

Chemistry 1000 Lecture 19: Hydrogen

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The nonmetallic (?) group 1 element

- Hydrogen is usually placed on periodic tables in group 1 due to its single (valence) electron.
- Diatomic gas at room temperature
- Electronegativity: 2.1
- Electrical resistivity of liquid hydrogen over 2200 K and above 140 GPa: $5 \times 10^{-6} \Omega \text{ m}$

Reactivity of H₂

- The H-H bond is very short \Longleftrightarrow strong.
- The strong H-H bond means that H₂ is not very reactive.
 - Reaction with O₂ requires a spark (free radicals) for initiation.
Contrast: reaction with alkali metals
 - Reaction with N₂ requires heat *and* pressure *and* a catalyst.

Hydrides

Binary hydrogen compounds (compounds of H and one other element) are called **hydrides**.

Types of hydrides:

Covalent hydrides: e.g. H_2O , CH_4

Some covalent hydrides (notably H_2O) display significant ionic character, as evidenced by their dissociation into ions in water.

Ionic hydrides: e.g. NaH , CaH_2

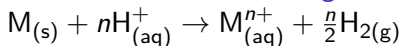
For H and Na, $\Delta\chi = 2.1 - 0.9 = 1.2$. We would normally predict this compound to be covalent, but it behaves as if it's an ionic compound of Na^+ and H^- .

Metallic hydrides: e.g. palladium hydride

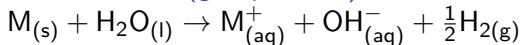
Preparation of hydrogen

Lab-scale processes

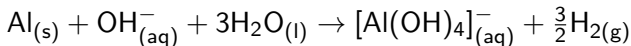
Reaction of a metal with a non-oxidizing acid:



Reaction of an active metal (group 1 or 2) with water:



Reaction of Al with base:



Electrolysis of water: $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$

Preparation of hydrogen

Industrial processes

Steam reforming of natural gas: $\text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{(g)} + 3\text{H}_{2(g)}$

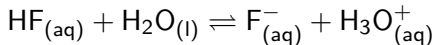
Coal gasification: $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{(g)} + \text{H}_{2(g)}$

Water gas shift reaction: $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{H}_{2(g)}$
Typically used with steam reforming or coal gasification

Electrolysis of water: May become a useful source of hydrogen if cheap/environmentally benign sources of electricity can be found.

Covalent hydrides

- Wide range of properties: some almost perfectly covalent (e.g. CH₄), some with substantial ionic character (e.g. HF)
- Because H sits right in the middle of the electronegativity scale, it can carry a partial positive charge (as in H₂O), essentially no charge (as in PH₃), or a partial negative charge (as in SiH₄).
- Ionic character and counterion hydration effects lead to Brønsted acidity, e.g.



Brønsted acid-base theory

Brønsted acid: proton donor

Brønsted base: proton acceptor

Strong acid: dissociates completely in water

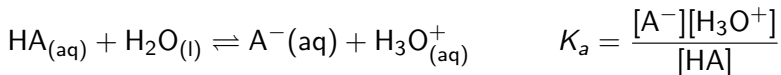
Common strong acids: HCl, HBr, HI, HNO₃, HClO₄, HClO₃,
H₂SO₄ (first proton)

Strong base: ionizes completely in water

Common strong bases: alkali metal hydroxides, alkaline
earth metal hydroxides (except Be(OH)₂)

Strength of acids

- K_a is the equilibrium constant for the dissociation of an acid:



- K_a range over several orders of magnitude, so it's convenient to use a logarithmic scale:

$$\text{p}K_a = -\log_{10} K_a$$

- Stronger acid \implies smaller $\text{p}K_a$

	HCl	HF	HOCl	HCN
$\text{p}K_a$:	< 0	3.18	7.54	9.21
	stronger			weaker

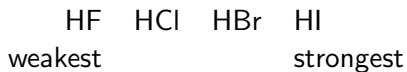
Ranking strong acids

Use one strong acid as a solvent for another.

If the reaction $\text{HA} + \text{HB} \rightleftharpoons \text{A}^- + \text{H}_2\text{B}^+$ occurs, then HA is a stronger acid than HB

Hydrohalic acids

- Ranked in order of strength:

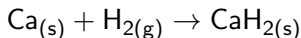
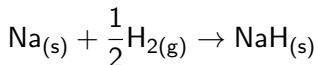


- Ionic radii:

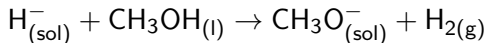
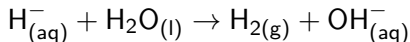
Ion	F^-	Cl^-	Br^-	I^-
r/pm	133	181	196	220

Ionic hydrides

- Group 1 and 2 metals (except Be and Mg) form ionic hydrides involving the H^- ion.
- H^- is isoelectronic with He: $1s^2$.
 \Rightarrow pseudo-halide ion?
- Made by direct reaction of the metal with hydrogen, e.g.



- The hydride ion is an extremely powerful base:



Metallic hydrides

- Typically non-stoichiometric compounds of a transition metal (or lanthanide or actinide) with hydrogen
- Alternative names: metal hydride, interstitial hydride
- Hydrogen molecules slip into the holes in the metal lattice.
- In some metals, the molecules dissociate, either into hydrogen atoms, or into H^+ and H^- .
- Palladium is the champion metallic hydride, absorbing up to 900 times its volume in H_2 .
- Proposed as hydrogen storage devices

Types of hydrides

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac, U, Pu									?							
Ionic hydrides		Metallic hydrides										Covalent hydrides						