This page examines at the effect of heat on the carbonates and nitrates of the Group 2 elements (beryllium, magnesium, calcium, strontium and barium). It explains how the thermal stability of the compounds changes down the group.

The effect of heat on the Group 2 carbonates

All the carbonates in this group undergo thermal decomposition to the metal oxide and carbon dioxide gas. The term "thermal decomposition" describes splitting up a compound by heating it.

All the Group 2 carbonates and their resulting oxides exist as white solids. If "X" represents any one of the elements, the following describes this decomposition:

\[ XCO_3(s) \rightarrow XO(s) + CO_2(g) \]

Down the group, the carbonates require more heating to decompose.

- The carbonates become more thermally stable down the group.

The effect of heat on the Group 2 Nitrates

The Group 2 nitrates undergo thermal decomposition to the metal oxide, nitrogen dioxide and oxygen gas. These compounds are white solids and brown nitrogen dioxide and oxygen gases are also given off when heated. Magnesium and calcium nitrates normally crystallize with water, and the solid may dissolve in its own water of crystallization to make a colorless solution before it starts to decompose.

Again, if "X" represents any one of the elements:

\[ 2X(NO_3)_2(s) \rightarrow 2XO(s) + 4NO_2(g) + O_2 (g) \]

Down the group, the nitrates must also be heated more strongly before they will decompose.

Group 2 nitrates also become more thermally stable down the group.

Summary

Both carbonates and nitrates of Group 2 elements become more thermally stable down the group. The larger compounds further down require more heat than the lighter compounds in order to decompose.

Explanations

This page offers two different explanations for these properties: polarizability and energetics. Detailed explanations are given for the carbonates because the diagrams are easier to draw, and their equations are also easier. Exactly the same arguments apply to the nitrates.

Explaining the trend in terms of the polarizing ability of the positive ion
A small 2+ ion has a lot of charge packed into a small volume of space. In other words, it has a high charge density and has a marked distorting effect on any negative ions which happen to be near it. A bigger 2+ ion has the same charge spread over a larger volume of space, so its charge density is lower; it causes less distortion to nearby negative ions.

**The structure of the carbonate ion**

A shorthand structure for the carbonate ion is given below:

\[
\text{\text{O}}\overset{\text{\text{-}}}{\text{C}}\overset{\text{\text{-}}}{\text{O}}
\]

This structure two single carbon-oxygen bonds and one double bond, with two of the oxygen atoms each carrying a negative charge. In real carbonate ions all the bonds are identical, and the charges are distributed over the whole ion, with greater density concentrated on the oxygen atoms. In other words, the charges are delocalized.

The next diagram shows the delocalized electrons. The shading is intended to show that there is a greater electron density around the oxygen atoms than near the carbon.

**Polarizing the carbonate ion**

If this ion is placed next to a cation, such as a Group 2 ion, the cation attracts the delocalized electrons in the carbonate ion, drawing electron density toward itself. The carbonate ion becomes polarized.
If the carbonate is heated the carbon dioxide breaks free, leaving the metal oxide.

The amount of heating required depends on the degree to which the ion is polarized. More polarization requires less heat. The smaller the positive ion is, the higher the charge density, and the greater effect it will have on the carbonate ion. As the positive ions get larger down the group, they affect on the carbonate ions near them less. More heat must be supplied for the carbon dioxide to leave the metal oxide.

In other words, the carbonates become more thermally stable down the group.

What about the nitrates?

The argument is exactly the same for the Group 2 nitrates. The small cations at the top of the group polarize the nitrate ions more than the larger cations at the bottom do. This process is much more difficult to visualize due to interactions involving multiple nitrate ions.

Enthalpy changes

The enthalpy changes for the decomposition of the various carbonates indicate that the reactions are strongly endothermic, implying that the reactions likely require constant heating to proceed. Remember that the reaction in question is the following:

\[XCO_{3(s)} \rightarrow XO_{(s)} + CO_{2(g)}\]

The calculated enthalpy changes (in kJ mol\(^{-1}\)) are given in the table below (there is no available data for beryllium carbonate).

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>(\Delta H)</th>
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<tbody>
<tr>
<td>MgCO(_3)</td>
<td>+117</td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>+178</td>
</tr>
<tr>
<td>SrCO(_3)</td>
<td>+235</td>
</tr>
<tr>
<td>BaCO(_3)</td>
<td>+267</td>
</tr>
</tbody>
</table>

The reactions are more endothermic down the group, as expected, because the carbonates become more thermally stable, as discussed above.
Explaining the enthalpy changes

Here's where things start to get difficult! If you aren't familiar with Hess's Law cycles (or with Born-Haber cycles) and with lattice enthalpies (lattice energies), you aren't going to understand the next bit. Don't waste your time looking at it.

Using an enthalpy cycle

You can dig around to find the underlying causes of the increasingly endothermic changes as you go down the Group by drawing an enthalpy cycle involving the lattice enthalpies of the metal carbonates and the metal oxides. Lattice enthalpy is the heat needed to split one mole of crystal in its standard state into its separate gaseous ions. For example, for magnesium oxide, it is the heat needed to carry out 1 mole of this change:

\[ \text{MgO}_{(s)} \rightarrow \text{Mg}^{2+}_{(g)} + \text{O}^{2-}_{(g)} \]

Lattice Energy (LE): + 3889 kJ/mol

Lattice enthalpy is more usually defined as the heat evolved when 1 mole of crystal is formed from its gaseous ions. In that case, the lattice enthalpy for magnesium oxide would be -3889 kJ mol\(^{-1}\). The term we are using here should more accurately be called the "lattice dissociation enthalpy".

The cycle we are interested in looks like this:

You can apply Hess's Law to this, and find two routes which will have an equal enthalpy change because they start and end in the same places.
For reasons we will look at shortly, the lattice enthalpies of both the oxides and carbonates fall as you go down the Group. But they don't fall at the same rate. The oxide lattice enthalpy falls faster than the carbonate one. If you think carefully about what happens to the value of the overall enthalpy change of the decomposition reaction, you will see that it gradually becomes more positive as you go down the Group.

\[ \Delta H + LE(XO) = LE(XCO_3) - \Delta H_{\text{const}} \]

\[ \Delta H = LE(XCO_3) - LE(XO) - \Delta H_{\text{const}} \]

These values both fall as you go down the Group.

Explaining the relative falls in lattice enthalpy

The size of the lattice enthalpy is governed by several factors, one of which is the distance between the centres of the positive and negative ions in the lattice. Forces of attraction are greatest if the distances between the ions are small. If the attractions are large, then a lot of energy will have to be used to separate the ions - the lattice enthalpy will be large.

The lattice enthalpies of both carbonates and oxides fall as you go down the Group because the positive ions are getting bigger. The inter-ionic distances are increasing and so the attractions become weaker.

<table>
<thead>
<tr>
<th>ionic radius (nm)</th>
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<tbody>
<tr>
<td>Mg²⁺</td>
</tr>
<tr>
<td>Ca²⁺</td>
</tr>
<tr>
<td>O²⁻</td>
</tr>
</tbody>
</table>
The lattice enthalpies fall at different rates because of the different sizes of the two negative ions - oxide and carbonate. The oxide ion is relatively small for a negative ion (0.140 nm), whereas the carbonate ion is large (no figure available).

In the oxides, when you go from magnesium oxide to calcium oxide, for example, the inter-ionic distance increases from 0.205 nm (0.140 + 0.065) to 0.239 nm (0.140 + 0.099) - an increase of about 17%.

In the carbonates, the inter-ionic distance is dominated by the much larger carbonate ion. Although the inter-ionic distance will increase by the same amount as you go from magnesium carbonate to calcium carbonate, as a percentage of the total distance the increase will be much less.

Some made-up figures show this clearly.

I can't find a value for the radius of a carbonate ion, and so can't use real figures. For the sake of argument, suppose that the carbonate ion radius was 0.3 nm. The inter-ionic distances in the two cases we are talking about would increase from 0.365 nm to 0.399 nm - an increase of only about 9%.

The rates at which the two lattice energies fall as you go down the Group depends on the percentage change as you go from one compound to the next. On that basis, the oxide lattice enthalpies are bound to fall faster than those of the carbonates.

**What about the nitrates?**

The nitrate ion is bigger than an oxide ion, and so its radius tends to dominate the inter-ionic distance. The lattice enthalpy of the oxide will again fall faster than the nitrate. If you constructed a cycle like that further up the page, the same arguments would apply.

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**Contributors**

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