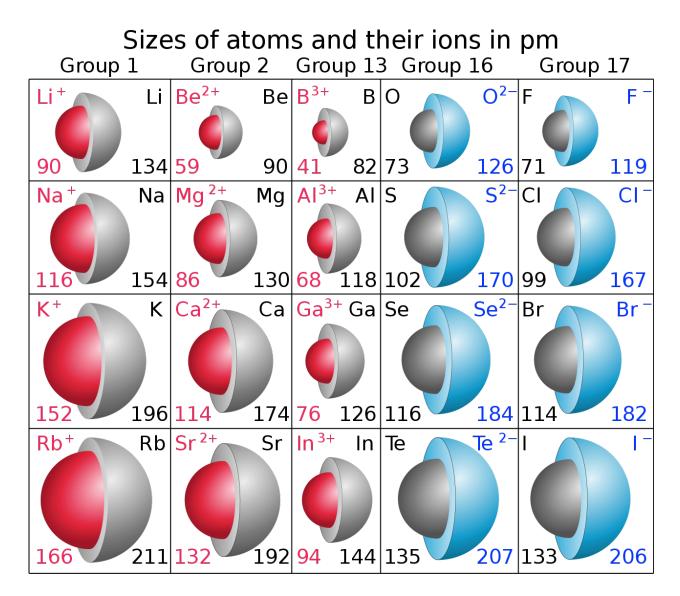
**Mg** not like Be or the rest of the group. It is intermediate between purely ionic and purely covalent.

#### Mg<sup>2+</sup> is highly polarizing (relatively small size and high charge) and therefore does form some non-ionic compounds in addition to ionic compounds

In order to form ionic bonds an atom must lose electrons easily to become positively charged. The amount of energy is their Ionization energy. The lower the ionization enthalpy, the easier it is to form a cation and thus an ionic bond. The ionization enthalpies of Alkali and Alkaline Earth metals are low compared to other groups in the periodic table, but there is a catch with Lithium and Beryllium (and to some extent Magnesium). They have the highest covalent character within their groups. The reason for this anomalous behavior is the unusual degree of attraction to the nucleus compared to other members of the group. **This is because they have their last electrons in a 2s orbital which is much closer to the nucleus compared to the other members of their series**. This leads to higher effective nuclear charge or stronger attraction from the nucleus and thus makes the removal of their electrons more difficult. This leads to bit of a higher ionization enthalpy and a but less ionic character.



 $Mg(OH)_2$  like Be(OH)\_2 is more covalent than the other M(OH)\_2 compounds in the group which dissolve readily in H<sub>2</sub>O to give basic solutions (ionic oxides which are basic) whereas covalent oxides, if they dissolve, are acidic) (actually, the reality is that Be<sup>2+</sup> and Mg<sup>2+</sup> form amphoteric oxides)

# **Calcium, Strontium, Barium and Radium**

These comprise a rather close-knit group with properties that vary gradually with increasing size  $Ca \rightarrow Ra$ 

- electropositive nature increases
- hydration energies of the salts increase

#### - insolubility of most salts increase

The solubility decreases down the group because the hydration enthalpy (tendency to be surrounded by water) decreases from Be<sup>2+</sup>to Ba<sup>2+</sup> as the size of the cation increases down the group. Sulfates, carbonates, nitrates etc.,

- larger cations tend to stabilize larger anions  $O_2^{2-}, O_2^{-}, I_3^{--}$ 

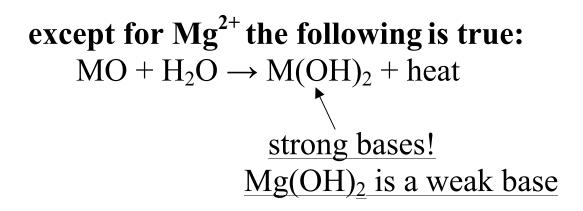
### **Binary Compounds of Group IIA**

Oxides

MO white, high-melting crystalline materials NaCl fcc structures

most important member is:  $CaCO_3 \rightarrow CaO + CO_{2(g)}$  $\Delta H = 178.1 \text{ kJ/mol}$ 

CaO is made on a vast scale for the cement industry (from limestone)



**Magnesium hydroxide** has limited solubility, meaning not very much is going to dissolve so it produces only a low concentration of **hydroxides**. Therefore it acts like a **weak base**.

### Halides all are ionic

 $MX_2$  can be made from dehydration of hydrates  $MX_2 \cdot xH_2O$  (the number of waters, x, can vary)

Solubilities of  $MX_2$  decrease as you go down the group except for  $MF_2$  compounds which are more soluble for:  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ 

- **Q** Why?
- ▲  $Mg^{2^+}$  is rather small so contact with F<sup>-</sup> is good in the crystal packing → stabilizes the crystal giving a high lattice energy & Ba<sup>2+</sup> is large, does not make good contact with F<sup>-</sup> in a crystal

#### **Summary**

Periodic Chemical Properties as developed in Chapter 8 are evident in Alkaline Earths, Group IIA

Be

- covalent even with electronegative elements e.g. BeF<sub>2</sub>, [BeF<sub>4</sub>]<sup>2-</sup>, [Be(OH<sub>2</sub>]<sup>2+</sup>
- 2. forms no simple  $Be^{2+}$  ionic compounds
- 3. forms four-coordinate compounds
- 4. forms covalent Be-C bonds as in BeR<sub>2</sub> (R = alkyl)
- 5. oxide BeO and hydroxide Be(OH)<sub>2</sub> are amphoteric
- 6. halides  $[BeX_2]_n$  are covalent polymers
- 7. hydride  $[BeH_2]_n$  is also a covalent polymer

Mg

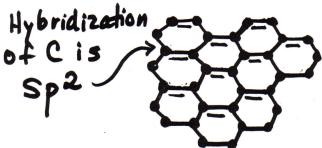
- 1. forms ionic substances that have partial ionic character
- 2. forms many ionic compounds with uncomplexed  $Mg^{2+}$
- 3. MgO is basic and the Mg(OH)<sub>2</sub> is only weakly basic due to low solubility
- 4. forms ionic MgX<sub>2</sub> halides
- 5.  $MgH_2$  is partially covalent

Ca, Sr, Ba

- 1. form only ionic substances
- 2. do not form covalent bonds
- 3. MO are basic and the M(OH)<sub>2</sub> are strong bases with increasing solubilities with larger cations
- MH<sub>2</sub> are strongly H<sup>-</sup> (hydride) based, ionic compounds

# <u>Carbon</u> <u>Allotropes</u> (two main ones)

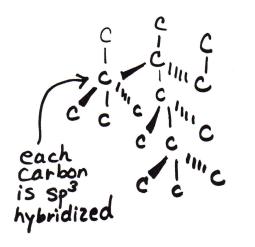
- 1. graphite  $C_{(s)}$
- 2. diamond  $C_{(s)}$
- 1. <u>Graphite</u> sheets of carbon atoms linked in hexagon shapes



This is a sheet, held together by C-C bonds

- Rings of carbon atoms "lock" together; this allows them to conduct electricity in the sheet
- The next sheet or layer on top is held only by weak van der Waals forces

2. Diamond



- each carbon is tetrahedral (sp<sup>3</sup>)
- the network is threedimensional
- hard to break the C-C bonds so diamond is hardest substance known
- diamond is used as an abrasive (cutting tools)

### **Other forms of Carbon**

3. <u>Charcoal</u> is mostly graphitic carbon but it is prepared by heating wood without oxygen

cellulose (C, H, O)  $\xrightarrow{\Delta}$  C + H<sub>2</sub>O

Finely powdered charcoal is <u>activated</u> <u>charcoal</u>. It absorbs a variety of molecules from air and water so it is used in filters. 4. <u>Coke</u> is similar to charcoal but it is made by heating soft (bituminous) coal. Coke is used to reduce oxides to metals.

coal (C, H)  $\xrightarrow{\Delta}$  C + small chain hydrocarbons

5. <u>Carbon black</u> is finely divided carbon made by heating hydrocarbons or paraffins (wax).

ex.  $CH_4 + O_{2(g)} \rightarrow C_{(s)} + 2H_2O$ imited supply only

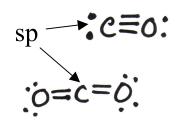
6. <u>Fullerenes</u> C<sub>60</sub>, C<sub>70</sub> Buckminsterfullerene "Bucky-Balls"

"Bucky-Balls", C<sub>60</sub>, look like soccer balls. Their shapes have 60 vertices and 32 faces with 20 hexagons and 12 pentagons

 $C_{70}$  is similar but is "pinched" around the middle and is larger than  $C_{60}$ 

#### Oxides of Carbon

- A. CO carbon monoxide
- B. CO<sub>2</sub> carbon dioxide



- A. Carbon monoxide CO
- Preparation:

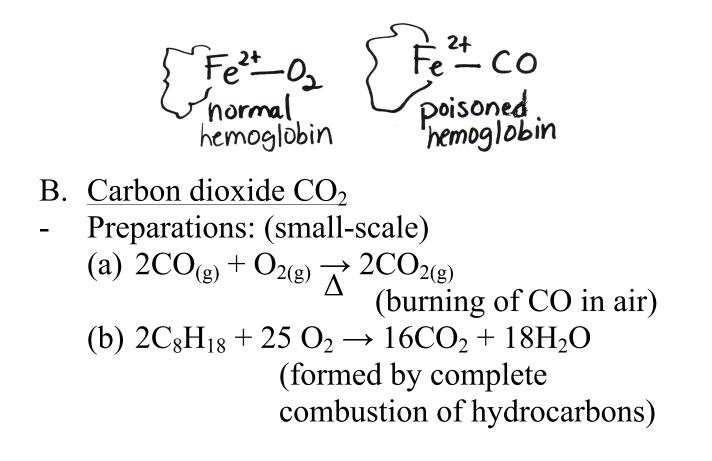
impure CO is found wherever fuels are burned – it is mixed with  $CO_2$  and sometimes other hydrocarbons

- Used as a fuel in the "water gas" reaction

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1000 \text{ °C}} \boxed{CO_{(g)} + H_{2(g)}}$$
  

$$\stackrel{\text{fuel}}{CO_{(g)} + H_{2(g)}} + O_{2(g)} \xrightarrow{\text{burn}} CO_2 + H_2O$$

- Used as a reducing agent. CO is used to <u>reduce</u> metal oxides to metals. ex. FeO + CO  $\rightarrow_{\Lambda}$  Fe + CO<sub>2</sub>
- poisonous to red-blooded animals. Why?
   because CO is very poisonous to our
   respiratory cycle. It binds to the Fe<sup>2+</sup> (heme)
   ion in hemoglobin and blocks it from
   carrying O<sub>2</sub> to the cells.



**Industrial Production:** CO<sub>2</sub> is a <u>by-product</u> of the Haber-Bosch process. A by-product is not a major product but a minor one.

 $CO_2$  is used to make urea Reaction of  $CO_2$  to make urea:

 $CO_{2(g)} + 2NH_{3(g)} \xrightarrow{200 \text{ atm}}_{185 \text{ °C}} (NH_2)_2CO + H_2O$ (urea) structure il Structure Il NH2 NH2

Use of urea:

Urea is a solid, unlike NH<sub>3</sub>. It can be easily shipped into agricultural areas and mixed into the soil. It then slowly reacts with H<sub>2</sub>O to give back NH<sub>3</sub> and CO<sub>2</sub>.  $(NH_2)_2CO + H_2O \rightarrow CO_2 + 2NH_3$ 

Other Sources of CO<sub>2</sub> by heating metal carbonates  $CaCO_{3(s)} \xrightarrow{\frown} \Delta \rightarrow CaO_{(s)} + CO_{2(g)}$ (limestone) (lime)

<u>lime</u> or <u>CaO</u> (limestone is CaCO<sub>3</sub>) is <u>calcium oxide</u> which is an important chemical

16-18 million tons of lime are produced annually in the U.S.

What is it used for?

- metallurgical industry
- chemical industry
- waste water treatment
- "scrubbing" SO<sub>2</sub> from smoke stack gases
- making <u>cement</u>

```
<u>Cement</u> – Portland cement
lime powder (CaO)
+ sand (SiO<sub>2</sub>)
+ clay (SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> oxides)
<u>heat</u>
<u>Portland Cement</u>
C-Si-O-Si-O-Si-.... strong bonds
```