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## s-Block chemistry

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### Answers to worked examples

#### WE 26.1 Estimating the enthalpy change of formation of lithium nitride (Li<sub>3</sub>N).

Estimate a value for the enthalpy change of formation of Na<sub>3</sub>N and comment on the stability of this compound with respect to the elements. Use the data in Tables 26.2 (p.1161), 2.6 (p.117) and 5.5 (p.246).

#### Strategy

Construct a Born–Haber cycle for the formation of Na<sub>3</sub>N from the elements. Use the Kapustinskii equation (Equation 5.10, p.257) to estimate the lattice enthalpy.

#### Solution

The calculation is analogous to the one for Li<sub>3</sub>N. 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 5.10),  $\Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$

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

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

The formation of  $\text{Na}_3\text{N}$  is endothermic. This helps explain why, in contrast to  $\text{Li}_3\text{N}$ ,  $\text{Na}_3\text{N}$  is unknown.

## Answers to boxes

### Box 26.1 Why is sodium peroxide more stable to heating than lithium peroxide?

Estimate  $\Delta_r H^\circ$  for the decomposition of  $\text{K}_2\text{O}_2$  to  $\text{K}_2\text{O}$ . The ionic radius of  $\text{K}^+$  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 5.10, p.257) before the cycle can be used to calculate  $\Delta_r H^\circ$ .

#### Solution

From the enthalpy cycle in Box 26.1 (p.1164),

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

Using the Kapustinskii equation (Equation 5.10),  $\Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$  for the lattice enthalpies of  $\text{K}_2\text{O}$  and  $\text{K}_2\text{O}_2$ ,

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

$$\Delta_{\text{latt}} H^\circ(\text{K}_2\text{O}_2) \approx \Delta_{\text{latt}} U^\circ(\text{K}_2\text{O}_2) = \frac{(107900 \text{ pm kJ mol}^{-1}) \times 3 \times 1 \times 2}{(138 + 180) \text{ pm}} = +2040 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_r H^\circ &= \Delta_{\text{latt}} H^\circ(\text{K}_2\text{O}_2) + \Delta_x H^\circ - \Delta_{\text{latt}} H^\circ(\text{K}_2\text{O}) \\ &= (+2040 \text{ kJ mol}^{-1}) + (+845 \text{ kJ mol}^{-1}) - (+2330 \text{ kJ mol}^{-1}) \\ &= +555 \text{ kJ mol}^{-1} \end{aligned}$$

### Box 26.3 Building materials

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

#### Strategy

Calcium hydroxide based cements require carbon dioxide to harden ('go off). The final cement is based on the material,  $\text{CaCO}_3$  (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 26.5 Chlorophylls

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 11.6, p.537). 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. 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;
  - adding beryllium to sodium hydroxide solution;
  - heating strontium carbonate.

### Strategy

Consider the strongest bonds that can be formed in each case. In the case of the group 1 metals, remember to take into account the relative sizes of cations and anions (remembering that large cations favour large anions according to HSAB theory, p xx)

### Solution

- $2 \text{Cs (s)} + 2 \text{H}_2\text{O (l)} \rightarrow 2 \text{CsOH (aq)} + \text{H}_2 \text{(g)}$
- $\text{Rb (s)} + \text{O}_2 \text{(g)} \rightarrow \text{RbO}_2 \text{(s)}$
- $4 \text{LiNO}_3 \text{(s)} \rightarrow 2 \text{Li}_2\text{O (s)} + 4 \text{NO (g)} + 3 \text{O}_2 \text{(g)}$
- $\text{Be (s)} + 4 \text{OH}^- \text{(aq)} \rightarrow [\text{Be(OH)}_4]^{2-} \text{(aq)}$
- $\text{SrCO}_3 \text{(s)} \rightarrow \text{SrO (s)} + \text{CO}_2 \text{(g)}$

2. Use a Born–Haber cycle and the data below to explain why  $\text{NaCl}_2$  doesn't exist. Assume the radius of  $\text{Na}^{2+}$  is the same as  $\text{Mg}^{2+}$ .

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

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

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

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

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

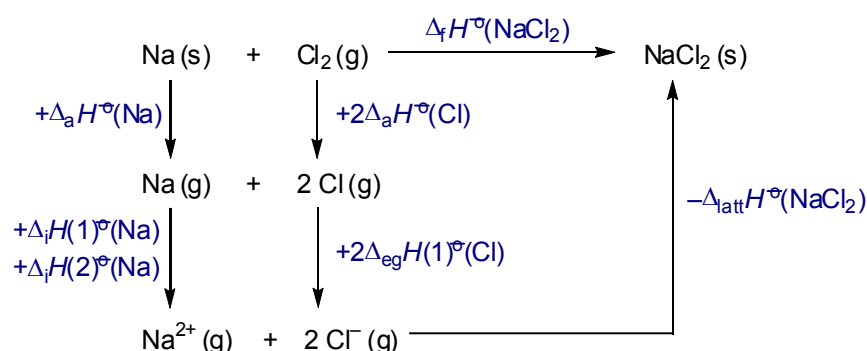
$$\Delta_{\text{eg}} H(1)^\circ(\text{Cl}) = -349 \text{ kJ mol}^{-1}$$

### Strategy

First draw an enthalpy cycle for the formation of  $\text{NaCl}_2$ . While the lattice enthalpy for  $\text{NaCl}_2$  is not known, it can be calculated using the Kapustinskii equation (Equation 5.10, p.257) by assuming the radius of  $\text{Na}^{2+}$  is the same as  $\text{Mg}^{2+}$ .

### Solution

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



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 5.10),  $\Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$  to estimate

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

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

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

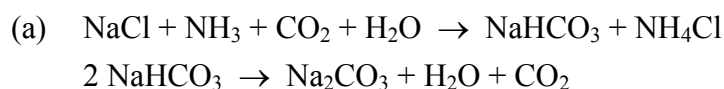
The enthalpy change of formation of  $\text{NaCl}_2$  is strongly endothermic, so it is unstable with respect to the elements. The most important factor is the very large positive value of  $\Delta_f H(2)^\circ(\text{Na})$ .

3. The Solvay process is used industrially to prepare sodium carbonate. It consists of two stages.
- Write a balanced equation for the overall reaction in each stage.
  - The  $\text{CO}_2$  is generated by heating limestone. The  $\text{CaO}$  formed in this reaction is converted into  $\text{Ca(OH)}_2$  by reaction with water, and then reacted with  $\text{NH}_4\text{Cl}$  to generate ammonia. Write a balanced equation for the *overall* Solvay process, and show that the only by-product is  $\text{CaCl}_2$ .

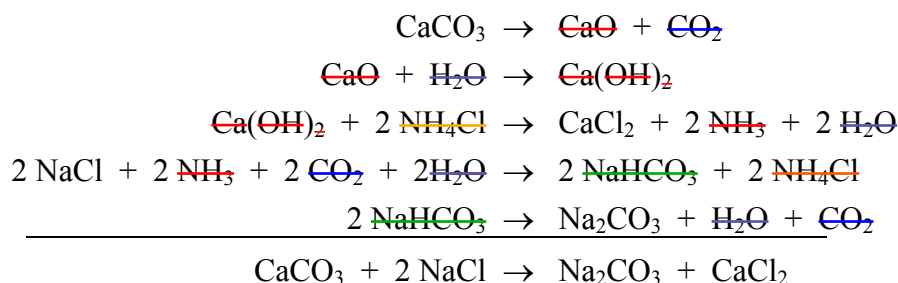
### Strategy

Write equations for each stage of the process and cancel out the terms that appear on both sides.

### Solution



- (b) Take these equations together with those for the conversions of  $\text{CaCO}_3$  to  $\text{CaO}$ ,  $\text{Ca(OH)}_2$  and  $\text{CaCl}_2$ , and add them together, cancelling out the terms that appear on both the left and right hand sides.



4. 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.

5. The structure of BeCl<sub>2</sub> is shown in Figure 26.9 (p.1178). 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 4.2, p.183).

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*<sup>3</sup> hybridization of the beryllium atom.

6. 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<sub>4</sub> contains small cations and large anions, whereas BaSO<sub>4</sub> contains large cations and large anions. The higher solubility of MgSO<sub>4</sub> is driven by the more negative Gibbs energy of hydration of the Mg<sup>2+</sup> ion, which has a higher magnitude than that of the larger Ba<sup>2+</sup> ion.

MgF<sub>2</sub> contains small cations and small anions, whereas BaF<sub>2</sub> contains large cations and small anions. The high negative Gibbs energies of hydration for Mg<sup>2+</sup> and F<sup>-</sup> are not high enough in magnitude to overcome the very high lattice Gibbs energy for MgF<sub>2</sub>. For BaF<sub>2</sub> the large cation ensures the lattice Gibbs energy is lower, but the Gibbs energy of hydration of F<sup>-</sup> is still highly negative.

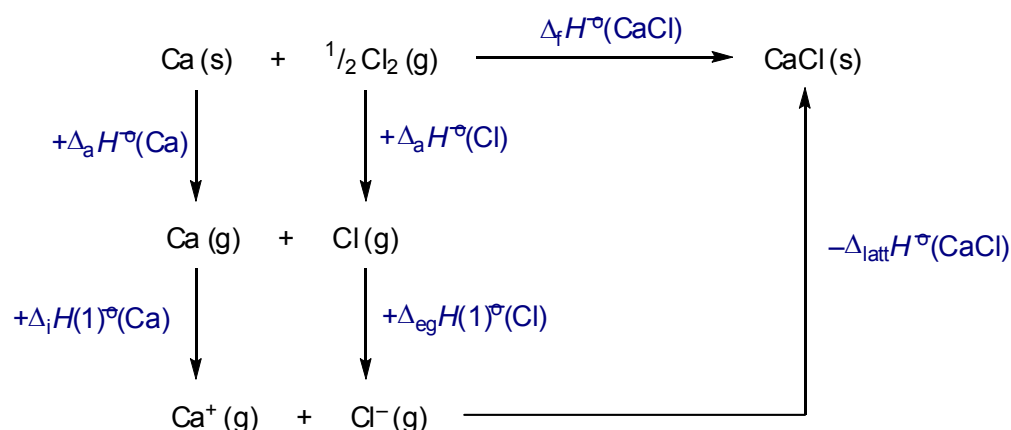
7. Use a Born–Haber cycle to calculate the enthalpy change of formation of calcium(I) chloride. Does your answer help explain why this compound is unknown? If not, what else could help?

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 5.10),  $\Delta_{\text{latt}} U = \frac{kvz_+z_-}{r_+ + r_-}$  to estimate a value for  $\Delta_{\text{latt}} H^\ominus(\text{CaCl})$

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

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

Substituting these values,

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

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).



