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)?
Hydrogen Production

Laboratory Scale

\[ \text{Zn}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g) \]

Steam Reforming

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow{1000^\circ C} \text{Ni}_{\text{cat}} \rightarrow \text{CO}(g) + 3\text{H}_2(g) \]

\[ \Delta H_{\text{rxn}}^\circ \approx +49.3 \frac{\text{kcal}}{\text{mol}} \]

\[ \text{C}(s) + \text{H}_2\text{O}(g) \xrightarrow{1000^\circ C} \rightarrow \text{CO}(g) + \text{H}_2(g) \]

\[ \Delta H_{\text{rxn}}^\circ \approx +31.4 \frac{\text{kcal}}{\text{mol}} \]

Driven by entropy!

Water-Gas Shift Reaction

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \xrightarrow{300^\circ C} \rightarrow \text{CO}_2(g) + \text{H}_2(g) \]

\[ \Delta H_{\text{rxn}}^\circ \approx -9.8 \frac{\text{kcal}}{\text{mol}} \]
**Hydrogen Use**

**Ammonia Production**

\[ N_2(g) + 3H_2(g) \xrightarrow{450^\circ C, 100 \text{ atm}} 2NH_3(g) \]

\[ \Delta H_{rxn}^\circ \approx -11 \text{ kcal/mol} \]

**Medicinal Chemistry**

L-DOPA (Parkinson’s)

**Food Chemistry**

Linoleic acid

\[ \text{linoleic acid} + H_2 \xrightarrow{[\text{Ni}]} \text{oleic acid} \]
The Hydrogen Economy

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

\[ H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \]

\[ \Delta H_{rxn}^\circ \approx -57.8 \frac{kcal}{mol} \]

The problem: our hydrogen comes from fossil fuels

\[ CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \]

\[ \Delta H_{rxn}^\circ \approx +49.3 \frac{kcal}{mol} \]

\[ CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \]

\[ \Delta H_{rxn}^\circ \approx -9.8 \frac{kcal}{mol} \]

\[ 4H_2(g) + 2O_2(g) \rightarrow 2H_2O(g) \]

\[ \Delta H_{rxn}^\circ \approx -231 \frac{kcal}{mol} \]

\[ CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \]

\[ \Delta H_{rxn}^\circ \approx -192 \frac{kcal}{mol} \]

Same overall result as burning methane: same energy out, same \( CO_2 \) out.
To be clean, \( H_2 \) must come from something other than fossil fuels.
Types of Hydrogen Compounds

Metallic Hydrides
- conducting hydrides (MgH₂, NiHₓ)
- often non-stoichiometric, i.e., [MHₓ] where x < 1 (PdHₓ)

Saline Hydrides
- salt-like solids of alkali and alkaline earth metals
- non-conducting
- characterized by a reduced hydrogen, i.e., [M⁺H⁻]

Molecular Hydrides
- electron precise compounds: CH₄, SiH₄, GeH₄
- basic covalent hydrides: NH₃, PH₃, AsH₃
- weak-acid covalent hydrides: H₂O, H₂S
- strong-acids: HF, HCl, HI
- electron-deficient hydrides: B₂H₆
- anionic hydrides: BH₄⁻, AlH₄⁻
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
  - 2nd row and lower are endoergic – as such, compounds like SiH$_4$ are extremely reactive

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kcal/mol
Hydride Synthesis and Reactivity

Synthesis

• Direct reaction (radical based) \[ 2E + H_2 \rightarrow 2HE \]

• Protonation (transfer of H\(^+\)) \[ E^- + H_2O \rightarrow HE + OH^- \]

• Metathesis (transfer of H\(^-\)) \[ EX + MH \rightarrow MX + HE \]

Reactivity Patterns

• Homolytic cleavage \[ HE \rightarrow H^* + E^* \]

• Hydride Transfer \[ HE \rightarrow E^+ + H^- \]

• Proton Transfer \[ HE \rightarrow E^- + H^+ \]
Alkali & Alkaline Earth Metals

Naturally occurring in various minerals

- rock salt (NaCl)
- carnallite (KCl•MgCl₂•6H₂O)
- beryl (Be₃Al₂(SiO₃)₆)
- limestone (CaCO₃)
- dolomite (CaCO₃•MgCO₃)
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

\[
M^0 \xrightarrow{NH_3(l)} M^+ \left( NH_3 \right)_n + e^- \left( NH_3 \right)_n
\]

- Dilute Solutions
  - dark blue in color ($\lambda_{max} \approx 1500$ 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⁺, Sr²⁺
dibenzo-14-crown-4
120-150 pm
Li⁺, Mg²⁺
benzo-15-crown-5
170-220 pm
Na⁺, Ca²⁺

Alkalides

\[ 2Na^0 + [2.2.2\text{cryptand}] \xrightarrow{EtNH_2(l)} [Na(\text{cryptand})]^+ + Na^- \]

Electrides

\[ Cs^0 + 18\text{crown} 6 \longrightarrow [Cs(\text{crown})]^+ + e^- \]
Cs\textsuperscript{+}(15c5)\textsubscript{2}e\textsuperscript{-}
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

\[ 2Li^0 + RX \xrightarrow{\text{solvent}} LiR + LiX \]

- 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⁻
More Organolithium Chemistry

Aryl derivatives accessible by metal-halogen exchange

\[ tBuLi + PhI \xrightarrow{\text{solvent}} PhLi + tBuX \]

Unsaturated derivatives accessible by transmetallation

\[ \text{tetravinyl tin} + 4PhLi \xrightarrow{\text{solvent}} SnPh_4 + 4Li\text{vinyl lithium} \]

General Reactivity

\[ RLi + X_2 \rightarrow RX + LiX \]

\[ RLi + HX \rightarrow RH + LiX \]

\[ RLi + R'X \rightarrow RR' + LiX \]
Organomagnesium (Grignard) Chemistry

\[ Mg^0 + RX \rightarrow RMgX \]

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

Sample Reactivity

- Formation of primary alcohols

\[ RMgX + O_2 \rightarrow ROOMgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{2HX} 2ROH + 2MgX_2 \]

- Formation of substituted alcohols

\[ \text{[Diagram]} + RMgX \rightarrow \text{[Diagram]} \rightarrow \text{[Diagram]} \xrightarrow{HX} MgX_2 + \text{[Diagram]} \]
Organomagnesium Reactivity

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

$\text{RMgX}$
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