Chem 241

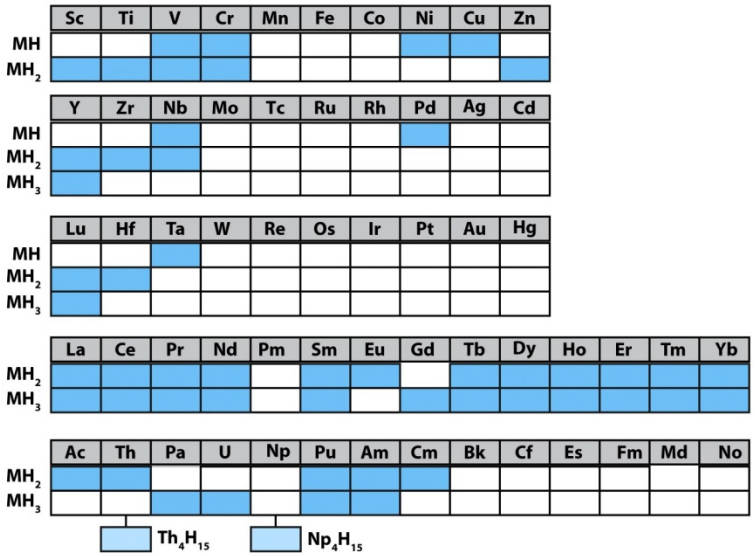
Lecture 27

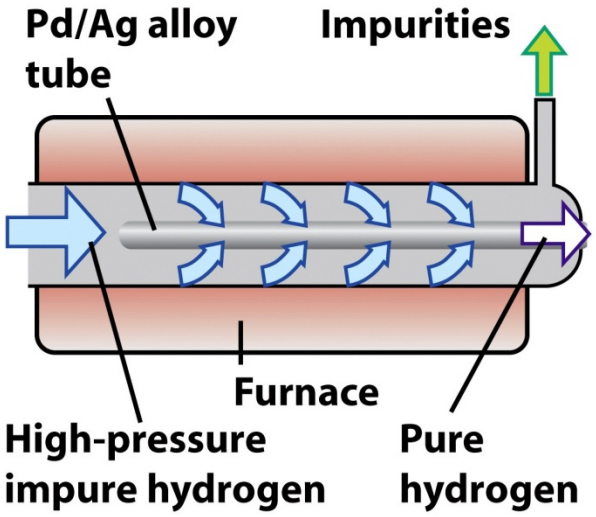
Recap

Fuel Cells
Reactions
Types of Compounds

Metallic Hydrides

Metallic Hydrides: non-stoichiometric, electrically conducting solid.



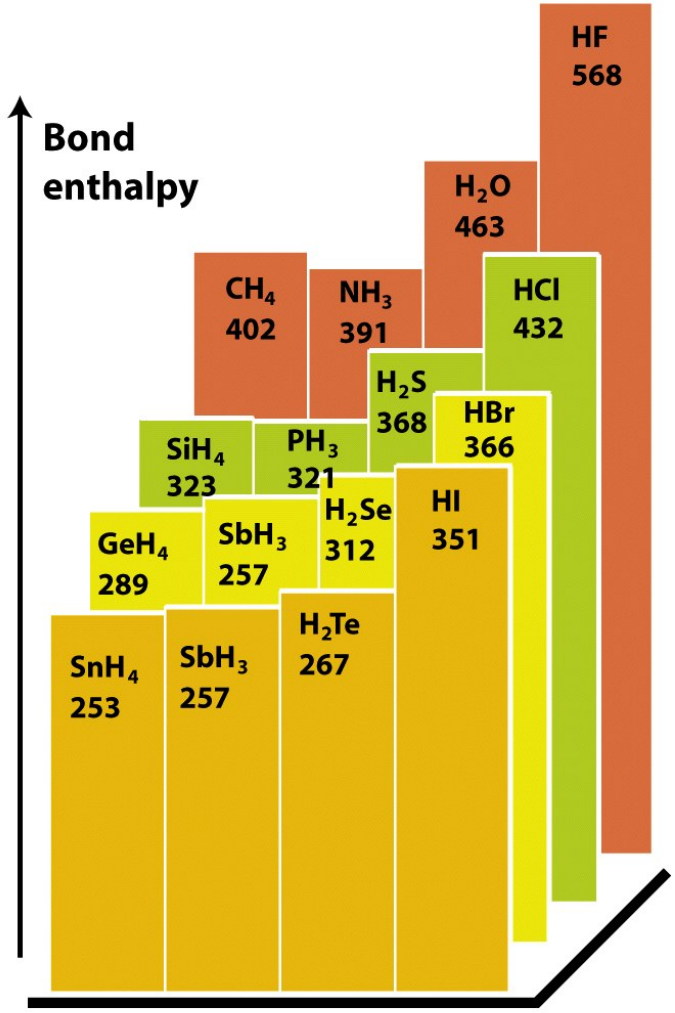


Stability

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)	BeH_2(s)	B_3H_6(g)	CH_4(g)	NH_3(g)	H_2O(l)	HF(g)
	−68.4	(+20)	+86.7	−50.7	−16.5	−237.1	−273.2
3	NaH(s)	MgH_2(s)	AlH_3(s)	SiH_4(g)	PH_3(g)	H_2S(g)	HCl(g)
	−33.5	−35.9	(−1)	+56.9	+13.4	−33.6	−95.3
4	KH(s)	CaH_2(s)	Ga_2H_6(s)	GeH_4(g)	AsH_3(g)	H_2Se(g)	HBr(g)
	(−36)	−147.2	> 0	+113.4	+68.9	+15.9	−53.5
5	RbH(s)	SrH_2(s)		SnH_4(g)	SbH_3(g)	H_2Te(g)	HI(g)
	(−30)	(−141)		+188.3	+147.8	> 0	+1.7
6	CsH(s)	BaH_2(s)					
	(−32)	(−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

Batteries

$$\mathrm{H_2O + M + e^- \leftrightharpoons OH^- + MH.}$$

$$\mathrm{Ni(OH)_2 + OH^- \leftrightharpoons NiO(OH) + H_2O + e^-.}$$

NiMH

Homework

Finish reading Chapter 9
Start reading Chapter 10

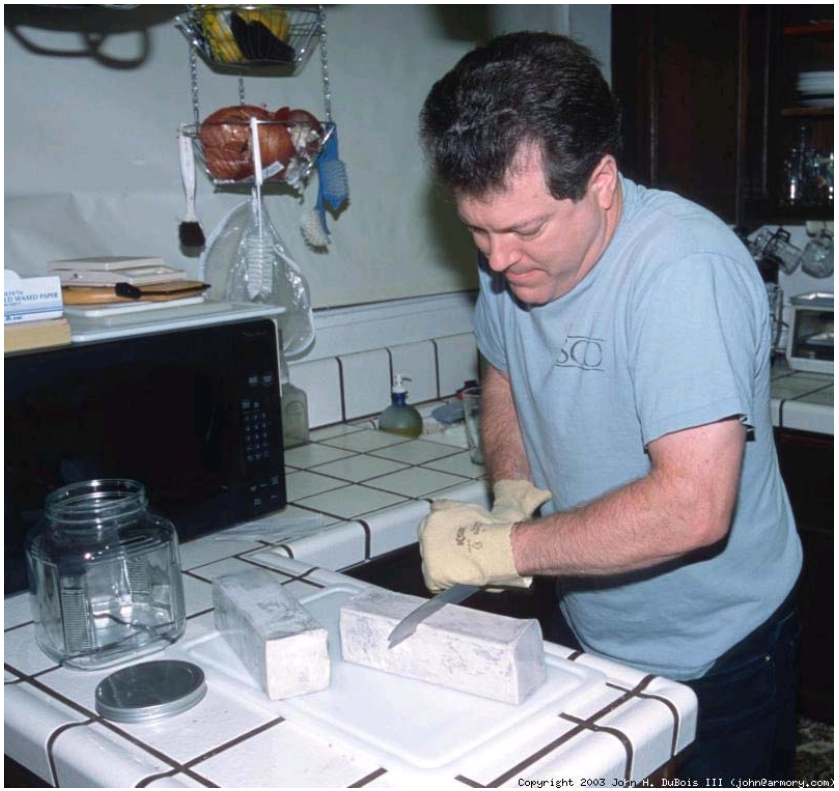
Chapter 9 Exercise:
3, 7, 9, 12, 14, 15

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

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.

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 ujsed as fertilizers.
3. K(NO_3) and $KClO_3$ are used in fireworks
4. KBr allegedly reduces the libido.

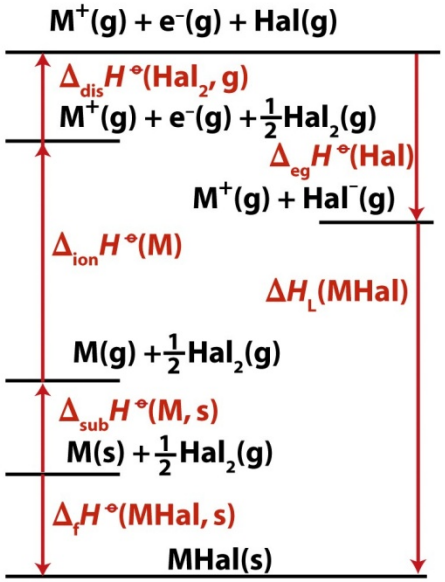
Rb and Cs.

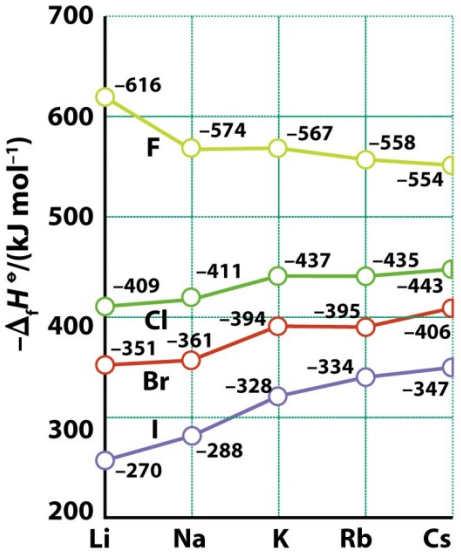
1. Glasses for fiber optic applications.
2. photoelectric cells
3. Night vision equip.
4. The “atomic clock” is a Cs clock and is used in the official definition of a second and a meter.

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.