

# Chem 241

## Lecture 30



# Homework

Finish Reading Chapter 10

Start Reading Chapter 11

Chapter 10 exercises

3, 4, 5, 6, 7, 8, 10

# Announcement

**\*\*Reminder \*\* Friday, April 23: EXAM 3!!!**



# Recap

Nitrogen compounds

Solubility

Metal Solutions

Crown ethers and Cryptands

Organometallics

Alkali Earth Metals

Diagonal Relationship  $\text{Be} \leftrightarrow \text{Al}$

Be



# Mg Uses

- e. Biologically important
  - Central element in chlorophyll
  - Counter ion to ATP/ADP, nucleic acids
  - Ave. adult human contains 25 g.
  - Lewis acid center in enzymes
  - “milk of Magnesia” is  $\text{Mg}(\text{OH})_2$
  - Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- f. Light alloys (particularly with Al), aircraft. Structural metal.
- g. MgO is used for refractory lining for furnaces
- h. Grignard reagents in organic synthesis
- i. Flares and fireworks



# Ca

Ca (latin Calx, meaning lime)

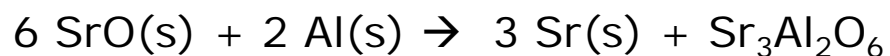
- a. 5<sup>th</sup> most abundant element in Earth's crust
- $\text{CaCO}_3$  is limestone.
- b. major component of biominerals, including bone, teeth, shells; (ave adult human contains 1 kg of Ca)
- c. Important to cell signaling, nerve impulses
- d. extracted by electrolysis of  $\text{CaCl}_2$ , which is a by-product of the Solvay process for making  $\text{Na}_2\text{CO}_3$ .



# Sr

Sr (named for Scottish village, Strontian, where Sr ores are found.)

a. extracted by electrolysis of molten  $\text{SrCl}_2$ , or by reduction of  $\text{SrO}$  with  $\text{Al}$ :

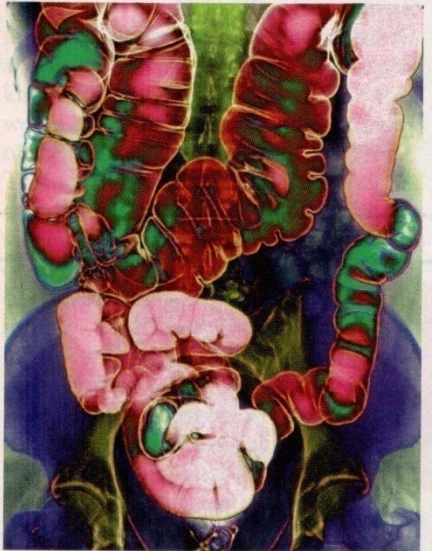


b. metal reacts vigorously with water, powder ignites in air.

c. Uses include fireworks (red), glass manufacture



# Group II: Alkaline earths

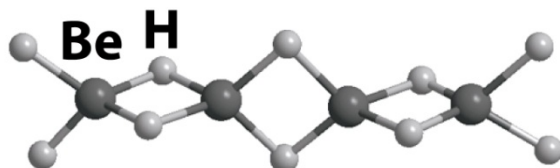


5. Ba (Gr. Barys, meaning heavy)
  - a. Produced by electrolysis of molten  $\text{BaCl}_2$  or reduction of  $\text{BaO}$  with Al (see Sr).
  - b. very reactive with water; ignites in air.
  - c. uses include
    - x-ray imaging ( $\text{BaSO}_4$ ), rat poison ( $\text{BaCO}_3$ ), glassmaking, BaS used to remove unwanted body hair.
  - d. Most salts are quite toxic.
  
6. Ra
  - a. Discovered by the Curies in 1898 after extraction from the U mineral, pitchblende.
  - b. Pitchblende contains about 1g of Ra/10 tons of ore, and it took the Curies 3 years to isolate 0.1 g of  $\text{RaCl}_2$ .
  - c. Once used to treat malignant tumors, and in luminous paint.



# Hydrides

- With the exception of Be, the metals in GpII make ionic compounds. Be(II) because of its small size (high charge density) forms covalent compounds
- A. Hydrides
  - 1.  $\text{BeH}_2$  is a covalent, polymeric hydride that cannot be prepared by direct reaction with  $\text{H}_2$ . Instead, made from reaction of alkyl Be compounds.



2. All other Gp II metals make ionic hydrides by direct interaction with  $\text{H}_2$ . These hydrides react with water to make  $\text{H}_2$ :  $\text{MH}_2 + 2 \text{H}_2\text{O} \rightarrow \text{M(OH)}_2 + \text{H}_2$



# Halides

- 1. Again, all the halides of Be are covalent, all other Gp II metals form ionic halides.
- 2. Preparations
  - a.  $\text{BeF}_2$  is made by thermal decomposition of  $(\text{NH}_4)_2[\text{BeF}_4]$ .
  - b.  $\text{BeCl}_2$  can be made from the oxide.  
$$\text{BeO} + \text{C} + \text{Cl}_2 \rightarrow \text{BeCl}_2 + \text{CO}$$
  - c.  $\text{BeCl}_2$  can also be made by direct reaction of the metal with the gas, which is how the Br- and I- is made.
  - d. Anhydrous  $\text{MgX}_2$  is prepared by direct combination because the hydrated salts partially hydrolyze upon heating. (polarizing power of Mg)
  - e. The  $\text{MX}_2$  halides of Ca, Sr, Ba, and Ra can be prepared by heating the hydrates.



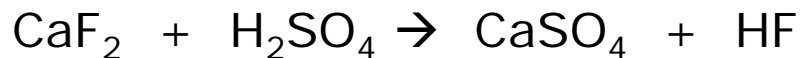
# Structures and solvation

- a. Fluorides of Ca, Sr, Ba adopt the fluorite structure ( $\text{CaF}_2$ )
- b. All other halides have layered structures due to the polarizing power of the  $2+$  cations and the increased polarizability of X.
  - $\text{MgCl}_2$  adopts the  $\text{CdCl}_2$  structure (viewed as ccp in  $\text{Cl}^-$  with  $\text{Mg}^{2+}$  in a layer between).
  - $\text{MgI}_2$  and  $\text{CaI}_2$  adopt the closely related  $\text{CdI}_2$  structure (hcp in  $\text{Cl}^-$ ).
- c. Solubility
  - All the  $\text{F}^-$  salts except  $\text{BeF}_2$  are insoluble in water
  - Salts of the other halides are all soluble in water.
  - In general, salts of uninegative anions with GpII ions are soluble, but less so than the corresponding GpI ions because the high hydration energy of the M(II) ions overcomes the lattice energy. The salts of GpII with dinegative anions are generally insoluble (increased lattice energy wins).



# Properties and uses

$\text{CaF}_2$  (fluorspar) is the only industrial source of  $\text{F}_2$  and HF:



c.  $\text{CaCl}_2$  is deliquescent and is used as a drying agent. It is also a more effective deicer for roads because the dissolution is exothermic, and the minimum freezing mixture is  $-55\text{ C}$  compared to  $-18\text{ C}$  for  $\text{NaCl}$ .



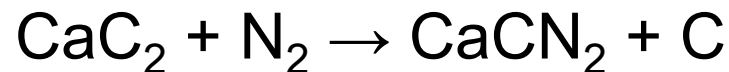
# Oxides and Hydroxides

- 1. Reaction of GpII metals with  $O_2$  forms normal oxides,  $MO$ , with the exception of Ba, which forms a peroxide.
  - a. BeO has the Wurtzite structure
  - b. All other  $MO$  have the NaCl structure
- 2.  $MO$  ( $M = Mg, Ca, Sr, Ba$ ) are more commonly prepared by thermal decomposition of the carbonate
  - $MCO_3 \rightarrow MO + CO_2$
- 3. The peroxides,  $MO_2$ , are strong oxidizing agents and decompose to the oxides. Their stability increases down the group.
- 4. All hydroxides are made by dissolving the oxides in water.
- 5. The basicity and solubility of the hydroxides increases down the group. ( $Be(OH)_2$  is amphoteric.)



# Carbides

- 1.  $\text{Be}_2\text{C}$  is an anionic material containing the  $\text{C}^{4-}$  ion. It has an antifluorite structure and reacts with water to form methane.
  - $\text{Be}_2\text{C} + 4 \text{H}_2\text{O} \rightarrow 2 \text{Be}(\text{OH})_2 + \text{CH}_4$
- 2.  $\text{MC}_2$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ ) contain the  $\text{C}_2^{2-}$  anion and react with water to form acetylene ( $\text{C}_2\text{H}_2$ )
  - $\text{MC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{M}(\text{OH})_2 + \text{C}_2\text{H}_2$
- 3. Both kinds of carbides produce a flammable gas.  $\text{CaC}_2$  was used in miner's lamps and headlights, and its use as a source of acetylene was the foundation of Union Carbide.
- 4. Calcium carbide reacts with nitrogen at high temperature to form calcium cyanamide:



# Salts of oxoacids

- 1. Carbonates and Bicarbonates
  - a. With the exception of "BeCO<sub>3</sub>", all are sparingly soluble in water. Bicarbonates are soluble. BeCO<sub>3</sub> exists as a soluble hydrate that is susceptible to hydrolysis because of the high charge density of Be(II).
    - $[\text{Be}(\text{OH}_2)_4]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Be}(\text{H}_2\text{O})_3(\text{OH})]^+ + \text{H}_3\text{O}^+$
  - b. MCO<sub>3</sub> (M = Mg...) decompose to the oxides upon heating.
  - c. CaCO<sub>3</sub> is limestone, chalk, marble etc. and is used to neutralize acid soils:
    - $\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
  - d. CaCO<sub>3</sub> is not very soluble, but solubility is increased if CO<sub>2</sub> is dissolved in the water because of the increased solubility of the bicarbonate:
    - $\text{CaCO}_3 + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$
    - The reaction is responsible for the decay of marble statues and facades. It is reversible, and thus is the reaction leading to the formation of stalactites and stalagmites in caves. Also temporary hardness.



# Salts of oxoacids

- $\text{CaCO}_3 + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$
- Heating ocean and calcite
- Cement
- Whiting in ceramics
- Used to be used as chalk,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



# Sulfates

- a. Gypsum and alabaster are  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .
- b. When the dihydrate is heated, it forms the hemihydrate,  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , also known as “plaster of Paris” from where it was first mined. When mixed with water it forms the dihydrate, and expands and hardens (plaster casts).
- c. the dihydrate is also used in wallboard, which is fire retardant because of the release of water vapor upon heating (endothermic, steam barrier is inert)
- d.  $\text{CaSO}_4$  and  $\text{MgSO}_4$  are responsible for permanent hardness of water. (Not reversed by boiling, needs ion exchange).



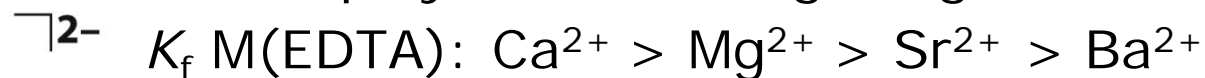
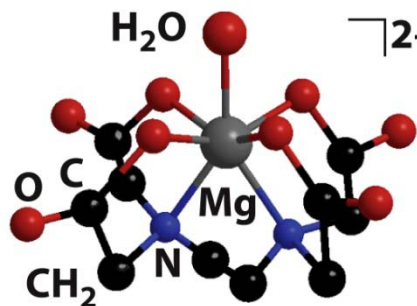


# Group II: Alkaline earths

## III. Coordination Compounds and Organometallics

### A. Coordination compounds

1. In general, the coordination compounds of GpII are more stable than those of GpI, reflecting the higher charge and increased covalent character of the coordinate bonds.
2. Classified as hard acids, the most stable complexes are formed with polydentate charged ligands such as EDTA.



the Mg(EDTA) complex has CN = 7, with one water molecule, and the Ca complex is either 7 or 8 coordinate with 1 – 2 aqua ligands.

3. Only Be forms stable complexes with simple ligands (*e.g.*, unidentate ligands).

# Organometallics

- 1. Be
  - Be organometallics are pyrophoric, and unstable in water. Can be made by transmetallation of Be metal with  $\text{HgR}_2$ , reaction of  $\text{BeCl}_2$  with RLi or with Grignard reagents,  $\text{RMgCl}$ .
  - Structures are similar to hydrides, polymeric with 3c,2e bonds in solid, dimers with large R,  $\text{CN}=2$  only in vapor or with large R.
- 2. Mg
  - Grignard reagents are important in organic synthesis; serve as a source of  $\text{R}^-$ .
  - Synthesis:  $\text{Mg(s)} + \text{RBr} \rightarrow \text{RMgBr}$ ; usually requires activation to overcome passivating oxide layer. (a little  $\text{I}_2$  or  $\text{Br}_2$  can be added to make the soluble halide which dissolves and presents a fresh reactive surface. )
  - The structure of a Grignard reagent is complicated.
    - $\text{CN} = 2$  only exists in solution for large R groups. Usually tetrahedral solvate of  $\text{Mg}^{2+}$  with  $\text{R}^-$  and  $\text{Cl}^-$  counterions
- 3. Ca, Sr, Ba form analogs of Grignards that are ionic and unstable.



# Homework

- Finish Reading Chapter 11
- Start Reading Chapter 12
- Exercises Chapter 12:  
2, 3, 5, 6, 7, 9, 11

