Chem 241

Lecture 28

Recap

Metallic Hydrides
Stability
Synthesis of Hydrides
Reactions of Hydrides
Alkali Metals

Homework

Finish reading Chapter 9
Start reading Chapter 10

Chapter 9 Exercise:
3, 7, 9, 12, 14, 15

Group I: Alkali Metals

Diagonal relationship

- A. Many times, the chemical properties of the first element in a group are similar to those of the second element in the next group. This is because the atomic radii, and thus the chemical properties, are similar.
  - 1. Li and Mg salts exhibit some covalent character (small cations are highly polarizing)
  - 2. Li and Mg form oxides, the rest of group I form peroxides or superoxides with O_2.
  - 3. Li is the only group I element that forms a nitride Li_3N, Mg does (as do all other Gp II elements)
  - 4. Li salts of carbonate, phosphate and fluoride are Insoluble, rest of Gp I are soluble, Gp II insoluble.
  - 5. Li and Mg carbonates decompose thermally to oxides other group I carbonates do not decompose.

Occurrence and Extraction

Most common method for production is electrolysis

1. Li (lithos, greek for stone)

   Found in low abundance as the minerals spodumene, $LiAlSi_2O_6$, and lepidolite, $K_2Li_3\ Al_4Si_7O_{21}(F, OH)_3$

   $$2\ LiCl(l) \rightarrow 2Li\ (l) + Cl_2.$$

2. Na (from NaCl) using Down's process (electrolysis of molten NaCl.) This is also used for commercial production of Cl_2.

3. K occurs naturally as potash (KOH) and carnelite, $KCl{\cdot}MgCl_2{\cdot}6H_2O$.

$$Na(l) + KCl(l) \rightleftharpoons NaCl(l) + K(g)$$

Salt Ponds

Occurrence and Extraction

Rb - Latin *rubidus*, deep red

Cs - Latin, *caesius*, sky blue

Were discovered by Robert Bunsen in 1861.

Both elements are found as minor constituents in Lepidolite.

$$2\ RbCl\ (l) + Ca(l) \rightarrow CaCl_2\ (l) + 2\ Rb\ (l)$$

Common Uses

A. Li

1. alloys used in aircraft (low density)
2. Li_2CO_3 is used to treat bipolar disorders (manic depression
3. Lithium batteries
    a. rechargeable batteries in computers, cell phones, etc.
    b. Uses $LiCoO_2$ as an anode, graphite (C) (with Li) as cathode

$$\mathrm{LiCoO_2} \leftrightarrows \mathrm{Li_{x-1}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-}$$

$$x\mathrm{Li^+} + x\mathrm{e^-} + 6\mathrm{C} \leftrightarrows \mathrm{Li_xC_6}$$

Sodium

1. Essential for maintenance of osmotic control, electrolytic balances and current (nerve action), the stability of polyelectrolytes (e.g., DNA) and the the uptake of nutrients. Gradients are maintained at the expense of energy (Na,K-ATPase) so that K is high in the cell and Na low, and vice versa outside the cell.

2. Na is used in the reductive extraction of rarer metals (e.g., K, but also Ti from $TiCl_4$).

3. Na vapor lamps

4. Large quantities of NaCl are used to de-ice roads; for production of NaOH (a large commodity chemical), and as table salt, baking soda, etc.

5. Preservative - NaCl

K, Rb and Cs

K

1. KOH is used in the manufacture of soft liquid soap.
2. KCl (and K_2SO_4) are used as fertilizers.
3. K(NO_3) and $KClO_3$ are used in fireworks
4. KBr allegedly reduces the libido.

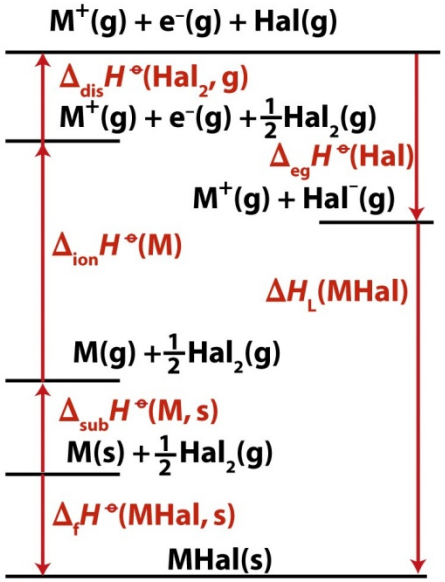
Rb and Cs.

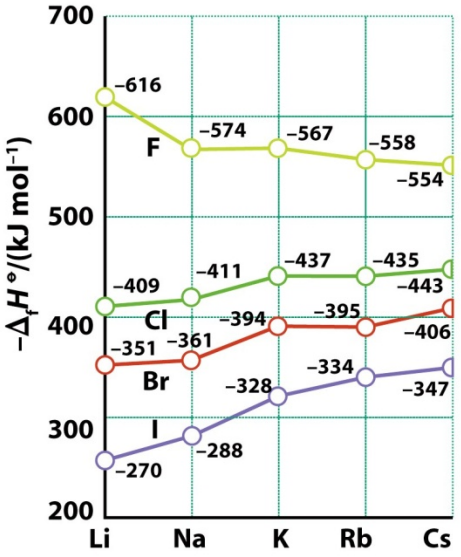
1. Glasses for fiber optic applications.
2. photoelectric cells
3. Night vision equip.
4. The “atomic clock” is a Cs clock and is used in the official definition of a second and a meter.

The second is the duration of 9,192,631,770 periods of the radiation of the caesium 133 atom.

Halides

- MX. Have NaCl structure, except CsCl, CsBr, and CsI (CsCl structure).
- ΔH_f for the reaction of the elements is large and negative (spontaneous) and becomes less negative F- → I- for a given M.
- For different M(s), ΔH_f gets more negative down the group, except for F-, which gets less negative down the group.
- These trends can be traced to the dominance of ΔH_L for F- salts, and to ΔH_{sub} and IE for the others using a Born-Haber cycle.





Oxides

•1. Upon reaction of the metals with O_2, Li forms an oxide, (Li_2O), Na forms a peroxide (Na_2O_2) and K, Rb, Cs form superoxides (MO_2).

•2. All of these oxides are basic in water:

•$Li_2O + H_2O \rightarrow 2\ Li^+(aq) + 2\ OH^-(aq)$

•$Na_2O_2 + H_2O \rightarrow 2\ Na^+ + 2\ OH^- + H_2O_2$

•$2\ KO_2 + 2\ H_2O \rightarrow 2\ K^+ + 2\ OH^- + H_2O_2 + O_2$.

3.Normal oxides (M_2O) can be prepared from peroxides or superoxides by heating.

Hydroxides

They are made, usually hygroscopic, and used as detergents and soaps.

Carbonates

GpI elements form soluble carbonates (M_2CO_3), with the exception of Li, which is only sparingly soluble

The Solvay process

$2\ NaCl + CaCO_3 \rightleftharpoons Na_2CO_3 + CaCl_2$

Main uses: glass manufacture and water softeners.

Not as harsh as hydroxides → German Pretzels, boiling bones, toothpaste

Hydrocarbonates

Na_2CO_3 (*aq*) + CO_2(*g*) + H_2O(*l*) → 2 $NaHCO_3$(*s*)

Reversed when heated.

Neutralize Acids

$KHCO_3$ is used as a buffer in wine production, low pH liquid detergents, as an additive in soft drinks and as an antacid.

Oxosalts

Na_2SO_4

a. By-product of HCl production

$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

b. Principle use is in processing wood pulp for brown paper bags and cardboard.

c. Also used in glass manufacture, detergents, mild laxative.

d. $Na_2S_2O_3$ (thiosulfate) is a mild reducing agent used in photography. $Na_2S_2O_4$ (thionite) is used as a reducing agent in biochemical applications.

e. $NaNO_3$ and KNO_3. The sodium salt is deliquescent and used in making fertilizers and explosives. The K salt occurs naturally (saltpetre) and is used in gunpowder, matches, fertilzers, etc.

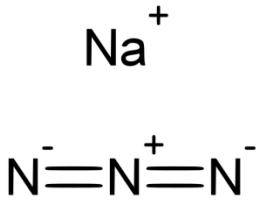
Nitrogen Compounds

Nitrides

$6\ Li\ (s) + N_2\ (g) \rightarrow 2\ Li_3N$

Azide

$2\ NaNH_3(s) + N_20\ (g) \rightarrow NaN_3\ (s) + NaOH\ (s) + NH_3\ (g)$



Solubility and Hydration

1. All common salts of GpI 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

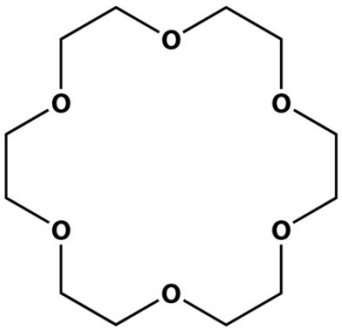
Liquid Ammonia Solutions

$Na(s) \rightarrow Na^{+}(am) + e^{-}(am)$

Coordination compounds

A. Coordination Compounds. GpI 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.

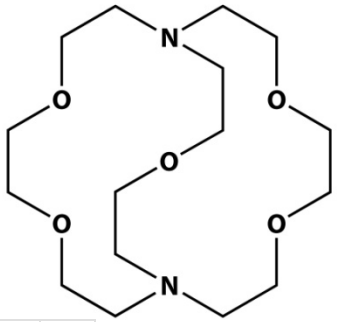


3 18-crown-6

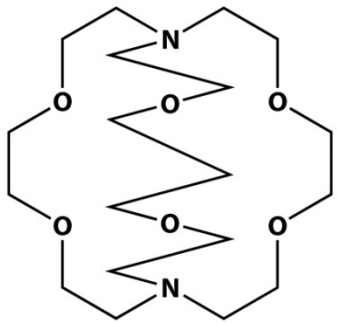
a. Crown ethers, such as 18-crown-6, form complexes that are stable in non-aqueous solvents.

b. Cryptands form complexes that are even stable in water

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



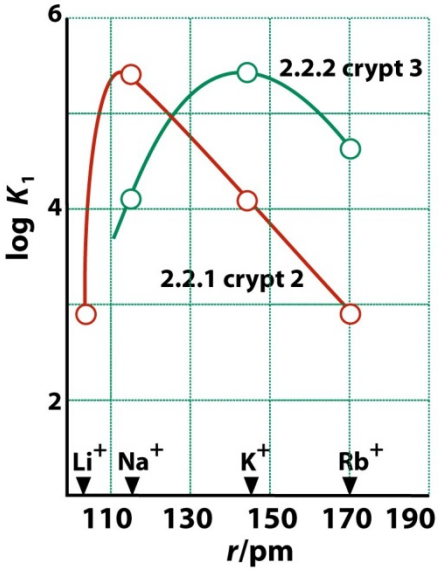
2.2.1 crypt



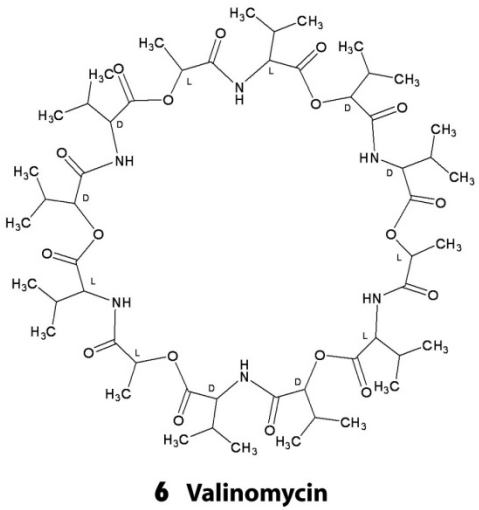
5 2.2.2 crypt

Group I: Alkali Metals

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



4. Biological ion channels that transport Na^+ or K^+ use a similar strategy.



6 Valinomycin

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

Organometallics

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

$$Na + C_5H_5 \rightarrow Na^+(C_5H_5)^-$$

often forming highly colored organic anions

2. Alkyls

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

$$RCl \text{ (ex: } R = C_4H_9) + 2\ Li \rightarrow RLi + LiCl$$

3. Inorganic synthesis

$$BCl_3 + 3\ RLi \rightarrow R_3B + 3\ LiCl$$

Homework

Finish Reading Chapter 10

Start Reading Chapter 11

Chapter 10 exercises

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