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: $5 \times 10^{-6}\,\Omega\,\mathrm{m}$

Reactivity of H_2

- The H-H bond is very short $\Longleftrightarrow$ strong.
- The strong H-H bond means that H_2 is not very reactive.
  - Reaction with O_2 requires a spark (free radicals) for initiation. Contrast: reaction with alkali metals
  - Reaction with N_2 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:

$$\mathrm{M_{(s)} + \mathit{n}H^+_{(aq)} \rightarrow M^{\mathit{n}+}_{(aq)} + \frac{\mathit{n}}{2}H_{2(g)}}$$

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

$$\mathrm{M_{(s)} + H_2O_{(l)} \rightarrow M^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(g)}}$$

Reaction of Al with base:

$$\mathrm{Al_{(s)} + OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow [Al(OH)_4]^-_{(aq)} + \frac{3}{2}H_{2(g)}}$$

Electrolysis of water: $\mathrm{H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}}$

Preparation of hydrogen

Industrial processes

Steam reforming of natural gas: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$

Coal gasification: $C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$

Water gas shift reaction: $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

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. CH_4), 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 H_2O), essentially no charge (as in PH_3), or a partial negative charge (as in SiH_4).
- Ionic character and counterion hydration effects lead to Brønsted acidity, e.g.

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons F^-_{(aq)} + H_3O^+_{(aq)}$$

Brønsted acid-base theory

Brønsted acid: proton donor

Brønsted base: proton acceptor

Strong acid: dissociates completely in water

Common strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, $HClO_3$, H_2SO_4 (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:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-(aq) + H_3O^+_{(aq)} \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

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

$$pK_a = -\log_{10} K_a$$

- Stronger acid $\Longrightarrow$ smaller pK_a

	HCl	HF	HOCl	HCN
pK_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 $HA + HB \rightleftharpoons A^- + H_2B^+$ occurs, then HA is a stronger acid than HB

Hydrohalic acids

- Ranked in order of strength:

	HF	HCl	HBr	HI
weakest				strongest

- 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.

$$Na_{(s)} + \frac{1}{2}H_{2(g)} \rightarrow NaH_{(s)}$$

$$Ca_{(s)} + H_{2(g)} \rightarrow CaH_{2(s)}$$

- The hydride ion is an extremely powerful base:

$$H^-_{(aq)} + H_2O_{(l)} \rightarrow H_{2(g)} + OH^-_{(aq)}$$

$$H^-_{(sol)} + CH_3OH_{(l)} \rightarrow CH_3O^-_{(sol)} + H_{2(g)}$$

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**