the higher decomposition temperature as the lattice enthalpy of the nitrite decomposition product is lower.
- (b) LiH has the higher decomposition temperature as decomposition is to the elements. It has the more negative enthalpy change of formation (driven by the higher lattice enthalpy).
- (c) SrCO_3 has the higher decomposition temperature as the lattice enthalpy of the oxide decomposition product is lower (Li_2CO_3 similar to MgCO_3).

5. A Group 1 metal, M, burns in air to produce X. M also reacts with water to form Y, giving off a combustible gas Z. When Y is heated, it gives off steam and decomposes to X. Identify M, X, Y and Z.

Strategy

Consider the chemistry of the Group 1 metals and their compounds, concentrating on the differences that occur going down the group.

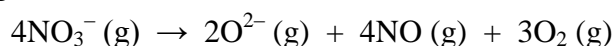
Solution

All Group 1 metals react with water to form the hydroxide and hydrogen, so the flammable gas Z is H₂. The only Group 1 hydroxide to decompose on heating is LiOH, which decomposes to lithium oxide, Li₂O, and steam. Therefore M is Li, Y is LiOH and X is Li₂O. As a confirmation, lithium burns in air to form the oxide as opposed to the peroxide or superoxide.

6. Construct an enthalpy cycle for the decomposition of a Group 1 nitrate to an oxide. Using the Kapustinskii equation to estimate values of the lattice energies, calculate values for the decomposition of lithium nitrate to lithium oxide and potassium nitrate to potassium oxide. Use the calculated values to predict which of these nitrates decomposes on heating to the oxide.

Values for ionic radii are given in Tables 6.4 (p.286), 6.5 (p.286) and 6.9 (p.297).

The enthalpy change for the reaction



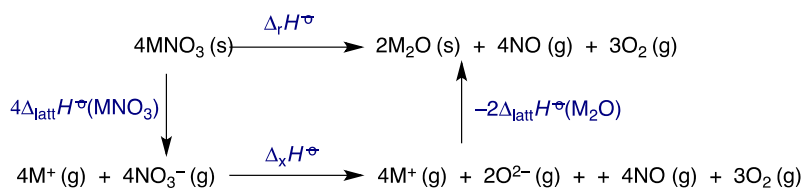
is +2160 kJ mol⁻¹.

Strategy

Construct an enthalpy cycle for the decomposition of MNO₃ to M₂O, and use it to calculate $\Delta_r H^\ominus$ for both M = Li and K. Estimate the lattice energies of MNO₃ and M₂O using the Kapustinskii equation and the data given. Use the relative magnitudes of ΔH for Li and K to predict which is the more likely to decompose on heating.

Solution

The enthalpy diagram is as shown below.



From the tables, the cationic radius for Li^+ is 76 pm, the cationic radius for K^+ is 138 pm, the anionic radius for O^{2-} is 140 pm, and the thermochemical radius for NO_3^- is 189 pm.

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$

$$\Delta_{\text{latt}} H^\ominus(\text{LiNO}_3) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 1 \cdot 1}{(76 + 200) \text{ pm}} = 782 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(\text{KNO}_3) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 1 \cdot 1}{(138 + 200) \text{ pm}} = 638 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(\text{Li}_2\text{O}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 1 \cdot 2}{(74 + 140) \text{ pm}} = 3030 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(\text{K}_2\text{O}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 1 \cdot 2}{(138 + 140) \text{ pm}} = 2330 \text{ kJ mol}^{-1}$$

Putting these values into the enthalpy cycle for $\text{M} = \text{Li}$:

$$\Delta_{\square} H^\ominus = (4 \times 782 \text{ kJ mol}^{-1}) + (2160 \text{ kJ mol}^{-1}) + (-2 \times 3030 \text{ kJ mol}^{-1}) = -772 \text{ kJ mol}^{-1}$$

For $\text{M} = \text{K}$:

$$\Delta_{\square} H^\ominus = (4 \times 638 \text{ kJ mol}^{-1}) + (2160 \text{ kJ mol}^{-1}) + (-2 \times 2330 \text{ kJ mol}^{-1}) = +52 \text{ kJ mol}^{-1}$$

(3 SF)

The value is much less endothermic for $\text{M} = \text{Li}$, suggesting this is more favourable than the reaction with $\text{M} = \text{K}$. Indeed, LiNO_3 is the only Group 1 nitrate to decompose to the oxide on heating (the others decompose to the nitrites).

7. Which of the following pairs of Group 1 compounds would you expect to be more soluble in water?
- LiNO_3 or CsNO_3
 - LiOH or RbOH
 - NaBr or CsBr .

Strategy

Consider how the solubility of the Group 1 salts is affected by the size of the cations and anions.

Solution

- (a) Nitrate is a large anion, so compounds with small cations tend to be more soluble than those with large anions. LiNO_3 is more soluble than CsNO_3 .
- (b) Hydroxide is a small anion, so compounds with large anions tend to be more soluble than those with small cations. RbOH is more soluble than LiOH .
- (c) Bromide is a large anion, so compounds with small cations tend to be more soluble than those with large anions. NaBr is more soluble than CsBr .

8. Suggest how the crown ether shown on p.1198 could be used to separate mixtures of Li^+ and K^+ .

Strategy

Crown ethers are ring like compounds which have central cavities that vary in size according to the size of the ring which contain a number of donor oxygen atoms. The larger the ring, the more oxygen donors are available to bind the central cation. Group 1 cations form complexes with the crown ethers that vary in stability according to the size match between cation and crown ether. More stable complexes are less soluble and can be separated from a mixture.

Solution

Lithium forms much more stable complexes with [12]crown-4 as it is small enough to fit into the cavity, whereas K^+ is not. Salts of the Li-crown complex have different solubility properties to those of K^+ , so are easy to separate.

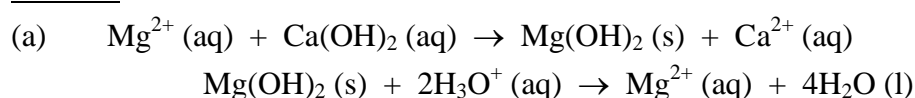
9. Magnesium chloride is prepared by reacting sea water with Ca(OH)_2 to precipitate Mg(OH)_2 , reacting this with hydrochloric acid, and then evaporating the solution slowly to give crystals of magnesium chloride.
- (a) Write balanced equations for these reactions, ignoring any water of crystallization.

- (b) A sample of MgCl_2 obtained from this process contains 18.5% magnesium by mass. Assuming there are no impurities, how many molecules of water does the MgCl_2 crystallize with?

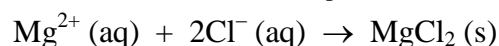
Strategy

The first part of this question involves writing a balanced equation for the acid hydrolysis of the magnesium hydroxide. In part (b), the mass of the hydrated magnesium chloride can be calculated using the $A_r(\text{Mg})$ and the fact that magnesium constitutes 18.5% by weight of the hydrate.

Solution



evaporation



- (b) $A_r(\text{Mg}) = 24.31$. Since magnesium makes up 18.5% of the sample of magnesium chloride, the molar mass of the sample = $\frac{100}{18.5} \times 24.31 \text{ g mol}^{-1} = 131 \text{ g mol}^{-1}$.

Of the total molar mass, MgCl_2 contributes $24.31 \text{ g mol}^{-1} (1 \times \text{Mg}) + 70.90 \text{ g mol}^{-1} (2 \times \text{Cl}) = 95.2 \text{ g mol}^{-1}$. This leaves $(131 \text{ g mol}^{-1} - 95.2 \text{ g mol}^{-1}) = 36 \text{ g mol}^{-1}$. Dividing this by the molar mass of water (18.0 g mol^{-1}) gives 2.

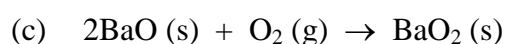
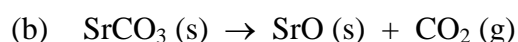
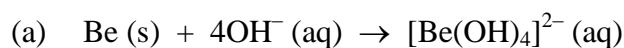
Therefore the sample is $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$.

- 10.** Identify the products and write balanced equations for the following reactions:
- adding beryllium to sodium hydroxide solution;
 - heating strontium carbonate;
 - heating barium oxide in air.

Strategy

Consider the strongest bonds that can be formed in each case. Remember to take into account the relative sizes of cations and anions (remembering that large cations favour large anions).

Solution



11. When magnesium burns in air, both magnesium oxide and magnesium nitride are formed. Suggest how you could obtain a pure sample of magnesium oxide from this mixture.

Strategy

In order to produce the pure oxide, the magnesium nitride bonds need to be replaced with magnesium oxide bonds.

Solution

Add water to the mixture to convert both the nitride and the oxide into the hydroxide. Then heat the hydroxide to get a pure sample of MgO.

12. The structure of BeCl_2 is shown in Figure 26.9 (p.1187). What is the geometry around the beryllium centres? Use this to predict a value for the Cl–Be–Cl bond angle. What is the most likely hybridization of the beryllium atom?

Strategy

Decide what sort of hybridization is present in the molecule by examining the geometry around the Be. Bond angles will be maximised to place the orbitals as far away from each other as possible (see VSEPR theory in Section 5.2, p.223).

Solution

The geometry around each beryllium centre is approximately tetrahedral, so the angle is likely to be close to 109.5°. This angle is consistent with sp^3 hybridization of the beryllium atom.

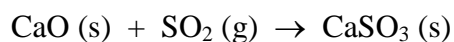
13. Calcium oxide is being used increasingly to reduce air pollution by the desulfurization of flue gases from power stations which contain SO_2 . Suggest how this reacts with CaO.

Strategy

The desulfurization process involves trapping the sulfur dioxide in the form of an insoluble calcium salt.

Solution

Calcium oxide reacts with sulfur dioxide to give calcium sulfite



14. Magnesium sulfate is more soluble in water than barium sulfate, but magnesium fluoride is less soluble than barium fluoride. Explain these observations in terms of the Gibbs energies involved.

Strategy

The solubility of the ionic salts varies according to the hydration enthalpy of the ions within them. Small highly charged ions have a greater effect on the surrounding water molecules due to a higher charge over size ratio (charge density). Solving this question is a matter of working out which ions would be more easily hydrated.

Solution

$MgSO_4$ contains small cations and large anions, whereas $BaSO_4$ contains large cations and large anions. The higher solubility of $MgSO_4$ is driven by the more negative

Gibbs energy of hydration of the Mg^{2+} ion, which has a higher magnitude than that of the larger Ba^{2+} ion.

MgF_2 contains small cations and small anions, whereas BaF_2 contains large cations and small anions. The high negative Gibbs energies of hydration for Mg^{2+} and F^- are not high enough in magnitude to overcome the very high lattice Gibbs energy for MgF_2 . For BaF_2 the large cation ensures the lattice Gibbs energy is lower, but the Gibbs energy of hydration of F^- is still highly negative.

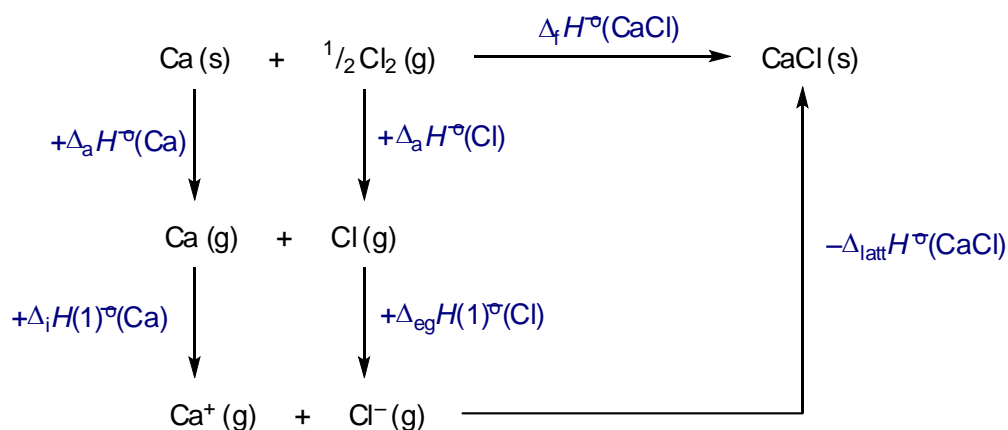
15. Use a Born–Haber cycle to calculate the enthalpy change of formation of calcium(I) chloride. Does your answer help explain why this compound is unknown? If not, what else could help?

Strategy

Construct the Born–Haber cycle for CaCl , using the Kapustinskii equation to calculate the lattice enthalpy for CaCl .

Solution

The Born-Haber cycle below allows you to calculate $\Delta_f H^\ominus(\text{CaCl})$.



$$\Delta_a H^\ominus(\text{Ca}) = +178 \text{ kJ mol}^{-1}$$

$$\Delta_a H^\ominus(\text{Cl}) = +121 \text{ kJ mol}^{-1}$$

$$\Delta_i H(1)^\ominus(\text{Ca}) = +590 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) = -349 \text{ kJ mol}^{-1}$$

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$ to estimate a

value for $\Delta_{\text{latt}} H^\ominus(\text{CaCl})$

$$\Delta_{\text{latt}}H^\ominus \approx \Delta_{\text{latt}}U^\ominus = \frac{k n z_+ z_-}{r_+ + r_-} \quad k = 107900 \text{ pm kJ mol}^{-1}$$

The ionic radius for Cl^- , r_- , is 181 pm. Since Ca^+ compounds are unknown, the ionic radius of Ca^+ is also unknown. A reasonable assumption is that the ionic radius of Ca^+ is similar to that of the ionic radius of the neighbouring ion K^+ (138 pm).

Substituting these values,

$$\Delta_{\text{latt}}H^\ominus(\text{CaCl}) \approx \Delta_{\text{latt}}U^\ominus(\text{CaCl}) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 1 \cdot 1}{(138 + 181) \text{ pm}} = +676 \text{ kJ mol}^{-1}$$

From the Born–Haber cycle:

$$\begin{aligned} \Delta_f H^\ominus(\text{CaCl}) &= \Delta_a H^\ominus(\text{Ca}) + \Delta_i H(1)^\ominus(\text{Ca}) + \Delta_a H^\ominus(\text{Cl}) + \Delta_{\text{eg}} H(1)^\ominus(\text{Cl}) - \Delta_{\text{latt}} H^\ominus(\text{CaCl}) \\ &= (+178 \text{ kJ mol}^{-1}) + (+590 \text{ kJ mol}^{-1}) + (+121 \text{ kJ mol}^{-1}) + (-349 \text{ kJ mol}^{-1}) \\ &\quad - (+676 \text{ kJ mol}^{-1}) \\ &= -136 \text{ kJ mol}^{-1} \end{aligned}$$

This is a negative value, so CaCl is stable with respect to the elements. To understand why it doesn't exist you need to also consider whether it is stable with respect to disproportionation. (See Worked Example 26.2 for more details).

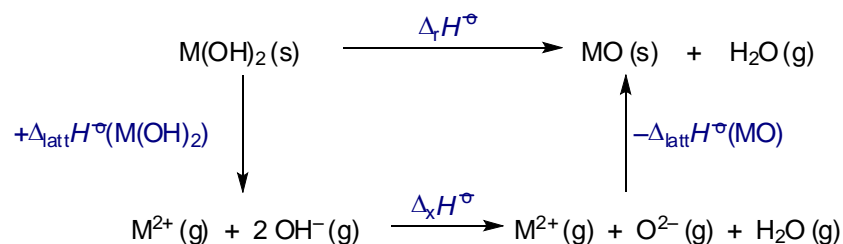
16. Use an enthalpy cycle to predict whether $\text{Mg}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ has a higher decomposition temperature.

Strategy

Construct a general energy cycle for $\text{M}(\text{OH})_2$ and use the Kapustinskii equation to calculate the lattice energy for both the hydroxides and oxides of Mg and Ba.

Solution

The enthalpy cycle below breaks down the decomposition reaction into three steps,



The only terms that involve the metal are the lattice enthalpies of $M(OH)_2$ and MO .

$$\Delta_r H^\ominus = -\Delta_{\text{latt}} H^\ominus(M(OH)_2) + \Delta_x H^\ominus + \Delta_{\text{latt}} H^\ominus(MO)$$

Using the Kapustinskii equation (Equation 6.11), $D_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$ to estimate the lattice enthalpies for $M(OH)_2$ and MO ,

$$\Delta_{\text{latt}} H^\ominus \approx \Delta_{\text{latt}} U^\ominus = \frac{k \eta z_+ z_-}{r_+ + r_-} \quad k = 107900 \text{ pm kJ mol}^{-1}$$

From Table 6.4 (p.286) the radii of the cations are 72 pm for Mg^{2+} and 149 pm for Ba^{2+} . From Tables 6.5 (p.286) and 6.9 (p.297) the radii of the anions are 140 pm for O^{2-} and 152 pm for OH^- . Substituting these values into the Kapustinskii equation,

$$\Delta_{\text{latt}} H^\ominus(Mg(OH)_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 2 \cdot 1}{(72 + 152) \text{ pm}} = +2890 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(Ba(OH)_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 3 \cdot 2 \cdot 1}{(135 + 152) \text{ pm}} = +2260 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(MgO) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 2 \cdot 2}{(72 + 140) \text{ pm}} = +4070 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{latt}} H^\ominus(BaO) = \frac{(107900 \text{ pm kJ mol}^{-1}) \cdot 2 \cdot 2 \cdot 2}{(135 + 140) \text{ pm}} = +3140 \text{ kJ mol}^{-1}$$

Therefore,

$$\begin{aligned} \Delta_r H^\ominus(Mg(OH)_2) &= \Delta_{\text{latt}} H^\ominus(Mg(OH)_2) + \Delta_x H^\ominus - \Delta_{\text{latt}} H^\ominus(MgO) \\ &= (+2890 \text{ kJ mol}^{-1}) + \Delta_x H^\ominus - (+4070 \text{ kJ mol}^{-1}) \\ &= -1180 \text{ kJ mol}^{-1} + \Delta_x H^\ominus \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\ominus(Ba(OH)_2) &= \Delta_{\text{latt}} H^\ominus(Ba(OH)_2) + \Delta_x H^\ominus - \Delta_{\text{latt}} H^\ominus(BaO) \\ &= (+2260 \text{ kJ mol}^{-1}) + \Delta_x H^\ominus - (+3140 \text{ kJ mol}^{-1}) \\ &= -880 \text{ kJ mol}^{-1} + \Delta_x H^\ominus \text{ kJ mol}^{-1} \end{aligned}$$

As $\Delta_{\text{x}}H^{\circ}$ is constant for both metals, $\Delta_{\text{r}}H^{\circ}$ is lower for magnesium. This means that decomposition is more favourable for $\text{Mg}(\text{OH})_2$, so it occurs at a lower temperature.

17. Explain why beryllium nitrate dissolves in water to give an acidic solution.

Strategy

Beryllium is small highly charged cation and therefore has a high charge density. Ions with high charge density are fully hydrated in solution. The high charge density means that the water molecules will be polarised.

Solution

The high charge density of Be^{2+} ensures it is hydrated in solution and that the O–H bonds are sufficiently polar for hydrolysis to occur:



18. Beryllium compounds are mainly covalent, whereas other Group 2 compounds are predominantly ionic. Discuss the evidence for this statement, and suggest factors that contribute to it.

Strategy

Describe the ways in which the chemistry of beryllium and its compounds differs from that for the heavier Group 2 elements. Consider how the small size of the Be^{2+} ion would affect ionic bonding.

Solution

Evidence for the covalent character of beryllium is given in Section 26.9 (p.1194). The small size of Be^{2+} means that the charge density on this ion is very much higher than that on the other Group 2 ions and this makes the free Be^{2+} ion strongly polarizing. It draws the electrons of neighbouring ions towards itself, which gives these bonds a much higher degree of covalent character than equivalent bonds of other Group 2 cations.

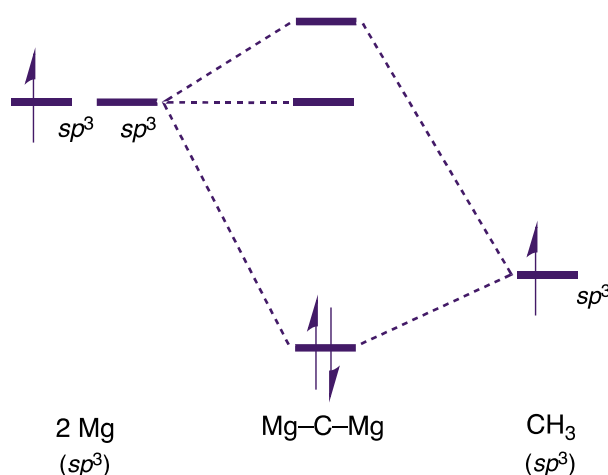
19. The solid state structure of dimethylmagnesium is polymeric, with bridging methyl groups. By considering the magnesium and carbon atoms as sp^3 hybridized, show how the bonding in this compound can be described as 3-centre 2-electron bonding.

Strategy

3-centre 2-electron bonding is described in Section 5.7 (p.249). In the case of $MgMe_2$, use the model to describe the bonding in a $Mg-C-Mg$ fragment, using sp^3 hybrid orbitals on each atom. Firstly consider the in-phase and out-of-phase combinations of the two Mg orbitals. Then, determine how these combinations interact with a carbon sp^3 orbital. If the orbitals have the correct symmetry to interact they will generate a bonding and an antibonding combination. If not, a non-bonding orbital will result. Finally, work out the appropriate number of electrons, and place them into the molecular orbitals using the aufbau principle.

Solution

The bonding in each $Mg-C-Mg$ fragment is very similar to that described for B_2H_6 in Section 5.7 (p.250). The in-phase combination of Mg sp^3 orbitals has the correct symmetry to interact with the carbon sp^3 orbital, and this gives rise to a bonding and an anti-bonding orbital. The out-of-phase combination of Mg sp^3 orbitals does not have the correct symmetry to interact with the carbon sp^3 orbital, so this gives a non-bonding orbital. This leads to the partial MO energy level diagram shown below.



There are two electrons to place into the scheme. One comes from the methyl fragment, and one comes from the two magnesium orbitals (each Mg starts with two

electrons, so formally gives rise to two sp^3 hybrid orbitals with one electron in, and two empty sp^3 hybrid orbitals).