Hydrogen
Isotopes

$^1\text{H}$, $^2\text{H}$ (D), $^3\text{H}$ (T)

Nuclear Spin Moments: $T_{1/2} = 12.33$ y

$I = \frac{1}{2}$, $1$, $\frac{1}{2}$

Deuterium – Isolated by chemical exchange $\text{H}_2\text{S}/\text{H}_2\text{O}$; electrolysis of water; fractional distillation; diffusion rates in palladium foil.

Tritium – Neutron bombardment of $^6\text{Li}$ as a Mg or Al alloy.

$$^6\text{Li} + ^1\text{n} \rightarrow ^4\text{He} + ^3\text{H}$$
Ortho & Para Hydrogen

<table>
<thead>
<tr>
<th></th>
<th>H-H</th>
<th>D-D</th>
<th>T-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s = 1$</td>
<td>$\uparrow\downarrow$</td>
<td>$\uparrow\downarrow$</td>
<td>$\uparrow\uparrow$</td>
</tr>
<tr>
<td>$s = 0$</td>
<td>$\uparrow\downarrow$</td>
<td>$\uparrow\uparrow$</td>
<td>$\uparrow\downarrow$</td>
</tr>
</tbody>
</table>

Spin isomerism in molecular hydrogen: the interchange between isomers is forbidden as long as the bond is strong. Hydrogenation catalysts catalyse interchange. The spin isomers differ principally in thermal conductivity. $s = 0$, para for H and T is 100% at 0 K; $s = 1$, ortho 75% at RT. For D $s = 1$ ortho is 100% at 0 K and 66.7% at RT.
# Hydrogen Ions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H· → H⁺ + e⁻</td>
<td>ΔH = +1311 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>Li· → Li⁺ + e⁻</td>
<td>ΔH = +520 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>F· → F⁺ + e⁻</td>
<td>ΔH = +1680 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>H· + e⁻ → H⁻</td>
<td>ΔH = -72 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>Li· + e⁻ → Li⁻</td>
<td>ΔH = -57 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>F· + e⁻ → F⁻</td>
<td>ΔH = -333 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>2 H· + H⁺ → H₃⁺</td>
<td>ΔH = -770 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>2 H· → H₂</td>
<td>ΔH = -436 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>H₂ + H⁺ → H₃⁺</td>
<td>ΔH = -337 kJ/mol</td>
<td></td>
</tr>
</tbody>
</table>

The H₂ bond is very strong, low reactivity. Source of energy for the atomic hydrogen or "plasma torch".
Three-Center Two-electron Bonding in Hydrogen and Boron

$3c-2e$

$3c-2e$
# Protonic Acids

## Trends in Bronsted Acidities of Hydrides

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>NH₃</th>
<th>H₂O</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ</td>
<td>46</td>
<td>35</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>PH₃</td>
<td>H₂S</td>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>7</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

Acid Strength increases l - r across the periodic table with electronegativity but not down. Bond strength decreases faster than does the electronegativity.

\[
\text{HF} + \text{H}_2\text{O} \xrightarrow{100\%} \text{H}_2\text{O} \cdots \text{HF} \xleftarrow{\sim 3\%} \text{H}_3\text{O}^+ + \text{F}^-
\]
# Strengths of Oxo-Acids and the Stability of their Conjugate Bases

<table>
<thead>
<tr>
<th>Oxo-Acid</th>
<th>pKₐ</th>
<th>Δ-charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCl</td>
<td>7.2</td>
<td>0.5</td>
</tr>
<tr>
<td>HOClO</td>
<td>2.0</td>
<td>0.33</td>
</tr>
<tr>
<td>HOClO⁻</td>
<td>-1</td>
<td>0.25</td>
</tr>
<tr>
<td>HOClO⁻⁻</td>
<td>-10</td>
<td></td>
</tr>
</tbody>
</table>

Delocalization of charge on the anion makes it less basic, more stable.

If the number of monovalent oxygens does not change little change in acid strength occurs.
**Strengths of Oxo-Acids - Electronegativity**

\[ HXO_n \quad n = \text{constant} \quad X = \text{Cl} > \text{Br} > \text{I} \]

**Polyprotic Acids – Successive Dissociations**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2S )</td>
<td>( HS^- )</td>
<td>( \Delta pK_a )</td>
<td>( H_3PO_4 )</td>
<td></td>
</tr>
<tr>
<td>( pK_a )</td>
<td>7</td>
<td></td>
<td>2.15</td>
<td>( \Delta pK_a )</td>
</tr>
<tr>
<td>( H_2Se )</td>
<td>( HSe^- )</td>
<td>12</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>( pK_a )</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_2Te )</td>
<td>( HTe^- )</td>
<td>11</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>( pK_a )</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta \Delta \Delta \Delta \]

**Strengths of Oxo-Acids - Electronegativity**

\[ HXO_n \quad n = \text{constant} \quad X = \text{Cl} > \text{Br} > \text{I} \]
The Hydrogen Bond

Unique characteristics of the Hydrogen atom.

- $1s$ atomic orbital is spherical and *gerada* (the wavefunction is “+” throughout).

- Polarized $\delta^+$ when bonded to elements $\chi > 2.5$.

- Interacts strongly with lone pairs of F, O, N but much less strongly with Cl, Br, I, S, P.

- Interaction above is strongest when $A-H \ B$ angle is $180^\circ$. 
The Hydrogen Bond

An incipient to full 3c-4e bond:
The Hydrogen Bond

- Finite Groups: $\text{HF}_2^-$; carboxylic acid dimers
- Infinite Chains: HF, HCN
- Infinite Layers: $\text{B(OH)}_3$; \{ $\text{N}_2\text{H}_5^+$ FHF$^-$ \}
- 3-D Networks: water ice, $\text{NH}_4\text{F}$, $\text{H}_2\text{O}_2(\text{s})$, $(\text{K}^+)$ $\text{H}_2\text{PO}_4^-$.

Hydrogen bonding is the predominant influence in the macro-structures of proteins, DNA, RNA, polysaccharides, etc.
**Acidity in Non-aqueous Solvents and Anhydrous Acids – Hammett Acidity & the Henderson-Hasselbalch Equation.**

\[
B + H^+ \rightleftharpoons BH^+
\]

**Hammett Acidity Function for anhydrous & concentrated acids** becomes in dilute aqueous solution

\[
-H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \quad \Rightarrow \quad pH = pK_a - \log \frac{[BH^+]}{[B]}
\]

<table>
<thead>
<tr>
<th>Acid</th>
<th>-$H_0$</th>
<th>Acid</th>
<th>-$H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₃F / SbF₅ / SO₃</td>
<td>&gt; 16</td>
<td>HF</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>15.2</td>
<td>H₃PO₄</td>
<td>5.0</td>
</tr>
<tr>
<td>HSO₃F</td>
<td>12.6</td>
<td>H₂SO₄ (63% aq)</td>
<td>4.9</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>11.0</td>
<td>HCO₂H</td>
<td>2.2 (-3.7/0.1 M)</td>
</tr>
</tbody>
</table>
Binary Metal Hydrides

dihydrogen:  H-H  d = 74 pm  EN = 2.1

H·  \( r_{\text{cov}} = 37 \text{ pm; } r_{\text{vdw}} = 120 \text{ pm; } r_{\text{Bohr}} = 53 \text{ pm} \)

H⁺  \( r_{\text{calc}} = 10^{-3} \text{ pm } \)  This is a bare proton!

H⁻  \( r_{\text{calc}} = 208 \text{ pm } r_{\text{expt}} = 130 – 154 \text{ pm} \)

cf  F⁻  \( r_{\text{ionic}} = 154 \text{ pm } \)  I⁻  \( r_{\text{ionic}} = 220 \text{ pm} \)

The hydride ion is about the size of F⁻ but has a high polarizability like I⁻ ion. Hydride structures are highly variable, the H⁻ ion is very sensitive to its environment.
Arbitrary Classification of Binary Hydrides

- Ionic Hydrides – Saline, “salt-like” hydrides contain the discrete $\text{H}^-$ ion. Groups 1, 2, 3 and lanthanides having group oxidation state. Uses: reducing agents, portable $\text{H}_2$ sources, anionic polymerization catalysts.

- Metallic Hydrides – Tend to be non-stoichiometric sufficient metal electrons are not involved in M-H bonding to preserve delocalized metallic bonding. $\text{MH}_2$ of Group 3 and lanthanides, Eu & Yb excepted, transition metal hydrides.
Arbitrary Classification of Binary Hydrides, cont.

- **Covalent Hydrides** – Generally those involving 2-center, 2-electron (2c-2e) bonds. Volatile hydrides of groups 14-17.

- **Electron Deficient Hydrides** – Tend to be polymeric and involve multicenter bonding. Hydrides of Be, (Mg), B, Al, Ga.
Metallic Hydrides

- Electrical Conductivity drops a hundred fold.
- Magnetism may decrease or increase due to specific effects of “dilution”. Hydrides may be paramagnetic, ferromagnetic or antiferromagnetic.
- Ductility decreases as H composition increases, “hydrogen embrittlement”.
- Density decreases as H composition increases. Useful in “powder metallurgy”. Thermal decomposition leads to very reactive often pyrophoric metal, also very pure dihydrogen.
Metallic Bonding – Band Theory

Overlap of metal atomic orbitals to form molecular orbitals:

Example: Li metal \(2s^1\) electron configuration

The overlap of a very large number of metal atoms produces a two band structure. The upper band is "empty" but is separated from the lower, "filled" band by a band gap \(\Delta E << kT\).

A metallic conductor has a band gap \(\Delta E << kT\).

The electron population in the upper band, and the "hole" population in the lower band is optimum. Electron and "hole" conduction is limited only by thermal disorder.

- Thermal energies continually create "holes" and a fuzzy cut-off energy called the "Fermi Level".
- Electron motion is random when no electric field is applied.
- An electric field destabilizes orbitals having electrons migrating toward the negative pole, stabilizes electrons migrating toward the positive pole. A net transfer of electrons in the bulk metal, an induced current.
Network Bonding – Band Theory

- A semiconductor has a band gap $\Delta E \sim kT$. Small electron population in the upper band, a few "holes" in the lower band. Marginal conduction heavily influenced by doping!

- An insulator has a band gap $\Delta E \gg kT$. No electron population in the upper band, no "holes" in the lower band. No conduction!

- The upper or conduction band conducts better as it increases in electron population.

- The lower or valence band conducts better as the "hole" population increases.
Theory of Metal Hydride Bonding

Alloy Model – A hydrogen atom, H\(^+\), loses its electron to the metal conduction band and is incorporated into the lattice as H\(^+\). The result is considered an alloy and metallic.

Hydride Model – A hydrogen atom, H\(^-\), gains an electron from the metal conduction band and the resulting H\(^-\) produces an ionic hydridic type bond. The remaining metallic electrons provide the residual bulk metallic character.
Alloy Model – Supporting Evidence

- Hydrogen in TM hydrides are very mobile in the lattice, very low barrier to diffusion.

- Proton NMR produce very narrow resonances.

- In Pd the magnetic susceptibility falls as H₂ is added; interpreted as filling conduction band, pairing of electrons increasing diamagnetism.

- When an electric field potential is applied hydrogen migrates to the cathode.
Hydride Model – Supporting Evidence

- A natural explanation for the gradual disappearance of metallic properties.
- Structural Studies – M-H distances are compatible with 130 pm radius for hydride ion. Similarities between hydride & halide lattices.
- Lattice energy calculations correlate well with experiment.
- Hydride/Oxide are compatible as solid solutions. O²⁻/H⁻ is okay but not O²⁻/H⁺
- Theoretical calculations: ΔHᶠ for TM hydrides.
Results of Theoretical Calculations

- $\Delta H_f$ of TM hydrides approach zero in gps 7 & 8.
- Entropy effects in $\Delta H_f$ calculations give rise to non-stoichiometric compositions.
- Give insight into the $H_2$ absorbing power and catalytic function in hydrogenations.

Hydride model seems to be gaining favor primarily as a result of successes in theoretical calculations. Experimentally neither has been disproved by available evidence. Neither model has allowed for covalency. Both yield similar results in practice.
Rationalization of Evidence for Alloy Model

- Wide H-NMR resonance bands are observed in many TM hydrides, e.g. TiH$_2$, at RT and below which become narrower at 50°C up.

\[ H^-_{(immobile)} \rightarrow H^+_{(mobile)} + 2e^- \text{ (excited to conduction band)} \]

- PdH$_{0.6}$ which is diamagnetic, remains so if it is carefully dehydrided. The diamagnetism is due to the expanded lattice not filling of the conduction bands.

- Hydrogen migration in an electric field is not so simplistic, ionic hydrides show similar effects.
Mid-d-block Metal Hydrogen Interactions

- TM hydrides become less stable across d-block and down each group. Except for Pd no true stable hydrides form below and to the right of Cr. Each of these elements strongly adsorb hydrogen, lack of hydride stability likely due to stronger metal-metal bonding in these elements.

- Many of these elements form exceptionally broad “alpha (solution phases)” where reversible structural changes occur, but do not form “beta (hydride) phases” even at high H₂ pressures.
The Palladium-Hydrogen System

- Forms readily at 25 C and 1 atm pressure.
- \( \Delta H_f = -9.5 \text{ kcal/mol} \) (exothermic!)
- \( \alpha \text{ PdH}_{0.03} \ a_{lattice} = 389 \text{ pm} \); \( \beta \text{ PdH}_{0.6} \ a_{lattice} = 401.8 \text{ pm} \) at 300C only the \( \alpha \) phase forms up to 1000 atm \( \text{H}_2 \). Most catalytic systems operate at 300C. A hypothetical PdH has a NaCl structure with \( a_{lattice} = 411 \text{ pm} \).
- A silver alloy (up to 20%) exhibits increased permeability to \( \text{H}_2 \) vs \( \text{D}_2 \) and \( \text{T}_2 \).
Unique Features of Pd-H$_2$ System

- Pd/αPdH have lattices of same symmetry.
- Only hydride where O$_h$ lattice sites fill first.
- Has never been made stoichiometric.
- Most extensive alpha phase at moderate temperatures.
- Has a very high hydrogen mobility.

This uniqueness and early discovery strongly influenced ideas of metal hydride bonding and led to the concept of “interstitial” dissolution.
Covalent Hydrides

Volatile Hydrides:

a) $M_nH_{2n+2}$ in Gp 14 & hydrides of Gps 15, 16, 17 where valence electrons equal or exceed the number of orbitals, employ 2c-2e bonding.

b) Electron deficient hydrides of boron where deficiency can be satisfied by dimerization.

Nonvolatile Hydrides: Electron deficient hydrides where deficiency is greater and polymerize to satisfy deficiency. $BeH_2$ $AlH_3$
Complex Metal Hydrides

K$_2$ReH$_9$ – A Re(VII) species, tricapped, trigonal prismatic, fluxional, pnmr $\tau = 19.1$ ppm. IR $\nu = 1869, 1795, 1779$ cm$^{-1}$. The ReH bond is strong $d_{\text{Re-H}} = 168$ pm, stable for weeks in aqueous alkaline solution, Tc similar.

NaBH$_4$ – A tetrahedral BH$_4^-$ anion, soluble in and stable to water, a good reducing agent.

LiAlH$_4$ – A versatile, powerful reducing agent, very soluble in ether, reacts violently to water. Structure does not contain the AlH$_4^-$ anion
Complex Metal Hydrides

Bonding Transitions in a Family:

\[ \text{Ba(BH}_4\text{)}_2, \text{Sr(BH}_4\text{)}_2, \text{Ca(BH}_4\text{)}_2 \parallel \text{Mg(BH}_4\text{)}_2, \text{Be(BH}_4\text{)}_2 \]

\[ \text{M(BH}_4\text{)}_3 \quad \text{M = Ga, In, Tl(III)} \]

unstable \( T < RT \)
Hydrogen as a Ligand

Formation of 2c-2e M-H bonds:

a) Protonation: \( \text{H}^+ + :\text{M}^- \)
b) Radical: \( \text{H}\cdot + \cdot\text{M} \)

c) Metathesis: \( \text{H}:^- + \text{M}^+ \)

d) Coordination: \( \text{nH}^- + \text{M} \rightarrow \text{MH}_n^{n^-} \)

e) Hydrogenolysis: \( \text{H}_2 + 2\text{M} \)

f) Oxidative Addition: \( \text{H}_2 + \text{M} \)

g) Elimination: \( \text{R-CH}_2\text{CH}_2\cdot-\text{M} \)
Hydrogen as a Ligand

Formation of 2c-2e M-H bonds – Protonation:

\[
H^+ + Fe(CO)_5 \longrightarrow [HFe(CO)_5]^+ \\
Na_2Fe(CO)_4 \xrightarrow{H_2O} Na[HFe(CO)_4] \xrightarrow{H_3PO_4} H_2Fe(CO)_4
\]

Radical:

Hydrogenolysis:

\[
Fe(CO)_5 + H_2 \xrightarrow{h\nu} H_2Fe(CO)_4 + CO \\
Co_2(CO)_8 + H_2 \xrightarrow{h\nu} 2 HCo(CO)_4
\]
Hydrogen as a Ligand

Formation of 2c-2e M-H bonds - Metathesis:

Heterolytic Splitting:

\[
\text{RuCl}_6^{3-} + \text{H}_2 \rightarrow [\text{HRuCl}_5]^{3-} + \text{HCl}
\]

Coordination:

Hydride Addition:

\[
4 \text{LiH} + \text{Rh} \rightarrow \text{Li}_4\text{RhH}_4 \xrightarrow{1/2 \text{H}_2} \text{Li}_4\text{RhH}_5
\]

Ligand Exchange:

\[
(\eta^5-\text{C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl} + \text{NaBH}_4 \rightarrow (\eta^5-\text{C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}
\]

\[
(\eta^5-\text{C}_5\text{H}_5)\text{Fe(CO)}_3^+ + \text{NaBH}_4 \xrightarrow{-\text{CO}} (\eta^5-\text{C}_5\text{H}_5)\text{Fe(CO)}_2\text{H}
\]
Hydrogen as a Ligand

Formation of 2c-2e M-H bonds:

Oxidative Addition:

\[
\begin{align*}
\text{Ir} & \quad \text{Cl} & \quad \text{C} & \quad \text{O} & \quad \text{P}(\text{Ph})_3 \\
(\text{Ph})_3\text{P} & \quad & & & \quad \text{H}_2
\end{align*}
\]

(β) Elimination:

\[
\begin{align*}
\text{Rh} & \quad \text{Cl} & \quad \text{H} & \quad \text{CH}_2\text{CH}_3 & \quad \text{P}(\text{Ph})_3 \\
(\text{Ph})_3\text{P} & \quad & & \quad \text{P}(\text{Ph})_3 & \quad (\text{Ph})_3\text{P}
\end{align*}
\]
Hydrogenation of Olefins

Oxidative Addition

Reductive Elimination

(β) Elimination

H₂ → (Ph)₃P

Cl

Rh

P(Ph)₃

CH₂CH₃

H₂C=CH₂

H₃CCH₂
Hydrogen as a Ligand – 3 center

Bent: (3c-2e)

\[
\begin{align*}
\text{(OC)}_3\text{Fe} & \quad \text{Fe(CO)}_3 \\
\text{C} & \quad \text{CC} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[\Psi_3\]  
anti-bonding

Linear: (3c-4e)

\[
\begin{align*}
\text{(OC)}_5\text{Cr} & \quad \text{H} \quad \text{Cr(CO)}_5 \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} \\
\end{align*}
\]

\[\Psi_2\]  
non-bonding

\[\Psi_1\]  
bonding
Hydrogen as a Ligand – 4-center bonding

$H_4Re_4(CO)_{12}$

4c-2e bonding

$d_{\text{Re-Re}} = 289.6 - 294.5$ pm

H atoms bridge each triangular face
Metal Bonding in Di-Hydrogen Ligands

Increasing $\pi$–backdonation to the $\text{H}_2 \, \sigma^*$-orbital will result in weakening the H-H bond and result in two M-H bonds.