

Hard and Soft Acids and Bases

1965- Ralph Pearson introduced the hard-soft-acid-base (HSAB) principle.

“Hard acids prefer to coordinate the hard bases and soft acids to soft bases”

This very simple concept was used by Pearson to rationalize a variety of chemical information.

1983 – the qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability.

A less polarizable atom or ion is “hard” and a more easily polarized atom or ion is “soft”

The Quantitative Definition of hardness:

$$N = (\text{I.P.} - \text{E.A.}) / 2$$

The average of ionization potential and electron affinity

Actually, the electronegativity, X , of a neutral species is the same

$$X = (\text{I.P.} - \text{E.A.}) / 2$$

One can relate n (**hardness**) to the gap between the HOMO and LUMO:

$$2n = (E_{\text{LUMO}} - E_{\text{HOMO}})$$

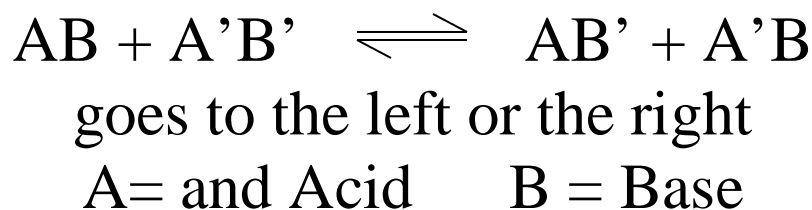
E (energy)

HOMO and LUMO orbitals (molecules) or simply highest occupied and lowest unoccupied orbitals in atoms participate in the bonding more than any other levels.

(The lower the energy of the HOMO and the higher the energy of the LUMO, the more stable the species is thermodynamically)

The greater the n value - the more hard the species is.

Basically, HSAB theory endeavors to help one decide if



Hard and Soft Acids and Bases

Hard acid: High positive charge
 Small size
 Not easily polarizable

Hard base: Low polarizability
 High electronegativity
 Not easily oxidized

Soft acid: Low positive charge
 Large size; easily oxidized
 Highly polarizable

Soft base: High polarizability
 Diffuse donor orbital
 Low electronegativity
 Easily oxidized

Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.

This statement is neither an explanation or a theory. It is simply a guideline that helps one to qualitatively predict the relative stability of acid-base adducts.

Lewis acids: A^+

Lewis bases: $B:$ or $B:^-$

A^{+n} the smaller and more highly charged, the harder it will be

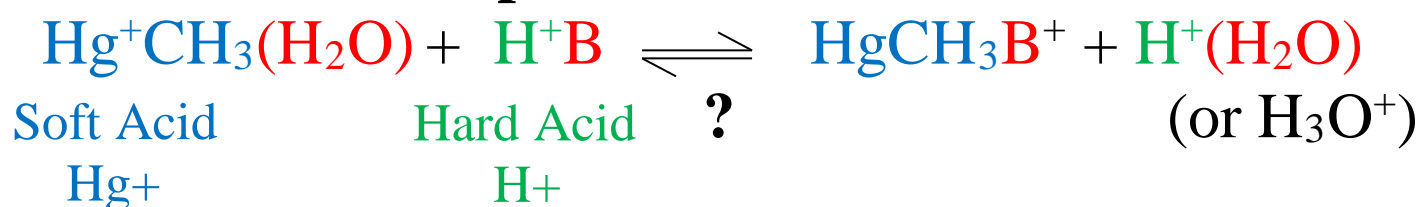
$B:$ or $B:^-$ the larger the atom (or ion) the softer it will be

Classification of hard and soft acids

Listings of hard and soft acids and bases are the result of observing the preferences for reactions to go to the right or left.

Example: a given base, B, may be classified as hard or soft based on the equilibrium:

This is how the Bases are ordered experimentally, namely comparing how the **Base, B, compares to the **Base H₂O** in a competition reaction**



There is a competition here between the acid **H⁺** and **CH₃Hg⁺** for **H₂O** as a base versus the new base **B**

If **B** is softer than H₂O then → to the right

If **B** is harder than H₂O then ← to the left

We look at the equilibrium constants to see if there is a tendency to proceed to the right or to the left

Reaction	<i>K</i>
1. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HF} \rightleftharpoons \text{CH}_3\text{HgF} + \text{H}_3\text{O}^+$	4.5×10^{-2}
2. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HCl} \rightleftharpoons \text{CH}_3\text{HgCl} + \text{H}_3\text{O}^+$	1.8×10^{12}
3. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HBr} \rightleftharpoons \text{CH}_3\text{HgBr} + \text{H}_3\text{O}^+$	4.2×10^{15}
4. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HI} \rightleftharpoons \text{CH}_3\text{HgI} + \text{H}_3\text{O}^+$	1×10^{18}
5. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}_3\text{O}^+$	5×10^{-7}
6. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{SH}^- \rightleftharpoons [\text{CH}_3\text{HgS}]^- + \text{H}_3\text{O}^+$	1×10^7
7. $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+ + \text{HSCN} \rightleftharpoons \text{CH}_3\text{HgSCN} + \text{H}_3\text{O}^+$	5×10^6


So this series of reaction Equilibrium Constants helps us to determine how H_2O ranks with respect to F^- , Cl^- , Br^- , I^- , OH^- , SH^- , SCN^-

Important to remember that the listings in the tables do not have a sharp dividing line between them. These terms, “hard” & “soft”, are relative

Some are borderline and even though within the same category are not all of the same degree of “hardness” and “softness”

e.g. although all alkali metals in ionic form M^+ are “hard”, the larger, more polarizable, Cs^+ ion is much softer than Li^+

- also N: compounds are not all equal

H_3N : versus  pyridine is much more polarizable

common
soft
species

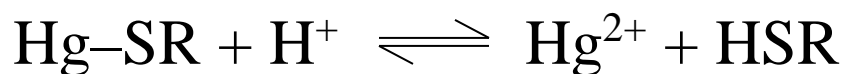
}

PR_3 , SR_2 , are “soft bases”
 Hg^{2+} , Pd^{2+} , Pt^{2+} are soft acids

common
hard
species

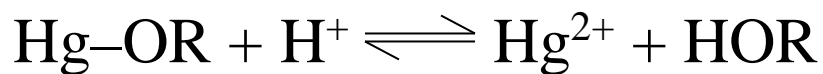
}

NH_3 , ROH , H_2O are “hard” bases
 Ti^{4+} , Si^{4+} , Co^{3+} are “hard acids”

RS⁻ versus RO⁻

does this reaction proceed to the left or right?

LEFT because **SR⁻** is soft and **Hg⁺** is soft



left or right?

RIGHT because **OR⁻** is hard and **H⁺** is hard

Table 7.6 Classification of hard and soft acids

Hard acids

H^+ , Li^+ , Na^+ , K^+ (Rb^+ , Cs^+)
 Be^{+2} , $Be(CH_3)_2$, Mg^{+2} , Ca^{+2} , Sr^{+2} (Ba^{+2})
 Sc^{+3} , La^{+3} , Ce^{+4} , Gd^{+3} , Lu^{+3} , Th^{+4} , U^{+4} , UO_2^{+2} , Pu^{+4}
 Ti^{+4} , Zr^{+4} , Hf^{+4} , VO^{+2} , Cr^{+3} , Cr^{+6} , MoO^{+3} , WO^{+4} , Mn^{+2} , Mn^{+7} , Fe^{+3} , Co^{+3}
 BF_3 , BCl_3 , $B(OR)_3$, Al^{+3} , $Al(CH_3)_3$, $AlCl_3$, AlH_3 , Ga^{+3} , In^{+3}
 CO_2 , RCO^+ , NC^+ , Si^{+4} , Sn^{+4} , CH_3Sn^{+3} , $(CH_3)_2Sn^{+2}$
 N^{+3} , RPO_2^+ , $ROPO_2^+$, As^{+3}
 SO_3 , RSO_2^+ , $ROSO_2^+$
 Cl^{+3} , Cl^{+7} , I^{+5} , I^{+7}
 HX (hydrogen-bonding molecules)

Borderline acids

Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2}
 Rh^{+3} , Ir^{+3} , Ru^{+3} , Os^{+2}
 $B(CH_3)_3$, GaH_3
 R_3C^+ , $C_6H_5^+$, Sn^{+2} , Pb^{+2}
 NO^+ , Sb^{+3} , Bi^{+3}
 SO_2

Soft acids

$Co(CN)_5^{-3}$, Pd^{+2} , Pt^{+2} , Pt^{+4}
 Cu^+ , Ag^+ , Au^+ , Cd^{+2} , Hg^+ , Hg^{+2} , CH_3Hg^+
 BH_3 , $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3 , Tl^+ , $Tl(CH_3)_3$
 CH_2 , carbenes
 Pi-acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, *etc.*
 HO^+ , RO^+ , RS^+ , RSe^+ , Te^{+4} , RTe^+
 Br_2 , Br^+ , I_2 , I^+ , ICN , *etc.*
 O , Cl , Br , I , N , $RO\cdot$, $RO_2\cdot$
 M^0 (metal atoms) and bulk metals

Table 7.7 Classification of hard and soft basesHard Bases

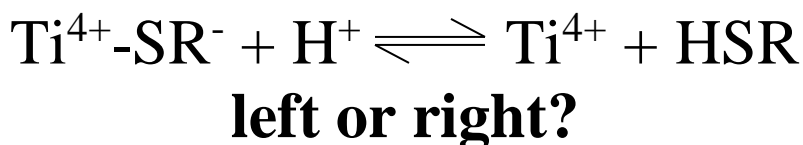
NH_3 , RNH_2 , N_2H_4
 H_2O , OH^- , O^{2-} , ROH , RO^- , R_2O
 CH_3COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^-
 F^- (Cl^-)

Borderline bases

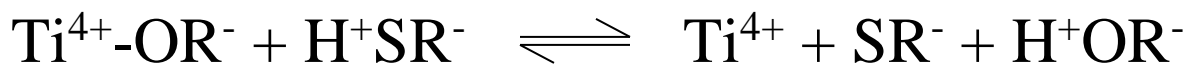
$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, N_3^- , N_2
 NO_2^- , SO_3^{2-}
 Br^-

Soft bases

H^-
 R^- , C_2H_4 , C_6H_6 , CN^- , RNC , CO
 SCN^- , R_3P , $(\text{RO})_3\text{P}$, R_3As
 R_2S , RSH , RS^- , $\text{S}_2\text{O}_3^{2-}$
 I^-



Remember it is all relative



Ti^{4+} is hard and OR^- is hard

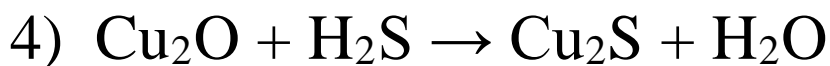
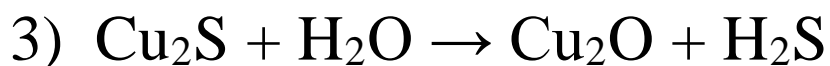
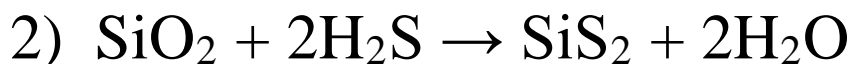
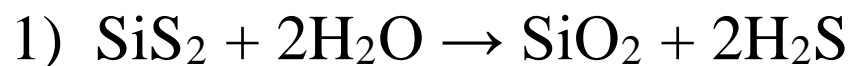
H^+ is hard but not as hard as Ti^{4+} because of charge and OR^- is hard

So reaction tends to the LEFT

Predict which way the following reactions will go.



How about the following?



Which ones will proceed as written?

R (1) Si^{4+} (hard) S^{2-} (soft) O^{2-} (hard) H^+ (hard)

L (2) Si^{4+} (hard) O^{2-} (hard)

L (3) Cu^+ (soft) S^{2-} (soft) O^{2-} (soft)

R (4) Cu^+ (hard) S^{2-} (soft) O^{2-} (hard)

(1) and (4) will proceed as written

Hydrogen: It's compounds and Selected Uses

Hydrogen is a very important element. Not only does it combine with carbon to give numerous organic compounds, but also serves as a fuel and as a reducing agent for both metal-oxides and non-metals. Hydrogen forms more compounds than any other element, including carbon!

Some Physical Properties

Hydrogen is the lightest element. It boils at -225.8°C . The bond dissociation energy $\text{H-H} \rightarrow \text{H} + \text{H}$ is 104.4 kcal/mole. The molecule is thus very thermally stable. At a temperature of 1727°C only 1% of H_2 molecules in a sample of the gas will be dissociated to atoms.

Isotopes of Hydrogen

Hydrogen has three isotopes: **hydrogen** (^1H); **deuterium** (^2H or **D**) and **tritium** (^3H or **T**).

Deuterium, a natural isotope of hydrogen sometimes labeled D, has one neutron in addition to the one electron and one proton present in "normal" hydrogen.

It is present in seawater, for example, as D_2O or HDO ; the ratio of D:H being 1:5000.

The other isotope of hydrogen, tritium, is sometimes depicted as T. It has two neutrons in addition to the one electron and one proton. Tritium is radioactive and does not exist in nature. The diatomics that are possible are H_2 , D_2 , T_2 , HD , HT , DT .

The two hydrogen isotopes play a very important role in nuclear fusion reactions which release a very large amount of energy, which if harnessed, can replace conventional fuels.

In nuclear reactions the energy released is given per atom rather than per mole as in chemical reactions. One $ev/atom$ is equal to 23.06 $kcal/mole$. The fusion reaction between D and T is the basis for the hydrogen bomb. It produces 4He and a neutron along with the 17.6 Mev of energy. This weapon requires the use of an atomic bomb (fission reaction) as a detonator to establish momentary temperatures of up to one million degrees to get the fusion reaction going.

Attempts have been made to fuse two deuterium atoms (obtained from seawater) to yield useful energy. It is doubtful that such energy will become available for everyday use in this century, but the available fuel supplies of oil and coal can be expected to be exhausted sometime in the future if other energy substitutes are not found. Note that the population of this Earth was 2.4 billion in 1944 and is ~7.7 billion. The necessity for alternate sources of energy is thus obvious. The possibility for obtaining energy from fusion reactions appears to be good even though it may turn out to be expensive. It should be realized that if it can be harnessed by fusion, the energy contained in one cubic kilometer of seawater is equivalent to the world's total supply of petroleum!!

One type of nuclear fusion device

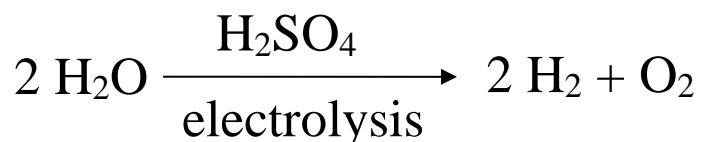
A **tokamak** (Russian: Токама́к) is a device which uses a powerful magnetic field to confine a hot plasma in the shape of a torus. The tokamak is one of several types of magnetic confinement devices being developed to produce controlled thermonuclear fusion power. As of 2016, it is the leading candidate for a practical fusion reactor (a **torus** is a surface of revolution generated by revolving a circle in three-dimensional space about an axis that is coplanar with the circle.)

Preparation of Hydrogen

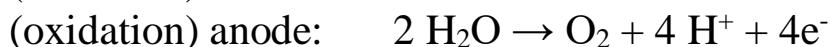
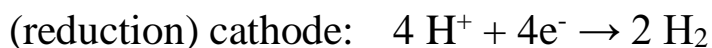
Hydrogen is expensive to prepare. It is prepared by **electrolysis of water**, a process that requires the use of expensive electricity. Research has been going on for many years to develop methods of obtaining hydrogen by the splitting of water using light energy, but the long term practicality of this procedure has yet to be established.

Electrolysis. For electrolysis to occur, an electrolyte (i.e., ions) must be present in the water. Sulfuric acid can be used for this purpose. Illustrative reactions are shown below.

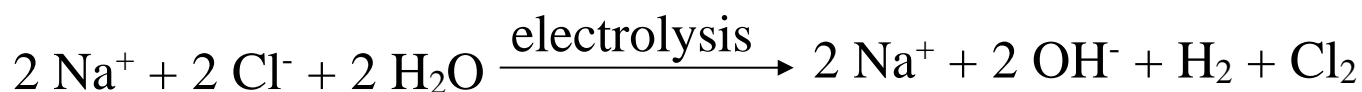
1. Electrolysis of Water:



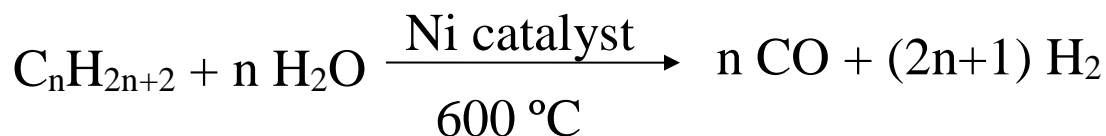
The half reactions are:



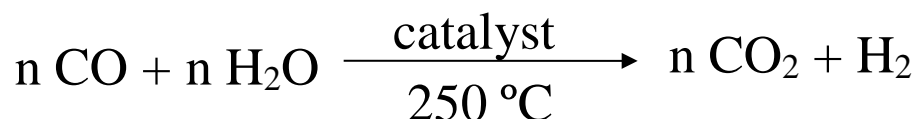
2. Electrolysis of Brine (an aqueous NaCl Solution):



3. Steam Reforming of Hydrocarbons:



The CO thus produced also can be further converted to hydrogen by the **water-gas shift reaction**:



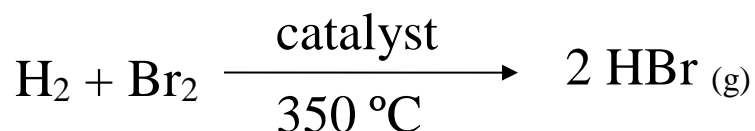
The CO₂/H₂ product is bubbled through water leaving hydrogen behind. (The CO₂ is soluble in H₂O). Any untreated CO cannot be allowed to escape in the atmosphere as it is very toxic, so the water-gas shift reaction must be made to go to completion.

The hydrocarbons used for steam reforming are CH₄ (methane) and C₂H₆ (ethane).

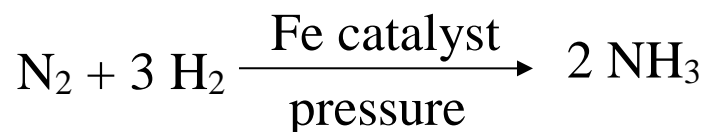
Reactions of Hydrogen

Some important reactions that involve hydrogen and illustrate its reactivity are:

1. Preparation of HBr



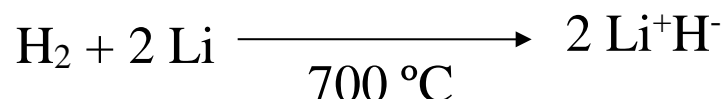
2. Preparation of Ammonia (Haber-Bosch Process)



The conversion of N_2 per pass is only 17% because of inefficiency of the reaction in spite of the catalysis. The unreacted gases are recirculated. It is noteworthy that the conversion per pass was 15% when this process was first invented in 1915. Evidently not much has changed since then...

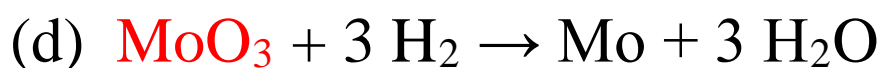
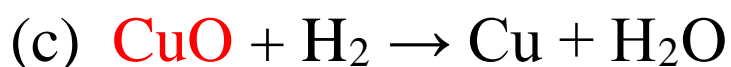
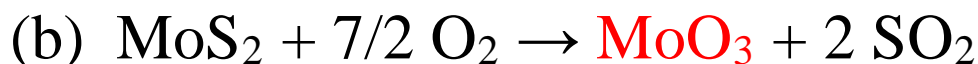
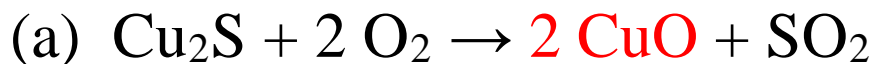
Ammonia is one of the most highly produced inorganic chemicals. There are numerous large-scale ammonia production plants worldwide, producing a total of 175 million tons of ammonia in 2016. China produced 31.9% of the worldwide production, followed by Russia with 8.7%, India with 7.5%, and the United States with 7.1%. 80% or more of the ammonia produced is used for fertilizing agricultural crops. Ammonia is also used for the production of plastics, fibers, explosives, nitric acid and intermediates for dyes and pharmaceuticals.

3. Formation of Hydrides



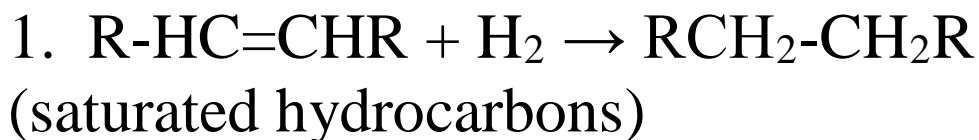
LiH is a white crystalline solid that melts at 680°C .

4. Isolation of Pure Metals from Ores by Reduction with H₂

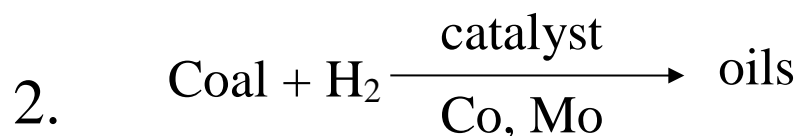


Molybdenum (Mo) is used in special steels where strength and corrosion resistance are required.

5. Hydrogenation Reactions



The hydrogenation of double bonds, which occur in vegetable oils, yields solid fats (i.e. Crisco).



6. CO + H₂ Synthesis Reactions

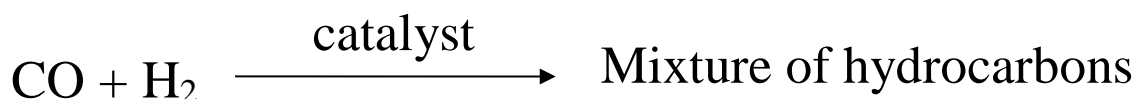
Synthesis gas which is a mixture of CO and H₂ is obtained from coal and can be converted to organic compounds.

Exemplary reactions are:



Methanol added to gasoline increases its octane value

7. Fischer-Tropsch (FT) Synthesis



Catalysts: Co, Fe, Mo

This process was used by Germany during World War II to manufacture gasoline from coal.

Compounds of Hydrogen that contain one other element (compounds with only two element types are called **Binary Compounds**)

1. Ionic or salt-like hydrides

Na⁺H⁻ contains the hydride ion H⁻

2. Molecular or Covalent hydrides



3. Interstitial Hydrides

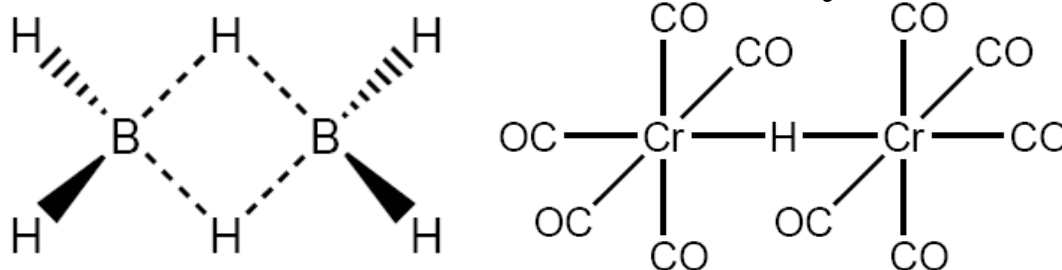
Interstitial hydrides are compounds prepared by absorption of H_2 into transition element metals or alloys. The hydrogen is usually present in the atomic form as H_2 . These hydrides can be used for the storage of hydrogen (fuel storage) because the H_2 can be easily liberated by heat. Typical examples are $\text{TiH}_{1.7}$ and LaNi_5H_6 .

It turns out that more hydrogen can be stored in such hydrides on a volume basis than by liquefying hydrogen.

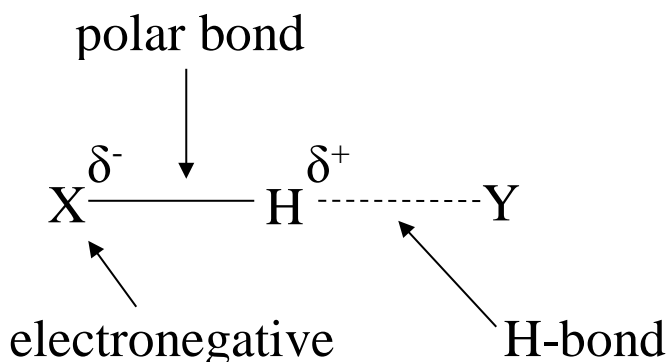
Bonding features of Hydrogen

(1) Numerous M_xH_y hydride materials are known that are often non-stoichiometric

(2) Formation of 3-center bonds via Hydride bridges



(3) The Hydrogen Bond

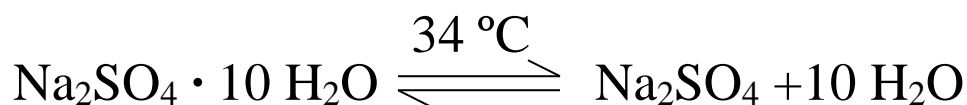


Largely Electrostatic between Y and H

Bottom Line:

Main chemistry is loss of an electron to give H^+ and gain of an electron to give H^-

(4) Water of Crystallization – Hydrates. In some compounds, water is an integral part of the crystalline material as indicated below.



This reversible adsorption accounts for the desiccant (dehydrating) action of anhydrous sodium sulfate. The interaction between water and the Na^+ or $[SO_4]^{2-}$ ion within the crystal is weak, thus water evolution can occur at a low temperature.

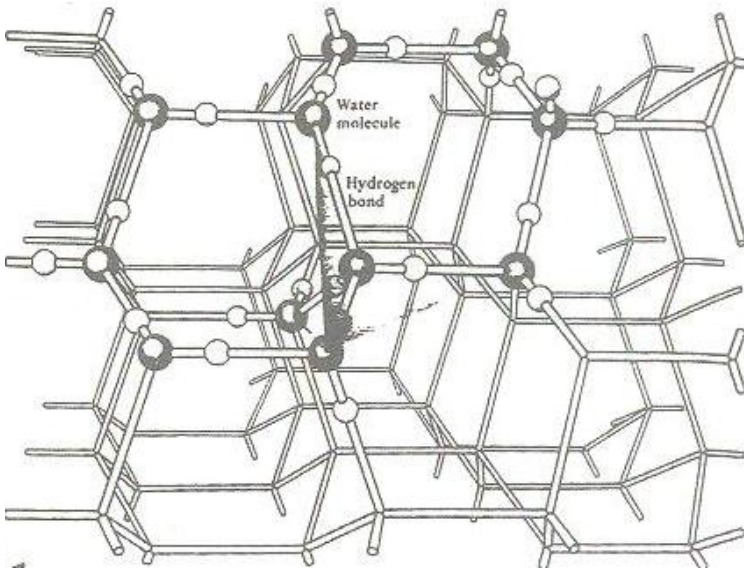
(5) Coordinate Covalent Bonding. Water can form coordinate covalent bonds in a number of metal salts, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Anhydrous copper sulfate is white but the penthydrate is blue due to the coordination of water molecules about the copper atom. In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, four water molecules are bonded with the water coordinated onto the cupric ion. It is thus properly formulated as $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$. Copper sulfate pentahydrate becomes anhydrous (loses all its water) at temperatures above $250\text{ }^\circ\text{C}$ (as opposed to $100\text{ }^\circ\text{C}$ or $217\text{ }^\circ\text{C}$) because it is much more difficult to release H_2O coordinated to a metal!)

The acidic behavior in water solutions of some metal salts can be explained by the strong coordination of water to the metal atom. For example, aluminum nitrate hexahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, is best represented by the formula $[\text{Al}(\text{H}_2\text{O})_6](\text{NO}_3)_3$. The six water molecules form six strong Al-O bonds. The acidic behavior of this compound results from the hydrolysis of the hydrated aluminum ion:

Hydrolysis:



Ice I Tetrahedral O atom arrangements

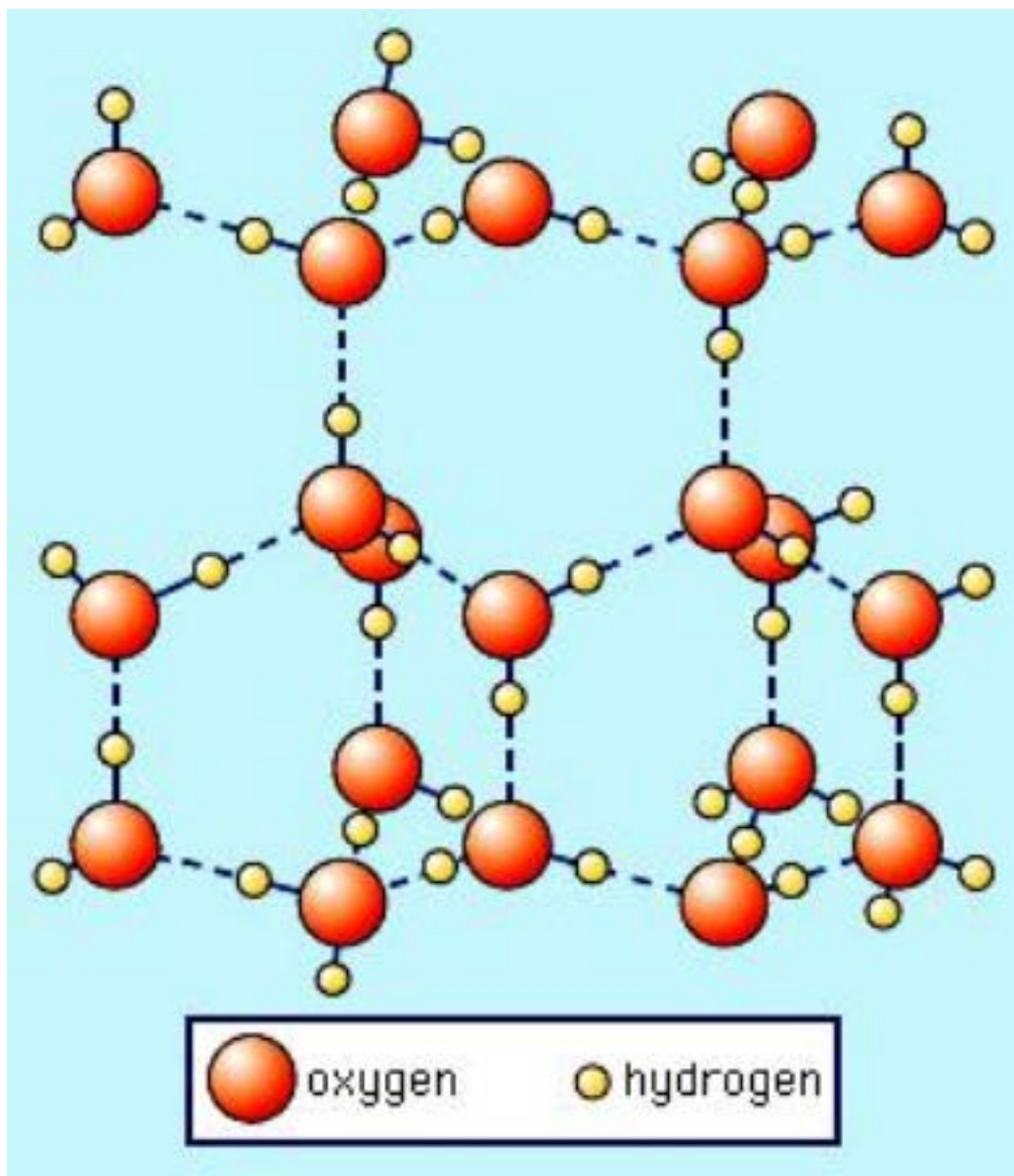


There are at least eighteen crystalline phases (where the oxygen atoms are in fixed positions relative to each other, but the hydrogen atoms may or may not be disordered, and three amorphous (non-crystalline) phases

Hydrogen Bonding in Ice

In the solid state (**ice**), intermolecular interactions lead to a highly ordered but loose **structure** in which each oxygen atom is surrounded by four hydrogen atoms; two of these hydrogen atoms are covalently bonded to the oxygen atom, and the two others (at longer distances) are hydrogen bonded to the oxygen atoms

Why is water more dense than Ice?



This is an image of the hexagonal crystalline form of ordinary ice (Ice I/h) taken from S.S. Zumdahl, Chemistry, 3rd ed., copyright © 1993 by D.C. Heath and Company:

O---O distances are 2.75\AA

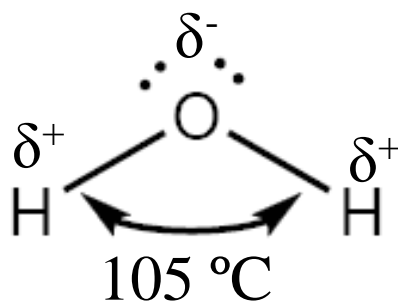
The dashed lines represent hydrogen bonds. Liquid water actually has a similar "open" structure also due to hydrogen bonding. But in the case of liquid water, the hydrogen bonds are not rigid and semi-permanent as in ice. So imagine that in the image above, the hydrogen bonding network collapses. This is what happens when enough thermal energy is present to break the rigid hydrogen bonds resulting in melting. Clearly, once this crystalline structure is no longer forced into place by the rigid hydrogen bonding in ice, it can collapse into itself, resulting a greater density of water molecules.

Thus the liquid form of water, although engaged in transient hydrogen bonding, is not as open and expanded as when held into it's solid form by the rigid, semi-permanent hydrogen bonding.

Water

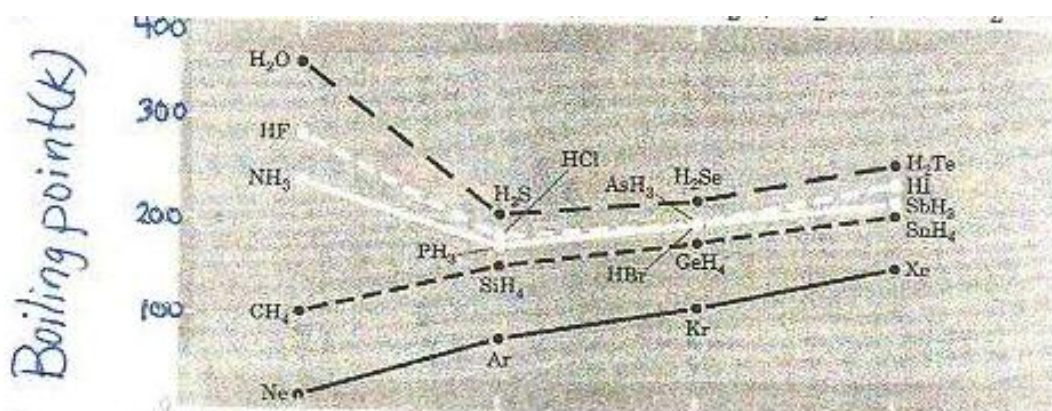
Water is a most abundant and interesting compound. This supplement to the notes emphasizes some of its important properties.

Bonding Aspects. Because of the electronegativity difference between hydrogen and oxygen, the O-H bonds in water are highly polar. The δ in the diagram below indicates a partial charge.



The H-O-H angle is 105°. We can think of water as having two lone pairs of electrons on the oxygen atom. The resulting repulsion between these electron pairs and the two O-H bond electron pairs would then cause the H-O-H angle to be less than tetrahedral (109.5°).

Hydrogen Bonding. Several of the properties of water can be attributed to its ability to form extensive hydrogen bonding in the solid and liquid phases. Only the gaseous phase can exist as discrete molecules. In the solid and liquid phases, aggregates are held together in the three-dimensional network by 1.77Å. Hydrogen bonds are weak in comparison to normal covalent bonds (8-34 kJ/mole), and vary in strength from molecule to molecule. The H-bond in water is 21 kJ/mole and is directional; that is, it is usually between a lone pair of electrons on an atom of one molecule and the positive pole of another molecule. Hydrogen Bonding plays a vital role in biological processes, especially in holding protein structures intact, and it is responsible for the high boiling point of water. We can obtain the boiling point of water as a function of molecular weight in the absence of hydrogen bonding from a plot of the boiling points of its congeners, H₂S, H₂Se, and H₂Te.



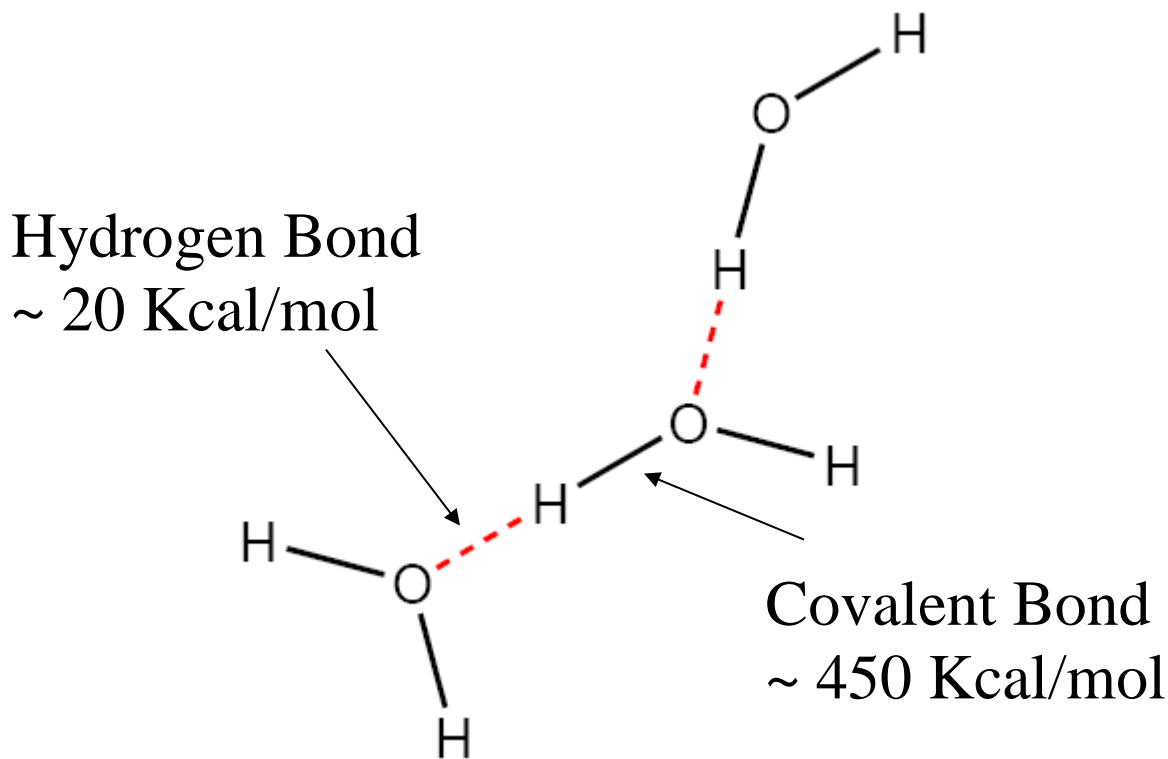
Appropriate data for such a plot are: Mol. Wt. Compound b.p.(°C)

18	H ₂ O	100
34	H ₂ S	-60.3
81	H ₂ Se	-41.3
129.6	H ₂ Te	-2

The boiling points of H₂S, H₂Se, and H₂Te increase with increasing molecular weight, but the b.p. of water is some 200°C higher than that expected (-90°C) by extrapolation. Hydrogen bonding is almost negligible in H₂S, H₂Se, and H₂Te, mostly because of the large size of the central atom.

Hydrogen Bonding in water gives it very special properties

1. Very high boiling point
2. VERY LOW DENSITY OF SOLID FORM (ICE)
3. “Glue” for proteins and DNA



Bottom Line: LIFE AS WE KNOW IT WOULD NOT EXIST WITHOUT HYDROGEN BONDING!

WHY?

H₂O would be a gas at room temperature (we would not be here!)

H₂O solid (ice) would not float – lakes would freeze from the bottom up and aquatic life would not be capable of existing.

Water-Containing Compounds. Water is known to form hydrates and compounds called clathrates with various elements.

(a) Clathrate Compounds. Clathrates are cage-like compounds of water in which other molecules or atoms can be trapped. For example, Xenon forms compounds of the composition $\text{Xe} \cdot 7.3 \text{H}_2\text{O}$, and chlorine $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$. Water in the solid state forms pockets or cage-like holes where the Xe atoms and Cl_2 molecules fit.

Hydrocarbons like methane, CH_4 , and butane, C_4H_{10} , also form clathrate compounds with water. It is presently believed that xenon and chloroform (CHCl_3) act as anesthetics by forming clathrate compounds with water within connecting parts of the nervous system, thus blocking the transmission of pain. It is also believed that methane gas is trapped under the sea by forming clathrate compounds with water.

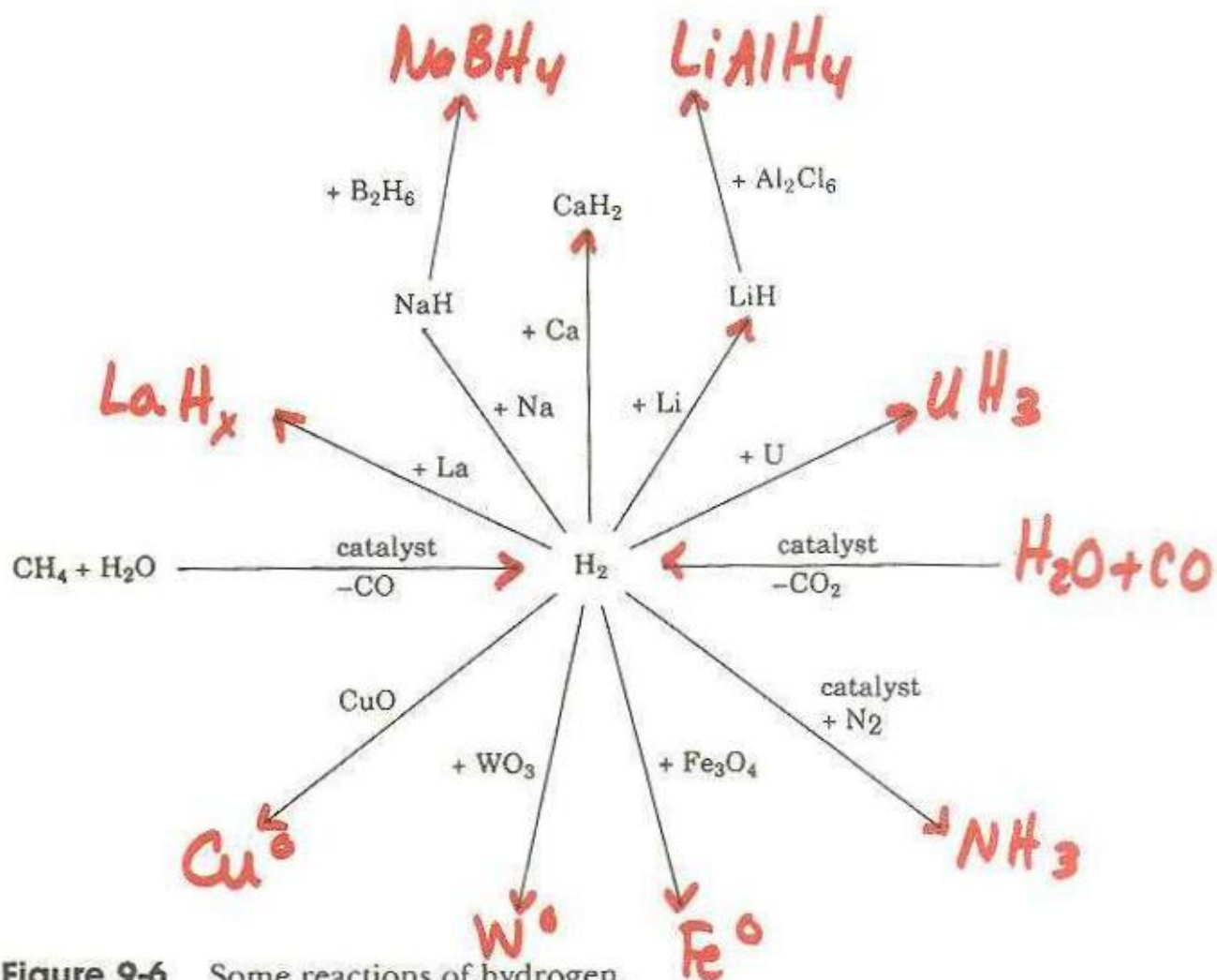


Figure 9-6 Some reactions of hydrogen.