Chapter 8
Hydrogen

CHEM 462
Wednesday, Nov. 3
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What comes now

- From this point on, we will be discussing more “descriptive chemistry” - this requires integration of the principles covered up to now.
- I’ll try to explain how to use the principles to help organize the descriptive facts, but this takes practicing chemists a long time to do well.
- There is no way we can do more than scratch the surface of selected topics, so I will have to “pick and choose” what I talk about. You will see more divergence from the text in several places.

Remember general trends and Periodic Table

- Electronegativities (and related ionization energies and electron affinities).
- Radii - cation and anion
- Polarizabilities
- Bonding summary:
  - Octet rule for sp-block elements
  - Hydridization, π-bonding
  - Covalency, ionicity
Hydrogen is Unique!

- Fairly large ionization energy, small electron affinity ... never is present in compounds as a ‘naked’ cation, forms an anion only with highly electropositive cations in the solid state
- No core electrons — highly polarizing, makes fairly strong bonds with many elements
- Most bonds have substantial covalency, even if polar

Hydrogen doesn’t belong . . .

- …to the group I metals: Although hydrogen makes a monocation in aqueous solution, “H⁺” isn’t at all like a group I cation. Reactivity of elemental hydrogen is not at all like alkali metals either.
- …to the halogens: Although the element exists as a diatomic molecule like the halogens, it is much less reactive, rarely reacts to give H⁻, and the H-H bond is quite strong (436 kJ/mol). Covalent hydrogen compounds have structural similarity to halogen compounds, but very different reactivity.

“Hydrides”

- Traditional categories:
  - ionic
  - covalent
  - metallic
- Divisions between categories are not entirely sharp
“Hydride” periodic geography

Examples to be discussed.

“Interstitial” hydrogen in metallic hydrides

Basic physical and chemical properties

- H₂ is low-boiling (26 K), low melting (20 K) colorless gas. Strong bond (436 kJ/mol⁻¹).
- Basic reactions to make covalent “hydrides”:
  - \(2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)\) \(\Delta H = -488\) kJ
  - \(\text{H}_2(g) + \text{F}_2(g) \rightarrow 2 \text{HF}(g)\) \(\Delta H = -542\) kJ
  - \(3 \text{H}_2(g) + \text{N}_2(g) \rightarrow 2 \text{NH}_3(g)\) \(\Delta H = -92\) kJ

Bonds broken are strong, but strong bonds made are too, and are more numerous. (Slow rxns. at r.t.)
Covalent hydrides have low b.p.s...  

<table>
<thead>
<tr>
<th></th>
<th>boiling points</th>
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<tbody>
<tr>
<td>CH₄</td>
<td>-164 °C</td>
<td></td>
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<tr>
<td>SiH₄</td>
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<td>PH₃</td>
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<tr>
<td>B₂H₆</td>
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Some H-bond strengths:
- [F−H−F]⁻ 165 kJ/mol
- F−H…FH 30 kJ/mol
- HO−H…OH₂ 25 kJ/mol
- H₂N−H…NH₃ 17 kJ/mol

Hydrogen bonds and water

- H-bonds give water some special properties:
  - high melting & boiling points, essential for our existence
  - structure of ice is very “open” and very stable
  - density of water increases slightly on melting, so ice floats
- H-bonds also important in structure of biomolecules like proteins, DNA, ...
Hydrogen bonding in Ice

Ice has a very "open" diamond-like structure, in liquid H$_2$O collapse occurs when a few H-bonds break. Liquid H$_2$O is therefore denser than ice.

A Personal Favorite!

[Zr$_6$BCl$_{18}$]$^-$ ions trapped in "ice cages"

Two Forms of Hydrogen (H$_2$):
Ortho and Para

Two special circumstances peculiar to hydrogen conspire to give quantum mechanical wavefunction symmetry a dramatic effect on the macroscopic thermal properties (e.g., heat capacity) of H$_2$.

- Rotational levels in H$_2$ are relatively widely spaced – and because H$_2$ is a homonuclear diatomic, they alternate in symmetry as a function of $J$, the rotational quantum number. ($J =$ even – symmetric; $J =$ odd antisymmetric)
- The nuclear spin states have opposite symmetry too! ($I =$ 1 - symmetric; $I =$ 0 - antisymmetric)
Nuclear Spins

- The nuclear spins couple into triplet ($I = 1$) and singlet ($I = 0$) total nuclear spin states.
- The triplet state is symmetric (ortho), the singlet is antisymmetric (para).

Rotational Levels

- The ortho and para forms correspond to the odd and even rotational levels.
- As long as the interconversion between levels is slow, the two forms have distinct thermal properties!

Some Statistical Thermo Relations

\[
\begin{align*}
E_J &= \frac{J(J+1)\hbar^2}{2I} ; \quad g_J = 2J+1 \\
q_{\text{tot}} &= \sum_J g_J e^{-E_J/kT} ; \quad \text{partition fct. (sum over states)} \\
q_{\text{para}} &= \sum_{\text{odd } J} g_J E_J = \sum_{\text{odd } J} (2J+1)e^{-J(J+1)\hbar^2/2kT} \\
q_{\text{ortho}} &= 3 \sum_{\text{even } J} g_J E_J = 3 \sum_{\text{even } J} (2J+1)e^{-J(J+1)\hbar^2/2kT} \\
U_{\text{tot}} &= RT \left( \frac{\partial \ln q_{\text{tot}}}{\partial T} \right) ; \quad C_{\text{tot}} = \left( \frac{\partial U_{\text{tot}}}{\partial T} \right)
\end{align*}
\]
Hydrogen as a reducing agent

- H₂ and hydrides are important reducing agents.
- For metals whose hydrides are nonexistent or aren’t very strong reductants, H₂ can be used industrially, e.g.,
  \[ \text{CuO}(s) + \text{H}_2 \rightarrow \text{Cu}(s) + \text{H}_2\text{O}(g) \]
  \[ \text{MO}_3(s) + 3 \text{H}_2 \rightarrow \text{M}(s) + 3\text{H}_2\text{O}(g); \ M = \text{Mo}, \text{W} \]
  \[ \text{NH}_4\text{MO}_4(s) + \ \text{xs} \ \text{H}_2 \rightarrow \]
  \[ \text{M}(s) + 4\text{H}_2\text{O}(g) + \text{NH}_3(g); \ M = \text{Tc}, \text{Re} \]

LiBH₄, NaBH₄: reducing agents

\[ 4 \text{NaH}(s) + \text{B}(\text{OCH}_3)_3(s) \rightarrow \]
\[ \text{NaBH}_4(s) + 3 \text{NaOCH}_3(s) \]
\[ \downarrow \text{NH}_3 \text{ or } (i-\text{Pr})\text{NH}_3 \]
soluble \ (industrial)

Lab: MH(s) + B₂H₆ \rightarrow 2 MBH₄ \quad M = \text{Li, Na}
\ (in \text{Et}_2\text{O or diglyme})

\text{NaBH}_4 \text{ selective for aldehyde, acid chloride, and ketone reductions; LiBH}_4 \text{ more powerful, less selective}