

Topics

Occurrence and extraction
Applications
Physical properties
Reactivity of the metals
Halides
Oxides and hydroxides
Salts of oxoacids
Aqueous solution chemistry
Complexes with *N*- and *O*-donors
Diagonal relationships



1	2		13	14	15	16	17	18	
H									He
Li	Be		B	C	N	O	F		Ne
Na	Mg		Al	Si	P	S	Cl		Ar
K	Ca		Ga	Ge	As	Se	Br		Kr
Rb	Sr	d-block	In	Sn	Sb	Te	I		Xe
Cs	Ba		Tl	Pb	Bi	Po	At		Rn
Fr	Ra								

12.1 Introduction

The group 2 metals – beryllium, magnesium, calcium, strontium, barium and radium – are collectively known as the *alkaline earth metals*. The relationships between them are very similar to those among the alkali metals. However, Be stands apart from the other group 2 metals to a *greater* extent than does Li from its homologues. For example, whereas Li^+ and Na^+ salts (with a common counter-ion) usually crystallize with the same structure type, this is not true for Be(II) and Mg(II) compounds. Beryllium compounds tend either to be covalent or to contain the hydrated $[\text{Be}(\text{OH}_2)_4]^{2+}$ ion. The high values of the enthalpy of atomization (Appendix 10) and ionization energies (Appendix 8) of the Be atom, and the small size and consequent high charge density of a

naked Be^{2+} ion, militate against the formation of naked Be^{2+} . It is noteworthy that Be is the only group 2 metal not to form a stable complex with $[\text{EDTA}]^{4-}$ (see Table 7.7).

Radium is radioactive and is formed as ^{226}Ra (α -emitter, $t_{\frac{1}{2}} = 1622$ yr) in the ^{238}U decay series. Uses of radium-226 in cancer treatment have generally been superseded by other radioisotopes. The properties of radium and its compounds can be inferred by extrapolation from those of corresponding Ca, Sr and Ba compounds.

We have already described some aspects of the chemistry of the group 2 elements as follows:

- ionization energies of metals (Section 1.10);
- bonding in diatomic Be_2 (Section 2.3);
- bonding schemes for BeCl_2 (Sections 2.8 and 5.2);
- structures of metals (Table 6.2);
- structures of halides and oxides, see CaF_2 , CdI_2 and NaCl structures (Section 6.11);
- lattice energy treatment of disproportionation of CaF into Ca and CaF_2 (Section 6.16);
- solubility products, e.g. for CaF_2 (Section 7.9);
- hydration of metal ions (Section 7.9);
- saline hydrides, MH_2 (Section 10.7).

12.2 Occurrence, extraction and uses

Occurrence

Beryllium occurs mainly as the silicate mineral *beryl*, $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$ (silicates, see Section 14.9). It is also found in many natural minerals including *bertrandite*,



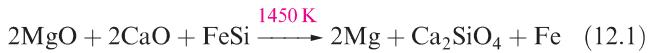
Fig. 12.1 Crystals of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the Cueva de los Cristales in the Naica mine system in Mexico.

$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$. Precious forms include *emerald* and *aquamarine*. Magnesium and calcium are the eighth and fifth most abundant elements, respectively, in the Earth's crust, and Mg is the third most abundant in the sea. The elements Mg, Ca, Sr and Ba are widely distributed in minerals and as dissolved salts in seawater. Some important minerals are *dolomite* ($\text{CaCO}_3 \cdot \text{MgCO}_3$), *magnesite* (MgCO_3), *olivine* ($(\text{Mg}, \text{Fe})_2\text{SiO}_4$), *carnallite* ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), CaCO_3 (in the forms of *chalk*, *limestone* and *marble*), *gypsum* ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), *celestite* (SrSO_4), *strontianite* (SrCO_3) and *barytes* (BaSO_4). Figure 12.1 shows 11 m long crystals of gypsum in Mexico's Cueva de los Cristales (Cave of Crystals). Their very slow growth over hundreds of thousands of years occurred because geothermally heated water originally filling the caves provided a constant temperature of 311 K which is the transition temperature between CaSO_4 (anhydrite) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

The natural abundances of Be, Sr and Ba are far less than those of Mg and Ca (Fig. 12.2).

Extraction

Of the group 2 metals, only Mg is manufactured on a large scale. The mixed metal carbonate dolomite is thermally decomposed to a mixture of MgO and CaO , and MgO is reduced by ferrosilicon in Ni vessels (eq. 12.1). Magnesium is then removed by distillation *in vacuo*.



Extraction of Mg by electrolysis of fused MgCl_2 is also important and is applied to the extraction of the metal from seawater. The first step is precipitation (see Table 7.4) of $\text{Mg}(\text{OH})_2$ by addition of $\text{Ca}(\text{OH})_2$ (*slaked lime*), produced from CaCO_3 (available as various calcareous deposits, see Fig. 11.6). Neutralization with

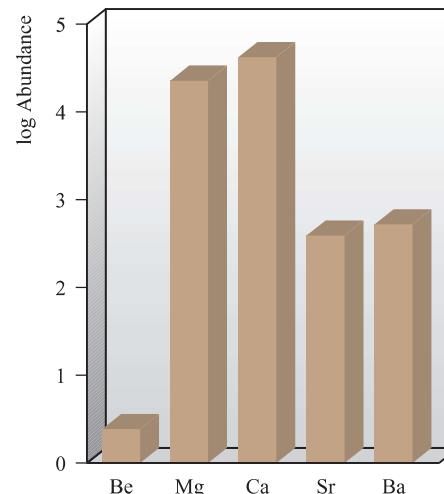
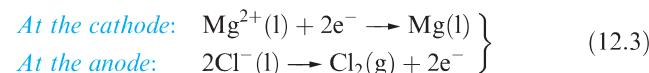
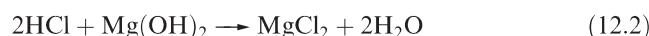


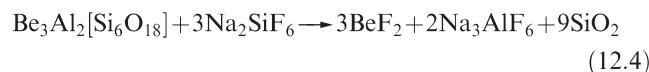
Fig. 12.2 Relative abundances in the Earth's crust of the alkaline earth metals (excluding Ra); the data are plotted on a logarithmic scale. The units of abundance are ppm.

hydrochloric acid (eq. 12.2) and evaporation of water gives $\text{MgCl}_2 \cdot x\text{H}_2\text{O}$, which, after heating at 990 K, yields the anhydrous chloride. This is followed by electrolysis of molten MgCl_2 and solidification of Mg (eq. 12.3).



Beryllium may be obtained from *beryl* by first heating with Na_2SiF_6 (eq. 12.4), extracting the water-soluble BeF_2 formed, and precipitating $\text{Be}(\text{OH})_2$.

Beryllium is also produced from *bertrandite* or *beryl* by extraction processes which involve leaching the ores with H_2SO_4 and steam, and conversion of beryllium sulfate to $\text{Be}(\text{OH})_2$. This is an intermediate compound in the production of Be, Be alloys and BeO. Production of the metal involves either reduction of BeF_2 with Mg, or electrolysis of BeCl_2 fused with NaCl.



The production of Ca is by electrolysis of fused CaCl_2 and CaF_2 . The metals Sr and Ba are extracted by reduction of the corresponding oxides by Al, or by electrolysis of MCl_2 ($\text{M} = \text{Sr, Ba}$).

Major uses of the group 2 metals and their compounds

Caution! Beryllium and soluble barium compounds are extremely toxic.

Beryllium is one of the lightest metals known, is non-magnetic, and has a high thermal conductivity and a very

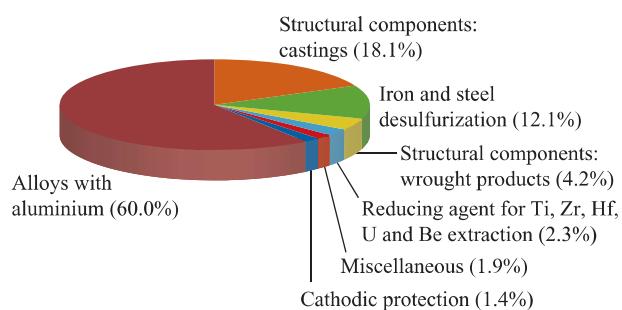


Fig. 12.3 Uses of Mg in the US in 2008 [data from US Geological Survey]; for a discussion of *cathodic protection*, see Box 8.4.

high melting point (1560 K). These properties, combined with inertness towards aerial oxidation, render it of industrial importance. It is used in the manufacture of body parts in high-speed aircraft and missiles, and in communication satellites. Because of its low electron density, Be is a poor absorber of electromagnetic radiation and, as a result, is used in X-ray tube windows. Its high melting point and low cross-section for neutron capture make Be useful in the nuclear energy industry.

Figure 12.3 summarizes the major uses of Mg. The presence of Mg in Mg/Al alloys imparts greater mechanical

strength and resistance to corrosion, and improves fabrication properties. Mg/Al alloys are used in aircraft and automobile body parts and lightweight tools. Die-casting of structural components accounted for 18.1% of the consumption of primary Mg in the US in 2008, compared with 57.0% in 2004. This corresponds not to a change in use of Mg, but to a fall in total Mg consumption (Box 12.1) which is largely associated with trends in the vehicle manufacturing industry. Miscellaneous uses (Fig. 12.3) include flares, fireworks and photographic flashlights, and medical applications such as indigestion powders (*milk of magnesia*, $\text{Mg}(\text{OH})_2$) and a purgative (*Epsom salts*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Both Mg^{2+} and Ca^{2+} ions are catalysts for diphosphate–triphosphate (see Box 15.11) transformations in biological systems; Mg^{2+} is an essential constituent of chlorophylls in green plants (see Section 12.8).

Uses of compounds of calcium far outnumber those of the metal. World production of CaO , $\text{Ca}(\text{OH})_2$, $\text{CaO}\cdot\text{MgO}$, $\text{Ca}(\text{OH})_2\cdot\text{MgO}$ and $\text{Ca}(\text{OH})_2\cdot\text{Mg}(\text{OH})_2$ was $\approx 296\,000\text{ Mt}$ in 2008 with China being by far the greatest producer. Calcium oxide (quicklime or lime) is produced by calcining limestone (see Fig. 11.6) and a major use is as a component in building mortar. Dry sand and CaO mixtures can be stored and transported. On adding water, and as CO_2 is absorbed,

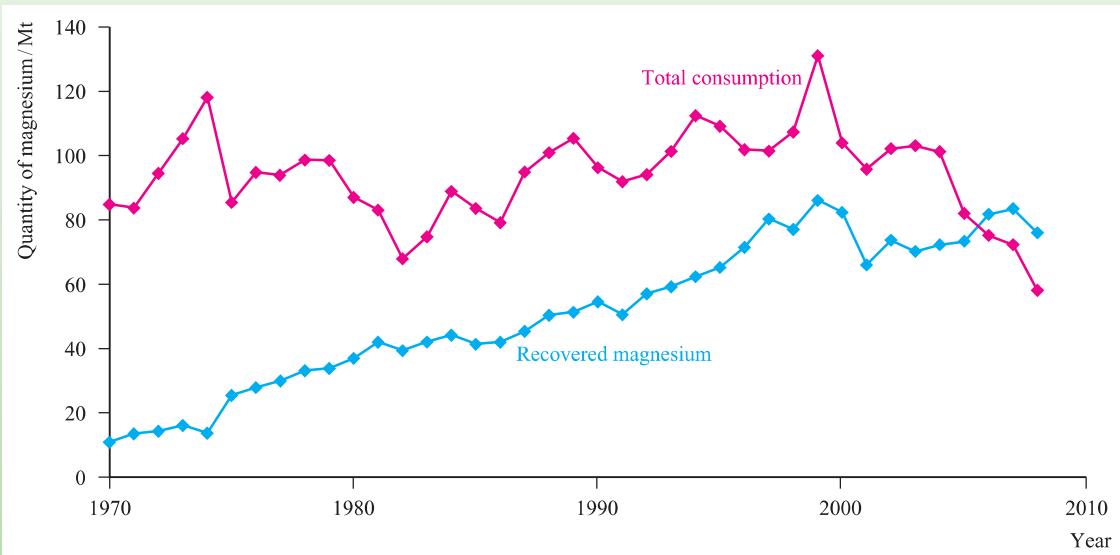


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Box 12.1 Recycling of materials: magnesium

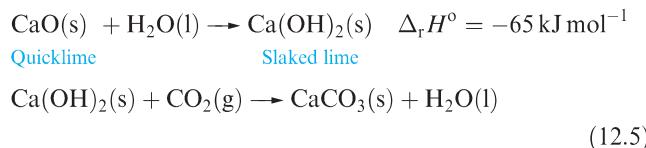
Recycling of materials became increasingly important during the last decades of the 20th century, and continues to have a significant influence on chemical industries. A large fraction of the total Mg consumed is in the form of Al/Mg alloys (see Fig. 12.3), and recycling of Al cans necessarily means recovery

of Mg. The graph below shows the variation in total consumption of primary Mg in the US from 1970 to 2008, and the increasing trend towards recovering the metal. The significant fall in total Mg consumption after 2004 is mainly associated with trends in the vehicle manufacturing industry.



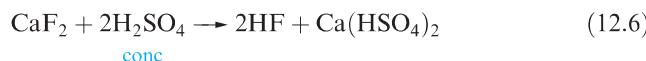
[Data from US Geological Survey]

the mortar sets as solid CaCO_3 (scheme 12.5). The sand in the mortar is a binding agent.



Other important uses of lime are in the steel industry (see Box 6.1), pulp and paper manufacturing, and extraction of Mg. Calcium carbonate is in huge demand in steel, glass, cement and concrete manufacturing (see Box 14.8), and the Solvay process (Fig. 11.6). Applications of CaCO_3 and Ca(OH)_2 with environmental significance are in desulfurization processes (see Box 12.2). Large quantities of Ca(OH)_2 are used to manufacture bleaching powder, $\text{Ca(OCl)}_2 \cdot \text{Ca(OH)}_2 \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (see Sections 17.2 and 17.9) and in water treatment (see eq. 12.29).

Calcium fluoride occurs naturally as the mineral fluorspar, and is commercially important as the raw material for the manufacture of HF (eq. 12.6) and F_2 (see Section 17.2). Smaller amounts of CaF_2 are used as a flux in the steel industry, for welding electrode coatings, and in glass manufacture. Prisms and cell windows made from CaF_2 are used in spectrophotometers.



The two mineral sources for strontium are the sulfate (*celestite*) and carbonate (*strontianite*). Trends in the commercial market for strontium have altered considerably over the last decade. Its main use was as a component ($\approx 8\%$ SrO) in colour television faceplate glass where its function was to block X-ray emissions from the cathode ray tube (CRT). However, this use of Sr has almost completely disappeared following the global uptake of flat screen televisions which incorporate only small amounts of SrCO_3 . Current commercial demands for Sr are in pyrotechnics ($\text{Sr(NO}_3)_2$), ceramic ferrite magnets (SrCO_3), alloys and pigments.

Barite (or *barytes*) is the mineral form of BaSO_4 . World production in 2008 was ≈ 8000 Mt, with China supplying over half this total. About 85% of global barite consumption is as a weighting material in oil- and gas-well drilling fluids. On a much smaller scale of application, the ability of BaSO_4 to stop the passage of X-rays leads to its use as a ‘barium meal’ in radiology for imaging the alimentary tract. Uses of Ba as a ‘getter’ in vacuum tubes arise from its high reactivity with gases including O_2 and N_2 .

12.3 Physical properties

General properties

Selected physical properties of the group 2 elements are listed in Table 12.1. The intense radioactivity of Ra makes

it impossible to obtain all the data for this element. Some general points to note from Table 12.1 are as follows:

- The general trend in decreasing values of IE_1 and IE_2 down the group (see Section 1.10) is broken by the increase in going from Ba to Ra, attributed to the *thermodynamic 6s inert pair effect* (see Box 13.4).
- High values of IE_3 preclude the formation of M^{3+} ions.
- Quoting a value of r_{ion} for beryllium assumes that the Be^{2+} ion is present in BeF_2 and BeO , a questionable assumption.
- There are no simple explanations for the irregular group variations in properties such as melting points and $\Delta_a H^\circ$.
- Values of E° for the M^{2+}/M couple are fairly constant (with the exception of Be), and can be explained in a similar way as for the group 1 metals (see Sections 8.7 and 11.3).

Flame tests

As for the alkali metals, emission spectra for the group 2 metals are readily observed and flame tests (see Section 11.3) can be used to distinguish between Ca-, Sr- and Ba-containing compounds: Ca (orange-red, but pale green when viewed through blue glass), Sr (crimson, but violet through blue glass), Ba (apple-green).

Radioactive isotopes

The isotope ^{90}Sr is a β -emitter ($t_{1/2} = 29.1$ yr) and a fission product of uranium. In the event of a nuclear energy plant disaster or through the dumping of nuclear waste, there is a danger that grass, and then milk, may be contaminated with ^{90}Sr and that it may be incorporated with calcium phosphate into bone.[†] For discussion of ^{226}Ra , see Section 12.1.

Self-study exercises

Refer to Section 10.3 for help if necessary.

1. ^{90}Sr decays by emission of a β -particle. Write an equation for the decay.
2. The product of the reaction in question 1 is also radioactive. It is a β -emitter and produces ^{90}Zr . Use this information to confirm that your answer to question 1 is correct.

(continued)

[†] For further details, see: N. Vajda and C.-K. Kim (2010) *Appl. Radiat. Isot.*, vol. 68, p. 2306 – ‘Determination of radiostrontium isotopes: A review of analytical methodology’.

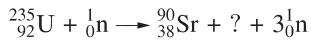
Table 12.1 Some physical properties of the group 2 metals, M, and their ions, M^{2+} .

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic number, Z	4	12	20	38	56	88
Ground state electronic configuration	[He]2s ²	[Ne]3s ²	[Ar]4s ²	[Kr]5s ²	[Xe]6s ²	[Rn]7s ²
Enthalpy of atomization, $\Delta_a H^\circ(298\text{ K})/\text{kJ mol}^{-1}$	324	146	178	164	178	130
Melting point, mp/K	1560	923	1115	1040	1000	973
Boiling point, bp/K	≈3040	1380	1757	1657	1913	1413
Standard enthalpy of fusion, $\Delta_{\text{fus}} H^\circ(\text{mp})/\text{kJ mol}^{-1}$	7.9	8.5	8.5	7.4	7.1	—
First ionization energy, $IE_1/\text{kJ mol}^{-1}$	899.5	737.7	589.8	549.5	502.8	509.3
Second ionization energy, $IE_2/\text{kJ mol}^{-1}$	1757	1451	1145	1064	965.2	979.0
Third ionization energy, $IE_3/\text{kJ mol}^{-1}$	14850	7733	4912	4138	3619	3300
Metallic radius, $r_{\text{metal}}/\text{pm}^{\ddagger}$	112	160	197	215	224	—
Ionic radius, $r_{\text{ion}}/\text{pm}^*$	27	72	100	126	142	148
Standard enthalpy of hydration of M^{2+} , $\Delta_{\text{hyd}} H^\circ(298\text{ K})/\text{kJ mol}^{-1}$	-2500	-1931	-1586	-1456	-1316	—
Standard entropy of hydration of M^{2+} , $\Delta_{\text{hyd}} S^\circ(298\text{ K})/\text{JK}^{-1}\text{ mol}^{-1}$	-300	-320	-230	-220	-200	—
Standard Gibbs energy of hydration of M^{2+} , $\Delta_{\text{hyd}} G^\circ(298\text{ K})/\text{kJ mol}^{-1}$	-2410	-1836	-1517	-1390	-1256	—
Standard reduction potential, $E^\circ_{M^{2+}/M}/\text{V}$	-1.85	-2.37	-2.87	-2.89	-2.90	-2.92

[‡] For 12-coordinate atoms.

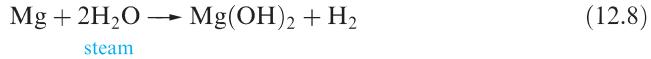
* For 4-coordination for Be^{2+} , and 6-coordination for other M^{2+} ions.

3. $^{90}_{38}\text{Sr}$ is formed as a fission product of $^{235}_{92}\text{U}$. Complete the following equation and determine the second fission product:



4. Why is $^{90}_{38}\text{Sr}$ considered to be especially dangerous when it is released into the environment?

However, Mg *amalgam* liberates H_2 from water, since no coating of oxide forms on its surface. Mg metal reacts with steam or hot water (eq. 12.8).



Beryllium and magnesium dissolve readily in non-oxidizing acids. Magnesium is attacked by nitric acid, whereas beryllium reacts with dilute HNO_3 but is passivated by concentrated nitric acid. Magnesium does not react with aqueous alkali, whereas Be forms an *amphoteric* hydroxide (see Section 12.6).

The metals Ca, Sr and Ba exhibit similar chemical behaviours, generally resembling, but being slightly less reactive than, Na. They react with water and acids liberating H_2 , and the similarity with Na extends to dissolution in liquid NH_3 to give blue solutions containing solvated electrons. From these solutions, it is possible to isolate hexaammines,

12.4 The metals

Appearance

Beryllium and magnesium are greyish metals, while the remaining group 2 metals are soft and silver-coloured. The metals are malleable, ductile and quite brittle. In air, the shiny surface of each metal quickly tarnishes.

Reactivity

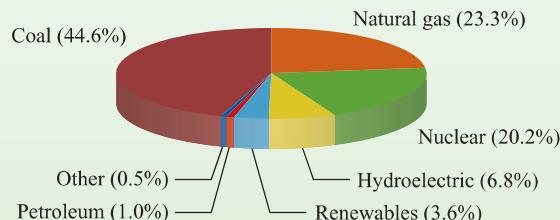
Beryllium and magnesium are passivated (eq. 12.7) and are kinetically inert to O_2 and H_2O at ambient temperatures.



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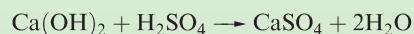
Box 12.2 Desulfurization processes to limit SO₂ emissions

Current awareness of the effects of environmental pollution has been instrumental in the development of *desulfurization processes*. This includes desulfurization of fossil fuels and flue gases from a variety of sources. Fossil fuels are the major source of fuel in electricity-generating power stations, and this is exemplified by the chart below which shows the source of fuel for the generation of electricity in the US in 2009:

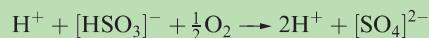
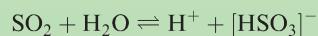


[Data: US Energy Information Administration]

The aim in a flue gas desulfurization process is to optimize the removal of SO₂ from emissions into the atmosphere. One important method of desulfurization in commercial operation throughout the world is based upon the neutralization reactions between Ca(OH)₂ or CaCO₃ and sulfuric acid. General equations for the neutralization reactions are:



Drax power station in the UK (shown opposite) operates six coal-fired boilers which produce superheated steam to drive turbines which generate electricity. About 7% of the electricity used in the UK is generated by this one power station. Different grades of coal contain varying amounts of sulfur, an upper limit being close to 2%. Each boiler at Drax power station consumes approximately 6300 tonnes of coal a day, and a 2% sulfur content by weight corresponds to 126 tonnes of sulfur being converted to SO₂. The photograph shows the main chimney (in the foreground) in addition to the cooling towers at Drax. When the power plant was first operational in the 1970s, gas emissions (CO₂, NO_x and SO₂) left the power station through the main chimney. The chimney was fitted with a flue gas desulfurization system in the 1990s and the emitted gases now pass through absorbers containing limestone, CaCO₃. Slaked lime, Ca(OH)₂, can also be used. The reactions shown below remove >90% of the SO₂ produced at the Drax power station, and the desulfurization system is capable of removing up to 280,000 tonnes of SO₂ per year. The reactions occurring are:



or



The Drax coal-fired power station in the UK uses desulfurization systems, installed between 1993 and 1996.

An advantage of the system is that CaSO₄·2H₂O, *gypsum*, is non-toxic and is not a waste product. It has a number of commercial applications, for example in the production of plaster of Paris (see Section 12.7) and cement (see Box 14.8).

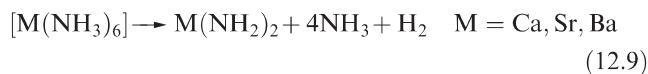
An alternative way of reducing sulfur emissions is to replace coal by biomass (timber and agricultural waste in addition to specifically grown crops). In 2007, Sembcorp Biomass Power Station was commissioned as a wood-fired power station in the UK, and uses wood from sustainable sources.

Ammonia can be used as an alternative to CaCO₃ and Ca(OH)₂ in desulfurization processes. The sulfuric acid (see above) combines with NH₃ to give [NH₄]₂[SO₄]. Like gypsum, ammonium sulfate is a commercially desirable chemical, and is recycled as a fertilizer.

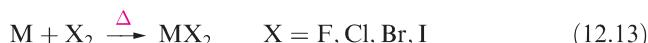
Further reading

- V.C. Baligar, R.B. Clark, R.F. Korcak and R.J. Wright (2011) *Adv. Agron.*, vol. 111, p. 51 – ‘Flue gas desulfurization product use on agricultural land’.
 - C. Li, Q. Zhang, N.A. Krotkov, D.G. Streets, K. He, S.-C. Tsay and J.F. Gleason, *Geophys. Res. Lett.* (2010) vol. 37, p. L08807/1 – ‘Recent large reduction in sulfur dioxide emissions from Chinese power plants observed by the ozone monitoring instrument’.
 - D. Stirling (2000) *The Sulfur Problem: Cleaning Up Industrial Feedstocks*, Royal Society of Chemistry, Cambridge.
 - S. Su, B. Li, S. Cui and S. Tao (2011) *Environ. Sci. Technol.*, vol. 45, p. 8403 – ‘Sulfur dioxide emissions from combustion in China: from 1990 to 2007’.
 - D. Wang, A. Bao, W. Kunc and W. Liss (2012) *Appl. Energy*, vol. 91, p. 341 – ‘Coal power plant flue gas waste heat and water recovery’.
 - C.F. You and X.C. Xu (2010) *Energy*, vol. 35, p. 4467 – ‘Coal combustion and its pollution control in China’.
 - www.draxpower.com
- See also Boxes 15.7, 16.5 and 22.5.

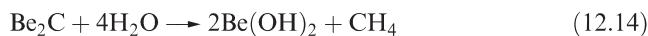
$[M(NH_3)_6]$ ($M = Ca, Sr, Ba$), but these slowly decompose to amides (eq. 12.9).



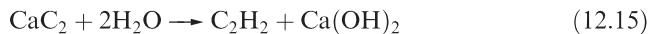
When heated, all the group 2 metals combine with O_2 , N_2 , sulfur or halogens (eq. 12.10–12.13).



Differences between the first and later members of group 2 are illustrated by the formation of hydrides and carbides. When heated with H_2 , Ca, Sr and Ba form saline hydrides, MH_2 , but Mg reacts only under high pressure. In contrast, BeH_2 (which is polymeric, Fig. 10.15) is prepared from beryllium alkyls (see Section 23.3). Beryllium combines with carbon at high temperatures to give Be_2C which possesses an antifluorite structure (see Section 6.11). The other group 2 metals form carbides MC_2 which contain the $[C\equiv C]^{2-}$ ion, and adopt NaCl-type structures that are elongated along one axis. Be_2C reacts with water according to eq. 12.14.

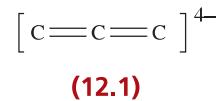


The carbides of Ca, Mg, Sr and Ba react with water to yield C_2H_2 . For CaC_2 , this reaction is a means of manufacturing ethyne (eq. 12.15) in areas of the world where coal is a more important feedstock for the chemical industry than oil, e.g. South Africa and China. Calcium carbide is made from CaO , which in turn is manufactured by calcining limestone (scheme 12.16). Production and consumption of CaC_2 in China accounts for 95% of the global demand. In Europe, the US and Japan, the production of CaC_2 has declined and it is manufactured, not for conversion to ethyne but to produce the nitrogenous fertilizer calcium cyanamide (eq. 12.17).



CaH_2 is used as a drying agent (see Box 12.3) but its reaction with water is highly exothermic.

The carbide Mg_2C_3 (which contains the linear $[C_3]^{4-}$ ion, 12.1, isoelectronic with CO_2) is formed by heating MgC_2 , or by reaction of Mg dust with pentane vapour at 950 K. Reaction of Mg_2C_3 with water produces $MeC\equiv CH$.

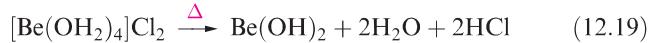
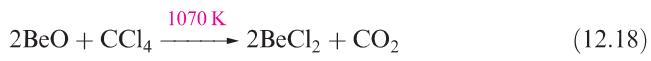


12.5 Halides

Beryllium halides

Anhydrous beryllium halides are covalent. The fluoride, BeF_2 , is obtained as a glass (sublimation point 1073 K) from the thermal decomposition of $[NH_4]_2[BeF_4]$, itself prepared from BeO and NH_3 in an excess of aqueous HF. Molten BeF_2 is virtually a non-conductor of electricity, and the fact that solid BeF_2 adopts a β -cristobalite structure (see Section 6.11) is consistent with its being a covalent solid. Beryllium difluoride is very soluble in water, the formation of $[Be(OH_2)_4]^{2+}$ (see Section 12.8) being thermodynamically favourable (Table 12.1).

Anhydrous $BeCl_2$ (mp 688 K, bp 793 K) can be prepared by reaction 12.18. This is a standard method of preparing a metal chloride that cannot be made by dehydration of hydrates obtained from aqueous media. In the case of Be, $[Be(OH_2)_4]^{2+}$ is formed and attempted dehydration of $[Be(OH_2)_4]Cl_2$ yields the hydroxide, not the chloride (eq. 12.19).



A **deliquescent** substance absorbs water from the surrounding air and eventually forms a liquid.

In the vapour state above 1020 K, $BeCl_2$ is monomeric and has a linear structure. At lower temperatures, the vapour also contains planar dimers. We return to the structures of gas-phase BeX_2 molecules later in the section. $BeCl_2$ forms colourless, deliquescent crystals containing infinite chains in which the coordination environment of each Be is tetrahedral. The Be–Cl distances are longer than in the monomer (Fig. 12.4). In Section 5.2, we described the bonding in monomeric $BeCl_2$ in terms of sp hybridization. In the polymer, each Be atom can be considered to be sp^3 hybridized and a localized σ -bonding scheme is appropriate in which each Cl donates a lone pair of electrons into an empty hybrid orbital on an adjacent Be atom (Fig. 12.4c). The formation of this chain demonstrates the Lewis acidity of beryllium dihalides. $BeCl_2$ acts as a Friedel–Crafts catalyst (i.e. like $AlCl_3$), and the formation of adducts is illustrated by $[BeF_4]^{2-}$, $[BeCl_4]^{2-}$ and $BeCl_2 \cdot 2L$ (L = ether, aldehyde, ketone).



APPLICATIONS

Box 12.3 Inorganic elements and compounds as drying agents

It is useful to distinguish between different classes of *drying agent* as being reagents that react with water either *reversibly* or *irreversibly*. The former can be regenerated, usually by heating, while the latter (sometimes classed as *dehydrating agents*) cannot. Caution is always needed when choosing a drying agent for the following reasons:

- the substance from which water is being removed may react with the drying agent;
- dehydrating agents often react vigorously with water and should not be used to dry very wet solvents, for which a pre-drying stage is appropriate;
- magnesium perchlorate, $Mg(ClO_4)_2$, although an extremely efficient drying agent, is best avoided because of the risk of explosions.

Many drying or dehydrating agents are compounds of group 1 or 2 metals. Concentrated H_2SO_4 , molecular sieves and silica gel are also commonly used to absorb water. Silica gel is a porous form of silica, SiO_2 , which is manufactured by coagulating acidified, aqueous solutions of sodium silicate. After washing to remove Na^+ and other ions, the precipitate is heated to drive off water. Although called a gel, silica gel is a microporous solid with a surface area of around $800\text{ m}^2\text{ g}^{-1}$. It is naturally colourless, but cobalt(II) salts (e.g. $[NH_4]_2[CoCl_4]$) are often added to act as an indicator. Such salts are blue in the absence of water and pink when hydrated. The photograph shows anhydrous cobalt-dyed silica gel spheres. Another highly effective dehydrating agent is phosphorus(V) oxide (see Section 15.10).

Agents for drying or predrying solvents

Typically, anhydrous salts that absorb water as solvate are suitable for removing water from solvents. Anhydrous $MgSO_4$, $CaCl_2$, $CaSO_4$, Na_2SO_4 and K_2CO_3 are hygroscopic and of these, $CaSO_4$ and $MgSO_4$ are particularly efficient and inert drying agents.

Drying agents that react irreversibly with H_2O

Drying agents in this category include Ca and Mg (for alcohols), CaH_2 (for a range of solvents, but not lower



Blue cobalt-dyed silica gel spheres; these turn pink when water is absorbed.

alcohols or aldehydes), $LiAlH_4$ (for hydrocarbons and ethers) and sodium. The latter, generally extruded as wire, is extremely efficient for removing water from hydrocarbons or ethers, but reacts with, for example, alcohols, and is not suitable for drying halogenated solvents.

Drying agents for use in desiccators and drying tubes

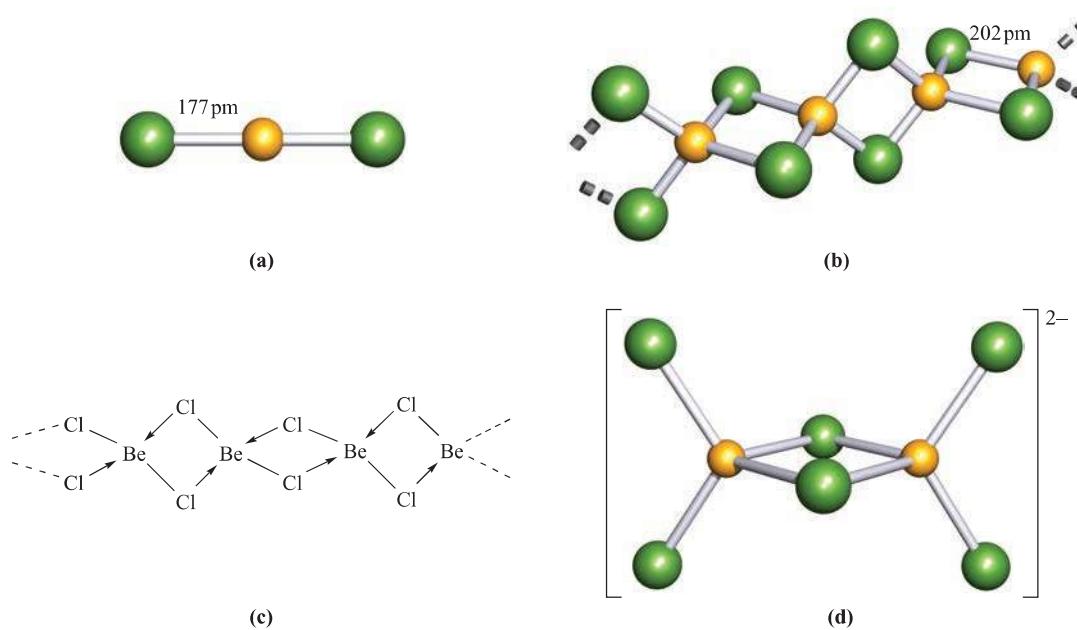
Suitable agents for drying samples in desiccators are anhydrous $CaCl_2$, $CaSO_4$, KOH and P_2O_5 . Gases may be dried by passage through drying tubes packed with a suitable agent, but possible reaction of the gas with the drying agent must be considered. Although P_2O_5 is a common choice for use in desiccators, reaction with water results in the formation of a brown, viscous layer on the surface of the anhydrous powder, thereby curtailing its dehydrating ability.

The reaction of $BeCl_2$ with $[Ph_4P]Cl$ in a 1 : 1 molar ratio produces $[Ph_4P]_2[Be_2Cl_6]$ containing the anion shown in Fig. 12.4d. The Be–Cl bonds involved in the bridging interactions are longer (210 pm) than the terminal bonds (196 pm), consistent with the differences observed on going from polymeric $BeCl_2$ to gas-phase $BeCl_2$ (Fig. 12.4). When $BeCl_2$ reacts with two equivalents of $[Ph_4P]Cl$, $[Ph_4P]_2[BeCl_4]$ is formed which contains the tetrahedral $[BeCl_4]^{2-}$ ion.

Worked example 12.1 Lewis acidity of $BeCl_2$

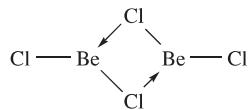
Suggest a structure for a dimer of $BeCl_2$ and explain how its formation illustrates $BeCl_2$ acting as a Lewis acid.

Each Be atom can accommodate up to eight electrons in its valence shell. In a $BeCl_2$ monomer, there are only four valence electrons associated with each Be atom. Each Be atom can therefore accept one or two lone pairs of electrons,



 **Fig. 12.4** (a) The linear structure of BeCl₂ in the gas phase. (b) The solid state polymeric structure of BeCl₂ is similar to that of BeH₂ (Fig. 10.15), although the bonding in these two compounds is *not* the same. (c) In BeCl₂, there are sufficient valence electrons to invoke 2c-2e Be–Cl bonds. (d) The structure of the [Be₂Cl₆]²⁻ ion in [Ph₄P]₂[Be₂Cl₆] determined by X-ray diffraction [B. Neumüller *et al.* (2003) *Z. Anorg. Allg. Chem.*, vol. 629, p. 2195]; the average Be–Cl terminal distance is 196 pm and the bridging Be–Cl distance is 210 pm. Colour code: Be, yellow; Cl, green.

thereby acting as a Lewis acid. Each Cl atom in monomeric BeCl₂ has three lone pairs of electrons. The dimer of BeCl₂ forms by donation of a lone pair of electrons from Cl to Be:



Each Be centre will be in a trigonal planar environment.

Self-study exercises

1. Rationalize why, on going from monomeric BeCl₂ to dimeric (BeCl₂)₂ to polymeric (BeCl₂)_n, the environment of the Be atom changes from linear to trigonal planar to tetrahedral.

[Ans. The number of electrons in the valence shell of Be changes from four to six to eight]

2. The recrystallization of BeCl₂ from diethyl ether solutions leads to a Lewis acid–base adduct. Draw the likely structure of the adduct and rationalize its formation in terms of the electron-accepting properties of BeCl₂.

[Ans. Tetrahedral BeCl₂·2Et₂O; O donates a lone pair of electrons to Be]

Halides of Mg, Ca, Sr and Ba

The fluorides of Mg(II), Ca(II), Sr(II) and Ba(II) are ionic, have high melting points, and are sparingly soluble in water, the solubility increasing slightly with increasing cation size (K_{sp} for MgF₂, CaF₂, SrF₂ and BaF₂ = 7.42×10^{-11} , 1.46×10^{-10} , 4.33×10^{-9} and 1.84×10^{-7} respectively). Whereas MgF₂ adopts a rutile structure (see Fig. 6.22), CaF₂, SrF₂ and BaF₂ crystallize with the fluorite structure (Fig. 6.19). In contrast to the behaviour of BeF₂, none of the later metal fluorides behaves as a Lewis acid.

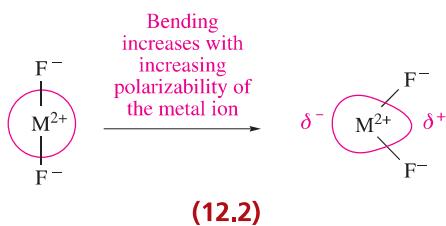
The structures of gaseous group 2 metal fluoride and later halide molecules are the subject of ongoing theoretical interest.[†] It has been suggested that the term ‘quasilinear’ be used for a species for which the calculated energy difference between linear and bent structures (with a change in angle of $>20^\circ$) is less than 4 kJ mol⁻¹. Using this definition leads to the structures given in Table 12.2. Of those compounds listed as quasilinear, SrBr₂ has the lowest energy barrier between a linear and bent structure. Some theoretical studies suggest only CaF₂, CaCl₂, SrCl₂ and SrBr₂ should be categorized as quasilinear, while in the extreme, only SrBr₂ should be considered quasilinear, with CaCl₂, CaBr₂, CaI₂ and SrI₂ being linear and CaF₂, SrCl₂ and BaI₂ being

[†] See: M. Kaupp (2001) *Angew. Chem. Int. Ed.*, vol. 40, p. 3534; M. Hargittai (2000) *Chem. Rev.*, vol. 100, p. 2233; K.J. Donald and R. Hoffmann (2006) *J. Am. Chem. Soc.*, vol. 128, p. 11236; M. Vasiliu, D. Feller, J.L. Gole and D.A. Dixon (2010) *J. Phys. Chem. A*, vol. 114, p. 9349.

Table 12.2 Structures of the monomeric group 2 metal dihalides, MX_2 . The term ‘quasilinear’ is explained in the text.

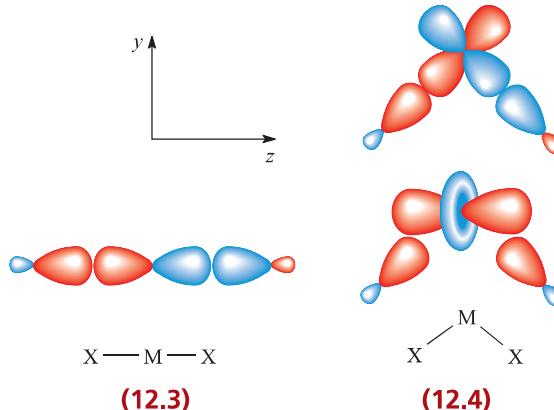
Metal	Halide			
	F	Cl	Br	I
Be	Linear	Linear	Linear	Linear
Mg	Linear	Linear	Linear	Linear
Ca	Quasilinear	Quasilinear	Quasilinear	Quasilinear
Sr	Bent	Quasilinear	Quasilinear	Quasilinear
Ba	Bent	Bent	Bent	Quasilinear

bent. The most bent of the dihalides is BaF₂. It has a bond angle in the region of 110–126° (values come from a range of theoretical and experimental data) and the calculated energy to convert bent BaF₂ to a linear molecule is $\approx 21 \text{ kJ mol}^{-1}$. The preference for bent structures for the heaviest metals combined with F, Cl or Br (see Table 12.2) has been explained in terms of both ‘inverse (or core) polarization’ and the participation of *d* atomic orbitals for Ca, Sr and Ba. Inverse polarization occurs when the metal ion is polarizable and is polarized by F[−] or Cl[−], or to a lesser extent, by Br[−]. This is represented in diagram 12.2. The polarization is termed ‘inverse’ to distinguish it from the polarization of a large, polarizable *anion* by a *cation* (see Section 6.13).



An alternative explanation focuses on the participation of d orbitals in the bonding in CaX_2 , SrX_2 and BaX_2 . Table 12.2 shows that Be and Mg form only linear gaseous dihalides. These two metals have only s and p atomic orbitals available for bonding and the best M–X orbital overlap is achieved for a linear molecule. This is shown in diagram 12.3 for an np orbital on M with the out-of-phase combination of X––X orbitals. For Ca, Sr and Ba, vacant $3d$, $4d$ and $5d$ orbitals, respectively, are available, but can only overlap efficiently with orbitals on the X atoms if the MX_2 molecule is bent. Two interactions must be considered as shown in diagram 12.4 (the axes are defined arbitrarily as shown). The out-of-phase combination of X––X orbitals only overlaps efficiently with the d_{yz} orbital of M if the MX_2 molecule is bent; opening the molecule up to a linear shape ‘switches off’ this orbital interaction. Although the interaction between the metal d_{z^2} orbital and the in-phase

combination of $X--X$ orbitals is most efficient when MX_2 is linear, it is still effective when the molecule is bent (diagram 12.4). The inverse polarization and participation of d atomic orbitals may both contribute to the problem of bent MX_2 molecules, and the explanation for the trend in shapes listed in Table 12.2 remains a matter for debate.



In addition to monomers of MX_2 being present in the vapour state, there is evidence that magnesium and calcium halides form dimers. Electron diffraction data are consistent with the presence of <5% Ca_2X_4 for calcium halides, while data at 1065 K for magnesium bromide indicate that 12% of the gaseous sample is composed of Mg_2Br_4 .

Worked example 12.2 Linear vs bent MX₂ molecules

What shape for the gas-phase molecule SrF₂ is consistent with the VSEPR model?

Sr is in group 2 and has two valence electrons.

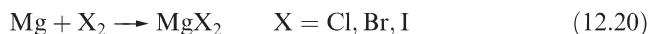
Each F atom provides one electron for bonding.

The valence shell of Sr in SrF_2 contains two bonding pairs of electrons and no lone pairs, therefore, by the VSEPR model SrF_2 should be a linear molecule.

Self-study exercises

1. Comment on the prediction of the VSEPR model for SrF_2 in the light of experimental observation.
[Ans. See text]
 2. For which of the following gas-phase species is the VSEPR model in agreement with experimental observations: BeCl_2 , BaF_2 , MgF_2 ?
[Ans. See text]
 3. Suggest a plausible structure for Mg_2Br_4 .
[Ans. Like Be_2Cl_4 in worked example 12.1]

Magnesium chloride, bromide and iodide crystallize from aqueous solution as hydrates which undergo partial hydrolysis when heated. The anhydrous salts are, therefore, prepared by reaction 12.20.



A *hygroscopic* solid absorbs water from the surrounding air but does not become a liquid.

Anhydrous MCl_2 , MBr_2 and MI_2 ($\text{M} = \text{Ca}$, Sr and Ba) can be prepared by dehydration of the hydrated salts. These anhydrous halides are *hygroscopic* and CaCl_2 (manufactured as a by-product in the Solvay process, see Fig. 11.6) is used as a laboratory drying agent (see Box 12.3), for road deicing and for dust control (see Box 12.4). In the solid state, many of the anhydrous halides possess complicated layer structures such as the CdI_2 -type structure (Fig. 6.23). Most of these halides are somewhat soluble in



ENVIRONMENT

Box 12.4 Winter road deicing and controlling dust on roads

In Section 11.2, we described the widespread use of NaCl for winter road deicing. In 2008, the US used ≈ 23 Mt of salt for the control of ice on roads. The great advantage of NaCl is that it is cheap. The disadvantages are that it is corrosive to motor vehicles and to concrete structures such as bridges and, when the snow melts, it is carried into water courses. The environmental effects that this has on water supplies and to fish and vegetation are a cause for concern and a topic of current research. Sodium chloride acts most effectively as a deicing agent at temperatures above -6°C (267 K).

Calcium chloride is also commonly applied as a road deicing agent. Its advantage over NaCl is that, when applied as solid anhydrous CaCl_2 , it is effective at temperatures as low as -32°C (241 K). An added benefit of using anhydrous CaCl_2 is that its dissolution into melted snow or ice is an exothermic process which results in further snow or ice melting. Aqueous solutions of CaCl_2 (sold as ‘liquid CaCl_2 ’) are also applied to roads. A solution that is 32% CaCl_2 by weight is an effective deicing agent down to -18°C (255 K). Two disadvantages of CaCl_2 are that it is significantly more corrosive than NaCl , and it is more expensive. One compromise is to pre-wet NaCl with CaCl_2 solution, and the application of ‘pre-wetted salt’ to roads is common practice.

While NaCl and CaCl_2 have been applied as winter road deicing agents for many years, their environmental disadvantages and corrosive properties make them far from ideal. The corrosive nature of chloride deicers makes them unsuitable for de-icing aircraft, and glycols are typically used for this purpose. An alternative to NaCl and CaCl_2 is the double salt calcium magnesium acetate (CMA), the potential of which was first recognized in the 1970s. CMA is manufactured by treating calcined dolomite (CaO.MgO) with acetic acid but, generated in this way, the product is about five times as expensive as NaCl . CMA is most efficient as a deicer above -7°C and therefore compares favourably with NaCl . However, CMA has many advantages. It is far less corrosive than chloride deicers, exhibits a low toxicity to vegetation and aquatic wildlife, and is biodegradable. Both NaCl and CaCl_2 are mobile in groundwater, and about 50% of NaCl applied to roads ends up in groundwater supplies. In contrast, CMA is poorly mobile in soil and shows a low tendency to reach groundwater. Current research into cheaper routes to its manufacture include oxidation of organic

food waste and fermentation processes, e.g. from calcined dolomite and whey lactose. The latter is converted to lactic acid by the bacterium *Lactobacillus plantarum*, and then to acetic and propanoic acids by *Propionibacterium acidipropionici*.

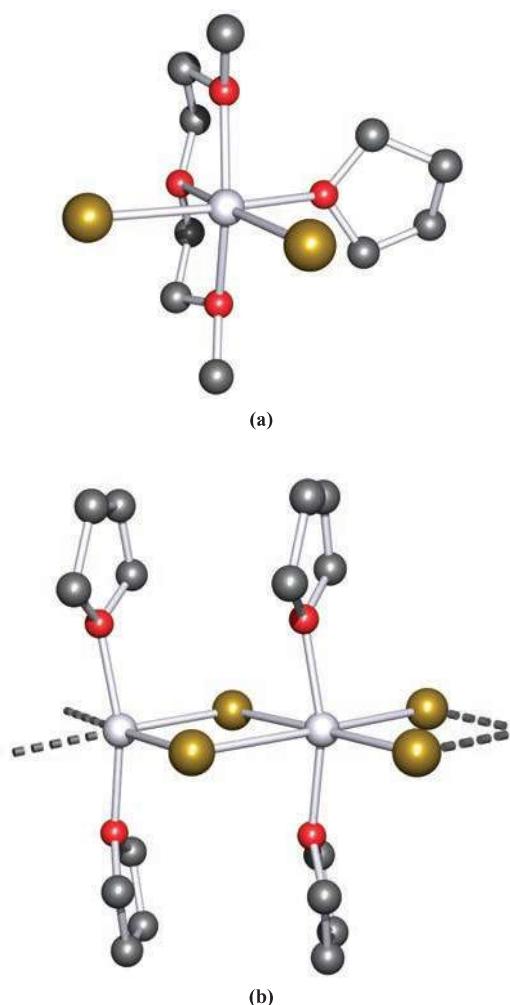
About 21% of CaCl_2 produced in North America is consumed in road deicing. A further 27% is used to control dust on unpaved roads. This application arises from the hygroscopic nature of CaCl_2 . Addition of anhydrous CaCl_2 , flaked CaCl_2 (78% CaCl_2 and 22% moisture) or ‘liquid CaCl_2 ’ (which dries out *in situ*) to dusty road surfaces provides a means of trapping water, thereby helping to aggregate the dust particles. In addition to reducing dust pollution, particle aggregation helps to slow down deterioration of the road surface. Canada, for example, uses CaCl_2 widely on its ‘dirt roads’, and in 2000, ≈ 100 kt were applied across the country.



Salt or pre-wetted salt is spread in huge amounts on roads in snow-belts.

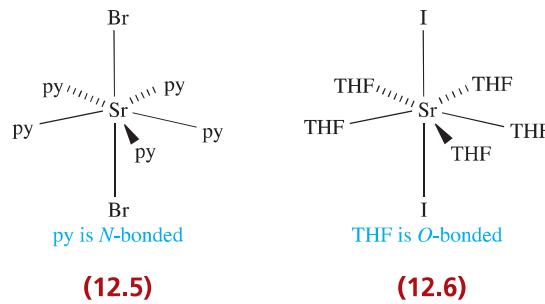
Further reading

- R.E. Jackson and E.G. Jobbág (2005) *Proc. Nat. Acad. Sci.*, vol. 102, p. 14487 – ‘From icy roads to salty streams’.
P.V. Vadlani, A.P. Mathews and G.S. Karr (2008) *World J. Microbiol. Biotechnol.*, vol. 24, p. 825 – ‘Low-cost propionate salt as road deicer: evaluation of cheese whey and other media constituents’.



 **Fig. 12.5** The structures (X-ray diffraction) of (a) $[\text{MgBr}_2(\text{diglyme})(\text{THF})]$ (diglyme = $\text{MeOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OMe}$) [N. Metzler *et al.* (1994) *Z. Naturforsch., Teil B*, vol. 49, p. 1448] and (b) $[\text{MgBr}_2(\text{THF})_2]$ [R. Sarma *et al.* (1977) *J. Am. Chem. Soc.*, vol. 99, p. 5289]; H atoms have been omitted. Colour code: Mg, pale grey; Br, gold; O, red; C, grey.

polar solvents such as ethers or pyridine, and a number of crystalline complexes have been isolated. Octahedral coordination has been confirmed by X-ray diffraction studies of complexes including *trans*- $[\text{MgBr}_2(\text{py})_4]$, *trans*- $[\text{MgBr}_2(\text{THF})_4]$, *cis*- $[\text{MgBr}_2(\text{diglyme})(\text{THF})]$ (Fig. 12.5a) and *trans*- $[\text{CaI}_2(\text{THF})_4]$. In $[\text{MgBr}_2(\text{THF})_2]$, octahedral coordination in the solid state is achieved by the formation of a chain structure (Fig. 12.5b); py = pyridine, THF = tetrahydrofuran (see Table 7.7). The larger sizes of the heavier metals permit higher coordination numbers, e.g. pentagonal bipyramidal *trans*- $[\text{SrBr}_2(\text{py})_5]$, **12.5**, and *trans*- $[\text{SrI}_2(\text{THF})_5]$, **12.6**. In organic chemistry, MgBr_2 is used as a catalyst for esterification reactions, and $\text{MgBr}_2 \cdot 2\text{Et}_2\text{O}$ is commercially available, being a catalyst for the conversion of aliphatic epoxides to the corresponding ketones.



12.6 Oxides and hydroxides

Oxides and peroxides

Beryllium oxide, BeO , is formed by ignition of Be or its compounds in O_2 . It is an insoluble white solid which adopts a wurtzite-type structure (see Fig. 6.21). The oxides of the other group 2 metals are usually prepared by thermal decomposition of the corresponding carbonate (eq. 12.21, for which temperature T refers to $P(\text{CO}_2) = 1$ bar).

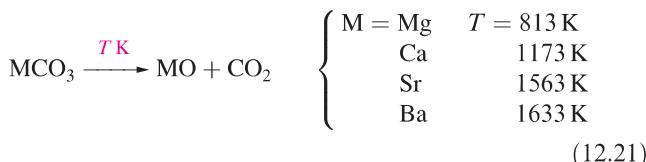


Figure 12.6 shows the trend in melting points of the oxides. MgO , CaO , SrO and BaO crystallize with an NaCl -type structure and the decrease in melting point reflects the decrease in lattice energy as the cation size increases (Table 12.1). The high melting point of MgO makes it suitable as a refractory material (see Box 12.5).

Refractory materials are suitable for use in furnace linings; such a material has a high melting point, low electrical conductivity and high thermal conductivity, and is chemically inert at the high operating temperatures of the furnace.

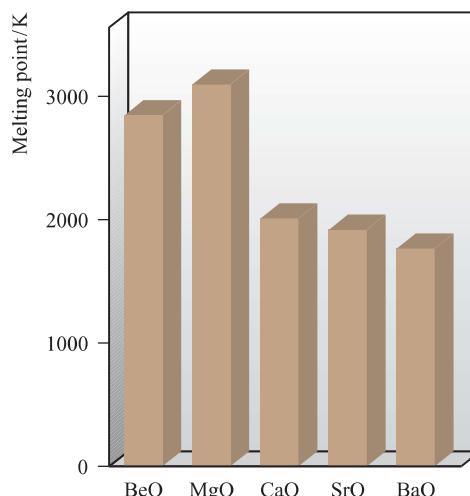


Fig. 12.6 The melting points of the group 2 metal oxides.



APPLICATIONS

Box 12.5 MgO: refractory material

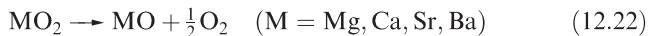
When one looks for a commercially viable refractory oxide, MgO (*magnesia*) is high on the list: it has a very high melting point (3073 K), can withstand heating above 2300 K for long periods, and is relatively inexpensive. Magnesia is fabricated into bricks for lining furnaces in steelmaking. Incorporating chromium ore into the refractory bricks increases their resistance to thermal shock. Magnesia bricks are also widely used in night-storage radiators: MgO conducts heat extremely well, but also has the ability to store it. In a radiator, the bricks absorb heat which is generated by electrically heated filaments during periods of ‘off-peak’ consumer rates, and then radiate the thermal energy over relatively long periods.



A blast furnace used in steel manufacturing.

The action of water on MgO slowly converts it to Mg(OH)₂ which is sparingly soluble. Oxides of Ca, Sr and Ba react rapidly and exothermically with water, and absorb CO₂ from the atmosphere (eq. 12.5). The conversion of CaO to calcium carbide and its subsequent hydrolysis (see eqs. 12.15 and 12.16) is industrially important.

Group 2 metal peroxides, MO₂, are known for M = Mg, Ca, Sr and Ba. Attempts to prepare BeO₂ have so far failed, and there is no experimental evidence for any beryllium peroxide compound.[†] As for the group 1 metal peroxides, the stability with respect to the decomposition reaction 12.22 increases with the size of the M²⁺ ion. This trend arises from the difference between the lattice energies of MO and MO₂ (for a given M) which becomes smaller as r_+ increases. $\Delta_{\text{lattice}}H^\circ(\text{MO}, \text{s})$ is always more negative than $\Delta_{\text{lattice}}H^\circ(\text{MO}_2, \text{s})$ (see worked example 12.3).



All the peroxides are strong oxidizing agents. Magnesium peroxide is manufactured by reacting MgCO₃ or MgO with H₂O₂, and is used in toothpaste and has environmental and agricultural applications as a slow O₂ release agent (see end-of-chapter problem 12.25). Calcium peroxide is

prepared by cautious dehydration of CaO₂·8H₂O, itself made by reaction 12.23.



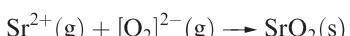
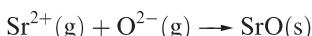
The reactions of SrO and BaO with O₂ (600 K, 200 bar pressure, and 850 K, respectively) yield SrO₂ and BaO₂. Pure BaO₂ has not been isolated and the commercially available material contains BaO and Ba(OH)₂. Reactions of the peroxides with acids (eq. 12.24) generate H₂O₂.



Worked example 12.3 Using the Kapustinskii equation

The lattice energies of SrO and SrO₂ are -3220 and $-3037 \text{ kJ mol}^{-1}$ respectively. (a) For what processes are these values defined? (b) Show that the relative magnitudes of these values are consistent with estimates obtained using the Kapustinskii equation.

(a) The lattice energies are negative values and therefore refer to the formation of 1 mole of crystalline lattice from gaseous ions:



[†] See: R.J.F. Berger, M. Hartmann, P. Pyykkö, D. Sundholm and H. Schmidbaur (2001) *Inorg. Chem.*, vol. 40, p. 2270 – ‘The quest for beryllium peroxides’.

(b) This part of the problem makes use of the relationship introduced at the end of Section 6.16: the Kapustinskii equation:

$$\Delta U(0\text{ K}) = -\frac{(1.07 \times 10^5)v|z_+||z_-|}{r_+ + r_-}$$

where: v = number of ions in the formula of the salt

$|z_+|$ = numerical charge on cation

$|z_-|$ = numerical charge on anion

r_+ = radius of cation in pm

r_- = radius of anion in pm

For SrO and SrO_2 :

$v = 2$ in each compound

$|z_+| = 2$ $|z_-| = 2$

$r_+ = 126\text{ pm}$ (see Appendix 6)

= constant for both compounds

The only variable is r_- .

Therefore:

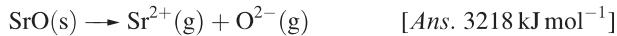
$$\Delta U(0\text{ K}) \propto -\frac{1}{126 + r_-}$$

Because the ionic radius of $[\text{O}_2]^{2-} > \text{O}^{2-}$, it follows from the equation above that $\Delta U(\text{SrO}_2)$ is less negative than $\Delta U(\text{SrO})$. This result is in agreement with the data given in the question.

Self-study exercises

Use data from the Appendices in the book where necessary.

1. Use the Kapustinskii equation to estimate a value for the process (at 0 K):

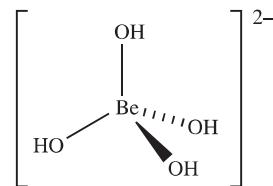


2. The values of the lattice energies of MgO , CaO and SrO are -3795 , -3414 and -3220 kJ mol^{-1} respectively. Show that this trend in values is consistent with the Kapustinskii equation.

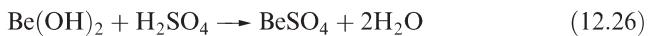
3. The difference between the lattice energies of CaO and CaO_2 is 270 kJ mol^{-1} . Will the difference between the lattice energies of MgO and MgO_2 be larger or smaller than 270 kJ mol^{-1} ? Use the Kapustinskii equation to rationalize your answer. [Ans. Larger]

Hydroxides

Beryllium hydroxide is amphoteric and this sets it apart from the hydroxides of the other group 2 metals which are basic. In the presence of excess $[\text{OH}]^-$, $\text{Be}(\text{OH})_2$ behaves as a Lewis acid (eq. 12.25), forming the tetrahedral complex ion 12.7, but $\text{Be}(\text{OH})_2$ also reacts with acids, e.g. reaction 12.26.



(12.7)

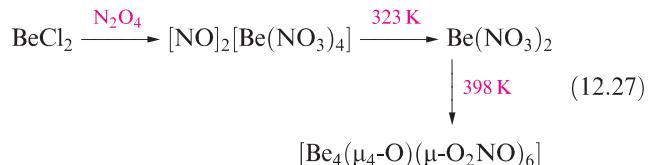


The water solubilities of $\text{M}(\text{OH})_2$ ($\text{M} = \text{Mg, Ca, Sr, Ba}$) increase down the group, as do their thermal stabilities with respect to decomposition into MO and H_2O . Magnesium hydroxide acts as a weak base, whereas $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are strong bases. *Soda lime* is a mixture of NaOH and $\text{Ca}(\text{OH})_2$ and is manufactured from CaO and aqueous NaOH . Soda lime is easier to handle than NaOH and is commercially available, being used, for example, as an absorbent for CO_2 , and in qualitative tests for $[\text{NH}_4]^+$ salts, amides, imides and related compounds which evolve NH_3 when heated with soda lime.

12.7 Salts of oxoacids

In this section, we give selected coverage of group 2 metal salts of oxoacids, paying attention only to compounds of special interest or importance.

Most beryllium salts of strong oxoacids crystallize as soluble hydrates. Beryllium carbonate tends to hydrolyse, giving a salt containing $[\text{Be}(\text{OH}_2)_4]^{2+}$ (see Section 12.8). BeCO_3 can be isolated only by precipitation under an atmosphere of CO_2 . This tendency towards hydrolysis is also illustrated by the formation of *basic beryllium acetate* $[\text{Be}_4(\mu_4-\text{O})(\mu-\text{O}_2\text{CMe})_6]$ (rather than $\text{Be}(\text{MeCO}_2)_2$) by the action of MeCO_2H on $\text{Be}(\text{OH})_2$. Figure 12.7 shows the structure of $[\text{Be}_4(\mu_4-\text{O})(\mu-\text{O}_2\text{CMe})_6]$; the central oxygen atom is bonded to four tetrahedral Be centres. A similar structure is observed in the basic nitrate $[\text{Be}_4(\mu_4-\text{O})(\mu-\text{O}_2\text{NO})_6]$ which is formed in reaction sequence 12.27.



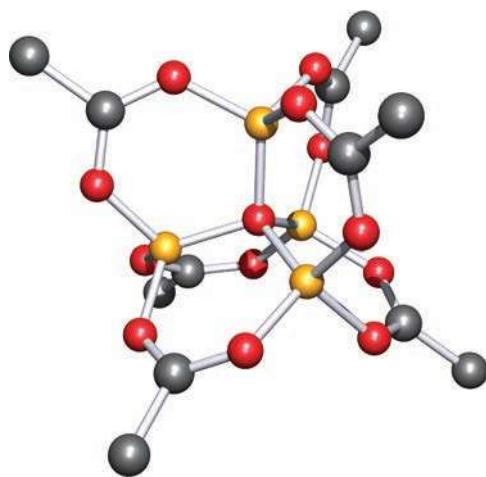
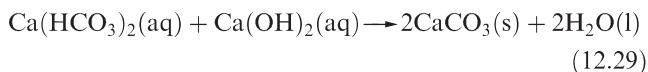
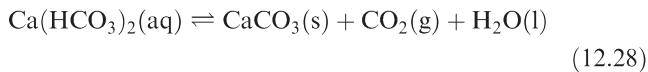


Fig. 12.7 The structure of basic beryllium acetate, $[\text{Be}_4(\mu_4\text{-O})(\mu\text{-O}_2\text{CMe})_6]$ (X-ray diffraction) [A. Tulinsky *et al.* (1959) *Acta Crystallogr.*, vol. 12, p. 623]; hydrogen atoms have been omitted. Colour code: Be, yellow; C, grey; O, red.

The carbonates of Mg and the later metals are sparingly soluble in water. Their thermal stabilities (eq. 12.21) increase with cation size, and this trend can be rationalized in terms of lattice energies. The metal carbonates are much more soluble in an aqueous solution of CO_2 than in water due to the formation of $[\text{HCO}_3]^-$. However, salts of the type ' $\text{M}(\text{HCO}_3)_2$ ' have not been isolated. *Hard water* contains Mg^{2+} and Ca^{2+} ions which complex with the stearate ions in soaps, producing insoluble 'scum' in household baths and basins. *Temporary hardness* is due to the presence of hydrogencarbonate salts and can be overcome by boiling (which shifts equilibrium 12.28 to the right-hand side causing CaCO_3 , or similarly MgCO_3 , to precipitate) or by adding an appropriate amount of $\text{Ca}(\text{OH})_2$ (again causing precipitation, eq. 12.29).

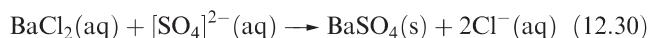


Permanent hardness is caused by other Mg^{2+} and Ca^{2+} salts (e.g. sulfates). The process of *water softening* involves passing the hard water through a cation-exchange resin (see Section 11.6). Washing-machine detergents contain 'builders' that remove Mg^{2+} and Ca^{2+} ions from washing water. Polyphosphates have been used for this purpose (see Box 15.11), but zeolites (see Section 14.9) are preferred.

Calcium carbonate occurs naturally in two crystalline forms, *calcite* and the metastable *aragonite*. In calcite, the Ca^{2+} and $[\text{CO}_3]^{2-}$ ions are arranged in such a way that each Ca^{2+} ion is 6-coordinate with respect to the carbonate

O atoms, whereas in aragonite, each Ca^{2+} ion is surrounded by nine O atoms. The energy difference between them is $<5\text{ kJ mol}^{-1}$ with calcite being the thermodynamically favoured form. However, aragonite is kinetically stable with respect to conversion to calcite. Aragonite can be prepared in the laboratory by precipitation of CaCO_3 from hot aqueous solution.

Sulfates of Mg and Ca have important applications and those of CaSO_4 are described in Section 16.2. CaSO_4 is a product of industrial desulfurization processes (see Box 12.2). Hydrated calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, *gypsum*) occurs naturally (see Fig 12.1). Gypsum crystals cleave easily owing to the presence of layers which are held together by hydrogen bonding. When gypsum is heated at $\approx 400\text{ K}$, it forms the hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (*plaster of Paris*), and if this is mixed with water, the material expands slightly as the dihydrate is regenerated (see Box 12.6). Barium sulfate is a sparingly soluble salt ($K_{\text{sp}} = 1.07 \times 10^{-10}$) and the formation of a white precipitate of BaSO_4 is used as a qualitative test for the presence of sulfate ions in aqueous solution (eq. 12.30).



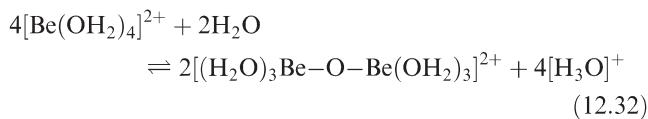
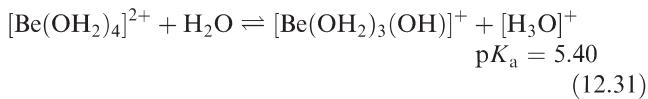
Calcium phosphate is described in Section 15.2.

A hydrate $\text{X}\cdot n\text{H}_2\text{O}$ in which $n = \frac{1}{2}$ is called a **hemihydrate**; if $n = 1\frac{1}{2}$, it is a **sesquihydrate**.

12.8 Complex ions in aqueous solution

Aqua species of beryllium

There is a high tendency to form $[\text{Be}(\text{OH}_2)_4]^{2+}$ in aqueous media. In ^{17}O -enriched water, exchange between coordinated water and solvent is slow on the NMR spectroscopic timescale, permitting the nature of the hydrated ion to be established. The tetrahedral coordination sphere ($\text{Be}-\text{O} = 162.0\text{ pm}$) has been established in the solid state structures of $[\text{Be}(\text{OH}_2)_4]\text{Cl}_2$ and $[\text{Be}(\text{OH}_2)_4][\text{O}_2\text{CC}\equiv\text{CO}_2]$ (Fig. 12.8). The charge density of Be^{2+} is high and solutions of beryllium salts are acidic (see Section 7.7). Reaction 12.31 is an over-simplistic representation of the acid dissociation, since various condensation processes occur, e.g. reaction 12.32, and hydroxido-bridged species are also present.





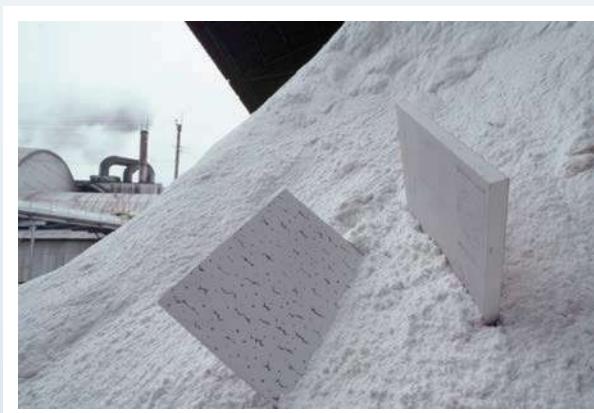
APPLICATIONS

Box 12.6 Gypsum plasters

The earliest known use of gypsum plaster was in Anatolia (part of modern-day Turkey) and Syria in about 6000 BC, and in about 3700 BC, the Egyptians used gypsum plaster in the inside of the pyramids. The building industry is the major consumer of gypsum plasters. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is mined on a large scale worldwide, and is calcined to form the β -hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. The hemihydrate is referred to as *plaster of Paris*, the name being derived from Montmartre in Paris where gypsum was quarried. Hydration of the hemihydrate with a carefully controlled amount of H_2O initially gives a slurry which hardens as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystallizes. Crystals are needle-like and it is their intergrowth that provides gypsum with its strength and suitability for the building trade. Calcined gypsum which is stored for long periods may age by absorbing water, and this affects the rehydration process. The setting process of gypsum plasters may be accelerated or slowed down by suitable additives, e.g. <0.1% of citric acid is sufficient to retard the crystallization process. Gypsum plasters suitable for applying to walls have been developed so that additives are already present with the hemihydrate. Building contractors commonly use prefabricated gypsum plasterboards and tiles. Plasterboards are fabricated by pouring a hemihydrate–water–additive slurry onto cardboard sheets ≈ 0.5 mm thick. After completing the lamination by applying a second sheet of cardboard, the plasterboard is dried. The incorporation of fibreglass (see Box 13.6) into plasterboards is also possible, giving fibreboard products. An advantage of gypsum plasterboards as partition walls is their degree of fire resistance.

In 2008, 159 Mt of gypsum was produced by mining worldwide. A second source referred to as ‘synthetic gypsum’ is produced in the flue gas desulfurization processes described in Box 12.2. The contribution made by synthetic gypsum to world supplies is growing in importance, and its production is

less expensive than mining natural gypsum. In 2008, 31% of gypsum consumed in the US was synthetic in origin. Recycling gypsum is also increasing. It can be salvaged from wallboard manufacturing, building demolition and house construction; approximately 10% of wallboard supplied for building a new house is scrapped. Recycled wallboard is crushed, and separated into paper and gypsum. The latter enters the production process for new prefabricated plasterboards along with mined and synthetic gypsum. The average new home in the US contains $\geq 570 \text{ m}^2$ of gypsum wallboard.



The Yoshino gypsum plant in Japan: recycling gypsum wallboards is an integral part of the manufacturing process which produces new gypsum plasterboards.

Statistical data: US Geological Survey.

Aqua species of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}

In contrast to the coordination number of four in the aquated Be^{2+} ion, each of the later group 2 metal ions can accommodate six or more water molecules in the first coordination sphere. In solution (^{17}O -labelled water), ^{17}O NMR spectroscopic data are consistent with the presence of $[\text{Mg}(\text{OH}_2)_6]^{2+}$, and crystallographic data on a range of salts confirm that this complex ion is octahedral. The $[\text{Mg}(\text{OH}_2)_6]^{2+}$ ion dissociates to some extent in aqueous solution ($\text{p}K_a = 11.44$).

In solution, the coordination number of the $[\text{Ca}(\text{OH}_2)_n]^{2+}$ ion depends on the concentration with $n \geq 6$. In the solid state, octahedral $[\text{Ca}(\text{OH}_2)_6]^{2+}$ is present in crystalline $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$, and a number of salts containing $[\text{Ca}(\text{OH}_2)_7]^{2+}$ have been structurally characterized. The geometry of the cation varies, e.g. pentagonal

bipyramidal in $[\text{Ca}(\text{OH}_2)_7][\text{Co}(\text{EDTA})]_2$ and capped octahedral in $[\text{Ca}(\text{OH}_2)_7][\text{Bi}(\text{EDTA})]_2 \cdot \text{H}_2\text{O}$ (see Fig. 19.8 for 7-coordinate geometries). $[\text{Ca}(\text{OH}_2)_8]^{2+}$ ions occur in $\text{CaK}[\text{AsO}_4] \cdot 8\text{H}_2\text{O}$. The large Sr^{2+} and Ba^{2+} ions can also accommodate more than six aqua ligands. The presence of $[\text{M}(\text{OH}_2)_8]^{2+}$ ions ($\text{M} = \text{Sr}, \text{Ba}$) in aqueous solution has been confirmed using the EXAFS technique (see Box 25.2). The single crystal structures of $[\text{Sr}(\text{OH}_2)_8][\text{OH}]_2$ and $[\text{Ba}(\text{OH}_2)_8][\text{OH}]_2$ have revealed hydrogen-bonded networks surrounding distorted square antiprismatic $[\text{M}(\text{OH}_2)_8]^{2+}$ ions. A similar coordination geometry has been observed for the $[\text{Sr}(\text{OH}_2)_8]^{2+}$ ion (Fig. 12.9) in a *host–guest complex* that involves an extensive hydrogen-bonded network with $[\text{Sr}(\text{OH}_2)_8]^{2+}$ ions in the cavities. The hydrated cations of Ca^{2+} , Sr^{2+} and Ba^{2+} do not undergo appreciable acid dissociation, and solutions of their salts derived from strong acids are neutral.

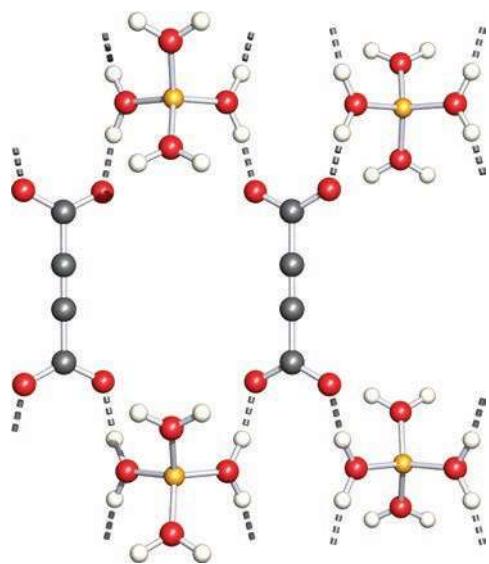


Fig. 12.8 Part of the packing diagram of $[\text{Be}(\text{OH}_2)_4][\text{O}_2\text{CC}\equiv\text{CCO}_2]$ showing hydrogen bonding between $[\text{Be}(\text{OH}_2)_4]^{2+}$ cations and $[\text{O}_2\text{CC}\equiv\text{CCO}_2]^{2-}$ anions; the structure was determined by neutron diffraction [C. Robl *et al.* (1992) *J. Solid State Chem.*, vol. 96, p. 318]. Colour code: Be, yellow; C, grey; O, red; H, white.

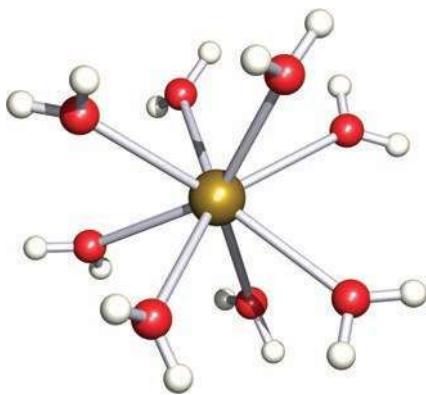


Fig. 12.9 The distorted square antiprismatic structure of the $[\text{Sr}(\text{OH}_2)_8]^{2+}$ ion present in a host–guest complex, the solid state structure of which has been determined by X-ray diffraction [M.J. Hardie *et al.* (2001) *Chem. Commun.*, p. 1850]. Colour code: Sr, gold; O, red; H, white.

In a **host–guest complex**, a molecule (the guest) occupies a cavity in the molecular structure of a larger molecular entity (the host). Intermolecular interactions are involved between the host and guest species. Examples are a metal ion within a crown ether or cryptand (ion–dipole interactions), hydrogen-bonded cages called **clathrates** that encapsulate guest molecules, and **inclusion compounds** in which guest molecules occupy channels in the structure of the host (van der Waals forces between host and guest).

Complexes with ligands other than water

The group 2 metal ions are hard acids and are preferentially coordinated by hard bases (see Table 7.9). In this section we consider complexes formed in aqueous solution in which the metal centre is coordinated by *O*- and *N*-donor ligands to give cationic species. Two important ligands are $[\text{EDTA}]^{4-}$ (see eq. 7.75) and $[\text{P}_3\text{O}_{10}]^{5-}$ (see Fig. 15.19). Both form water-soluble complexes with Mg^{2+} and the heavier metal ions, and are *sequestering agents* used in water-softening to remove Mg^{2+} and Ca^{2+} ions.

Macrocyclic ligands, including crown ethers and cryptands (see Sections 7.12 and 11.8), form stable complexes with Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . In an analogous manner to that noted for group 1 cations, selectivity corresponding to matching of cation (Table 12.1) and ligand-cavity sizes is observed. Thus, values of the stability constants for complexation with cryptand-222 (cavity radius 140 pm) in water follow the sequence $\text{Ba}^{2+} > \text{Sr}^{2+} \gg \text{Ca}^{2+} > \text{Mg}^{2+}$. An important class of macrocyclic ligands are the porphyrins and the parent compound is shown in Fig. 12.10a. Deprotonation of the two NH groups of a porphyrin gives a dianionic porphyrinato ligand. Chlorophylls, the pigments in green plants involved in photosynthesis, are porphyrinato derivatives containing Mg^{2+} coordinated within a square planar array of the four *N*-donor atoms. The structure of chlorophyll *a* is shown in Fig. 12.10b. The extensive conjugation in the ring system means that the molecule absorbs light in the visible region (λ_{max} 660 nm) and this initiates a series of reactions involving other systems containing Mn or Fe. Note that it is the *ligand* (not Mg^{2+}) that is involved in these redox reactions.

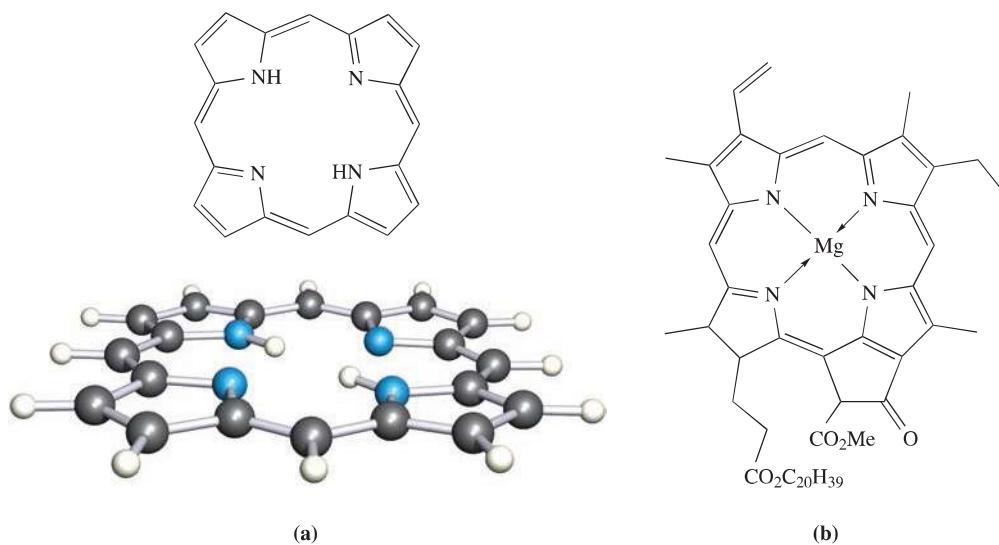
Self-study exercise

The fullerenes C_{60} and C_{70} are discussed in Chapter 14. When these fullerenes are reduced using barium in liquid ammonia, fulleride salts containing $[\text{Ba}(\text{NH}_3)_7]^{2+}$ and $[\text{Ba}(\text{NH}_3)_9]^{2+}$ counter-ions are obtained. Suggest possible structures for these cations.

[Ans. Refer to Figs. 10.14c and 19.9]

12.9 Complexes with amido or alkoxy ligands

In Section 12.5, we described group 2 metal halide complexes such as *trans*- $[\text{CaI}_2(\text{THF})_4]$ and *trans*- $[\text{SrBr}_2(\text{py})_5]$.

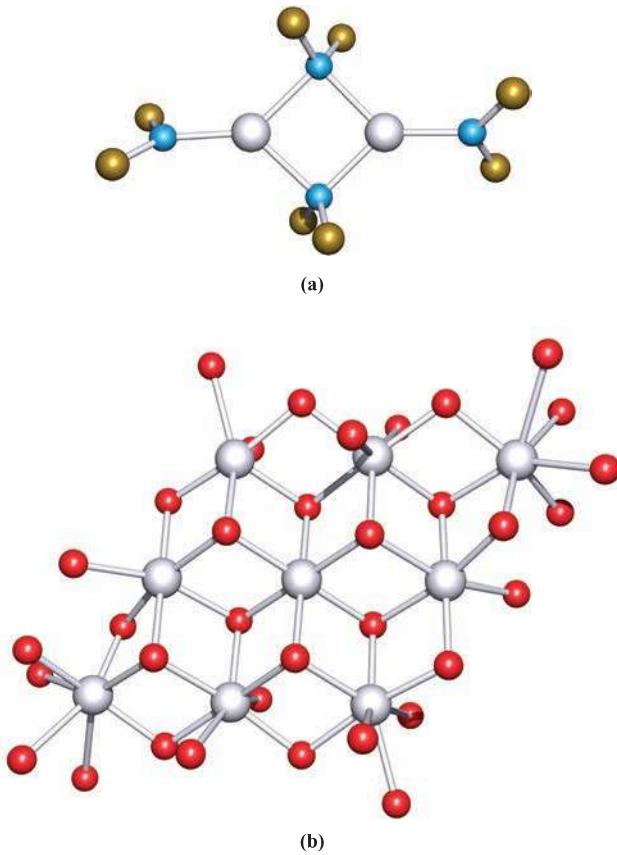


 **Fig. 12.10** The structures of (a) porphyrin and (b) chlorophyll *a*.

The number of complexes of the group 2 metals with *N*- or *O*-donor ligands continues to grow, notably those incorporating sterically demanding amido or alkoxy ligands.

With the bulky bis(trimethylsilyl)amido ligand, each of the M^{2+} ions forms at least one type of complex. In the gas phase, monomeric $[Be\{N(SiMe_3)_2\}_2]$ contains a linear $N-Be-N$ unit. In the solid state structure of $[Mg\{N(SiMePh_2)_2\}_2]$, $\angle N-Mg-N = 162.8^\circ$, the deviation from linearity being attributed to weak dipolar interactions between the electropositive metal centre and the electron density of the aromatic rings. Coordination numbers of 3 and 4 for $Mg(\text{II})$, $Ca(\text{II})$, $Sr(\text{II})$ and $Ba(\text{II})$ are seen in dimers $[M\{N(SiMe_3)_2\}_2]_2$ or solvated monomers, e.g. tetrahedral $[Ba\{N(SiMe_3)_2\}_2(\text{THF})_2]$. The structure of $[Ca\{N(SiMe_3)_2\}_2]_2$ is shown in Fig. 12.11a, and similar structures have been confirmed crystallographically for the analogous Mg , Sr and Ba compounds as well as for $[Mg\{N(CH_2Ph)_2\}_2]$.

While alkoxy derivatives of the alkaline earth metals have been known for many years, the area has undergone significant expansion since 1990. Much of this interest stems from the fact that calcium, strontium and barium alkoxides are potential precursors for high-temperature superconductors (see Chapter 28) and volatile compounds suitable for *chemical vapour deposition* (CVD) studies are being sought. Mononuclear complexes include several of the type $[M(\text{OR})_2(\text{THF})_3]$, e.g. $[Ca(\text{OC}_6\text{H}_2-2,6-\text{Bu}_2-4-\text{Me})_2(\text{THF})_3]$. Some interesting high nuclearity species have also been isolated, including $[Ba_4(\mu_4-\text{O})(\mu-\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_3-2,4,6)_6]$, formed by treating BaI_2 with $K[\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_3-2,4,6]$ in THF, and $[Ca_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}(\text{HOCH}_2\text{CH}_2\text{OMe})_2]$ (Fig. 12.11b), produced by reacting Ca metal with 2-methoxyethanol in hexane.



 **Fig. 12.11** The structures (determined by X-ray diffraction) of (a) $[Ca_2\{N(SiMe_3)_2\}_2\{\mu-N(SiMe_3)_2\}_2]$ in which the methyl groups have been omitted [M. Westerhausen *et al.* (1991) *Z. Anorg. Allg. Chem.*, vol. 604, p. 127] and (b) $[Ca_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}-(\text{HOCH}_2\text{CH}_2\text{OMe})_2]$ for which only the $Ca_9(\mu_3-\text{O})_8(\mu-\text{O})_8\text{O}_{20}$ core is shown (four of the ligands in $[Ca_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}-(\text{HOCH}_2\text{CH}_2\text{OMe})_2]$ are terminally attached, leaving four oxygen atoms non-coordinated to Ca^{2+} centres) [S.C. Goel *et al.* (1991) *J. Am. Chem. Soc.*, vol. 113, p. 1844]. Colour code: Ca, pale grey; O, red; N, blue; Si, gold.

12.10 Diagonal relationships between Li and Mg, and between Be and Al

In Section 11.3, we noted that the properties of Li and its compounds are often considered to be anomalous when compared with those of the later group 1 metals, and that a *diagonal relationship* exists between Li and Mg. In this section, we consider this relationship in detail and also describe a similar diagonal relationship between Be and Al. The positions of Li, Be, Mg and Al in the periodic table are shown below:

1	2	13
Li	Be	B
Na	Mg	Al
K	Ca	Ga

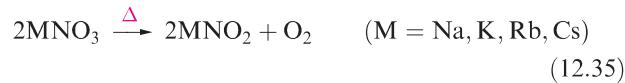
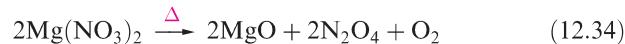
Table 12.3 lists selected physical properties of the first three elements in groups 1, 2 and 13. From a comparison of the properties of Li with those of Na and K, or of Li with Mg, it can be seen that Li resembles Mg more closely than it does the later members of group 1. A similar comparison between Be, Mg, Ca and Al leads to the conclusion that the physical properties of Be listed in Table 12.3 resemble those of Al more than they do those of the later group 2 metals. The Li^+ ion is small and highly polarizing, and this results in a degree of covalency in some of its compounds. On going from Li^+ to Be^{2+} , the ionic radius *decreases*, while on going down group 2 from Be^{2+} to Mg^{2+} , the ionic radius *increases*. The net result is that the sizes of Li^+ and Mg^{2+} are similar (Table 12.3), and we observe similar patterns in behaviour between lithium and magnesium despite the fact that they

are in different groups. The diagonal relationship that exists between Li^+ and Mg^{2+} is also observed between Be^{2+} and Al^{3+} , and between the Na^+ , Ca^{2+} and Y^{3+} ions.

Lithium and magnesium

Some of the chemical properties of Li that make it diagonally related to Mg rather than vertically related to the other alkali metals are:

- Lithium readily combines with N_2 to give the nitride, Li_3N ; Mg reacts with N_2 to give Mg_3N_2 .
- Lithium combines with O_2 to give the oxide Li_2O rather than a peroxide or superoxide (see eqs. 11.8–11.10); Mg forms MgO . The peroxides of both metals can be formed by reacting LiOH or $\text{Mg}(\text{OH})_2$ with H_2O_2 .
- Lithium and magnesium carbonates decompose readily on heating to give Li_2O and CO_2 , and MgO and CO_2 respectively; down the group, the carbonates of the group 1 metals become increasingly stable with respect to thermal decomposition (see eq. 11.19 and accompanying text).
- Lithium and magnesium nitrates decompose on heating according to eqs. 12.33 and 12.34, whereas NaNO_3 and the later alkali metal nitrates decompose according to eq. 12.35.



- The Li^+ and Mg^{2+} ions are more strongly hydrated in aqueous solution than are the ions of the later group 1 and 2 metals.
- LiF and MgF_2 are sparingly soluble in water; the later group 1 fluorides are soluble.

Table 12.3 Selected physical properties of the first three elements of groups 1, 2 and 13.

Property	Group 1			Group 2			Group 13		
	Li	Na	K	Be	Mg	Ca	B	Al	Ga
Metallic radius, r_{metal} / pm [†]	157	191	235	112	160	197	—	143	153
Ionic radius, r_{ion} / pm [‡]	76	102	138	27	72	100	—	54	62
Pauling electronegativity, χ^{P}	1.0	0.9	0.8	1.6	1.3	1.0	2.0	1.6	1.8
$\Delta_{\text{atom}}H^\circ(298\text{ K})$ / kJ mol ⁻¹	161	108	90	324	146	178	582	330	277

[†] For 12-coordinate atoms (see also Table 11.1).

[‡] For 6-coordination except for Be, which is for 4-coordination; the ionic radius refers to M^+ for group 1, M^{2+} for group 2, and M^{3+} for group 13.

- LiOH is much less soluble in water than the other alkali metal hydroxides; Mg(OH)₂ is sparingly soluble.
- LiClO₄ is much more soluble in water than the other alkali metal perchlorates; Mg(ClO₄)₂ and the later group 2 metal perchlorates are very soluble.

Beryllium and aluminium

Representative chemical properties of Be that make it diagonally related to Al rather than vertically related to the later group 2 metals are:

- The Be²⁺ ion is hydrated in aqueous solution, forming [Be(OH₂)₄]²⁺ in which the Be²⁺ centre significantly polarizes the already polar O–H bonds, leading to loss of H⁺ (see eq. 12.31); the pK_a value of 5.4

for [Be(OH₂)₄]²⁺ is close to that of [Al(OH₂)₆]³⁺ (pK_a = 5.0) which contains a highly polarizing Al³⁺ ion (see eq. 7.34).

- Be and Al both react with aqueous alkali, liberating H₂; Mg does not react with aqueous alkali.
- Be(OH)₂ and Al(OH)₃ are amphoteric, reacting with both acids and bases (see eqs. 12.25 and 12.26 for reactions of Be(OH)₂, and eqs. 7.41 and 7.42 for Al(OH)₃); the hydroxides of the later group 2 metals are basic.
- BeCl₂ and AlCl₃ fume in moist air, reacting to give HCl.
- Both Be and Al form complex halides, hence the ability of the chlorides to act as Friedel–Crafts catalysts.

Further examples of similarities between the behaviours of Be and Al can be found by comparing their reactivities (see Sections 12.4 and 13.4).

KEY TERMS

The following terms were introduced in this chapter. Do you know what they mean?

- | | | |
|--|--|---|
| <input type="checkbox"/> deliquescent | <input type="checkbox"/> water-softening agent | <input type="checkbox"/> clathrate |
| <input type="checkbox"/> hygroscopic | <input type="checkbox"/> (sequestering agent) | <input type="checkbox"/> inclusion compound |
| <input type="checkbox"/> refractory material | <input type="checkbox"/> hemihydrate | <input type="checkbox"/> porphyrin |
| <input type="checkbox"/> permanent and temporary hardness of water | <input type="checkbox"/> sesquihydrate | <input type="checkbox"/> amido ligand |
| | <input type="checkbox"/> host–guest complex | <input type="checkbox"/> alkoxy ligand |

FURTHER READING

K.M. Fromm (2002) *CrystEngComm*, vol. 4, p. 318 – An article that uses structural data to consider the question of ionic versus covalent bonding in group 2 metal iodide complexes.

N.N. Greenwood and A. Earnshaw (1997) *Chemistry of the Elements*, 2nd edn, Butterworth-Heinemann, Oxford – Chapter 5 gives a detailed account of the inorganic chemistry of the group 2 metals.

A.G. Massey (2000) *Main Group Chemistry*, 2nd edn, Wiley, Chichester – Chapter 5 covers the chemistry of the group 2 metals.

K.A. Walsh (2009) *Beryllium Chemistry and Processing*, ASM International, Ohio – A book that details sources, production, chemistry and metallurgy of beryllium.

A.F. Wells (1984) *Structural Inorganic Chemistry*, 5th edn, Clarendon Press, Oxford – A full account of the structural chemistry of the group 2 metals and their compounds.

Special topics

L. Addadi, ed. (2007) *CrystEngComm*, vol. 9, issue 12 – An issue dedicated to biominerization including that of CaCO₃.

K.M. Fromm and E.D. Gueneau (2004) *Polyhedron*, vol. 23, p. 1479 – ‘Structures of alkali and alkaline earth metal clusters with oxygen donor ligands’ (a review that includes comments on CVD).

D.L. Kepert, A.F. Waters and A.H. White (1996) *Aust. J. Chem.*, vol. 49, p. 117 – ‘Synthesis and structural systematics of nitrogen base adducts of group 2 salts’ (Part VIII in a series of papers covering this subject).

N.A.J.M. Sommerdijk and G. de With (2008) *Chem. Rev.*, vol. 108, p. 4499 – ‘Biomimetic CaCO₃ mineralization using designer molecules and interfaces’.

PROBLEMS

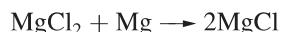
- 12.1 (a) Write down, in order, the names and symbols of the metals in group 2; check your answer by reference to the first page of this chapter. (b) Give a *general* notation that shows the ground state electronic configuration of each metal.
- 12.2 Using data in Table 7.4, determine the relative solubilities of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ and explain the relevance of your answer to the extraction of magnesium from seawater.
- 12.3 (a) Write an equation to show how Mg reacts with N_2 when heated. (b) Suggest how the product reacts with water.
- 12.4 The structure of magnesium carbide, MgC_2 , is of the NaCl type, elongated along one axis. (a) Explain how this elongation arises. (b) What do you infer from the fact that there is no similar elongation in NaCN which also crystallizes with a NaCl -type structure?
- 12.5 Write balanced equations for the following reactions:
 (a) the thermal decomposition of $[\text{NH}_4]_2[\text{BeF}_4]$;
 (b) the reaction between NaCl and BeCl_2 ;
 (c) the dissolution of BeF_2 in water.
- 12.6 (a) Suggest a likely structure for the dimer of BeCl_2 , present in the vapour phase below 1020 K. What hybridization scheme is appropriate for the Be centres? (b) BeCl_2 dissolves in diethyl ether to form monomeric $\text{BeCl}_2 \cdot 2\text{Et}_2\text{O}$; suggest a structure for this compound and give a description of the bonding.
- 12.7 MgF_2 has a TiO_2 -type structure. (a) Sketch a unit cell of MgF_2 , and (b) confirm the stoichiometry of MgF_2 using the solid state structure.
- 12.8 Discuss the trends in data in Table 12.4.
- 12.9 (a) How do anhydrous CaCl_2 and CaH_2 function as drying agents?
 (b) Compare the solid state structures and properties of BeCl_2 and CaCl_2 .

Table 12.4 Data for problem 12.8.

Metal, M	$\Delta_f H^\circ / \text{kJ mol}^{-1}$			
	MF_2	MCl_2	MBr_2	MI_2
Mg	-1113	-642	-517	-360
Ca	-1214	-795	-674	-535
Sr	-1213	-828	-715	-567
Ba	-1200	-860	-754	-602

- 12.10 How would you attempt to estimate the following?

(a) $\Delta_r H^\circ$ for the solid state reaction:



(b) $\Delta_r H^\circ$ for the reaction:



- 12.11 (a) Identify the conjugate acid–base pairs in reaction 12.24. (b) Suggest how BaO_2 will react with water.

- 12.12 (a) Determine $\Delta_r H^\circ$ for the reactions of SrO and BaO with water, given that values of $\Delta_f H^\circ(298 \text{ K})$ for SrO(s) , BaO(s) , $\text{Sr(OH)}_2\text{(s)}$, $\text{Ba(OH)}_2\text{(s)}$ and $\text{H}_2\text{O(l)}$ are -592.0, -553.5, -959.0, -944.7 and -285.5 kJ mol^{-1} respectively. (b) Compare the values of $\Delta_r H^\circ$ with that for the reaction of CaO with water (eq. 12.5), and comment on factors contributing to the trend in values.

- 12.13 (a) What qualitative test is used for CO_2 ? (b) What reaction takes place, and (c) what is observed in a positive test?

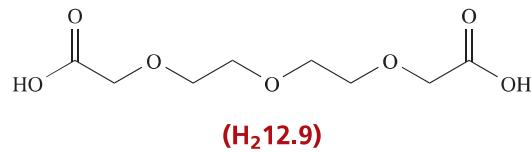
- 12.14 Discuss the data presented in Table 12.5.

- 12.15 Write a short account that justifies the so-called *diagonal relationship* between Li and Mg.

- 12.16 Suggest why MgO is more soluble in aqueous MgCl_2 solution than in pure water.

- 12.17 Suggest why Be^{2+} forms the tetrahedral ion $[\text{Be}(\text{OH}_2)_4]^{2+}$, while Mg^{2+} forms octahedral $[\text{Mg}(\text{OH}_2)_6]^{2+}$.

- 12.18 The reaction between $\text{Ca}(\text{OH})_2$ and $\text{H}_2\text{12.9}$ in aqueous solution leads to the formation of the complex $[\text{Ca}(\text{OH}_2)_2\text{12.9}]$. This crystallizes as a centrosymmetric dimer in which each Ca^{2+} centre is 8-coordinate. This contains a central $\text{Ca}_2(\mu\text{-O})_2$ unit in which each bridging O-donor involves a carboxylate group; only one oxygen atom of each carboxylate group is coordinated. Propose a structure for the centrosymmetric dimer.

**Table 12.5** Data for problem 12.14: $\log K$ for the formation of the complexes $[\text{M}(\text{crypt}-222)]^{n+}$.

M^{n+}	Na^+	K^+	Rb^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\log K$	4.2	5.9	4.9	2.0	4.1	13.0	>15

OVERVIEW PROBLEMS

- 12.19 Suggest explanations for the following observations.
- The energy released when a mole of crystalline BaO is formed from its constituent ions is less than that released when a mole of MgO forms from its ions. (Each compound possesses an NaCl-structure.)
 - Despite being a covalent solid, BeF₂ is very soluble in water.
 - At 298 K, Be adopts an hcp lattice; above 1523 K, the coordination number of a Be atom in elemental beryllium is 8.
- 12.20 Comment on the following statements.
- Na₂S adopts a solid state structure that is related to that of CaF₂.
 - [C₃]⁴⁻, CO₂ and [CN₂]²⁻ are isoelectronic species.
 - Be(OH)₂ is virtually insoluble in water, but is soluble in aqueous solutions containing excess hydroxide ions.
 - MgO is used as a refractory material.
- 12.21 Suggest products for the following reactions, and write balanced equations for the reactions. Comment on any of these reactions that are important in chemical manufacturing processes.
- CaH₂ + H₂O →
 - BeCl₂ + LiAlH₄ →
 - CaC₂ + H₂O →
 - BaO₂ + H₂SO₄ →
 - CaF₂ + H₂SO₄(conc) →
 - MgO + H₂O₂ →
 - MgCO₃ →
△
 - Mg in air →
△
- 12.22 (a) A group 2 metal, **M**, dissolves in liquid NH₃, and from the solution, compound **A** can be isolated. **A** slowly decomposes to **B** with liberation of NH₃ and a gas **C**. Metal **M** gives a crimson flame test; through blue glass, the flame appears pale purple. Suggest identities for **M**, **A**, **B** and **C**.
- (b) The group 2 metal **X** occurs naturally in great abundance as the carbonate. Metal **X** reacts with cold water, forming compound **D**, which is a strong base. Aqueous solutions of **D** are used in qualitative tests for CO₂. **X** combines

with H₂ to give a saline hydride that is used as a drying agent. Identify **X** and **D**. Write equations for the reaction of **X** with H₂O and of the hydride of **X** with H₂O. Explain how you would carry out a qualitative test for CO₂ using an aqueous solution of **D**.

- 12.23 (a) A 6-coordinate complex may be obtained by crystallizing anhydrous CaI₂ from THF solution at 253 K. In contrast, when anhydrous BaI₂ is crystallized from THF at 253 K, a 7-coordinate complex is isolated. Suggest structures for the two complexes, and comment on possible isomerism and factors that may favour one particular isomer in each case. Rationalize why CaI₂ and BaI₂ form complexes with THF that have different coordination numbers.
- (b) Which of the following compounds are sparingly soluble in water, which are soluble without reaction, and which react with water: BaSO₄, CaO, MgCO₃, Mg(OH)₂, SrH₂, BeCl₂, Mg(ClO₄)₂, CaF₂, BaCl₂, Ca(NO₃)₂? For the compounds that react with water, what are the products formed?

- 12.24 Each compound in List 1 has a matching description in List 2. Correctly match the partners. There is only one correct statement for each compound.

List 1	List 2
CaCl ₂	Polymeric in the solid state
BeO	Soda lime
Be(OH) ₂	Strong oxidizing agent
CaO	Used in qualitative analysis for sulfates
CaF ₂	Hygroscopic solid, used for de-icing
BaCl ₂	Amphoteric
BeCl ₂	Quicklime
MgO ₂	Crystallizes with a wurtzite-type structure
Ca(OH) ₂ /NaOH	A prototype crystal structure

INORGANIC CHEMISTRY MATTERS

- 12.25 Magnesium peroxide is used as a slow O₂ release agent in agriculture, ponds and lakes. It is manufactured by treating magnesium oxide or carbonate with H₂O₂. (a) Write equations for these reactions. (b) Suggest how the decomposition of magnesium peroxide depends upon pH by considering decomposition in neutral H₂O, dilute acid and dilute alkali.
- 12.26 Describe how sulfur-containing emissions from coal-fired power stations (a) arise, and (b) are controlled. (c) What are the products of standard desulfurization processes and how are they utilized?
- 12.27 Discuss how the properties of Mg lead to the following applications. (a) Professional camera bodies are made from magnesium alloys (>90% Mg). (b) Mg is used for cathodic protection of steel structures exposed to seawater. (c) Mg is used in fireworks. (d) Aluminium alloys used in the vehicle manufacturing industry contain up to 5% Mg.
- 12.28 World production of lime in 2008 was 296 Mt. The term ‘lime’ may refer to CaO (quicklime) and/or slaked lime (Ca(OH)₂), but is also used to encompass CaO, Ca(OH)₂, CaO·MgO, Ca(OH)₂·MgO and Ca(OH)₂·Mg(OH)₂. (a) How are CaO and CaO·MgO manufactured? (b) Describe the role of CaO in the building industry. (c) How is CaO converted to calcium carbide. Comment on recent trends in the industrial importance of this reaction. (d) In the paper industry, wood chips are converted to pulp by treatment with aqueous NaOH and Na₂S. Heating the spent liquor gives Na₂CO₃. Explain how treating this residue with Ca(OH)₂ followed by appropriate steps allows both NaOH and Ca(OH)₂ to be recovered.