

Greenwood & Earnshaw

2nd Edition

Chapter 3

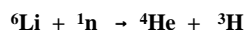
Hydrogen

Isotopes

¹ H	² H (D)	³ H (T)
Nuclear Spin Moments:		$T_{1/2} = 12.33 \text{ y}$
$I = 1/2$	1	$1/2$

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 ⁶Li as a Mg or Al alloy.

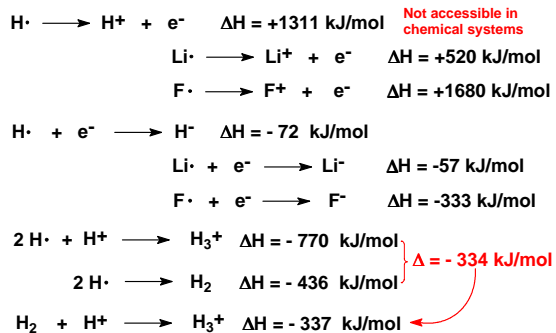


Ortho & Para Hydrogen

H-H	D-D	T-T
$\uparrow \uparrow \quad s = 1$	$\uparrow \downarrow \quad s = 0$	$\uparrow \uparrow \quad s = 1$
$\uparrow \downarrow \quad s = 0$	$\uparrow \uparrow \quad s = 1$	$\uparrow \downarrow \quad s = 0$

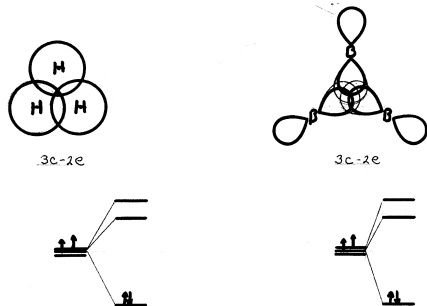
Spin isomerism in molecular hydrogen: the interchange between isomers is forbidden as long as the bond is strong. Hydrogenation catalysts catalyse interchange. The spin isomers differ principally in thermal conductivity. $s = 0$, para for H and T is 100% at 0 K; $s = 1$, ortho 75% at RT. For D $s = 1$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

Hydrogen Ions



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

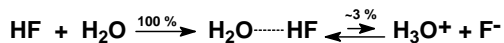


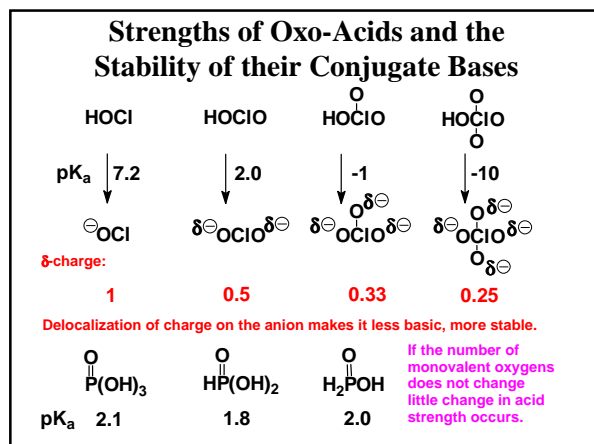
Protonic Acids

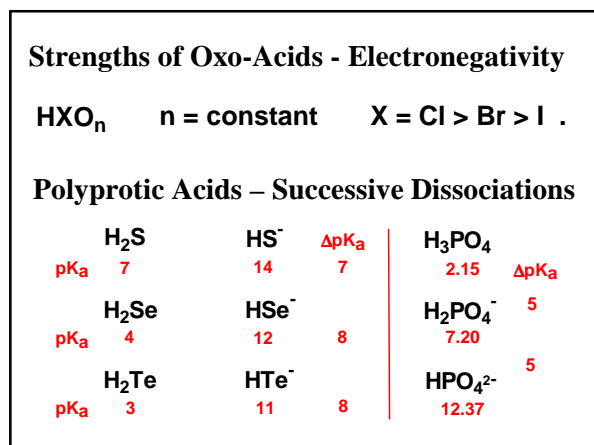
Trends in Bronsted Acidities of Hydrides

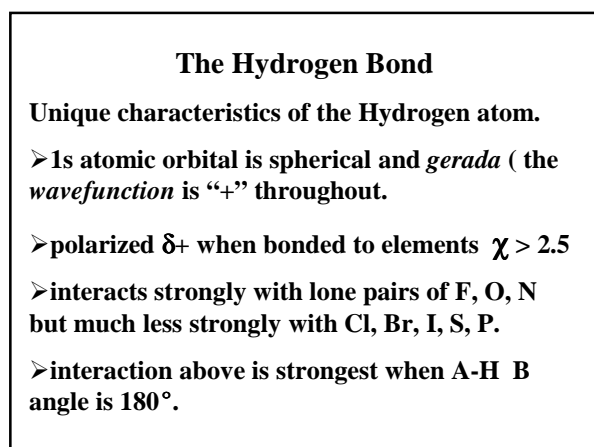
CH ₄	NH ₃	H ₂ O	HF
pK _a 46	35	16	3
	PH ₃	H ₂ S	HCl
	27	7	-1
		H ₂ Se	HBr
		4	-9
		H ₂ Te	HI
		3	-10

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



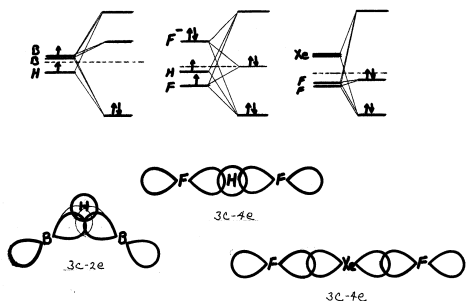






The Hydrogen Bond

An incipient to full 3c-4e bond:



The Hydrogen Bond

➤ Finite Groups: HF_2^- ; carboxylic acid dimers

➤ Infinite Chains: HF, HCN

➤ Infinite Layers: $\text{B}(\text{OH})_3$; $\{\text{N}_2\text{H}_5^+ \text{FHF}^-\}$

➤ 3-D Networks: water ice, NH_4F , $\text{H}_2\text{O}_{2(s)}$, $(\text{K}^+) \text{H}_2\text{PO}_4^-$.

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.



Hammett Acidity Function for anhydrous & concentrated acids becomes Henderson Hasselbalch Equation in dilute aqueous solution

$$\text{H}_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]} \Rightarrow \text{pH} = \text{p}K_a - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

Acid	$-\text{H}_0$	Acid	$-\text{H}_0$
$\text{HSO}_3\text{F} / \text{SbF}_5 / \text{SO}_3$	> 16	HF	10.2 (-3.2/0.1 M)
HF / SbF_5	15.2	H_3PO_4	5.0
HSO_3F	12.6	H_2SO_4 (63% aq)	4.9
H_2SO_4	11.0	HCO_2H	2.2 (-3.7/0.1 M)

Binary Metal Hydrides

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

H \cdot $r_{\text{cov}} = 37$ pm; $r_{\text{vdw}} = 120$ pm; $r_{\text{Bohr}} = 53$ pm

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

H $^-$ $r_{\text{calc}} = 208$ pm $r_{\text{expt}} = 130 - 154$ pm

cf F $^-$ $r_{\text{ionic}} = 154$ pm I $^-$ $r_{\text{ionic}} = 220$ 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 H $^-$ ion. Groups 1, 2, 3 and lanthanides having group oxidation state. Uses: reducing agents, portable 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. 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.

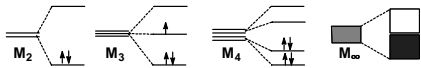
Metallic Hydrides

- **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 2s¹ 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* $\Delta E \ll kT$.

A metallic conductor has a *band gap* $\Delta E \ll kT$.

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^\bullet , 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^\bullet , 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 H_2 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. O^{2-}/H^- is okay but not O^{2-}/H^+
- Theoretical calculations: ΔH_f for TM hydrides.

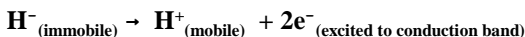
Results of Theoretical Calculations

- ΔH_f of TM hydrides approach zero in gps 7 & 8.
- Entropy effects in ΔH_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.



- $PdH_{0.6}$ 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 H_2 pressures.

The Palladium-Hydrogen System

- Forms readily at 25 C and 1 atm pressure.
- $\Delta H_f = -9.5$ kcal/mol (exothermic!)
- α PdH_{0.03} $a_{\text{lattice}} = 389$ pm; β PdH_{0.6} $a_{\text{lattice}} = 401.8$ pm at 300C only the α phase forms up to 1000 atm H₂. Most catalytic systems operate at 300C. A hypothetical PdH has a NaCl structure with $a_{\text{lattice}} = 411$ pm.
- A silver alloy (up to 20%) exhibits increased permeability to H₂ vs D₂ and T₂.

Unique Features of Pd-H₂ System

- Pd/ α PdH have lattices of same symmetry.
- Only hydride where O_n 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:

- 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.
- 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. BeH₂ AlH₃

Complex Metal Hydrides

K_2ReH_9 – A Re(VII) species, tricapped, trigonal prismatic, fluxional, pmr $\tau = 19.1$ ppm. IR $\nu = 1869, 1795, 1779$ cm^{-1} . The ReH bond is strong $d_{Re-H} = 168$ pm, stable for weeks in aqueous alkaline solution, Tc similar.

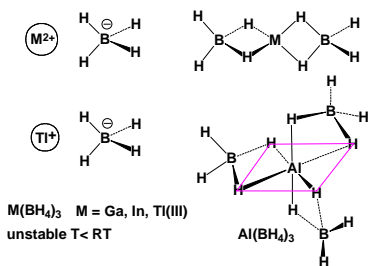
$NaBH_4$ – A tetrahedral BH_4^- anion, soluble in and stable to water, a good reducing agent.

$LiAlH_4$ – 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:

$Ba(BH_4)_2, Sr(BH_4)_2, Ca(BH_4)_2 \parallel Mg(BH_4)_2, Be(BH_4)_2$



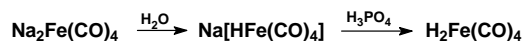
Hydrogen as a Ligand

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

- Protonation: $H^+ + :M^-$
- Radical: $H\cdot + \cdot M$
- Metathesis: $H:^- + M^+$
- Coordination: $nH:^- + M \rightarrow MH_n^{n-}$
- Hydrogenolysis: $H_2 + 2M$
- Oxidative Addition: $H_2 + M$
- Elimination: $R-CH_2CH_2-M$

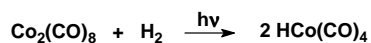
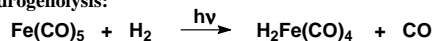
Hydrogen as a Ligand

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



Radical:

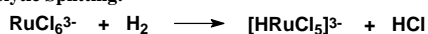
Hydrogenolysis:



Hydrogen as a Ligand

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

Heterolytic Splitting:



Coordination:

Hydride Addition:



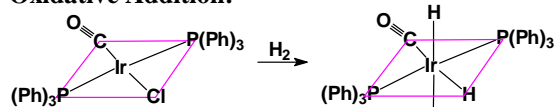
Ligand Exchange:



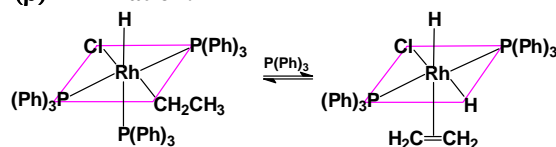
Hydrogen as a Ligand

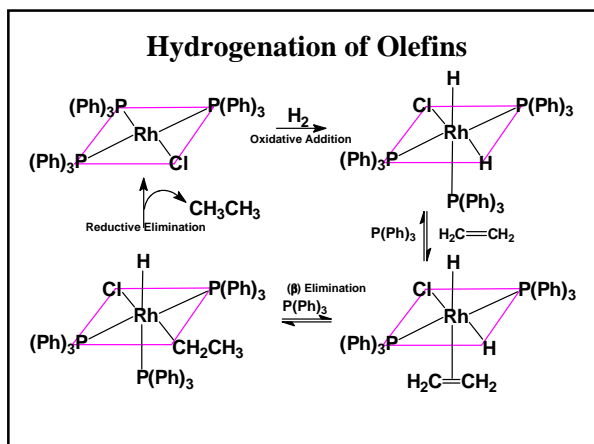
Formation of 2c-2e M-H bonds:

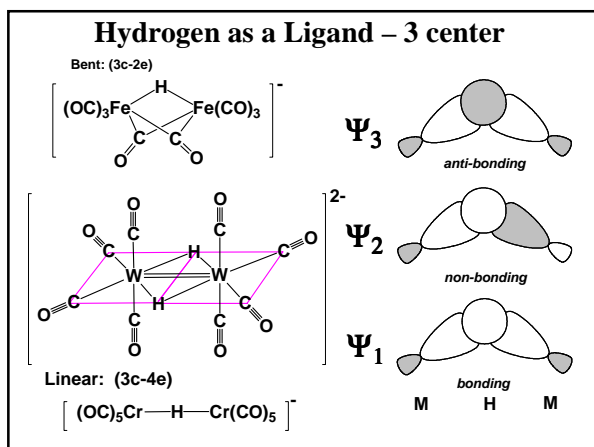
Oxidative Addition:

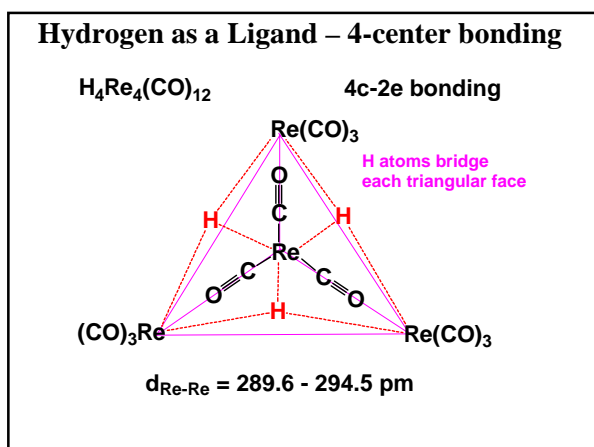


(β) Elimination:

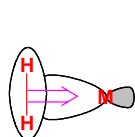




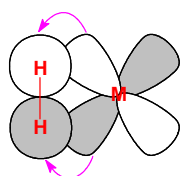




Metal Bonding in Di-Hydrogen Ligands



σ -Donation of bonding molecular orbital electron density to metal hybrid atomic orbitals.



π -Back-donation of metal electron density to hydrogen anti-bonding molecular orbitals.

Increasing π -backdonation to the H₂ σ^* -orbital will result in weakening the H-H bond and result in two M-H bonds.
