

## 12.3: Group II- Alkaline Earths

Group IIA also known as the **alkaline-earth metals**, include beryllium, magnesium, calcium, strontium, barium, and radium. The last member of the group, Ra, is radioactive and will not be considered here. All alkaline earths are silvery-gray metals which are ductile and relatively soft. However, the following table shows that they are much denser than the group IA metals, and their melting points are significantly higher. They are also harder than the alkali metals. This may be attributed to the general valence electron configuration  $ns^2$  for the alkaline earths, which involves two electrons per metal atom in metallic bonding (instead of just one as in an alkali metal).

Table 12.3.1: Properties of the Group IIA Alkaline-Earth Metals

Element	Symbol	Electron Configuration	Usual Oxidation State<	Radius/pm	
				Atomic	Ionic (M <sup>2+</sup> )
Barium	Ba	[Xe]6s <sup>2</sup>	+2	198	135
Beryllium	Be	[He]2s <sup>2</sup>	+2	89	31
Calcium	Ca	$[Ar]4s^2$	+2	174	99
Magnesium	Mg	[Ne]3s <sup>2</sup>	+2	136	65
Strontium	Sr	[Kr]5s <sup>2</sup>	+2	191	113

Symbol	Ionization Energy/MJ mol <sup>-1</sup>			Density/ g cm <sup>-3</sup>	Electro negativity	Melting Point (in °C)
	First	Second	Third			
Be	0.906	1.763	14.86	1.86	1.5	1278
Mg	0.744	1.467	7.739	1.74	1.2	651
Ca	0.596	1.152	4.918	1.54	1.0	839
Sr	0.556	1.071	4.21	2.60	1.0	769
Ba	0.509	0.972	3.43	3.51	0.9	725

First and second ionization energies for the alkaline earths (corresponding to removal of the first and second valence electrons) are relatively small, but the disruption of an octet by removal of a third electron is far more difficult. Like the alkali metals, the alkaline-earth atoms lose electrons easily, and so they are good reducing agents. Other trends among the data in the table are what we would expect. Ionization energies and electronegativities decrease from top to bottom of the group, and atomic and ionic radii increase. The radii of +2 alkaline-earth ions are much smaller than the +1 alkali-metal ions of the same period, because the greater nuclear charge holds the inner shells more tightly. This effect is sufficiently large that an alkaline earth below and to the right of a given alkali metal in the periodic table often has nearly the same ionic radius. Thus Na<sup>+</sup> (95 pm), can fit into exactly the same type of crystal lattice as Ca<sup>2+</sup> (99 pm), and these two elements are often found in the same minerals. The same is true of K<sup>+</sup> and Ba<sup>2+</sup>. Below is the table for alkali metals, to compare with the table of alkaline earth metals.

Table 12.3.2: Properties of the Group IA Alkali Metals

Element	Symbol	Electron Configuration	Usual Oxidation State	Radius/pm	
				Atomic	Ionic (M <sup>+</sup> )
Lithium	Li	[He]2s <sup>1</sup>	+1	122	60
Sodium	Na	[Ne]3s <sup>1</sup>	+1	157	95
Potassium	K	[Ar]4s <sup>1</sup>	+1	202	133
Rubidium	Rb	[Kr]5s <sup>1</sup>	+1	216	148
Cesium	Cs	[Xe]6s <sup>1</sup>	+1	235	169



Symbol	Ionization Energy/MJ mol <sup>-1</sup>		Density/ g cm <sup>-3</sup>	Electronegativity	Melting Point (in °C)
	First	Second			
Li	0.526	7.305	0.534	1.0	179
Na	0.502	4.569	0.97	0.9	98
K	0.425	3.058	0.86	0.8	64
Rb	0.409	2.638	1.52	0.8	39
Cs	0.382	2.430	1.87	0.7	28

Similarity of ionic radii also leads to related properties for Li and Mg. Since these two elements are adjacent along a diagonal line from the upper left to the lower right in the periodic table, their similarity is called a **diagonal relationship**. Diagonal relationships are mainly evident in the second and third periods: Be is similar to Al, and B is like Si in many ways.

Farther toward the right-hand side of the table such relationships are less pronounced. The most striking similarity between Li and Mg is their ability to form covalent bonds with elements of average electronegativity, such as C, while forming fairly ionic compounds with more electronegative elements, such as O or F. Two examples of covalent compounds are ethyllithium, CH<sub>3</sub>CH<sub>2</sub>Li, and diethylmagnesium, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Mg. Such compounds are likely in the case of Li and Mg but not the alkali or alkaline earths below them, because Li<sup>+</sup> and Mg<sup>2+</sup> are small enough to be strongly polarizing and thus form bonds with considerable covalent character.

## Chemical Reactions and Compounds

The alkaline earth metals react directly with most nonmetallic elements. forming Except for beryllium, the alkaline earths react directly with hydrogen gas to form hydrides,  $MH_2$ ; M = Mg, Ca, Sr, Ba, or Ra. Beryllium hydride,  $BeH_2$  can also be prepared, but not directly from the elements. Alkaline-earth metals combine readily with oxygen from the air to form oxides, MO. This follows the general reaction:

$$2\mathrm{M}(s) + \mathrm{O}_2(g) o 2\mathrm{MO}_2(s)$$

The following video shows the reaction of magnesium with oxygen:



In the video, magnesium is burned in air, and emits a bright white flame. A white powder of MgO remains after the reaction described by the equation:

$$2\mathrm{Mg}(s) + \mathrm{O}_2(g) \rightarrow 2\mathrm{MgO}_2(s)$$



It should also be noted that while MgO is the main product, nitrogen is also present in the air, and so some magnesium nitride is also produced according to the chemical equation:

$$Mg(s) + N_2(q) \rightarrow Mg_3N_2(s)$$

These oxides will coat the surface of the metal and prevent other substances from contacting and reacting with it. A good example of the effect of such an oxide coating is the reaction of alkaline-earth metals with water. Beryllium and magnesium react much more slowly than the others because their oxides are insoluble and prevent water from contacting the metal.

Alkaline-earth metals react directly with halogens to form salts:

$$\mathrm{M}(s)+\mathrm{Cl}_2(g) o\mathrm{MCl}_2(s)$$

Salt obtained by evaporating seawater (sea salt) contains a good deal of magnesium chloride and calcium chloride as well as sodium chloride. It also has small traces of iodide salts, accounting for the absence of simple goiter in communities which obtain their salt from the oceans. Simple goiter is an enlargement of the thyroid gland caused by iodine deficiency.

Alkaline earths also form sulfides: MS. In all these compounds the alkaline-earth elements occur as dipositive ions,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , or  $Ba^{2+}$ .

Similar compounds of Be can be formed by roundabout means, but not by direct combination of the elements. Moreover, the Be compounds are more covalent than ionic. The Be<sup>2+</sup> ion has a very small radius (31 pm) and is therefore capable of distorting (polarizing) the electron cloud of an anion in its vicinity. Therefore all bonds involving Be have considerable covalent character, and the chemistry of Be is significantly different from that of the other members of group IIA.

As in the case of the alkali metals, the most important and abundant alkaline earths, Mg and Ca, are in the third and fourth periods. Be is rare, although its strength and low density make it useful in certain special alloys. Sr and Ba occur naturally as the relatively insoluble sulfates SrSO<sub>4</sub> (strontianite) and BaSO<sub>4</sub> (barite), but these two elements are of minor commercial importance.

The most common ores of Mg and Ca are dolomite, MgCO<sub>3</sub>•CaCO<sub>3</sub>, after which an entire mountain range in Italy is named, and limestone, CaCO<sub>3</sub>, an important building material. Mg is also recovered from seawater on a wide scale. The oxides of the alkaline earths are commonly obtained by heating the carbonates. For example, lime, CaO, is obtained from limestone as follows:

$$\mathrm{CaCO}_3(s) \stackrel{\Delta}{\longrightarrow} \mathrm{CaO}(s) + \mathrm{CO}_2(g)$$

Except for BeO, which is covalently bonded, alkaline-earth oxides contain  $O^{2-}$  ions and are strongly basic. When treated with water (a process known as **slaking**), they are converted to hydroxides:

$${
m CaO}(s) + {
m H_2O}(l) 
ightarrow {
m Ca(OH)_2}(s)$$

Ca(OH)<sub>2</sub> (slaked lime) is an important strong base for industrial applications, because it is cheaper than NaOH.

MgO has an extremely high melting point  $(2800^{\circ}\text{C})$  because of the close approach and large charges of its constituent Mg<sup>2+</sup> and O<sup>2-</sup> ions in the crystal lattice. As a solid it is a good electrical insulator, and so it is used to surround metal-resistance heating wires in electric ranges. MgO is also used to line high-temperature furnaces. When converted to the hydroxide, Mg finds a different use. Mg(OH)<sub>2</sub> is quite insoluble in water, and so it does not produce a high enough concentration of hydroxide ions to be caustic. It is basic, however, and gram for gram can neutralize nearly twice the quantity of acid that NaOH can. Consequently a suspension of Mg(OH)<sub>2</sub> in water (milk of magnesia) makes an excellent antacid, for those who can stand its taste.

Because the carbonate ion behaves as a Brönstedt-Lowry base, carbonate salts dissolve in acidic solutions. In nature, water often becomes acidic because the acidic oxide  $CO_2$  is present in the atmosphere. When  $CO_2$  from the air dissolves in water, it can help dissolve limestone:

$$\mathrm{CO}_2(g) + \mathrm{H}_2\mathrm{O}(l) + \mathrm{CaCO}_3(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{HCO}_3^-(aq)$$

This reaction often occurs underground as rainwater saturated with  $CO_2$  seeps through a layer of limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of  $CaCO_3$ . In addition, the groundwater and well water in such areas becomes hard. **Hard water** contains appreciable concentrations of  $Ca^{2+}$ ,  $Mg^{2+}$ , and certain other metal ions. These form insoluble compounds with soap, causing curdy, scummy precipitates. Hard water can be softened by adding



 $Na_2CO_3$ , washing soda, which precipitates  $CaCO_3$ , or by **ion exchange**, a process in which the undesirable  $Ca^{2+}$  and  $Mg^{2+}$  ions are replaced in solution by  $Na^+$  ions, which do not precipitate soap. Most home water softeners work on the latter principle.

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