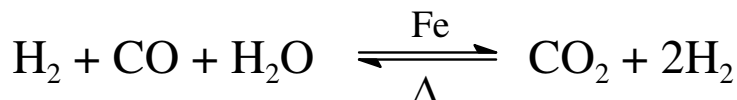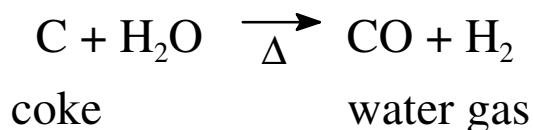# Hydrogen - The Element

- Discovered by Cavendish in 1766 and named by Lavoisier.
  Gk., *hydro* = water + *genes* = forming

- Most abundant element in the universe.
  - 90% of all atoms
  - ~3/4 of all mass

- Elemental form, $H_2(g)$, is rare in the atmosphere because hydrogen is reactive.

  - H_2 reacts with virtually all other elements (except noble gases), often explosively.

 - However, H_2 is not exceptionally reactive, due to the stability of its bond ($D = 434.1$ kJ/mol).

Synthesis

- Laboratory syntheses for impure $H_2(g)$

  - active metal in acid: $Zn + 2H^+ \rightarrow H_2 + Zn^{2+}$

  - hydrolysis of hydride: $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

  - electrolysis: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.82806$ V

- Industrial: Bosch process (water-gas shift reaction) – Reduction of H_2O over white-hot coke to produce "water gas", which makes more H_2 by the water-gas shift reaction.

$$C + H_2O \xrightarrow{\Delta} CO + H_2$$
$$\text{coke} \qquad\qquad \text{water gas}$$

$$H_2 + CO + H_2O \underset{\Delta}{\overset{Fe}{\rightleftharpoons}} CO_2 + 2H_2$$

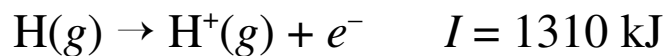 CO_2 removed by scrubbing: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

- Industrial: Cracking of light hydrocarbons.

$$CH_4 + H_2O \xrightarrow[Ni]{800^oC} CO + 3H_2$$

$$C_3H_6 + 3H_2O \xrightarrow[Ni]{800^oC} 3CO + 6H_2$$
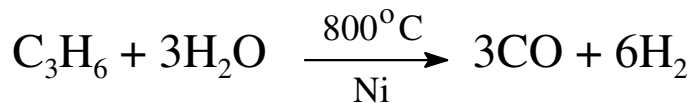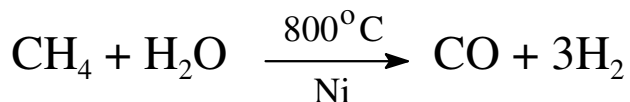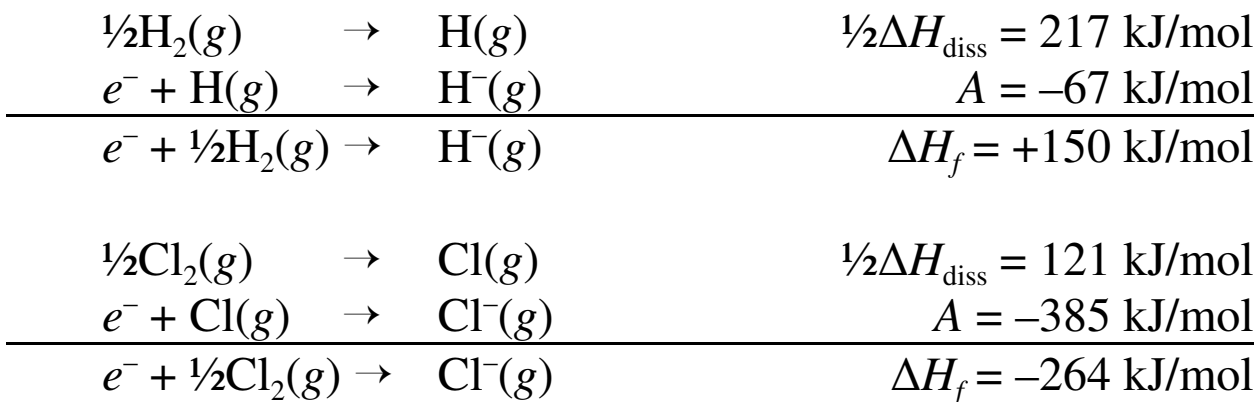
Classifying Hydrogen
Alkali Metal?

● Although Hydrogen forms H^+, like the alkali metals, it should not be classified as a group 1 element, because its ionization potential is too high.

$$H(g) \rightarrow H^+(g) + e^- \qquad I = 1310 \text{ kJ}$$
$$K(g) \rightarrow K^+(g) + e^- \qquad I = 418 \text{ kJ}$$
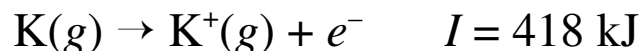
● H^+ requires stabilization and in solution only exists as molecular species such as NH_4^+, H_3O^+, etc.

● In compounds, H^+ only forms covalent compounds, unlike the alkali metals whose compounds are mainly ionic.

Classifying Hydrogen
Halogen?

● Hydrogen forms some compounds in which it is H^- (hydride ion), and it has a negative (favorable) electron affinity, like typical halogens.

● Unlike typical halides, the overall enthalpy of formation of the hydride ion is endothermic.

$\frac{1}{2}H_2(g)$	$\rightarrow$	$H(g)$	$\frac{1}{2}\Delta H_{diss} = 217$ kJ/mol
$e^- + H(g)$	$\rightarrow$	$H^-(g)$	$A = -67$ kJ/mol
$e^- + \frac{1}{2}H_2(g)$	$\rightarrow$	$H^-(g)$	$\Delta H_f = +150$ kJ/mol

$\frac{1}{2}Cl_2(g)$	$\rightarrow$	$Cl(g)$	$\frac{1}{2}\Delta H_{diss} = 121$ kJ/mol
$e^- + Cl(g)$	$\rightarrow$	$Cl^-(g)$	$A = -385$ kJ/mol
$e^- + \frac{1}{2}Cl_2(g)$	$\rightarrow$	$Cl^-(g)$	$\Delta H_f = -264$ kJ/mol

● H^- requires a small and very electropositive element to stabilize it in a crystal lattice.

● Radius of H^- is highly variable:

      126 pm in LiH   154 pm in CsH

Isotopes

$$^{2}_{1}H = D \qquad ^{3}_{1}H = T$$

● Deuterium is 0.0156% of naturally occurring hydrogen.

  • Often obtained as D_2O, produced after prolonged electrolysis of natural water.

  • D_2O is concentrated during electrolysis because reduction of H_2O is kinetically and thermodynamically favored over D_2O.

● Tritium is only about $1:10^{17}$ in natural hydrogen.

  • Tritium is a beta emitter with $t_{1/2} = 12.4$ yr.

  • Produced naturally by cosmic rays in the upper atmosphere.

  • Produced commercially in nuclear reactors:

$$^{6}_{3}Li + ^{1}_{0}n \longrightarrow ^{4}_{2}He + ^{3}_{1}H$$
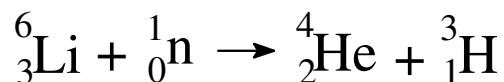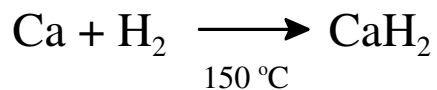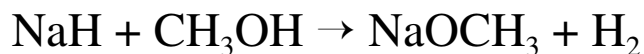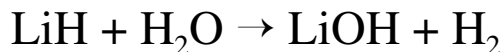
Compounds of Hydrogen

- Hydrogen compounds can be classified as the following five types:

  - Saline hydrides
  - Hydride complexes
  - Covalent hydrides
  - Macromolecular complexes
  - Interstitial hydrides

Saline Hydrides

- Group 1 and 2 elements form saline hydrides, which contain H^- ion, by direct combination:

$$Ca + H_2 \xrightarrow[150\ ^\circ C]{} CaH_2$$

- Saline hydrides react with protonic solvents to give H_2.

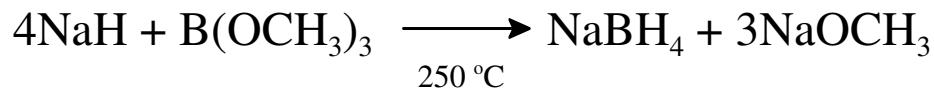$$LiH + H_2O \rightarrow LiOH + H_2$$
$$NaH + CH_3OH \rightarrow NaOCH_3 + H_2$$

- When molten saline hydrides are electrolyzed, H_2 is evolved at the anode.

$$H^- \rightarrow \tfrac{1}{2}H_2 + e^- \qquad -E^o = +2.25\ V$$
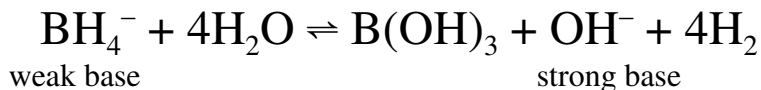
Hydride Complexes

- Most important are MH_4^- complexes of group 13 elements.

$$8LiH + Al_2Cl_6 \xrightarrow[(C_2H_5)_2O]{} 2LiAlH_4 + 6LiCl$$

$$4NaH + B(OCH_3)_3 \xrightarrow[250\ ^oC]{} NaBH_4 + 3NaOCH_3$$
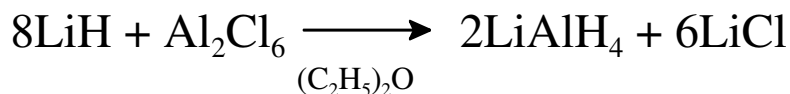
- Stability of MH_4^- complexes decreases with increasing atomic number of M and decreasing bond strength:
$$BH_4^- > AlH_4^- > GaH_4^- \gg InH_4^-$$
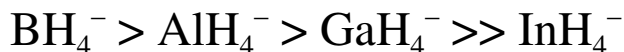
- Vigor of water hydrolysis is in the same order:
$$BH_4^- + 4H_2O \rightleftharpoons B(OH)_3 + OH^- + 4H_2$$
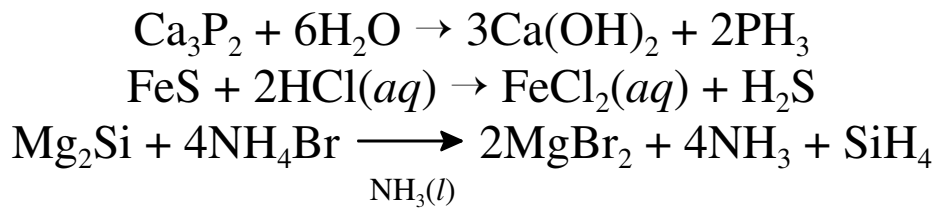weak base   strong base

  - BH_4^- reacts initially, making the solution basic, then dissolves without further hydrolysis.
  - GaH_4^- explodes on contact with water!

- MH_4^- compounds are more useful than saline hydrides in syntheses, because they are soluble in ether and their reactions are more controlled.
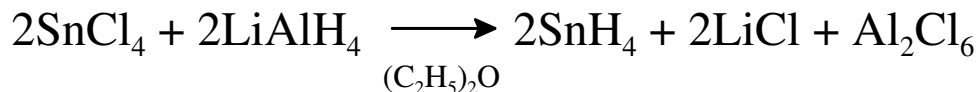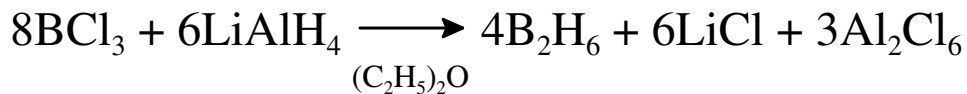
Covalent Hydrides

- Familiar covalent compounds in which H has a formal oxidation state of +1.

- Strength of X-H bond tends to increase with difference in electronegativity and decrease with mass of X (X = nonmetal, Sn, As, Sb).

- Direct combination is typical synthesis with electronegative elements:

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$
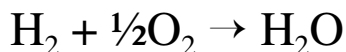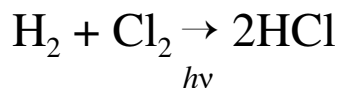
- With less electronegative elements, metal salts of the non-hydrogen element may be used:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$
$$FeS + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2S$$
$$Mg_2Si + 4NH_4Br \xrightarrow{NH_3(l)} 2MgBr_2 + 4NH_3 + SiH_4$$

- $LiAlH_4$ can also act as a hydrogenating agent:

$$8BCl_3 + 6LiAlH_4 \xrightarrow{(C_2H_5)_2O} 4B_2H_6 + 6LiCl + 3Al_2Cl_6$$

$$2SnCl_4 + 2LiAlH_4 \xrightarrow{(C_2H_5)_2O} 2SnH_4 + 2LiCl + Al_2Cl_6$$
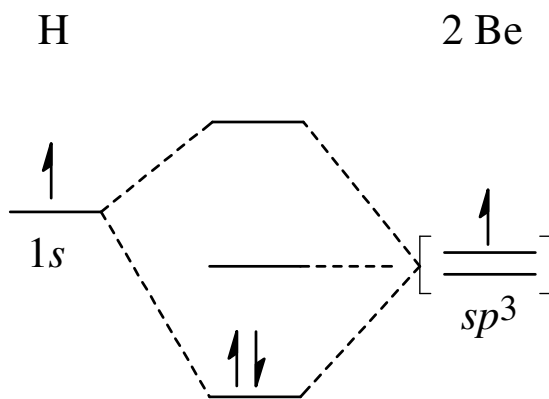
Macromolecular Hydrides

- BeH_2 and MgH_2 have similar reactivity to saline hydrides, but they are more covalent.

- The solids contain infinite chains of tetrahedrally coordinated Be or Mg with –H– bridges.

$$\left[\begin{array}{c} \overset{H}{\diagdown}Be\overset{H}{\cdots}Be\overset{H}{\diagup}Be\overset{H}{\cdots}Be\overset{H}{\diagup} \end{array} \right]_n$$
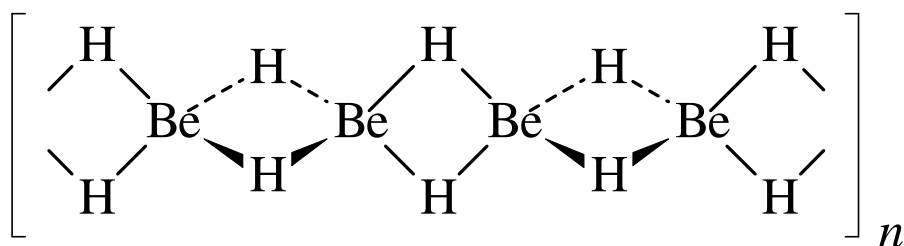
- The hydrogen bridges are electron-deficient 3c-2e bonds.

H   2 Be

$1s$ sp^3

Interstitial Hydrides

- Hydrogen reacts with most transition metals and lanthanides to form interstitial hydrides, M_xH_y, with no fixed stoichiometry.

- These are better regarded as phases, rather than true compounds.

- The hydrogen atoms occupy interstitial holes in the metallic structure.

- These phases are often catalytically important.

- CuH is a true hydride compound with a fixed stoichiometry.

Hydrogen Bonding

- Hydrogen bonding occurs when H in an X–H bond (X = N, O, F) is attracted to another very electronegative atom.

$$X–H\cdots Y \qquad (X = Y \text{ or } X \neq Y)$$
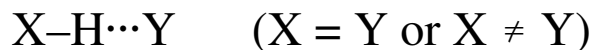
  - Weak hydrogen bonding may occur in cases such as HCN, HCl_2^-, etc.

- Most hydrogen bonding is weak (~4 – 40 kJ/mol), asymmetric, and nearly linear.
  - $O\cdots H$ bond in H_2O is $D \approx 21$ kJ/mol.
  - Strongest hydrogen bond is that in $F–H–F^-$ ($D \approx 212$ kJ/mol) in KHF_2, which is symmetrical and linear ($d_{HF} = 114.5$ pm).

- Most hydrogen bonds are a result of electrostatic attraction, but that in HF_2^- is better treated as a $3c$-$4e$ bond.


| Σ_g^+ | Σ_u^- | Σ_g^+ |
| bonding | nonbonding | antibonding |
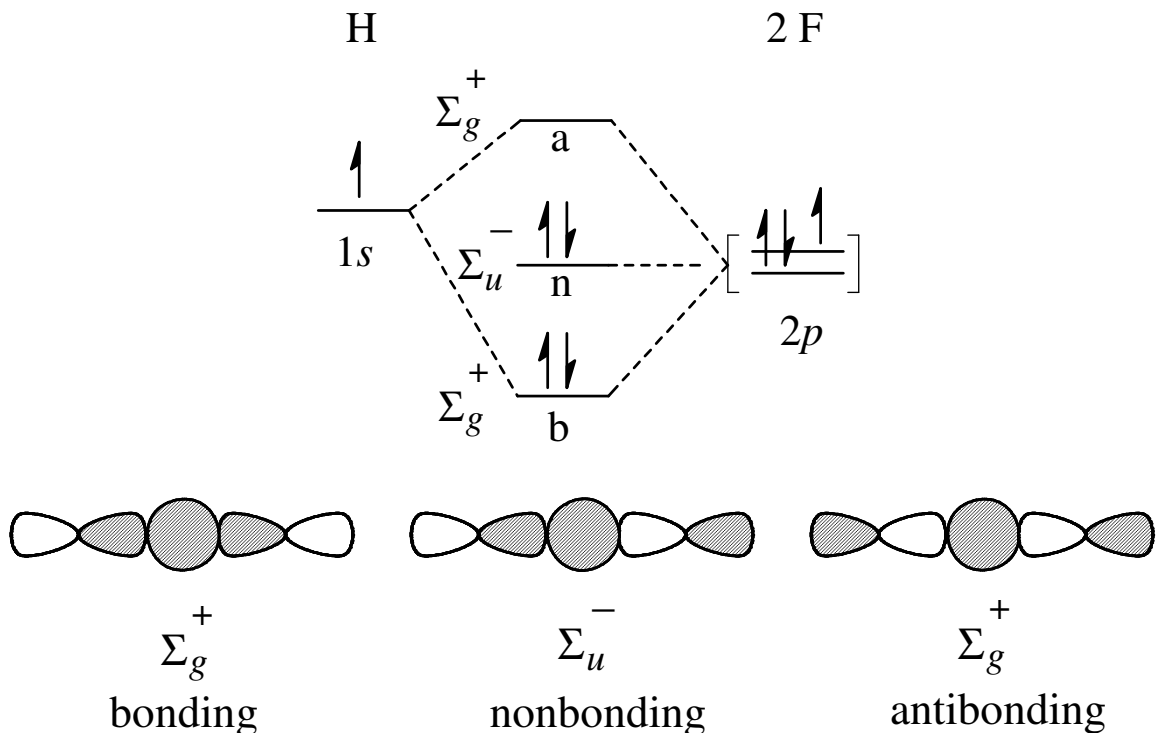
Physical Evidence of Hydrogen Bonding

1. X–Y distance much shorter than the sum of van der Waals radii.

   $r_{vw}(O) = 150$ pm $d_{O\text{-}O}(H_2O) = 276$ pm $< 2r_{vw}(O) = 300$ pm

2. X–H$\cdots$Y angle $\sim 109º - 180º$
   - Close to $180º$ is typical.

3. Changes in vibrational frequency
   - X–H stretch lowered (>100 cm^{-1}), broader, weaker
   - X–H bend raised

4. NMR changes
   - Line at lower field due to deshielding and inhibited electron circulation.
   - Line rises under bond breaking conditions (e.g., higher temperature, dilution)

5. Unusually high melting points, boiling points, and heats of vaporization.

Melting Points and Boiling Points of Molecular Hydrides
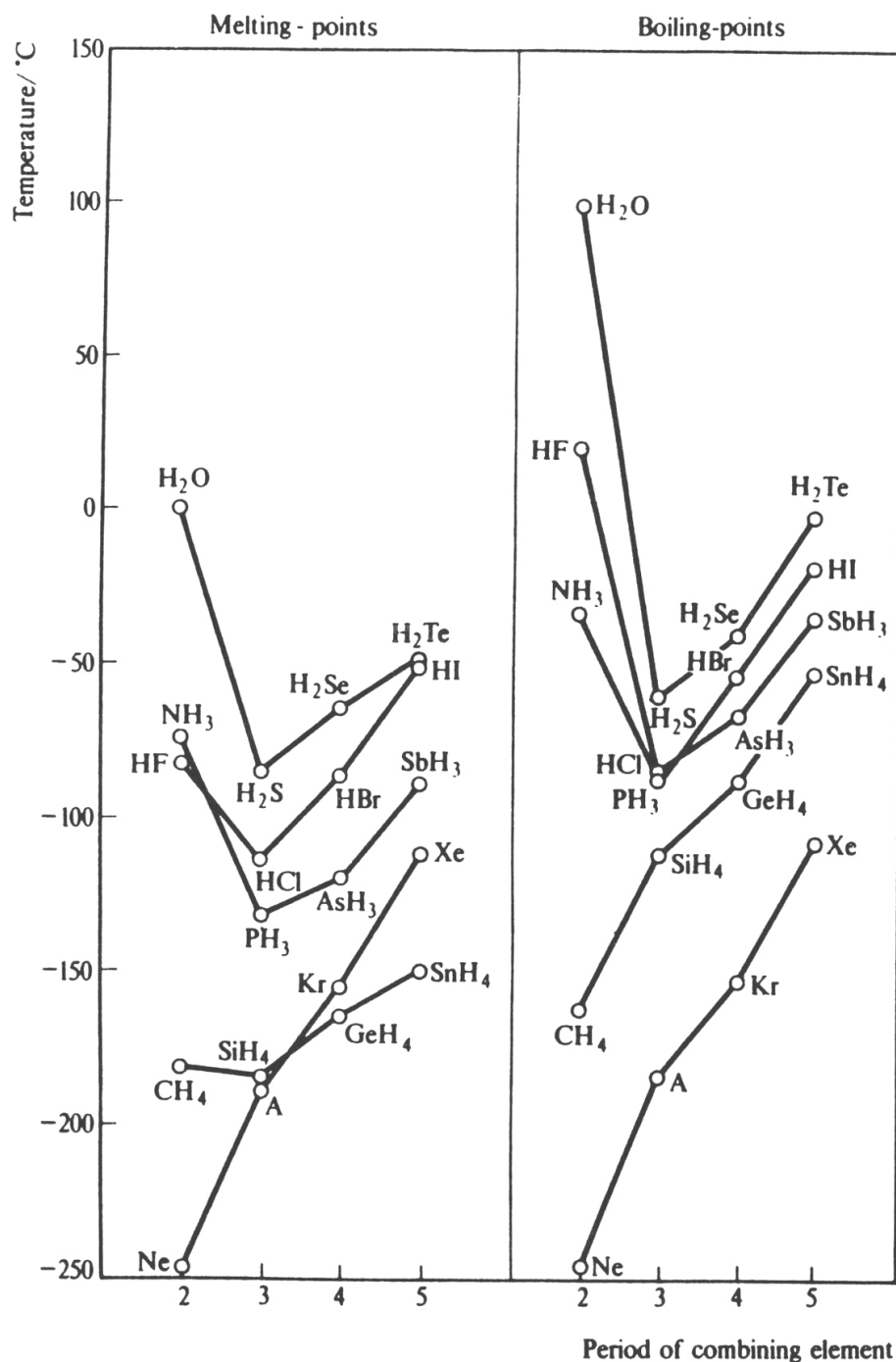
Melting- and boiling-points of the molecular hydrides and the noble gases. (After J.J. Lagowski (1973) *Modern Inorganic Chemistry*, Marcel Dekker, New York, p. 174.)
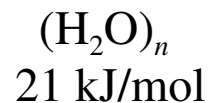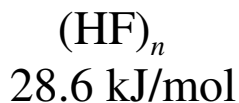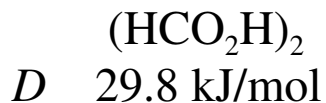
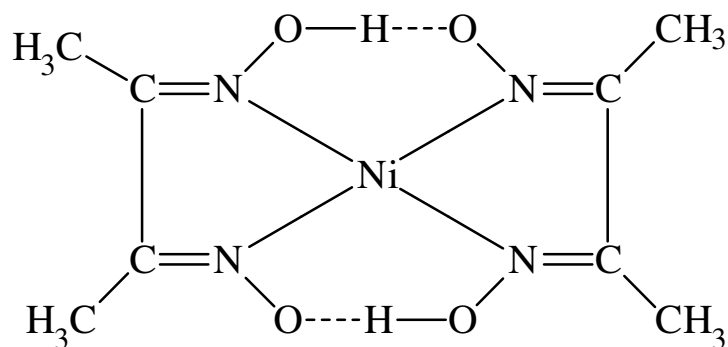# Enthalpies of Vaporization of Molecular Hydrides
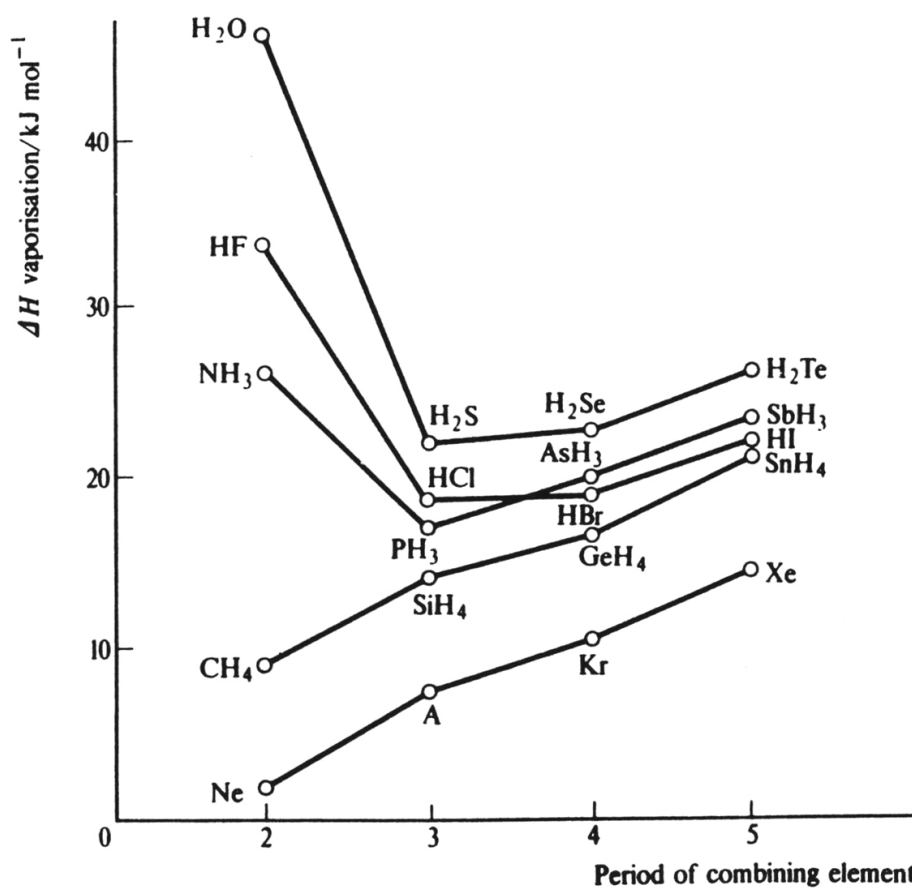
Enthalpies of vaporisation of molecular hydrides and noble gases at their boiling-points.

Intermolecular vs. Intramolecular Hydrogen Bonds

- Intermolecular hydrogen bonding (between molecules) is most common.

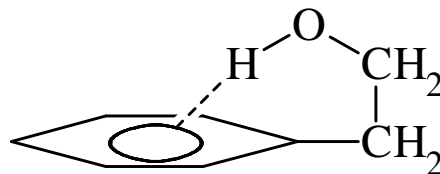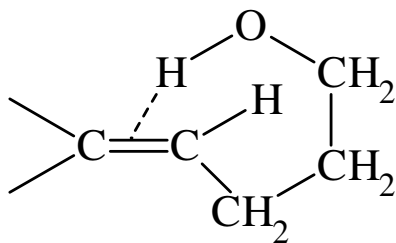| $(HCO_2H)_2$	$(HF)_n$	$(H_2O)_n$
D 29.8 kJ/mol	28.6 kJ/mol	21 kJ/mol

- Intramolecular cases are less common.

bis(dimethylglyoximato)nickel(II)

- A few cases of intramolecular bonds to polar double bonds or π-systems are known.

Water – Ice

- Water is extensively hydrogen bonded in both solid and liquid.

- Ice has at least nine structural modifications at various T and P conditions.

- At 0 ºC and 1 atm, the form is Ice I, an open structure built of puckered sheets of six-member oxygen rings held together by hydrogen bonds.
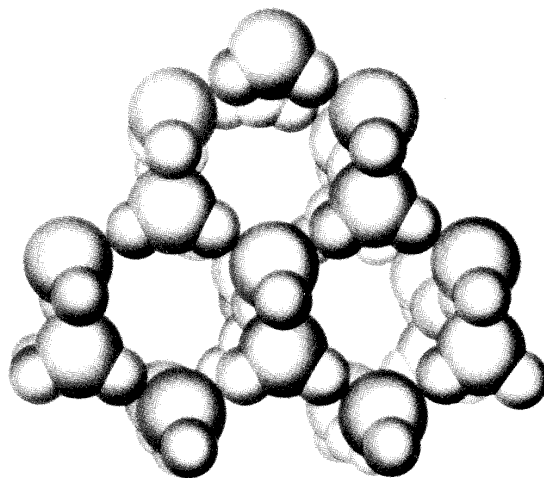
- Each O is tetrahedrally coordinated to four H atoms, two by hydrogen bonding and two by covalent bonding.

- Open shafts in Ice I make it less dense than liquid water, which is why ice floats on liquid water.

Water - Liquid

- Much of the solid structure is retained in liquid water.

- Short-range order exists, with non-network water in the interstices of the expanded network.

- Interstitial water makes the density greater than in ice.

- Maximum density occurs at 3.98 ºC.

Variation of Water Density with Temperature

Density (g/mL) vs **Deg C**
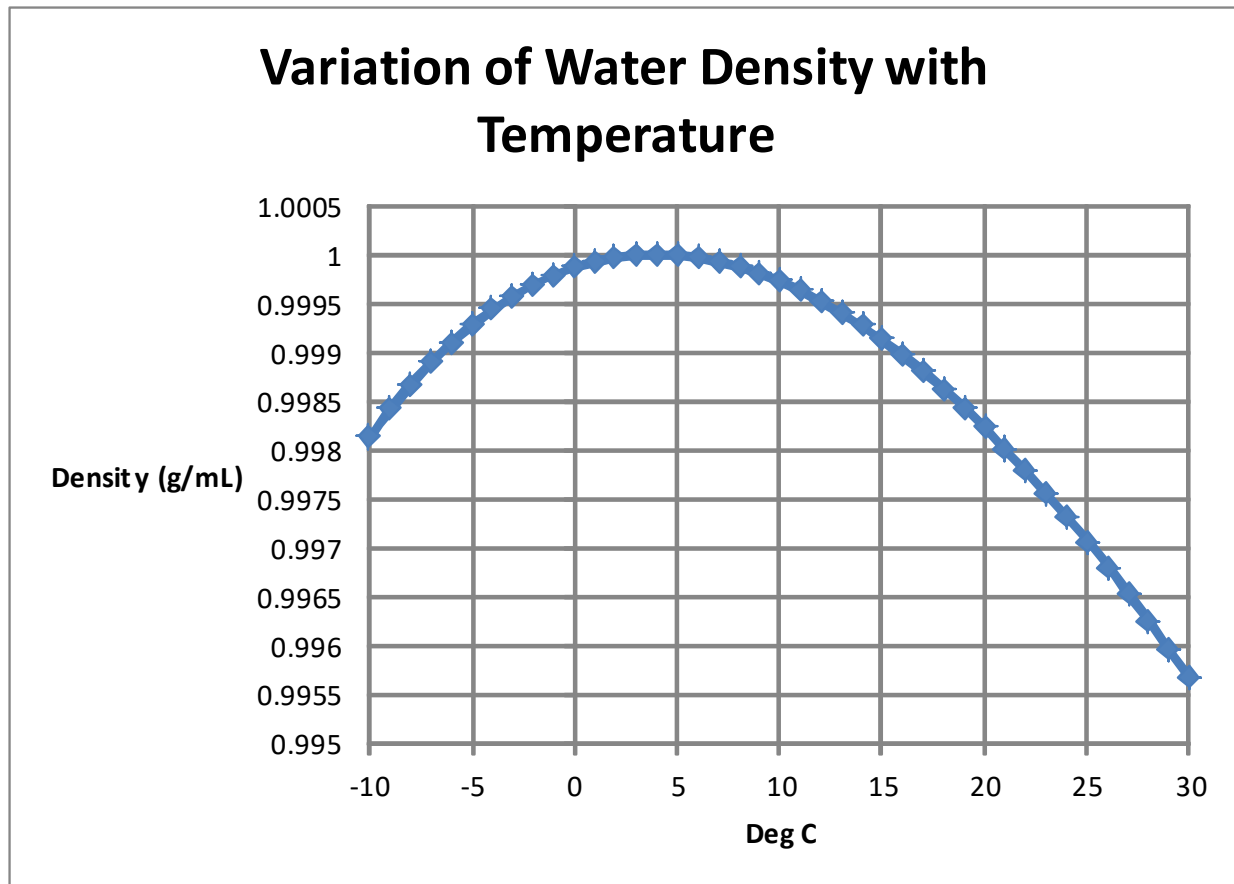
Hydroxonium Cations

- Hydronium ion exists mainly in aqueous solutions, but some ionic salts contain H_3O^+ and other hydroxonium ions.

- *p*-toluenesulfonic acid monohydrate is $[H_3O^+][CH_3C_6H_4SO_3^-]$.[1]

~C_{3v} H—O----H   O is 32.2 pm above 3H plane
         H
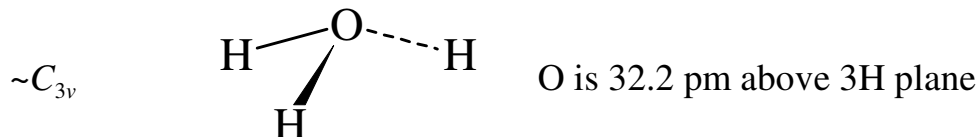
H–O (pm)	101.1	101.3	100.8
∠ H–O–H (º)	110.7	109.2	111.2

- $HClO_4 \cdot H_2O$ is $[H_3O^+][ClO_4^-]$, which is isomorphous with NH_4ClO_4.

- $H_5O_2^+$ exists in $HCl \cdot 2H_2O$, $HCl \cdot 3H_2O$, and $HClO_4 \cdot 2H_2O$.
    - Structurally, $H_5O_2^+$ is $H_2O \cdot H \cdot OH_2$, with short $O \cdots O$ distances (241-245 pm) and variable central H position from centrosymmetric $H_5O_2^+$ to the hydrate $H_3O^+ \cdot H_2O$.

- $HBr \cdot 4H_2O$ is actually $[H_7O_3^+][H_9O_4^+][Br^-]_2[H_2O]$.

- Higher hydronium ions can be considered to be H_3O^+ with one, two, or three waters of hydration.

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[1]Jan-Olof Lundgren and Jack M. Williams, *J. Chem. Phys.*, **1973**, *58*, 788.

Structure of $H_9O_4^+$ Cation[2]
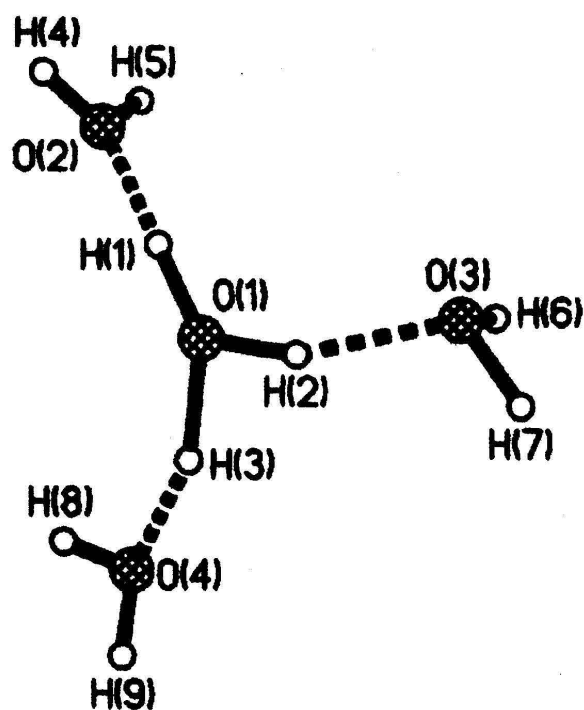
Structure of $H_9O_4^+$ in $[H_9O_4^+][CB_{11}H_6Br_6^-]$

distance	pm	angle	deg
O1···O2	250.5	O2–O1–O3	103.4
O1···O3	250.6	O2–O1–O4	117.0
O1···O4	253.2	O3–O1–O4	104.0

[2]Z. Xie, R. Bau, C. A. Reed, *Inorg. Chem.*, **1995**, *34*, 5403.