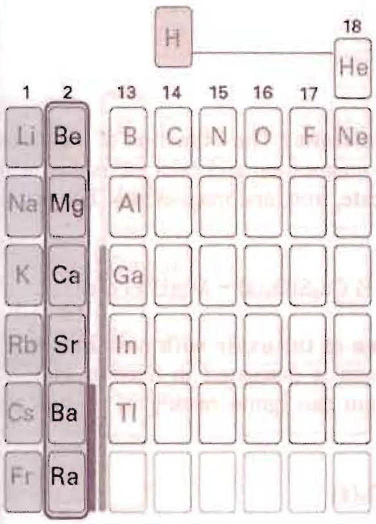
Chapter 11 The Group 2 Elements



The *Group 2* elements calcium, strontium, barium, and radium are known as the **alkaline earth metals.** All the elements are silvery white metals, but some aspects of the chemical properties of beryllium are more like those of a metalloid. The elements are harder, denser, and less reactive than the elements of Group 1 but are still more reactive than many typical metals. The elements form a limited number of complexes and organometallic compounds. The insolubility of some of the calcium compounds in particular leads to the existence of many inorganic minerals that provide the raw materials for the infrastructure of our built environment and provide the building blocks for the compounds from which many rigid biological structures are formed.

S11.1 Ionic or covalent? (a) $BeCl_2$? $BeCl_2$ is covalent because of a smaller radius and high electron density of Be^{2+}, the lightest group 2 metal ion; **(b) $BaCl_2$?** $BaCl_2$ is ionic because of the larger radius of Ba^{2+}, a heavier and more electropositive group 2 metal ion.

S11.2 Use lattice enthalpy considerations to explain why MgO_2 is less stable than BaO_2? MgO_2 has a lattice enthalpy of 3395 kJ mol^{-1} and BaO_2 has a lattice enthalpy of 2736 kJ mol^{-1} (see Self-Test 11.3). The decrease in enthalpy descending the group demonstrates that the stability of group 2 metal peroxides increases down the group. MgO_2 thermally decomposes easily to produce O_2 and MgO, compared to BaO_2, a stable peroxide.

S11.3 The lattice enthalpies for CaO and CaO_2? Use the Kapustinskii equation (equation 3.4), the ionic radii from Table 11.1, and the appropriate constants—which are $K = 1.21 \times 10^5$ MJ Å mol^{-1}, $n = 2$, $z^+_{Ca} = +2$, $z^-_{O} = -2$—the sum of the thermochemical radii, d_0, 140 pm + 99 pm = 239 pm = 23.9 Å and d = 3.45 Å, to find the lattice enthalpy of CaO. For calcium peroxide use $n = 2$, $z^+_{Ca} = +2$, $z^-_{O_2} = -2$, and d_0 = 180 pm + 99 pm = 279 pm = 27.9 Å. The lattice enthalpies of calcium oxide and calcium peroxide are 3465 kJ mol^{-1} and 3040 kJ mol^{-1}, respectively. The trend that the thermal stability of peroxides decreases down group 2 and that peroxides are less thermally stable than the oxides is confirmed.

S11.4 The pH of a saturated aqueous solution of $Ca(OH)_2$? The solubility of $Ca(OH)_2$ is $2.1\,1 \times 10^{-3}$ mol dm^{-1}, and the concentration of OH^- ions in the saturated aqueous solution is 4.22×10^{-3} mol dm^{-1}. Recalling that $[H^+][OH^-] = 1 \times 10^{-14}$, and solving for H^+, yields 2.36×10^{-12}, the calculated pH of the solution is 11.6.

S11.5 The lattice enthalpy of MgF_2? Using the Kapustinskii equation (equation 3.4) and the values of $K = 1.21 \times 10^5$ MJ Å mol^{-1}, $n = 3$, $z^+_{Mg} = +2$, $z^-_{F_2} = -1$, the sum of the thermochemical radii, d_0, 181 pm + 65 pm = 246 pm = 24.6 Å and d = 3.45 Å, the calculated lattice enthalpy of MgF_2 is 2991 kJ mol^{-1} will offset hydration enthalpy and reduce solubility compared to $MgCl_2$.

11.1 Why are compounds of beryllium covalent whereas those of the other group 2 elements are predominantly ionic? Be has large polarizing power and a high charge density due to its small radius. Descending group 2 elements increase in size, which leads to more electropositive and ionic character. This leads to predominantly ionic compounds with larger group 2 ions.

11.2 Why are the properties of beryllium more similar to aluminium than to magnesium? Because of a diagonal relationship between Be and Al arising from their similar atomic radii.

11.3 **Identify the compounds A, B, C, and D of the group 2 element M?**
$M + H_2O \rightarrow M(OH)_2$; $A = M(OH)_2$
$M(OH)_2 + CO_2 \rightarrow MCO_3$; $B = MCO_3$
$2MCO_3 + 5C \rightarrow 2MC_2 + 3CO_2$; $C = MC_2$
$MC_2 + 2H_2O \rightarrow M(OH)_2 + C_2H_2$
$M(OH)_2 + 2HCl \rightarrow MCl_2 + 2H_2O$; $D = MCl_2$.

11.4 **Give a balanced equation for the extraction of magnesium from dolomite?** The extraction of magnesium is mentioned in Section 11.1. The dolomite is heated in air to give the magnesium and calcium oxides, which are then heated in the presence of iron silicide to produce calcium silicate, iron, and magnesium. The reaction is shown below:

$$CaCO_3 + MgCO_3(s) \rightarrow MgO(s) + CaO(s) + 2\,CO_2(g) \xrightarrow{FeSi} ½\,Ca_2SiO_4(s) + Mg(l) + Fe(s)$$

11.5 **Give a balanced equation for the extraction of barium by reduction of the oxide with aluminium?** The extraction of barium by the reduction of barium oxide with aluminum is discussed in Section 11.1. The reaction produces aluminum oxide and three moles of barium. Barium can ignite readily in air and react vigorously with water, as shown below:

$$3BaO(s) + 2\,Al(s) \rightarrow 3\,Ba(l) + Al_2O_3(s)$$

11.6 **Why is magnesium hydroxide a much more effective antacid than calcium or barium hydroxide?** $Mg(OH)_2$ is sparingly soluble and mildly basic; $Ca(OH)_2$ is more soluble and so moderately basic; $Ba(OH)_2$ is soluble and is so strongly basic, that it also is a poison.

11.7 **Explain why group 1 hydroxides are much more corrosive than group 2 hydroxides?** Group 1 hydroxides are more soluble than group 2 hydroxides, and therefore have higher OH^- concentrations. The increase in OH^- concentration increases the corrosiveness of group 1 hydroxides.

11.8 **How do group 2 salts give rise to scaling from hard water?** Salts of divalent ions have low solubility. Temporary hardness of water occurs because of the formation of insoluble $CaCO_3$ from $CaHCO_3$ on heating, while permanent hardness is attributed to the presence of $CaSO_4$.

11.9 **Use the data in Table 1.8 and the Ketelaar triangle in Figure 2.2 to predict the nature of the bonding in $BeCl_2$, MgI_2, and BaF_2?** Covalent bonding corresponds with a small difference in electronegativity, and compounds that exhibit this sort of bonding, such as $BeCl_2$ and $MgCl_2$, lie at the base of the triangle on the LHS. Compounds with a greater differences in electronegativity, such as BaF_2, lie toward the top of the triangle and hence are ionic.

11.10 **Discuss the difference that you might expect between the structures of the two Grignard compounds C_2H_5MgBr and 2,4,6-$(CH_3)_3C_6H_2MgBr$?** In solution, C_2H_5MgBr will be tetrahedral with two molecules of solvent coordinated to the magnesium. The bulky organic group in 2,4,6-$(CH_3)_3C_6$ H_2MgBr leads to a coordination number of two.

11.11 **Predict the products of the following reactions?**
(a) $MgCl_2 + 2LiC_2H_5 \rightarrow 2LiCl + Mg(C_2H_5)_2$
(b) $Mg + (C_2H_5)_2Hg \rightarrow Mg(C_2H_5)_2 + Hg$
(c) $Mg + C_2H_5HgCl \rightarrow C_2H_5MgCl + Hg$