

# Chem 241

## Lecture 29



# Recap

Diagonal Relationship

Occurrence and Extraction of Alkali Elements

Common Uses

Halides

Oxides

Hydroxides

Carbonates

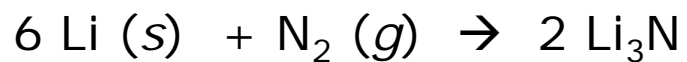
Hydrocarbonates

Oxosalts

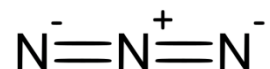


# Nitrogen Compounds

Nitrides



Azide



# Solubility and Hydration

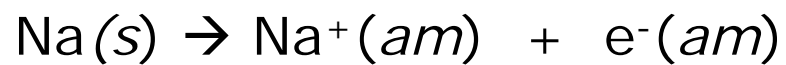
1. All common salts of Gpl metals are soluble in water, but the degree of solubility varies widely.
2. The most soluble are those where the cation and anion differ the most in size (lower lattice energy)
  - a. Li salts more soluble:  $F^- > Cl^- > Br^- > I^-$
  - b. Cs salts more soluble:  $I^- > Br^- > Cl^- > F^-$



# Metal Solutions

NaK – Sodium and Potassium alloy

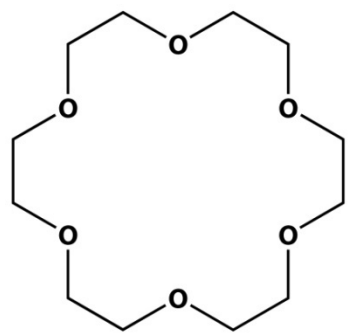
Liquid Ammonia Solutions



# Coordination compounds

A. Coordination Compounds. Gpl metals are classified as “hard” acids and are thus expected to make complexes with ligands that have mostly “hard” donor atoms (O and N) that maximize the ionic component of the bonding.

1. Most of the complexes formed are with polydentate ligands, particularly macrocycles, because of the weak binding with a single donor atom.

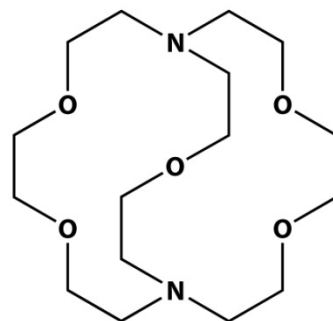


**3** 18-crown-6

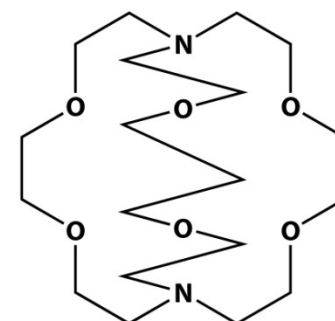
a. Crown ethers, such as 18-crown-6, form complexes that are stable in non-aqueous solvents.

b. Cryptands form complexes that are even stable in water

2. Can be used to pull salts into organic solvents.



**2.2.1** crypt



**5** 2.2.2 crypt

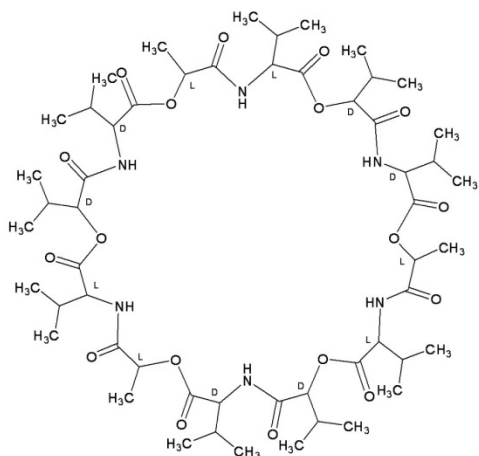


# Group I: Alkali Metals

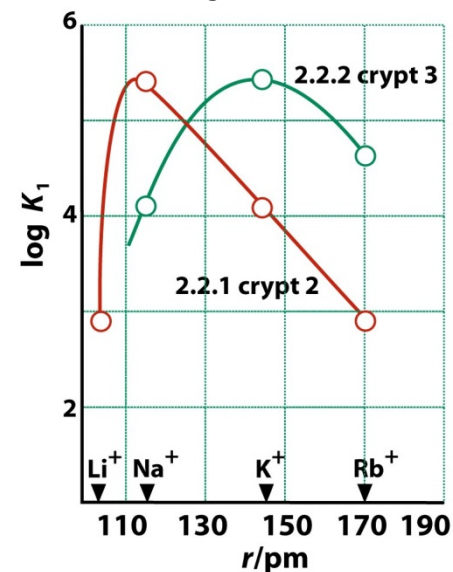
3. Preferentially bind metals based on cavity size and numbers of donor atoms.

4. Biological ion channels that transport  $\text{Na}^+$  or  $\text{K}^+$  use a similar strategy.

a. Valinomycin is an antibiotic that selectively binds  $\text{K}^+$  and transports it through bacterial cell membranes. This depolarizes the cell and results in cell death



6 Valinomycin



# Organometallics

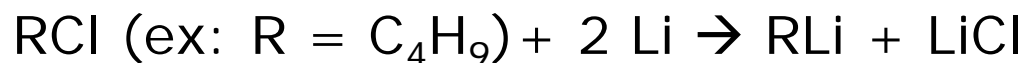
1. Generally reactive and often pyrophoric
  - a. Used to dry solvents such as THF, benzene etc.



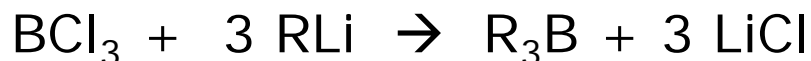
often forming highly colored organic anions

2. Alkyls

- a. Li alkyls are a source of good nucleophiles in organic chemistry (R-)



3. Inorganic synthesis





# Homework

Finish Reading Chapter 10

Start Reading Chapter 11

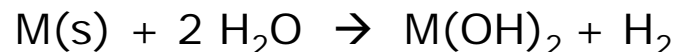
Chapter 10 exercises

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



# Alkaline Earths

- A. Harder metals than Group I due to stronger metal bonding associated with 2 valence electrons.  $ns^2$
- B. Many properties again related to atomic and ionic radius (size).
    - 1. reduction in size rel. to gp I responsible for
      - a. higher density
      - b. higher IE
      - c. increased reactivity down the group as radius inc. and IE decreases
      - d. more negative reduction potentials down the group.
        - Heavier metals are more easily oxidized
        - E.g., Ca, Sr, Ba react with water, Mg only with hot water.
- like gp I:



# Diagonal relationship (Be and Al)

- Form covalent hydrides, halides, and oxides (the Mg compounds are ionic)
- BeO and Al<sub>2</sub>O<sub>3</sub> are amphoteric (MgO is basic)
- In the presence of xs. OH<sup>-</sup>, Be and Al form [Be(OH)<sub>4</sub>]<sup>2-</sup> and [Al(OH)<sub>4</sub>]<sup>2-</sup>, Mg does not react.
- Be and Al form carbides that contain C<sup>4-</sup> and produce methane upon reaction with water, the rest of GpII forms carbides that contain C<sub>2</sub><sup>2-</sup> and produce acetylene upon reaction with water.



# Group II. Alkaline earths

**Table 11.1** Selected properties of the Group 2 elements

	Be	Mg	Ca	Sr	Ba	Ra
Metallic radius/pm	112	160	197	215	217	220
Ionic radius, $r(M^{2+})$ /pm	27	72	100	118	135	170
Ionization energy, $I$ /(kJ mol <sup>-1</sup> )	900	736	590	548	502	510
$E^\ominus(M^{2+}/M)$ /V	-1.85	-2.38	-2.87	-2.89	-2.90	-2.92
Density, $\rho$ /(g cm <sup>-3</sup> )	1.85	1.74	1.54	2.62	3.51	5.00
Melting point/°C	1280	650	850	768	714	700
$\Delta_{\text{hyd}}H^\ominus$ /(kJ mol <sup>-1</sup> )	-2500	-1920	-1650	-1480	-1360	-
$\Delta_{\text{sub}}H^\ominus$ /(kJ mol <sup>-1</sup> )	321	150	193	164	176	130

Table 11-1

*Shriver & Atkins Inorganic Chemistry, Fourth Edition*

© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Compounds of Mg, Ca, Sr, Ba are mostly ionic;  
Compounds of Be are covalent.



# Occurrence, Extraction and uses

Be

- a. Found as the semiprecious mineral beryl:  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , which is the basis for emeralds & aquamarines
- b. Extracted by heating beryl with  $\text{Na}_2\text{SiF}_6$  to produce  $\text{BeF}_2$  and then reduced with Mg.
- c. Be is unreactive in air due to a passivating layer of oxide (like Al). This makes it resistant to corrosion. This property, plus its light weight, led to alloys being used to make precision instruments, aircraft and missiles.
- d. Moderator in nuclear reactions because it has a high neutron-capture cross section and a high melting point.
- e. x-ray windows.
- f. Soluble Be salts are highly toxic.
  - Exposure to element as dust –berylliosis and lung cancer
  - Alters phosphate metabolism and accumulates in bone.
  - Interacts with DNA and RNA and is mutagenic.



# Mg

Mg (named for Greek city of Magnesia)

- a. 8<sup>th</sup> most abundant element in the Earth's crust.
  - Many minerals, inc. dolomite,  $\text{CaCO}_3\text{MgCO}_3$ , and magnesite,  $\text{MgCO}_3$ .
  - 3<sup>rd</sup> most abundant element in sea water (1l contains 1g)
- b. Extracted from seawater relying on the fact that  $\text{Mg}(\text{OH})_2$  is less soluble than  $\text{Ca}(\text{OH})_2$ .
- c. Also extracted from dolomite.

Heating in air converts it to the Ca and Mg oxides

Mixture is heated with ferrosilicon ( $\text{FeSi}$ ) to form  $\text{Ca}_2\text{SiO}_4$ , iron and Mg, which is a liquid at the high temp and can be removed by distillation.

- d. The pure metal is very reactive with  $\text{O}_2$  and water, but can be handled because of a passivating oxide layer. Can't be handled under  $\text{N}_2$  because of  $\text{Mg}_3\text{N}_2$  formation, and  $\text{SF}_6$  or  $\text{SO}_3$  are used, but pose environmental hazards (green house gas and acid rain)



# 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 intgition



# 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 signalling, 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  $\text{Al}$ :

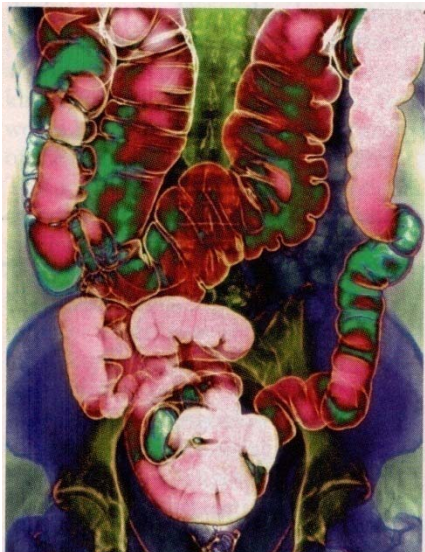


b. metal reacts vigorously with water, powder ignites in air.

c. Uses include fireworks (red), glass manufacture



# Group II: Alkaline earths



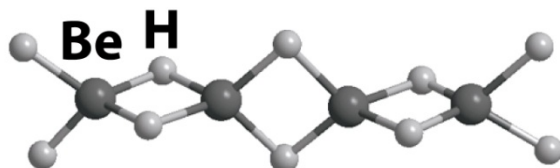
5. Ba (Gr. Barys, meaning heavy)
  - a. Produced by electrolysis of molten  $\text{BaCl}_2$  or reduction of  $\text{BaO}$  with Al (see Sr).
  - b. very reactive with water; ignites in air.
  - c. uses include
    - x-ray imaging ( $\text{BaSO}_4$ ), rat poison ( $\text{BaCO}_3$ ), glassmaking, BaS 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.



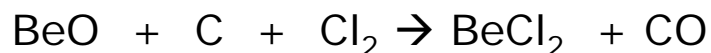
2. All other Gp II metals make ionic hydrides by direct interaction with  $\text{H}_2$ . These hydrides react with water to make  $\text{H}_2$ :  $\text{MH}_2 + 2 \text{H}_2\text{O} \rightarrow \text{M(OH)}_2 + \text{H}_2$

# 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.



- 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 GpII ions are soluble, but less so than the corresponding GpI ions because the high hydration energy of the  $\text{M}(\text{II})$  ions overcomes the lattice energy. The salts of GpII with dinegative anions are generally insoluble (increased lattice energy wins).

