

Hydrides

In chemistry, a **hydride** is the anion of hydrogen, H^- , or, more commonly, it is a compound in which one or more hydrogen centres have nucleophilic, reducing, or basic properties. In compounds that are regarded as hydrides, the hydrogen atom is bonded to a more electropositive element or group. Compounds containing hydrogen bonded to metals or metalloid may also be referred to as hydrides, even though in this case the hydrogen atoms can have a protic¹ character. Almost all of the elements form binary compounds with hydrogen, the exceptions being He, Ne, Ar, Kr, Pm, Os, Ir, Rn, Fr, and Ra

Bonds

Bonds between hydrogen and other elements range from highly to somewhat covalent. Some hydrides, e.g. boron hydrides, do not conform to classical electron-counting rules, and the bonding is described in terms of multi-centered bonds, whereas the interstitial hydrides often involve metallic bonding. Hydrides can be discrete molecules, oligomers or polymers, ionic solids, chemisorbed monolayers, bulk metals (interstitial), and other materials. While hydrides traditionally react as Lewis bases or reducing agents, some metal hydrides behave as hydrogen-atom donors and as acids.

Applications

- Hydrides such as sodium borohydride, lithium aluminium hydride, diisobutylaluminium hydride (DIBAL) and super hydride, are commonly used as reducing agents in chemical synthesis. The hydride adds to an electrophilic center, typically unsaturated carbon.
- Hydrides such as sodium hydride and potassium hydride are used as strong bases in organic synthesis. The hydride reacts with the weak Bronsted acid releasing H_2 .
- Hydrides such as calcium hydride are used as desiccants, i.e. drying agents, to remove trace water from organic solvents. The hydride reacts with water forming hydrogen and hydroxide salt. The dry solvent can then be distilled or vac transferred from the "solvent pot".

- Hydrides are important in storage battery technologies such as Nickel-metal hydride battery. Various metal hydrides have been examined for use as a means of hydrogen storage for fuel cell-powered electric cars and other purposed aspects of a hydrogen economy.
- Hydride complexes are catalysts and catalytic intermediates in a variety of homogeneous and heterogeneous catalytic cycles. Important examples include hydrogenation, hydroformylation, hydrosilylation, hydrodesulfurization catalysts. Even certain enzymes, the hydrogenase, operate via hydride intermediates. The energy carrier NADH reacts as a hydride donor or hydride equivalent

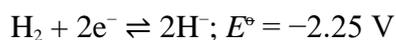
Hydride ion

Free hydride anions exist only under extreme conditions and are not invoked for homogeneous solution. Instead, many compounds have hydrogen centres with hydridic character.

Aside from electride, the hydride ion is the simplest possible anion, consisting of two electrons and a proton. Hydrogen has a relatively low electron affinity, 72.77 kJ/mol and reacts exothermically with protons as a powerful Lewis base.



The low electron affinity of hydrogen and the strength of the H–H bond ($\Delta H_{\text{BE}} = 436 \text{ kJ/mol}$) means that the hydride ion would also be a strong reducing agent



Types of hydrides

According to the general definition every element of the periodic table (except some noble gases) forms one or more hydrides. These substances have been classified into three main types according to the nature of their bonding

Ionic hydrides, which have significant ionic bonding character.

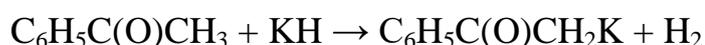
Covalent hydrides, which include the hydrocarbons and many other compounds which covalently bond to hydrogen atoms.

Interstitial hydrides, which may be described as having metallic bonding.

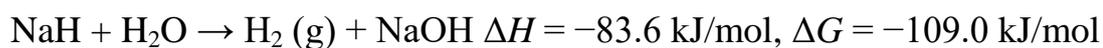
While these divisions have not been used universally, they are still useful to understand differences in hydrides.

Ionic hydrides

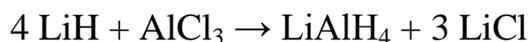
Ionic or saline hydride, is a hydrogen atom bound to an extremely electropositive metal, generally an alkali metal or alkaline earth metal. In these materials the hydrogen atom is viewed as a pseudohalide. Saline hydrides are insoluble in conventional solvents, reflecting their nonmolecular structures. Most ionic hydrides exist as "binary" materials involving only two elements including hydrogen. Ionic hydrides are used as heterogeneous bases and reducing reagents in organic synthesis.



Typical solvents for such reactions are ethers. Water and other protic solvents cannot serve as a medium for ionic hydrides because the hydride ion is a stronger base than hydroxide and most hydroxyl anions. Hydrogen gas is liberated in a typical acid-base reaction.



Often alkali metal hydrides react with metal halides. Lithium aluminium hydride (often abbreviated as LAH) arises from reactions of lithium hydride with aluminium chloride.



Covalent hydrides

According to some definitions, covalent hydrides cover all other compounds containing hydrogen. Some definitions limit hydrides to hydrogen centres that formally react as hydrides, i.e. are nucleophilic, and hydrogen atoms bound to metal centers. These hydrides are formed by all the true non-metals (except zero group elements) and the elements like Al, Ga, Sn, Pb, Bi, Po, etc., which are normally metallic in nature, i.e., this class includes the hydrides of p-block elements. In these substances the hydride bond is formally a covalent bond much like the bond made by a proton in a weak acid. This category includes hydrides that exist as discrete molecules, polymers or oligomers, and hydrogen that has been chemisorbed to a surface. A particularly important segment of covalent hydrides are complex metal hydrides, powerful soluble hydrides commonly used in synthetic procedures.

Molecular hydrides often involve additional ligands such as, diisobutylaluminium hydride (DIBAL) consists of two aluminum centers bridged by hydride ligands. Hydrides that are soluble in common solvents are widely used in organic synthesis. Particularly common are sodium borohydride (NaBH_4) and lithium aluminium hydride and hindered reagents such as DIBAL.

Interstitial hydrides or metallic hydrides

Interstitial hydrides most commonly exist within metals or alloys. They are traditionally termed 'compounds', even though they do not strictly conform to the definition of a compound; more closely resembling common alloys such as steel. In such hydrides, hydrogen can exist as either atomic, or diatomic entities. Mechanical or thermal processing, such as bending, striking, or annealing may cause the hydrogen to precipitate out of solution, by degassing. Their bonding is generally considered metallic. Such bulk transition metals form interstitial binary hydrides when exposed to hydrogen. These systems are usually non-stoichiometric, with variable amounts of hydrogen atoms in the lattice. In materials engineering, the phenomenon of hydrogen embrittlement results from the formation of interstitial hydrides. Hydrides of this type form according to either one of two main mechanisms. The first mechanism involves the adsorption of dihydrogen, succeeded by the cleaving of the H-H bond, the delocalisation of the hydrogen's electrons, and finally, the diffusion of the protons into the metal lattice. The other main mechanism involves the electrolytic reduction of ionised hydrogen on the surface of the metal lattice, also followed by the diffusion of the protons into the lattice. The second mechanism is responsible for the observed temporary volume expansion of certain electrodes used in electrolytic experiments.

Palladium absorbs up to 900 times its own volume of hydrogen at room temperatures, forming palladium hydride. This material has been discussed as a means to carry hydrogen for vehicular fuel cells. Interstitial hydrides show certain promise as a way for safe hydrogen storage. During last 25 years many interstitial hydrides were developed that readily absorb and discharge hydrogen at room temperature and atmospheric pressure. They are usually based on intermetallic compounds and solid-solution alloys. However, their application is still limited, as they are capable of storing only about 2 weight percent of hydrogen, insufficient for automotive applications.

Transition metal hydride complexes

Transition metal hydrides include compounds that can be classified as *covalent hydrides*. Some are even classified as interstitial hydrides and other bridging hydrides. Classical transition metal hydride feature a single bond between the hydrogen centre and the transition metal. Some transition metal hydrides are acidic, e.g., $\text{HCo}(\text{CO})_4$ and $\text{H}_2\text{Fe}(\text{CO})_4$. The anions $[\text{ReH}_9]^{2-}$ and $[\text{FeH}_6]^{4-}$ are examples from the growing collection of known molecular homoleptic metal hydrides.^[7] As pseudohalides, hydride ligands are capable of bonding with positively polarized hydrogen centres. This interaction, called dihydrogen bond is similar to hydrogen bonding which exists between positively polarized protons and electronegative atoms with open lone pairs.

Deuterides

Hydrides containing deuterium are known as *deuterides*. Some deuterides, such as LiD , are important fusion fuels in thermonuclear weapons