

**Chemistry of the Main Group  
Elements:  
Hydrogen, Alkali and Alkaline Earth  
Metals**

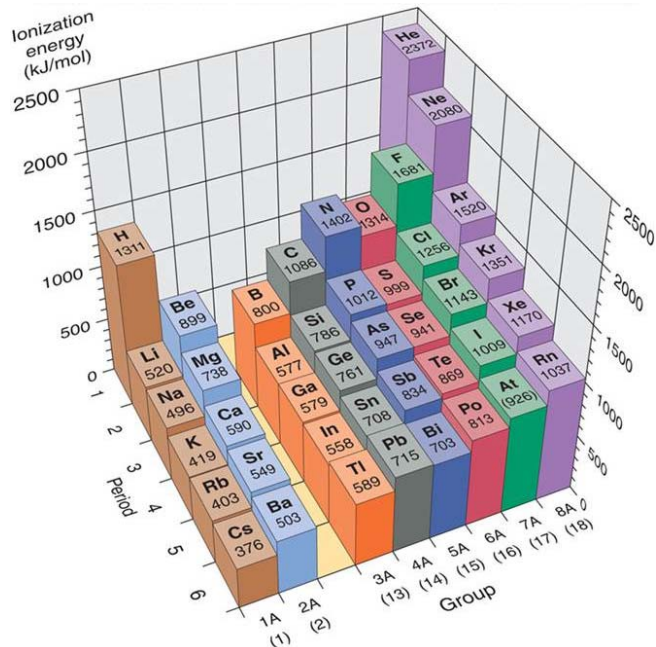
Sections 8.1-8.4

Wednesday, November 4, 2015

# Hydrogen

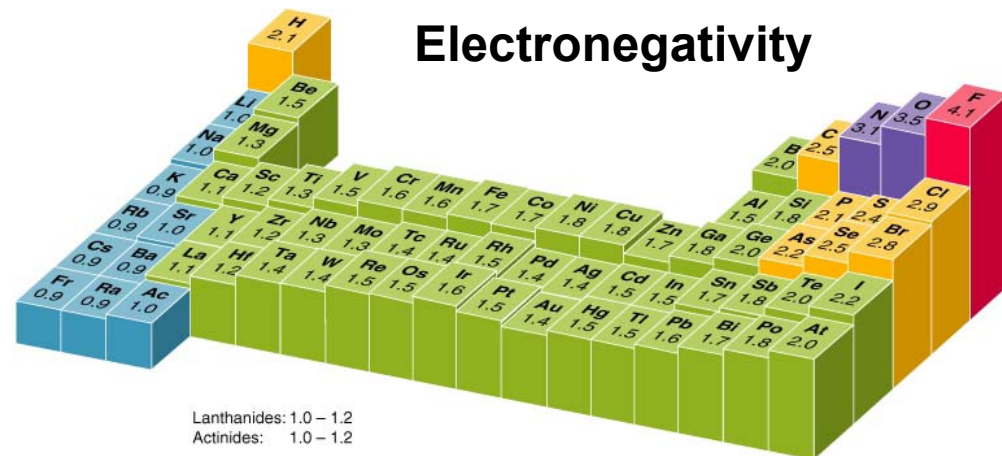
Obviously the simplest element, with a  $1s^1$  electron configuration.

- placement on the Periodic Table is questionable: is it an alkali metal, is it a halogen, or should it be placed above carbon (half-filled valence shell)?



**Ionization Energy**

1A (1)		Electron Affinity (kJ/mol)					8A (18)										
		3A (13)	4A (14)	5A (15)	6A (16)	7A (17)											
H	-72.8	B	-26.7	C	-122	N	+7	O	-141	F	-328	Ne	(+29)				
Li	-59.6	Al	-42.5	Si	-134	P	-72.0	S	-200	Cl	-349	Ar	(+35)				
Na	-52.9	Ga	-28.9	Ge	-119	As	-78.2	Se	-195	Br	-325	Kr	(+39)				
K	-48.4	In	-28.9	Sr	-5.03	Sn	-107	Sb	-103	Te	-190	I	-295	Xe	(+41)		
Rb	-46.9	Tl	-19.3	Cs	-45.5	Ba	-13.95	Pb	-35.1	Bi	-91.3	Po	-183	At	-270	Rn	(+41)

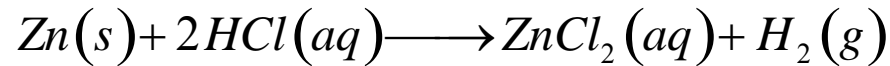


**Electronegativity**

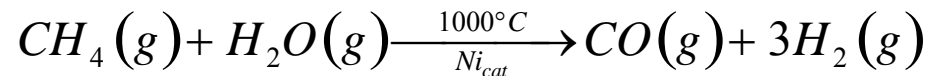
# Hydrogen Production

---

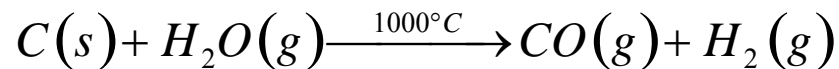
## Laboratory Scale



## Steam Reforming



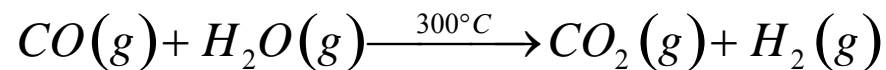
$$\Delta H_{rxn}^\circ \cong +49.3 \frac{\text{kcal}}{\text{mol}}$$



$$\Delta H_{rxn}^\circ \cong +31.4 \frac{\text{kcal}}{\text{mol}}$$

Driven by  
entropy!

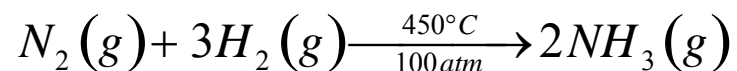
## Water-Gas Shift Reaction



$$\Delta H_{rxn}^\circ \cong -9.8 \frac{\text{kcal}}{\text{mol}}$$

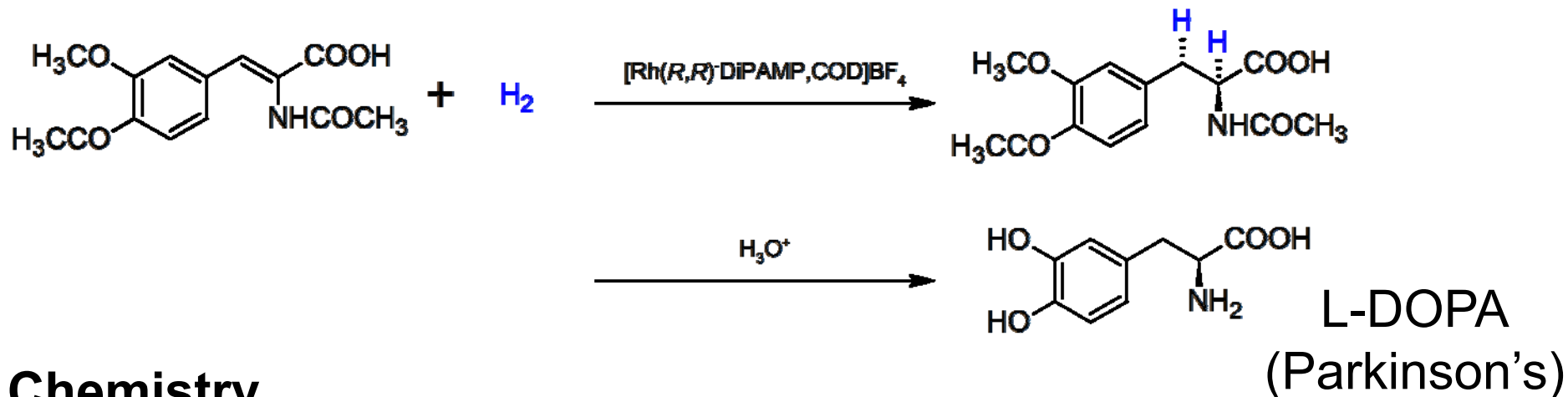
# Hydrogen Use

## Ammonia Production

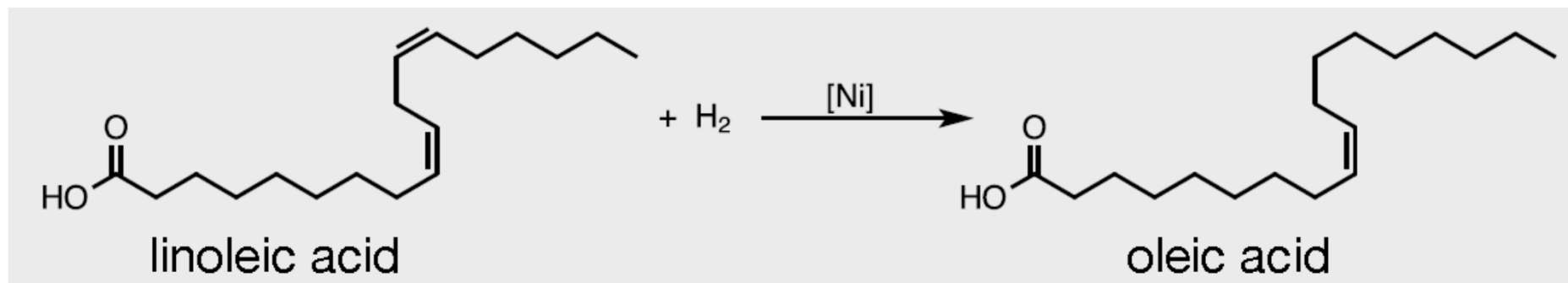


$$\Delta H_{rxn}^\circ \cong -11 \frac{\text{kcal}}{\text{mol}}$$

## Medicinal Chemistry



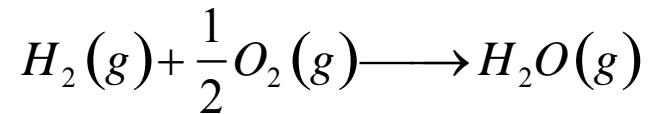
## Food Chemistry



# The Hydrogen Economy

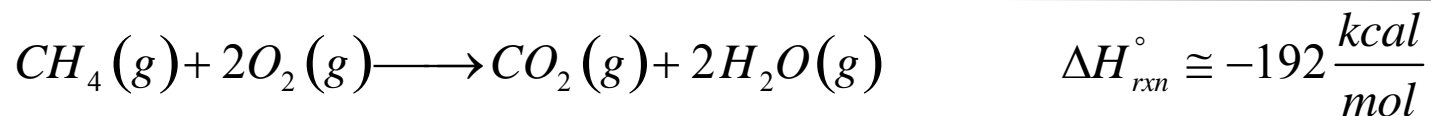
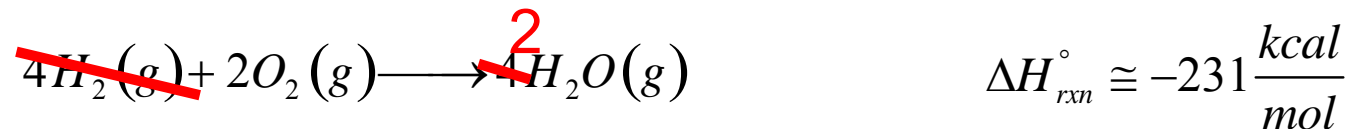
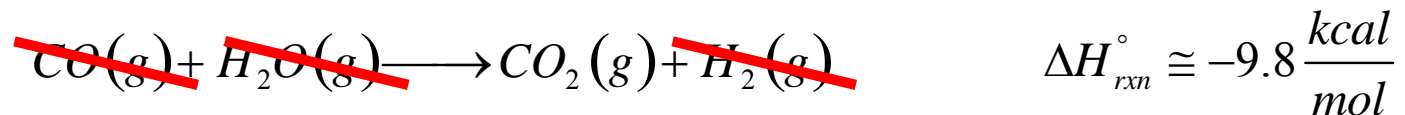
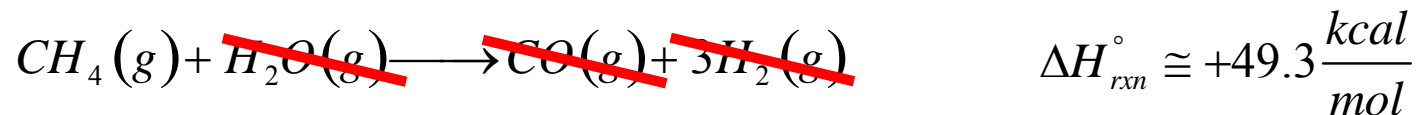
---

Hydrogen is an attractive fuel because of its high heat of combustion and zero pollution



$$\Delta H_{rxn}^\circ \cong -57.8 \frac{kcal}{mol}$$

The problem: our hydrogen comes from fossil fuels



Same overall result as burning methane: same energy out, same CO<sub>2</sub> out.  
**To be clean, H<sub>2</sub> must come from something other than fossil fuels.**

# Types of Hydrogen Compounds

---

## Metallic Hydrides

- conducting hydrides ( $\text{MgH}_2$ ,  $\text{NiH}_x$ )
- often non-stoichiometric, i.e.,  $[\text{MH}_x]$  where  $x < 1$  ( $\text{PdH}_x$ )

## Saline Hydrides

- salt-like solids of alkali and alkaline earth metals
- non-conducting
- characterized by a reduced hydrogen, i.e.,  $[\text{M}^+\text{H}^-]$

## Molecular Hydrides

- electron precise compounds:  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{GeH}_4$
- basic covalent hydrides:  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$
- weak-acid covalent hydrides:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$
- strong-acids:  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HI}$
- electron-deficient hydrides:  $\text{B}_2\text{H}_6$
- anionic hydrides:  $\text{BH}_4^-$ ,  $\text{AlH}_4^-$

# Hydride Stability

- Formation of saline hydrides generally is exoergic ( $\Delta G < 0$ )
- Formation of acids is mostly exoergic
- $\Delta G_f$  of covalent hydride compounds can be exoergic or endoergic
  - 2<sup>nd</sup> row and lower are endoergic – as such, compounds like  $\text{SiH}_4$  are extremely reactive

Period	Group						
	1 IA	2 IIA	13 IIIB	14 IVB	15 VB	16 VIB	17 VIIB
2	LiH(s) -16.4	BeH <sub>2</sub> (s) +4.8	B <sub>2</sub> H <sub>6</sub> (g) +20.7	CH <sub>4</sub> (g) -12.1	NH <sub>3</sub> (g) -3.9	H <sub>2</sub> O(l) -56.7	HF(g) -65.3
3	NaH(s) -8.0	MgH <sub>2</sub> (s) -8.6	AlH <sub>3</sub> (s) ~0	SiH <sub>4</sub> (g) +13.6	PH <sub>3</sub> (g) +3.2	H <sub>2</sub> S(g) -8.0	HCl(g) -22.8
4	KH(s) -8.6	CaH <sub>2</sub> (s) -35.2	Ga <sub>2</sub> H <sub>6</sub> (s) >0	GeH <sub>4</sub> (g) +27.1	AsH <sub>3</sub> (g) +16.5	H <sub>2</sub> Se(g) +3.8	HBr(g) -12.8
5	RbH(s) -7.2	SrH <sub>2</sub> (s) -33.6		SnH <sub>4</sub> (g) +45.0	SbH <sub>3</sub> (g) +35.3	H <sub>2</sub> Te(g) >0	HI(g) +0.4
6	CsH(s) -7.6	BaH <sub>2</sub> (s) -33.4					

kcal/mol

# Hydride Synthesis and Reactivity

---

## Synthesis

- **Direct reaction (radical based)**  $2E + H_2 \longrightarrow 2HE$
- **Protonation (transfer of H<sup>+</sup>)**  $E^- + H_2O \longrightarrow HE + OH^-$
- **Metathesis (transfer of H<sup>-</sup>)**  $EX + MH \longrightarrow MX + HE$

## Reactivity Patterns

- **Homolytic cleavage**  $HE \longrightarrow H^\bullet + E^\bullet$
- **Hydride Transfer**  $HE \longrightarrow E^+ + H^-$
- **Proton Transfer**  $HE \longrightarrow E^- + H^+$



# Alkali & Alkaline Earth Metals

Naturally occurring in various minerals



rock salt ( $\text{NaCl}$ )



carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ )



beryl ( $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ )



limestone ( $\text{CaCO}_3$ )



dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ )

# Alkali & Alkaline Earth Metals

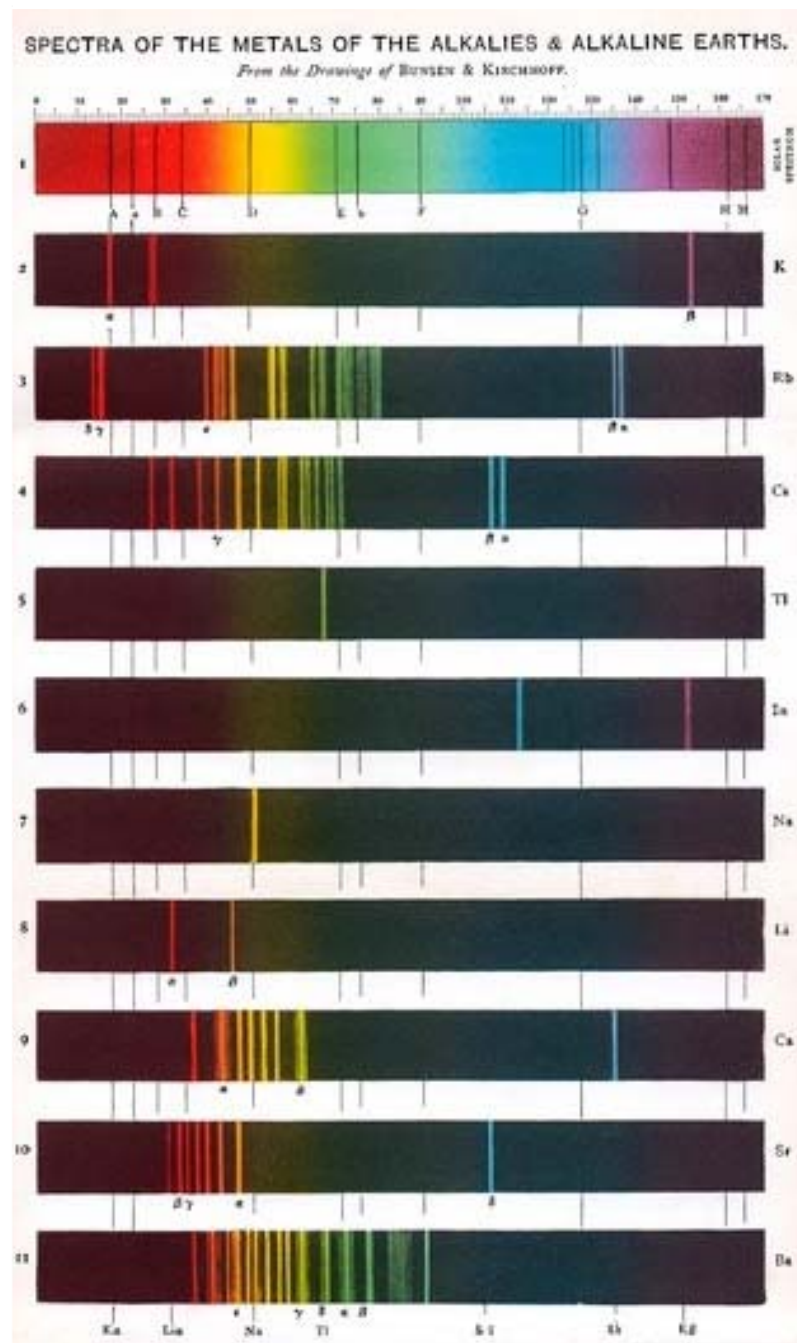
Li, Na and K were discovered by electrolysis (1807-1818)



Cs and Rb were discovered spectroscopically in mineral spa waters

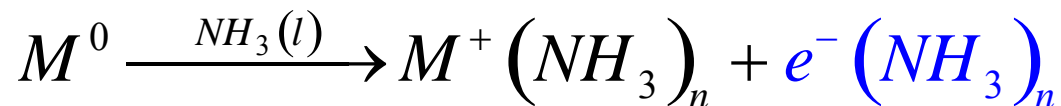
Lithium is a very important metal

- $\text{Li}_2\text{CO}_3$  – flux in porcelain enamels, hardening agent for glass, therapeutic for manic-depressive psychoses
- $\text{Li}^0$  – lightens and strengthens aircraft aluminum, alloyed with Mg for armor plate
- $\text{LiOH} - \text{CO}_2$  absorber in space capsules and submarines



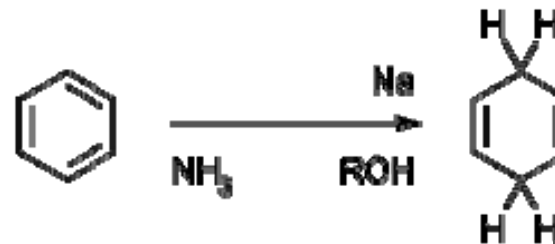
# Solvated Electron Solutions

All alkali metals (plus Ca, Sr, & Ba) dissolve in liquid ammonia



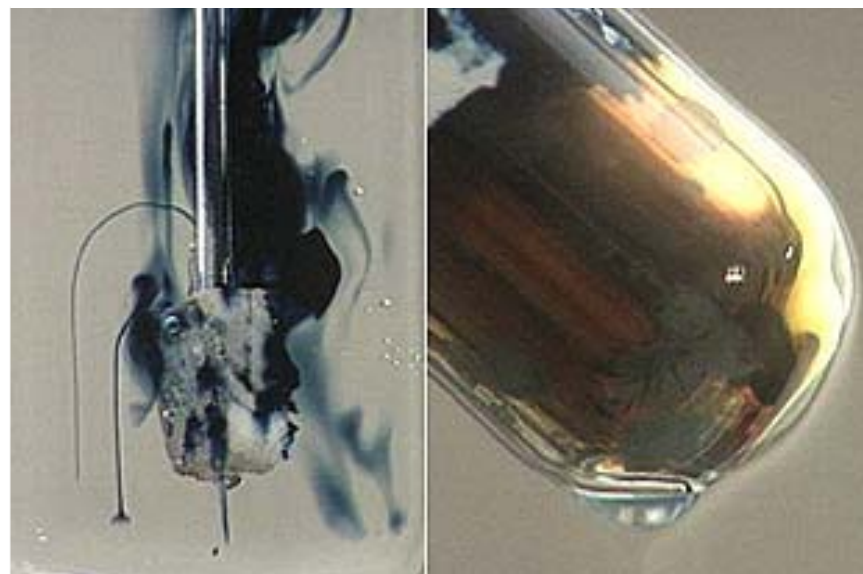
## • Dilute Solutions

- dark blue in color ( $\lambda_{\max} \cong 1500$  nm) diagnostic of a 'solvated electron'
- paramagnetic
- useful reducing agent (Birch reduction)



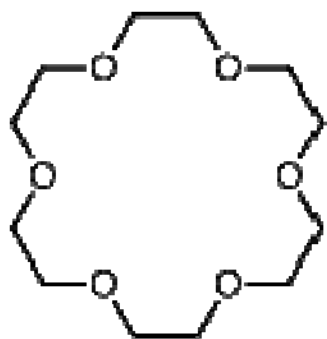
## • Concentrated Solutions

- metallic bronze color
- conductivity like a molten metal
- weakly paramagnetic

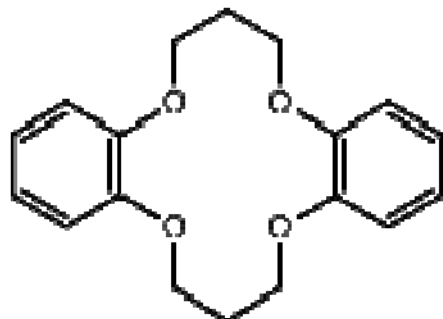


# Alkalides and Electrides

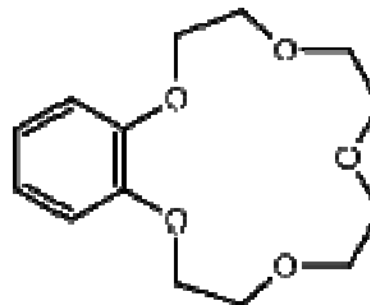
Crown ethers and cryptands are special Lewis bases designed to selectively bind metal cations.



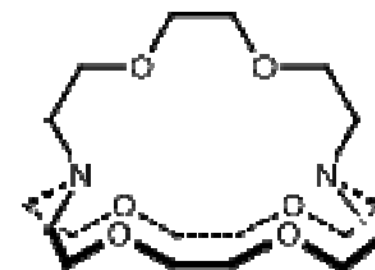
**18-crown-6**  
260-280 pm  
 $K^+$ ,  $Sr^{2+}$



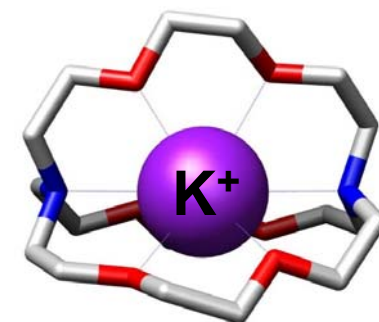
**dibenzo-14-crown-4**  
120-150 pm  
 $Li^+$ ,  $Mg^{2+}$



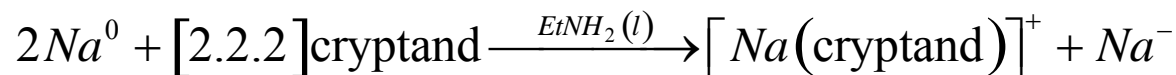
**benzo-15-crown-5**  
170-220 pm  
 $Na^+$ ,  $Ca^{2+}$



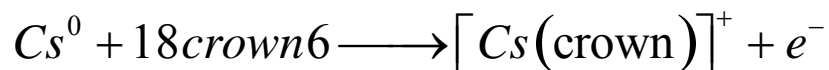
**[2.2.2] cryptand**



## Alkalides

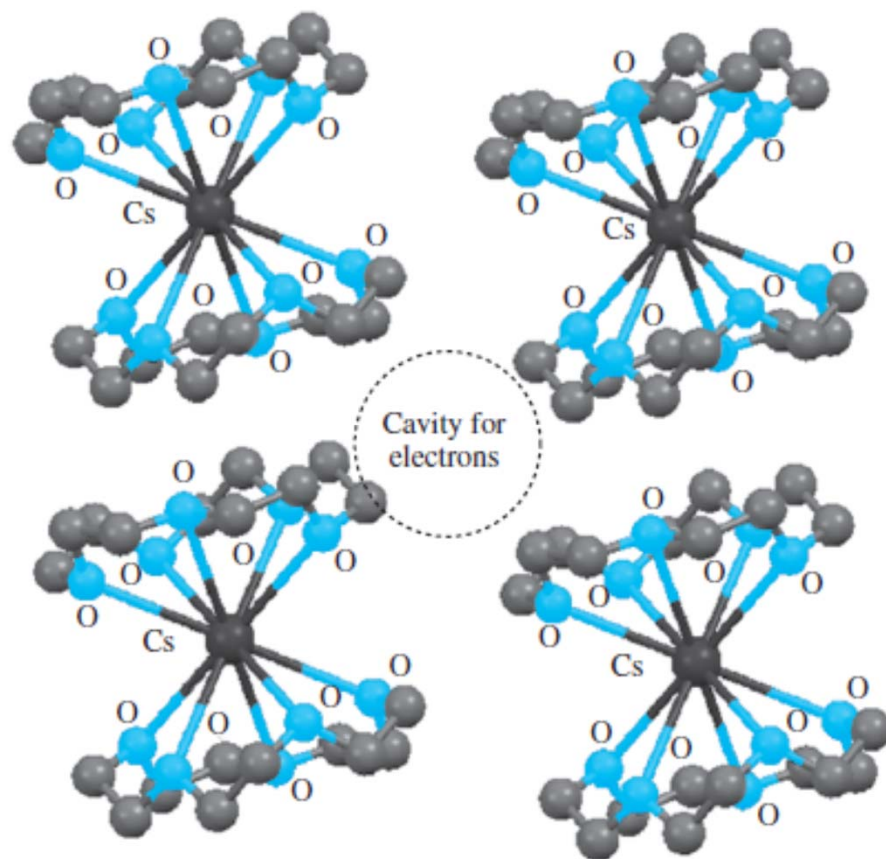


## Electrides



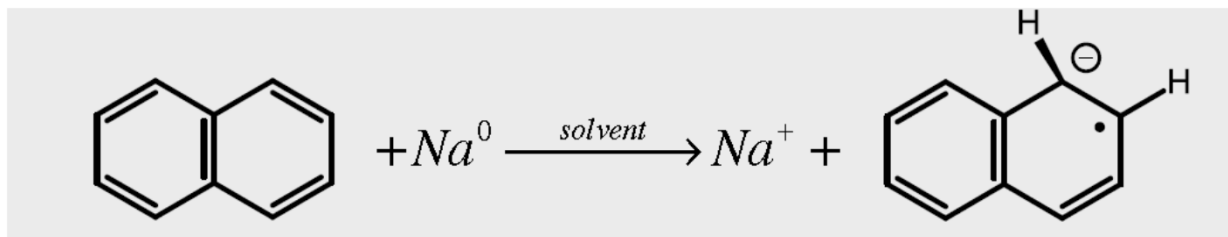


# Cs 15-crown-5 Sandwich Electride



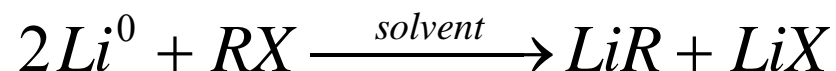
# Organometallic Chemistry

## Arene Reduction



- ethereal solvents (ether groups act as Lewis bases to prevent aggregation)
- reduced arene is deep green to deep blue
- similar to the solvated electron

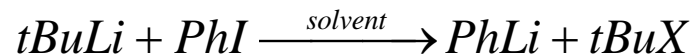
## Organolithium Reagents



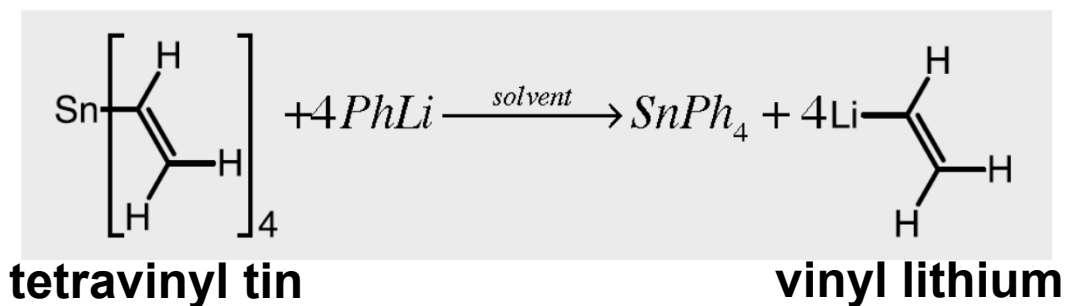
- alkane, arene, or ethereal solvents
- works best for alkyl derivatives
- most stable for R = Me, nBu, tBu
- LiR is actually a higher order cluster depending on R group
- LiR used as very strong base, or for nucleophilic addition of R<sup>-</sup>

# More Organolithium Chemistry

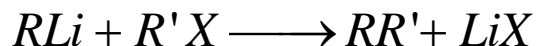
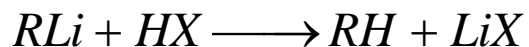
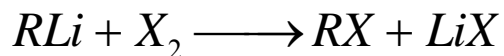
## Aryl derivatives accessible by metal-halogen exchange



## Unsaturated derivatives accessible by transmetalation

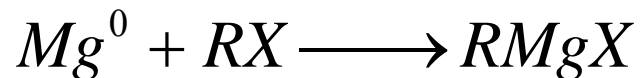


## General Reactivity



# Organomagnesium (Grignard) Chemistry

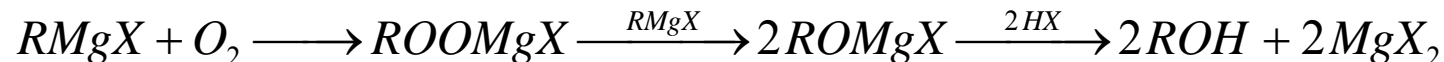
---



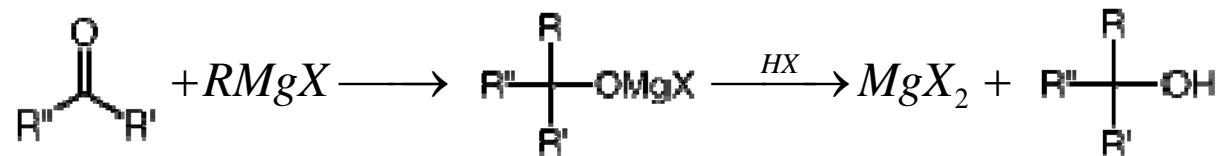
- reactivity is  $I > Br > Cl$  and alkyl  $>$  aryl
- mechanism is poorly understood

## Sample Reactivity

- Formation of primary alcohols



- Formation of substituted alcohols







# Organomagnesium Reactivity

In general Grignard reagents always react as the carbanion (nucleophile) to attack an electrophile:

