# Chem 241

## Lecture 26

# Announcement

Mistake we have class on the 3rd not 4th

Exam 3
Originally scheduled April 23rd (Friday)

APRIL/MAY

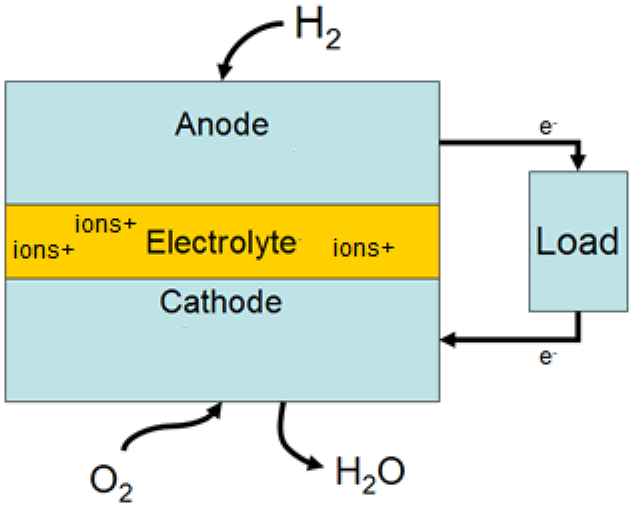
| M | T | W | T | F | S | S |
|---|---|---|---|---|---|---|
| 19 | 20 | 21 | 22 | 23 | 24 | 25 |
| 26 | 27 | 28 | 29 | 30 | 1 | 2 |
| 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 10 | 11 | 12 | 13 | | | |

# Recap

Hydrogen
Production

# Reactions of Hydrogen

Hydrogen can be homolytically cleaved on the metal surfaces.




$H_2 \rightarrow 2e^- + 2H^+$

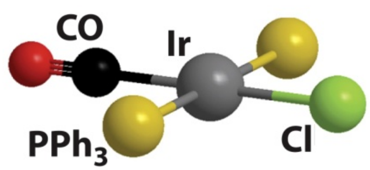
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

Hydrogen can be hetrolytically cleaved on the metal surfaces.

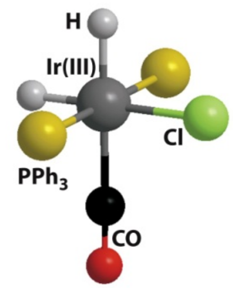
$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

# Reactions of Hydrogen

Hydrogen can coordinate to low oxidation metals.

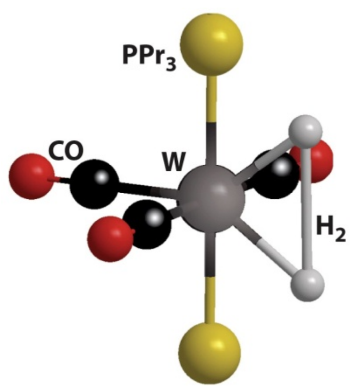



**1** $[IrClCO(PPh_3)_2]$




**2** $[IrCl(H)_2CO(PPh_3)_2]$

Molecular hydrogen can coordinate to metals.




**3** $[W(CO)_3(H_2)(P^iPr_3)_2]$

# Reactions of Hydrogen

Chain reactions

$Br_2$ + *hv* or Δ → Br• + •Br — Initiation

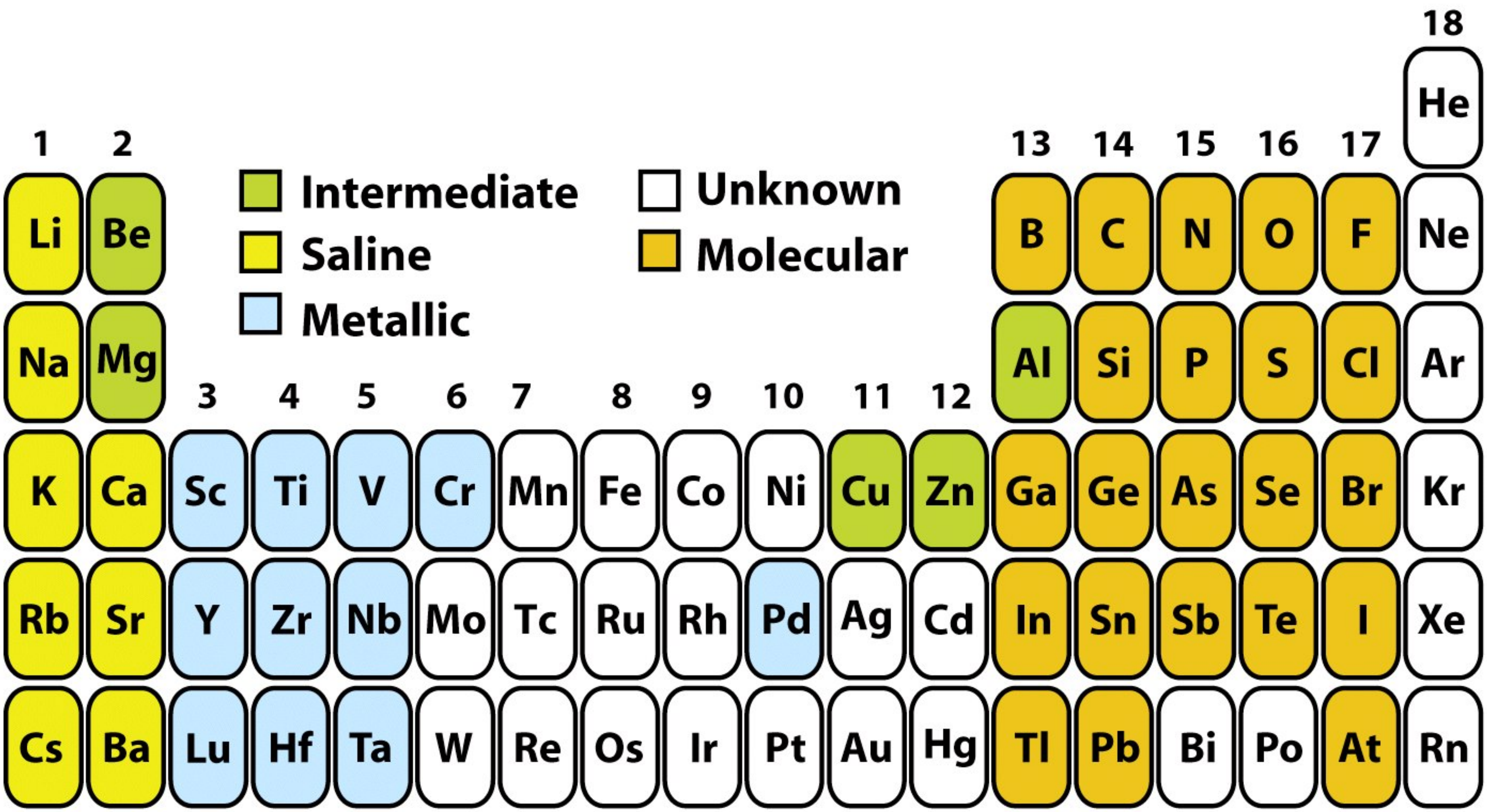
Br• + $H_2$ → HBr + H• — Propagation

X• + Y• → XY — Termination

Combustion

$2H_2 + O_2 \rightarrow 2H_2O \qquad \Delta_r H^o = -244\ \mathrm{kJ\ mol^{-1}}$

# Compounds of Hydrogen



# Molecular Hydrides

**Molecular Hydrides:** binary compounds of an element and hydrogen in the from of individual, discrete molecules.

Common for electronegative elements

**Electron Precise –** all valence electrons are in bonds.
**Electron Deficient** - too few to write a Lewis structure.
**Electron Rich –** has lone pairs on central atoms.

**Table 9.3** Bond angles (in degrees) for Group 15 and 16 hydrogen compounds

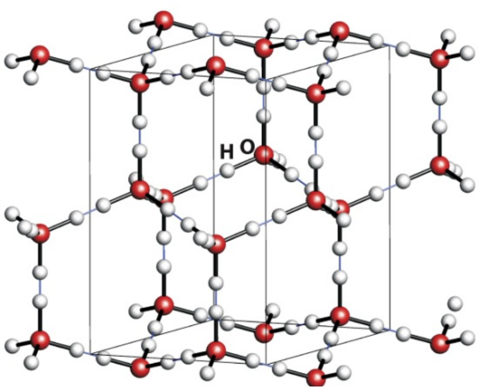
| | | | |
|---|---|---|---|
| $NH_3$ | 106.6 | $H_2O$ | 104.5 |
| $PH_3$ | 93.8 | $H_2S$ | 92.1 |
| $AsH_3$ | 91.8 | $H_2Se$ | 91 |
| $SbH_3$ | 91.3 | $H_2Te$ | 89 |

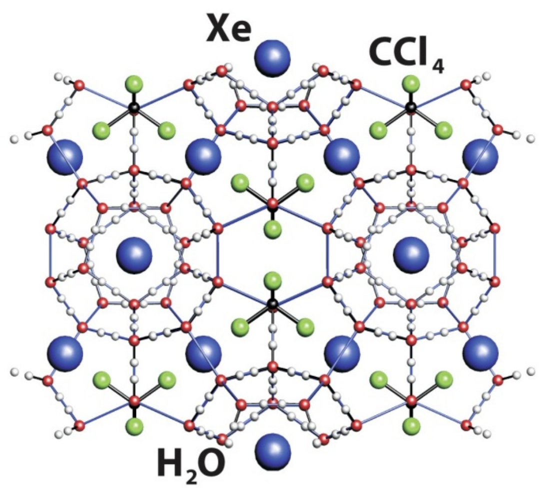
# Hydrogen Bonding

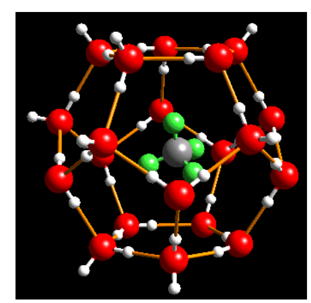
Because of the difference in electron negativity, the E-H bond is highly polar.

Imparts, high boiling points, densities changes, rigid structures.

Clathrate Structures, H-bond cages



# Saline Hydrides

**Saline Hydrides:** non-volatile, electrically non-conducting, crystalline solids

Groups 1 and 2

Used as drying agents.

$NaH(\mathit{s}) + H_2O(\mathit{l}) \rightarrow H_2(\mathit{g}) + NaOH(\mathit{aq})$

Making Other Hydrides

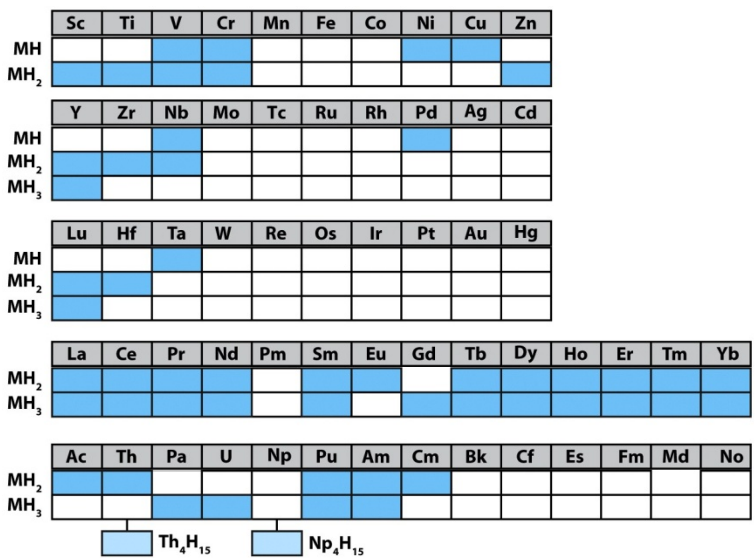
$NaH(\mathit{s}) + B(C_2H_5)_3(\mathit{et}) \rightarrow Na[HB(C_2H_5)_3](\mathit{et})$

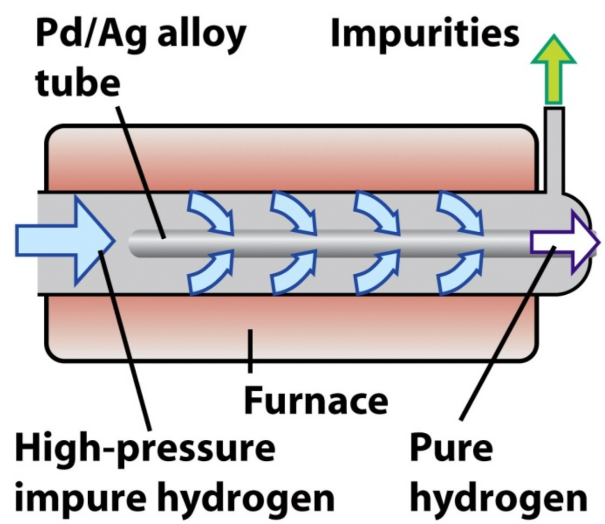
Deprotanting – carbon anion

$LiH(\mathit{s}) + H\text{-}CH_2R_w \rightarrow Li\text{-}CHR_w + H_2(\mathit{g})$

# Metallic Hydrides

**Metallic Hydrides:** non-stoichiometric, electrically conducting solid.



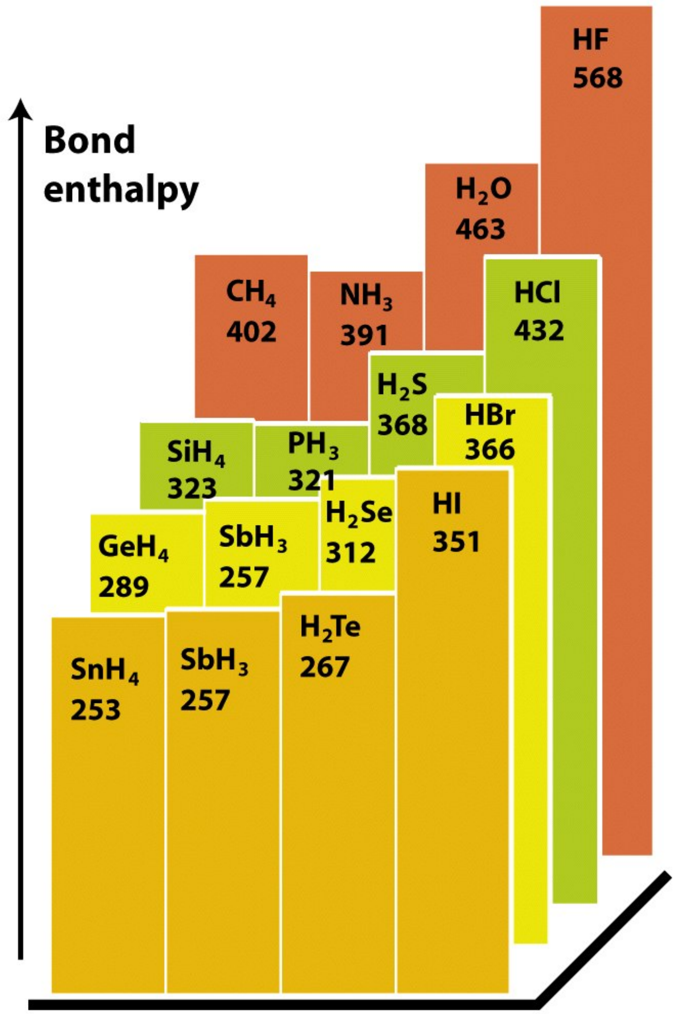



# Stability

**Table 9.6** Standard Gibbs energy of formation, $\Delta_f G^{\ominus}/(\text{kJ mol}^{-1})$, of binary *s*- and *p*-block hydrogen compounds at 25°C

| | Group | | | | | | |
|---|---|---|---|---|---|---|---|
| Period | 1 | 2 | 13 | 14 | 15 | 16 | 17 |
| 2 | $LiH(s)$ −68.4 | $BeH_2(s)$ (+20) | $B_2H_6(g)$ +86.7 | $CH_4(g)$ −50.7 | $NH_3(g)$ −16.5 | $H_2O(l)$ −237.1 | $HF(g)$ −273.2 |
| 3 | $NaH(s)$ −33.5 | $MgH_2(s)$ −35.9 | $AlH_3(s)$ (−1) | $SiH_4(g)$ +56.9 | $PH_3(g)$ +13.4 | $H_2S(g)$ −33.6 | $HCl(g)$ −95.3 |
| 4 | $KH(s)$ (−36) | $CaH_2(s)$ −147.2 | $Ga_2H_6(s)$ > 0 | $GeH_4(g)$ +113.4 | $AsH_3(g)$ +68.9 | $H_2Se(g)$ +15.9 | $HBr(g)$ −53.5 |
| 5 | $RbH(s)$ (−30) | $SrH_2(s)$ (−141) | | $SnH_4(g)$ +188.3 | $SbH_3(g)$ +147.8 | $H_2Te(g)$ > 0 | $HI(g)$ +1.7 |
| 6 | $CsH(s)$ (−32) | $BaH_2(s)$ (−140) | | | | | |

From *J. Phys. Chem. Ref. Data*, **11**, Supplement 2 (1982). Values in parentheses are based on $\Delta_f H^{\ominus}$ data from this source and entropy contributions.



# Synthesis

Direct Combination

$2E + H_2 \rightarrow 2\,EH$

Strong Base

$E^- + H_2O \rightarrow EH + OH^-$

Metathesis

$E^+H^- + EX \rightarrow E^+X^- + EH$

# Heterolytic Cleavage by Hydride Transfer

$E\text{-}H \rightarrow E^+ + H^-$

Reaction with a Proton Source

$CaH_2(s) + 2\ H_2O\ (l) \rightarrow Ca(OH)_2(s) + 2\ H_2(g)$

Methasis

$4LiH\ (s) + SiCl_4(et) \rightarrow 4LiCl(s) + SiH(g)$

Addition

$LiH(s) + B(CH_3)_3(g) \rightarrow Li[BH(CH_3)_3](et)$

# Homolytic Cleavage

E-H → E• + H•

$R_3SnH + R'X \rightarrow R'H + R_3SnCl$

RF < RCl < RBr < RI

# Heterolytic Cleavage by Proton Transfer

Chapter 4 → Bronsted Acids

# Homework

Finish reading Chapter 9
Start reading Chapter 10

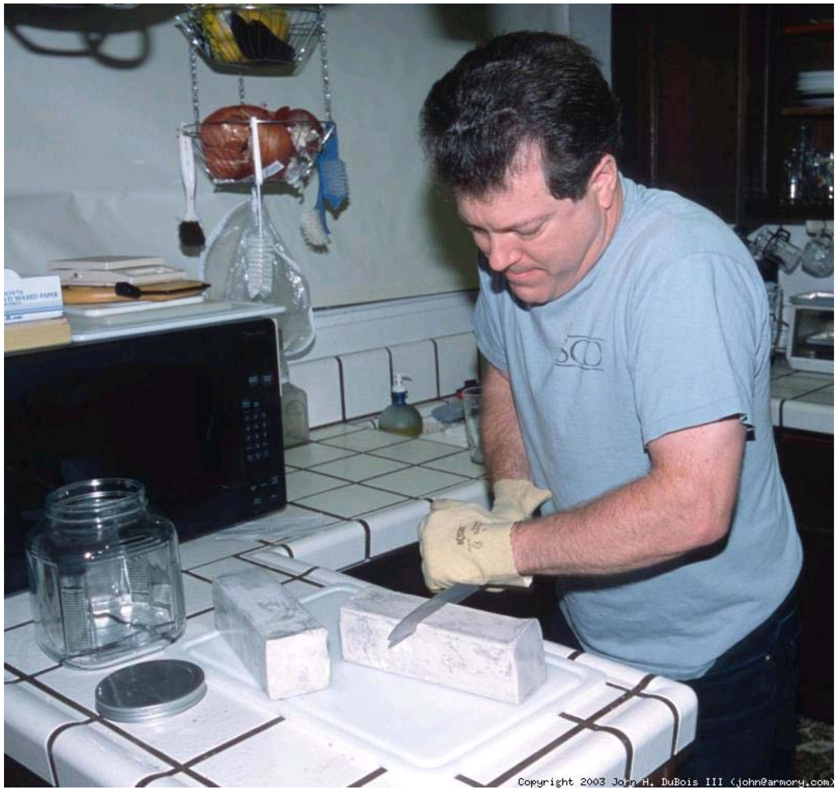
Chapter 9 Exercise:
3, 7, 9, 12, 14, 15

# Group I: Alkali Metals

## Properties of the Elements

- A. Electronic Configuration: $ns^1$
  - 1. Metals: Partially filled band containing one e- from each metal.
  - 2. Thus, good conductors of heat and electricity
  - 3. Soft because of weak metallic bonding
  - 4. Low melting points also a consequence of weak metallic bonding.
  - 5. Metals adopt bcc structure (CsCl), which is not close packed, thus they have low densities.
  - 6. The chemistry of Fr is not well known because of very low abundance and the fact that it is radioactive.

# Group I: Alkali Metals




# Group I: Alkali Metals

- B. Chemical properties correlate with the trend in atomic radii.

**Table 10.1** Selected properties of the Group 1 elements

| | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| Metallic radius/pm | 152 | 186 | 231 | 244 | 262 |
| Ionic radius/pm | 59 | 99 | 137 | 148 | 167 |
| Ionization energy/(kJ mol$^{-1}$) | 519 | 494 | 418 | 402 | 376 |
| Standard potential/V | −3.04 | −2.71 | −2.94 | −2.92 | −3.03 |
| Density/(g cm$^{-3}$) | 0.53 | 0.97 | 0.86 | 1.53 | 1.90 |
| Melting point/°C | 180 | 98 | 64 | 39 | 29 |
| $\Delta_{hyd}H^{\ominus}$/(kJ mol$^{-1}$) | −519 | −406 | −322 | −301 | −276 |
| $\Delta_{sub}H^{\ominus}$/(kJ mol$^{-1}$) | 161 | 109 | 90 | 86 | 79 |

**Table 10-1**
***Shriver & Atkins Inorganic Chemistry, Fourth Edition***

# Group I: Alkali Metals

Because they all have low IE, they are reactive and tend to form $M^+$ ions. Thus they all react with water to form $M^+$ ions, and the standard reduction potentials are all negative (spontaneous formation of $M^+$ in water.)

$$2M(s) + 2\,H_2O(l) \rightarrow 2\,MOH\,(aq) + H_2\,(g)$$

# Group I: Alkali Metals

- II. 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.