

BOX 10.1 The biological hydrogen cycle

Hydrogen is cycled by microbial organisms using metalloenzymes (Section 27.14). Although H_2 is present only to the extent of about 0.5 ppm at the Earth's surface, its levels are hundreds of times higher in anaerobic environments, such as wetland soils and sediments at the bottoms of deep lakes and hot springs. Hydrogen is produced in these O_2 -free zones as a waste product by strict anaerobes (fermentative bacteria) which break down organic material (biomass) using H^+ as an oxidant acting as a terminal electron acceptor. It is also produced by thermophilic organisms that derive their carbon and energy entirely from CO , and by nitrogen fixing bacteria, which yield H_2 as a byproduct of ammonia formation. Other microorganisms, many of them aerobic, use H_2 instead as a 'food' (a fuel) and are responsible for the formation of the familiar gases CH_4 (methanogens) and H_2S (*Desulfovibrio*) as well as nitrite and other products. Figure B10.1 summarizes some of the overall processes occurring in a freshwater environment.

In animals, including humans, the anaerobic environment of the large intestine is host to bacteria that form H_2 by the breakdown of carbohydrates. The mucus layer of the mouse intestine has been found to contain H_2 at levels above $0.04 \text{ mmol dm}^{-3}$, equivalent to a partial atmosphere of 5 per cent H_2 . In turn, this H_2 is utilized by methanogens, such as those found in ruminating mammals, to produce CH_4 and by other bacteria, including dangerous pathogens such as those of the *Salmonella* genus and *Helicobacter pylori*, which is responsible for gastric ulcers. High levels of H_2 in the breath have been used to diagnose conditions related to carbohydrate-intolerance and these levels may reach $>70 \text{ ppm}$ following lactose ingestion by lactose-intolerant patients.

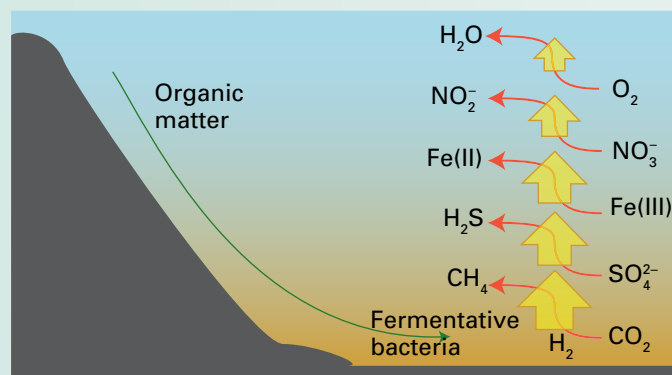


Figure B10.1 Some of the processes that contribute to the biological hydrogen cycle in a freshwater environment.

Industrial production of H_2 by microorganisms (*biohydrogen*) is an important area for research and development. There are two different approaches, each of which uses renewable energy. The first of these approaches is to use anaerobic organisms to ferment biomass from sources ranging from cultivated biomass (including seaweed) to domestic waste. The second involves manipulation of photosynthetic organisms such as green algae and cyanobacteria to produce H_2 as well as biomass. In either case H_2 can be extracted continuously by gas filters without the interruptions that would be required were harvesting required.

(a) The atom and its ions

Key points: The proton, H^+ , is always found in combination with a Lewis base and is highly polarizing; the hydride ion, H^- , is highly polarizable.

There are three isotopes of hydrogen: hydrogen itself (^1H), deuterium (D , ^2H), and tritium (T , ^3H); tritium is radioactive. The lightest isotope, ^1H (very occasionally called protium), is by far the most abundant. Deuterium has variable natural abundance with an average value of about 16 atoms in 100 000. Tritium occurs to the extent of only 1 in 10^{21} . The different names and symbols for the three isotopes reflect the significant differences in their masses and the chemical properties that stem from mass, such as the rates of diffusion and bond-cleavage reactions. The nuclear spin of ^1H ($I = \frac{1}{2}$) is exploited in NMR spectroscopy (Section 8.5) for identifying hydrogen-containing molecules and determining their structures.

The free hydrogen cation (H^+ , the proton) has a very high charge/radius ratio and it is not surprising to find that it is a very strong Lewis acid. In the gas phase it readily attaches to other molecules and atoms; it even attaches to He to form HeH^+ . In the condensed phase, H^+ is always found in combination with a Lewis base, and its ability to transfer between Lewis bases gives it the special role in chemistry explored in detail in Chapter 4. The molecular cations H_2^+ and H_3^+ have only a transitory existence in the gas phase and are unknown in solution. In contrast to H^+ , which is highly polarizing; the hydride ion, H^- , is highly polarizable because two electrons are bound by just one proton. The radius of H^- varies considerably depending on the atom to which it is attached. The lack of core electrons to scatter X-rays means that bond distances and angles involving a H atom in a compound are difficult to measure by X-ray diffraction: for this reason, neutron diffraction is used when it is crucial to determine the precise positions of H atoms.

(b) Properties and reactions

Key points: Hydrogen has unique atomic properties that place it in a special position in the periodic table. Dihydrogen is an inert molecule and its reactions require a catalyst or initiation by radicals.

Hydrogen's unique properties distinguish it from all other elements in the periodic table. It is often placed at the head of Group 1 because, like the alkali metals, it has only one electron in its valence shell. That position, however, does not truly reflect the chemical or

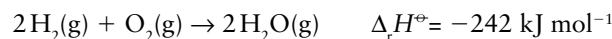
physical properties of the element. In particular, its ionization energy is far higher than those of the other Group 1 elements, so hydrogen is not a metal, although it may be found naturally in a metallic state where extreme pressures exist, such as the core of Jupiter. In some versions of the periodic table hydrogen is placed at the head of Group 17 because, like the halogens, it requires only one electron to complete its valence shell. But the electron affinity of hydrogen is far lower than that of any of the elements of Group 17 and the discrete hydride ion, H^- , is encountered only in certain compounds. To reflect its unique characteristics, we place H in its own special position at the head of the entire table.

Because H_2 has so few electrons, the intermolecular forces between H_2 molecules are weak, and at 1 atm the gas condenses to a liquid only when cooled to 20 K. If an electric discharge is passed through H_2 gas at low pressure, the molecules dissociate, ionize, and recombine, forming a plasma containing, in addition to H_2 , spectroscopically observable amounts of H , H^+ , H_2^+ , and H_3^+ .

The H_2 molecule has a high bond enthalpy (436 kJ mol^{-1}) and a short bond length (74 pm). The high bond strength results in H_2 being an inert molecule. However, it is still much easier to dissociate H_2 homolytically than heterolytically,¹ because in heterolytic dissociation energy is required to separate opposite charges:



Because of its inherently inert nature, reactions of H_2 do not occur readily unless a special activation pathway has been provided. These pathways include homolytic or heterolytic dissociation catalysed by molecules or active surfaces, and initiation of radical chain reactions. The explosive reaction of H_2 with O_2 , for instance



proceeds by a complex radical chain mechanism. Hydrogen is an excellent fuel for large rockets on account of its high specific enthalpy (the standard enthalpy of combustion divided by the mass), which is approximately three times that of a typical hydrocarbon (Box 10.2).

In addition to reactions that result in dissociation of the H–H bond, H_2 can also react reversibly without cleavage to form dihydrogen d-metal complexes (Section 10.6 and Section 22.7).

10.2 Simple compounds

The nature of the bonding in binary compounds of hydrogen (EH_n) is largely rationalized by noting that an H atom has a high ionization energy (1312 kJ mol^{-1}) and a low but positive electron affinity (73 kJ mol^{-1}). Although binary hydrogen compounds are often known as ‘hydrides’, very few actually contain a discrete H^- anion. The (Pauling) electronegativity of 2.2 (Section 1.9) is intermediate in value, so it is normally assigned the oxidation number -1 when in combination with metals (as in NaH and AlH_3) and $+1$ when in combination with nonmetals (as in H_2O and HCl).

(a) Classification of binary compounds

Key points: Compounds formed between hydrogen and other elements vary in their nature and stability. In combination with metals, hydrogen is often regarded as a hydride; hydrogen compounds with elements of similar electronegativity have low polarity.

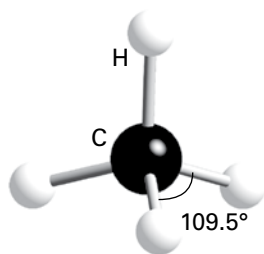
The binary compounds of hydrogen fall into three classes, although there is a range of structural types, and some elements form compounds with hydrogen that do not fall strictly into any one category:

1. **Molecular hydrides** exist as individual, discrete molecules; they are usually formed with p-block elements of similar or higher electronegativity than H. Their E–H bonds are best regarded as covalent.

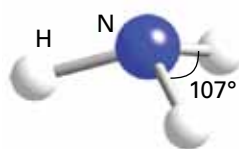
Familiar examples of molecular hydrides include methane, CH_4 (1), ammonia, NH_3 (2), and water, H_2O (3).

2. **Saline hydrides**, also known as *ionic hydrides*, are formed with the most electropositive elements.

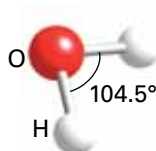
¹In homolytic dissociation the bond breaks symmetrically to give one product. In heterolytic dissociation the bond breaks unsymmetrically to give two different products.



1 Methane, CH_4



2 Ammonia, NH_3



3 Water, H_2O

BOX 10.2 Dihydrogen as a fuel

The use of H₂ as a fuel (an energy carrier) has been investigated seriously since the 1970s when oil prices first rose dramatically; interest has increased greatly in more recent times owing to environmental pressures on further use of fossil fuels. Hydrogen is clean burning, nontoxic, and its production from fully renewable resources is slowly but inevitably replacing its production from fossil carbon feedstocks. Table B10.1 compares the performance data for H₂ and other energy carriers, including hydrocarbon fuels and a lithium ion battery. Among all fuels, H₂ has the highest specific enthalpy (its standard enthalpy of combustion divided by its mass) but has a very low energy density (its standard enthalpy of combustion divided by its volume).

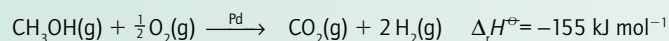
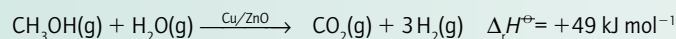
It is obvious that H₂ is an excellent fuel for vehicles provided the problems of on-board containment are solved (see Box 10.4). In addition to its choice as a rocket fuel (due to its high specific enthalpy), H₂ can be used in conventional internal combustion engines with little if any modification

Table B10.1 Specific enthalpies and energy densities of common energy carriers (1 MJ = 0.278 kWh)

Fuel	Specific enthalpy /(MJ kg ⁻¹)	Energy density /(MJ dm ⁻³)
Liquid H ₂ *	120	8.5
H ₂ at 200 bar*	120	1.9
Liquid natural gas	50	20.2
Natural gas at 200 bar	50	8.3
Petrol (gasoline)	46	34.2
Diesel*	45	38.2
Coal	30	27.4
Ethanol*	27	22.0
Methanol	20	15.8
Wood*	15	14.4
Lithium battery*	2.0	6.1
(Li _{1-x} CoO ₂ , see Box 11.1)		

* Denotes an energy carrier that is easily derived or recharged from renewable resources.

to their design or specifications. However, the most important way of utilizing H₂ in a vehicle is to react it in a fuel cell to produce electricity directly (Box 5.1). The efficient and reliable power output of H₂ fuel cells makes it viable to produce H₂ 'on board' by steam reforming of methanol, a transportable and energy-dense fuel. (Direct methanol fuel cells, discussed in Box 5.1, produce less power than H₂ fuel cells and are therefore less attractive for vehicles.) An automotive steam reformer (the principle of which is shown in Fig. B10.2) mixes methanol vapour with H₂O (steam) and with O₂ (air) to produce H₂ by the following reactions



The reactions, which occur over the temperature range 200–350°C, are controlled to ensure that the heat produced by the exothermic oxidation reaction just offsets that required for the reaction with steam and the vaporization of all components. Excessive heat results in production of CO, which poisons the Pt catalyst of the PEM fuel cell. The CO₂ and H₂ products are separated with a Pd membrane.

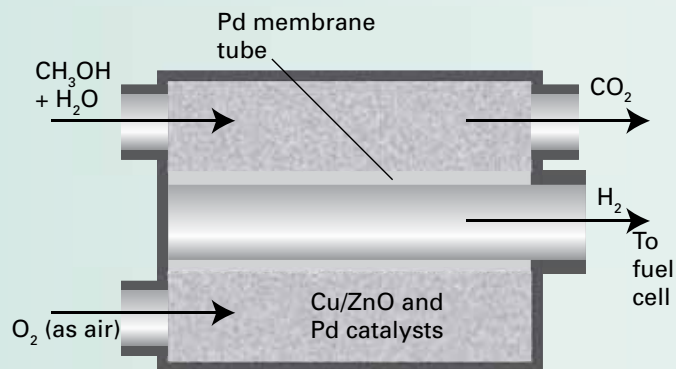


Figure B10.2 Schematic cross-sectional view of an on-board methanol reformer.

Saline hydrides, such as LiH and CaH₂, are nonvolatile, electrically nonconducting, crystalline solids although only those in Group 1 and the heavier elements of Group 2 should be regarded as hydride 'salts' containing H⁻ ions.

3. Metallic hydrides are non-stoichiometric, electrically conducting solids with a metallic lustre.

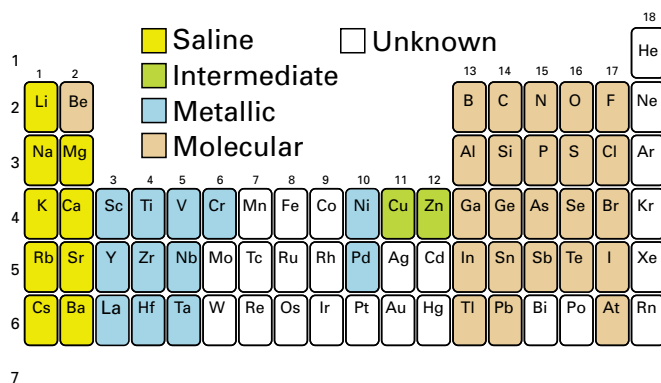
Metallic hydrides are formed with many d- and f-block elements (Table 3.12). The H atoms are often regarded as occupying interstitial sites within the metal structure although this occupation rarely occurs without expansion or phase change. Figure 10.2 (which reproduces Fig. 9.11) summarizes this classification and the distribution of the different classes through the periodic table. It also identifies 'intermediate' hydrides that do not fall strictly into any of these categories, and elements for which binary hydrides have not been characterized.

In addition to binary compounds, hydrogen is found in complex anions of some p-block elements, examples being the BH₄⁻ ion (tetrahydridoborate, also known in older texts as 'borohydride') in NaBH₄ or the AlH₄⁻ ion (tetrahydridoaluminate, also known in older texts as 'aluminiumhydride') in LiAlH₄.

(b) Thermodynamic considerations

Key points: In the s and p blocks, strengths of E–H bonds decrease down each group. In the d block, strengths of E–H bonds increase down each group.

Figure 10.2 Classification of the binary hydrogen compounds of the s-, p-, and d-block elements. Although some d-block elements such as iron and ruthenium do not form binary hydrides they do form metal complexes containing the hydride ligand.



The standard Gibbs energies of formation of the hydrogen compounds of s- and p-block elements reveal a regular variation in stability (Table 10.1). With the possible exception of BeH_2 (for which good data are not available) all the s-block hydrides are exergonic ($\Delta_f G^\ominus < 0$) and therefore thermodynamically stable with respect to their elements at room temperature. The trend is erratic in Group 13, in that only AlH_3 is exergonic at room temperature. In all the other groups of the p block, the simple hydrogen compounds of the first members of the groups (CH_4 , NH_3 , H_2O , and HF) are exergonic but the analogous compounds of their congeners become progressively less stable down the group, a trend that is illustrated by decreasing E–H bond energies (Fig. 10.3). The heavier hydrides become more stable on going from Group 14 across to the halogens. For example, SnH_4 is highly endergonic ($\Delta_f G^\ominus > 0$) whereas HI is barely so.

These thermodynamic trends can be traced to the variation in atomic properties. The H–H bond is the strongest single homonuclear bond known (apart from D–D or T–T bonds) and in order for a compound to be exergonic and stable with respect to its elements, it needs to have E–H bonds that are even stronger than H–H. For molecular hydrides of the p-block elements, bonding is strongest with the Period 2 elements and becomes progressively weaker down each group. The weak bonds formed by the heavier p-block elements are due to the poor overlap between the relatively compact H1s orbital and the more diffuse s and p orbitals of their atoms. Although d-block elements do not form binary molecular compounds, many complexes contain one or more hydride ligands. Metal–hydrogen bond strengths in the d block increase down a group because the 3d orbitals are too contracted to overlap well with the H1s orbital and better overlap is afforded by 4d and 5d orbitals.

(c) Reactions of binary compounds

Key point: The reactions of binary compounds of hydrogen fall into three classes depending on the polarity of the E–H bond.

In compounds where E and H have similar electronegativities, cleavage of the E–H bond tends to be homolytic, producing, initially, an H atom and a radical, each of which can go on to combine with other available radicals.

Table 10.1 Standard Gibbs energy of formation, $\Delta_f G^\ominus / (\text{kJ mol}^{-1})$ of binary s- and p-block hydrogen compounds at 25°C. Values in parentheses are estimates.

Period	Group						
	1	2	13	14	15	16	17
2	LiH(s) –68.4	$\text{BeH}_2(\text{s})$ (+20)	$\text{B}_2\text{H}_6(\text{g})$ +86.7	$\text{CH}_4(\text{g})$ –50.7	$\text{NH}_3(\text{g})$ –16.5	$\text{H}_2\text{O(l)}$ –237.1	HF(g) –273.2
3	NaH(s) –33.5	$\text{MgH}_2(\text{s})$ –35.9	$\text{AlH}_3(\text{s})$ (+91)	SiH_4 +56.9	$\text{PH}_3(\text{g})$ +13.4	$\text{H}_2\text{S(g)}$ –33.6	HCl(g) –95.3
4	KH(s) (–36)	$\text{CaH}_2(\text{s})$ –147.2	$\text{Ga}_2\text{H}_6(\text{s})$ > 0	$\text{GeH}_4(\text{g})$ +113.4	$\text{AsH}_3(\text{g})$ +68.9	$\text{H}_2\text{Se(g)}$ +15.9	HBr(g) –53.5
5	RbH(s) (–30)	$\text{SrH}_2(\text{s})$ (–141)		$\text{SnH}_4(\text{g})$ +188.3	$\text{SbH}_3(\text{g})$ +147.8	$\text{H}_2\text{Te(g)}$ > 0	HI(g) +1.7
6	CsH(s) (–32)	$\text{BaH}_2(\text{s})$ (–140)					

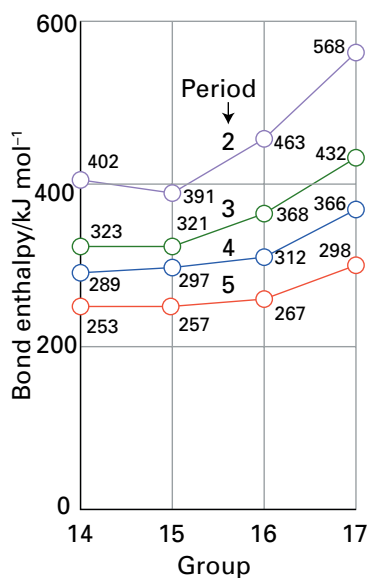


Figure 10.3 Average bond energies (kJ mol^{-1}) for binary molecular hydrides of p-block elements.



Common examples of homonuclear cleavage include the thermolysis and combustion of hydrocarbons.

In compounds where E is more electronegative than H, heterolytic cleavage occurs, releasing a proton.



The compound behaves as a Brønsted acid and is able to transfer H^+ to a base. In such compounds the H atom is termed **protonic**. Heterolytic bond cleavage also occurs in compounds where E is less electronegative than H, including saline hydrides



In this case the H atom is **hydridic** and an H^- ion is transferred to a Lewis acid. The reducing agents NaBH_4 and LiAlH_4 used in organic synthesis are examples of hydride-transfer reagents.

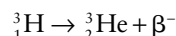
PART B: THE DETAIL

In this part of the chapter we present a more detailed discussion of the chemical properties of hydrogen, identifying and interpreting trends. We explain how dihydrogen is prepared on a small scale in the laboratory and how it is produced industrially from fossil fuels, then we outline methods for its production from water using renewable energy. We describe the reactions that dihydrogen undergoes with other elements and classify the different types of compounds formed. Finally we present the strategies for synthesizing various hydrogen-containing compounds.

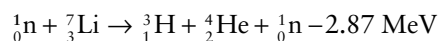
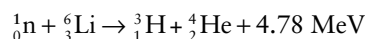
10.3 Nuclear properties

Key point: The three hydrogen isotopes H, D, and T have large differences in their atomic masses and different nuclear spins, which give rise to easily observed changes in IR, Raman, and NMR spectra of molecules containing these isotopes.

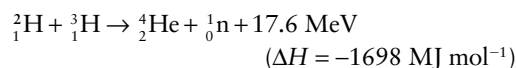
Neither ^1H nor ^2H (deuterium, D) is radioactive, but ^3H (tritium, T) decays by the loss of a β particle to yield a rare but stable isotope of helium:



The half-life for this decay is 12.4 years. Tritium's abundance of 1 in 10^{21} hydrogen atoms in surface water reflects a steady state between its production by bombardment of cosmic rays on the upper atmosphere and its loss by radioactive decay. Tritium can be synthesized by neutron bombardment of ^6Li or ^7Li .



Continuous production of tritium from lithium is a key step in the projected future generation of energy from nuclear fusion rather than nuclear fission. In a fusion reactor tritium and deuterium are heated to over 100 MK to give a plasma in which the nuclei react to produce ^4He and a neutron.



The neutron is used to bombard a lithium blanket that has been enriched in ^6Li to generate further tritium. This process carries far fewer environmental risks than fission of ^{235}U and is essentially renewable: of the two primary fuels required, deuterium is readily available from water, although the natural abundance of lithium is low (Chapter 11).

The physical and chemical properties of **isotopologues**, isotopically substituted molecules, are usually very similar, but not when D is substituted for H, as the mass of the substituted atom is doubled. Table 10.2 shows that the differences in boiling points and bond enthalpies are easily measurable for H_2 and D_2 . The difference in boiling point between H_2O and D_2O reflects the greater strength of the $\text{O}\cdots\text{D}-\text{O}$ hydrogen bond (Section 10.6) compared with that of the $\text{O}\cdots\text{H}-\text{O}$ bond because the zero-point energy (Section 8.4) of the former is lower. The compound D_2O is known as 'heavy water' and is used as a moderator in the nuclear power industry; it slows down emitted neutrons and increases the rate of induced fission.

A note on good practice An *isotopologue* is a molecular entity that differs only in isotopic composition. An *isotopomer* is an isomer having the same number of each isotopic atom but differing in their positions.

Reaction rates are often measurably different for processes in which $\text{E}-\text{H}$ and $\text{E}-\text{D}$ bonds, where E is another element, are broken, made, or rearranged. The detection of this **kinetic isotope effect** can often help to support a proposed reaction mechanism. Kinetic isotope effects are frequently observed when an H atom is transferred from one atom to another in an activated complex. For example, the electrochemical reduction of $\text{H}^+(\text{aq})$ to $\text{H}_2(\text{g})$ occurs with a substantial isotope effect, with H_2 being liberated much more rapidly. A practical consequence of the difference in rates of formation of H_2 and D_2 is that D_2O may be concentrated electrolytically, thus facilitating separation of

Table 10.2 The effect of deuteration on physical properties

	H_2	D_2	H_2O	D_2O
Normal boiling point/ $^\circ\text{C}$	-252.8	-249.7	100.0	101.4
Mean bond enthalpy/ (kJ mol^{-1})	436.0	443.3	463.5	470.9

the two isotopes: the pure D_2O that accumulates is then used to produce pure HD (by reaction with $LiAlH_4$) or D_2 (by electrolysis). In general, reactions involving D_2O occur more slowly than those involving H_2O and, not surprisingly, D_2O and D-substituted foods ingested in large quantities are poisonous for higher organisms.

Because the frequencies of molecular vibrations depend on the masses of atoms, they are strongly influenced by substitution of D for H. The heavier isotope results in the lower frequency (Section 8.4). The isotope effect can be exploited by observing the IR spectra of isotopologues to determine whether a particular infrared absorption involves significant motion of a hydrogen atom in the molecule.

The distinct properties of the isotopes make them useful as tracers. The involvement of H and D through a series of reactions can be followed by infrared (IR, Section 8.4) and mass spectrometry (Section 8.10) as well as by NMR spectroscopy (Section 8.5). Tritium can be detected by its radioactivity, which can be a more sensitive probe than spectroscopy.

Another important property of the hydrogen nucleus is its spin. The nucleus of hydrogen, a proton, has $I = \frac{1}{2}$; the nuclear spins of D and T are 1 and $\frac{1}{2}$, respectively. As explained in Chapter 8, proton NMR detects the presence of H nuclei in a compound and is a powerful method for determining structures of molecules, even proteins with molecular masses as high as 20 kDa. Figure 10.4 shows some typical 1H -NMR chemical shifts for some compounds of p- and d-block elements. Hydrogen atoms bonded to electronegative elements (protonic H atoms) display deshielded NMR signals (at more positive values of chemical shift), whereas hydrogens coordinated to metal ions with incomplete d subshells typically display more negative chemical shifts.

Molecular hydrogen, H_2 , exists in two forms that differ in the relative orientations of the two nuclear spins: in *ortho*-hydrogen the spins are parallel ($I = 1$), in *para*-hydrogen the spins are antiparallel ($I = 0$). At $T = 0$ hydrogen is 100 per cent *para*. As the temperature is raised, the proportion of the *ortho* form in a mixture at equilibrium increases until at room temperature there is approximately 75 per cent *ortho* and 25 per cent *para*. Most physical properties of the two forms are the same, but the melting and boiling points of *para*-hydrogen are about $0.1^\circ C$ lower than those of normal hydrogen, and the thermal conductivity of *para*-hydrogen is about 50 per cent greater than that of the *ortho* form. The heat capacities also differ.

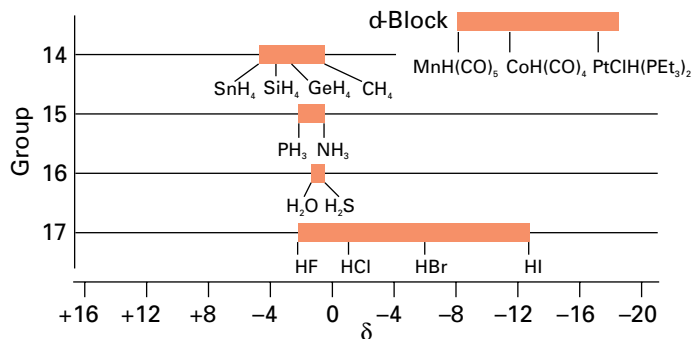


Figure 10.4 Typical 1H -NMR chemical shifts. The tinted boxes show families of elements together.

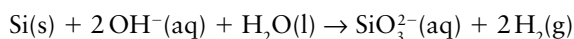
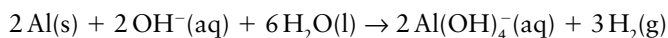
10.4 Production of dihydrogen

Hydrogen is important both as a raw material for the chemical industry and, increasingly, as a fuel. Although it is not present in significant quantities in the Earth's atmosphere or in underground gas deposits, there is a high biological turnover because various microorganisms use H^+ as an oxidant or H_2 as a fuel (Box 10.1). Industrially, most H_2 is produced from natural gas by using steam reforming (in the USA, about 95 per cent is produced in this way). Increasingly, H_2 is being produced by other methods, notably coal gasification (with carbon dioxide capture, Box 14.4) and thermally assisted electrolysis. In 2007, world production of H_2 was approximately 50 Mt. Most H_2 is used close to its site of production for the synthesis of ammonia (the Haber process), hydrogenation of unsaturated fats and large-scale manufacture of organic chemicals. In the future, H_2 may be produced from entirely renewable sources such as water and capturing the energy of sunlight.

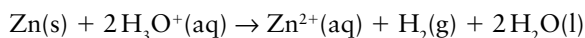
(a) Small-scale preparation

Key points: In the laboratory, H_2 is easily produced by the reactions of electropositive elements with aqueous acid or alkali, or by hydrolysis of saline hydrides. It is also produced by electrolysis.

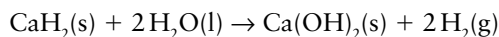
There are many straightforward procedures for preparing small quantities of pure H_2 . In the laboratory, H_2 is produced by reaction of Al or Si with hot alkali solution.



or, at room temperature, by reaction of Zn with mineral acids:



The reaction of metal hydrides with water provides a convenient way to obtain small amounts of H_2 outside the laboratory. Calcium hydride is particularly suited for this purpose as it is commercially available and inexpensive and it reacts with H_2O at room temperature:



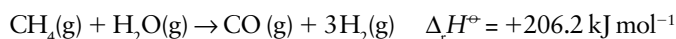
Calcium hydride is used as a portable H_2 generator and has important applications in remote places, such as filling meteorological balloons.

Pure H_2 is also produced in small amounts using a simple electrolysis cell; electrolysis of heavy water is also a convenient way to prepare pure D_2 .

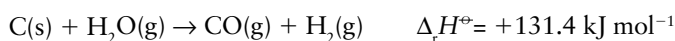
(b) Production from fossil sources

Key point: Most H_2 for industry is produced by high-temperature reaction of H_2O with CH_4 or a similar reaction with coke.

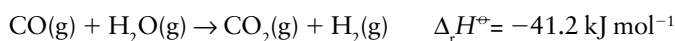
Hydrogen is produced in huge quantities to satisfy the needs of industry, in fact production is often integrated directly (without transport) into chemical processes that require H_2 as a feedstock. The main commercial process for the production of H_2 is currently *steam reforming*, the catalysed reaction of H_2O (as steam) and hydrocarbons (typically methane from natural gas) at high temperatures:



Increasingly, coal or coke is used. This reaction, which occurs at 1000°C, is



The mixture of CO and H₂ is known as *water gas* and further reaction with water (the water gas shift reaction) produces more H₂:



Overall, coal gasification (and hydrocarbon reforming) result in production of CO₂ and H₂.

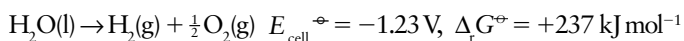


By implementing a system for capturing CO₂ from the mixture (Box 14.4), it is possible to use fossil fuels and minimize release of the greenhouse gas CO₂ into the atmosphere. However, this process is not a renewable route for H₂ production as it is based on the use of fossil fuels. Dihydrogen for immediate consumption by on-board fuel cells in vehicles is produced from methanol by using an automotive steam reformer (Box 10.2).

(c) Production from renewable sources

Key points: Production of H₂ by electrolysis of water is costly and viable only in areas where electricity is cheap or if it is a byproduct of an economically important process. Environmental pressures are driving technologies to produce H₂ more efficiently from surplus or renewable energy, including solar and biological sources.

Electrolysis is used to produce H₂ that is free from contaminants.



To drive this reaction, a large overpotential is required to offset the sluggish electrode kinetics, particularly for the production of O₂. The best catalysts are based on platinum, but it is too expensive to justify its use in large-scale plants. As a consequence, electrolysis of water is economical and environmentally benign only if the electrical power stems from cheap, renewable resources or if it is surplus to demand. These conditions are found in countries that have plenty of hydroelectric or nuclear energy. There is also scope for off-shore wind farms that can employ resources far from the electricity grids and are far from the population areas that are otherwise necessary for conventional power generation. Electrolysis is carried out using hundreds of cells arranged in series, each operating at 2 V with iron or nickel electrodes and aqueous NaOH (or an ion-selective membrane) as electrolyte (Fig. 10.5). Temperatures of 80–85°C are used to increase the electrolytic current and to lower the overpotential. The most important electrolytic H₂ production method is the *chlor-alkali process* (Box 11.2), in which H₂ is produced as a byproduct of NaOH manufacture. In this process the other gaseous product is Cl₂, which requires a lower overpotential than O₂.

As yet, however, only about 0.1 per cent of the global H₂ demand is produced by electrolysis, including that produced in the chlor-alkali process. This percentage could be improved by the development of cheap and efficient electrocatalysts to reduce the economically wasteful overpotential.

Hydrogen can be produced by fermentation, using anaerobic bacteria that use cultivated biomass or biological waste as their energy source (Box 10.1). Research is also under way to establish how best to produce H₂ by exploiting solar energy directly either through physical methods (solar-powered thermolysis or photo-

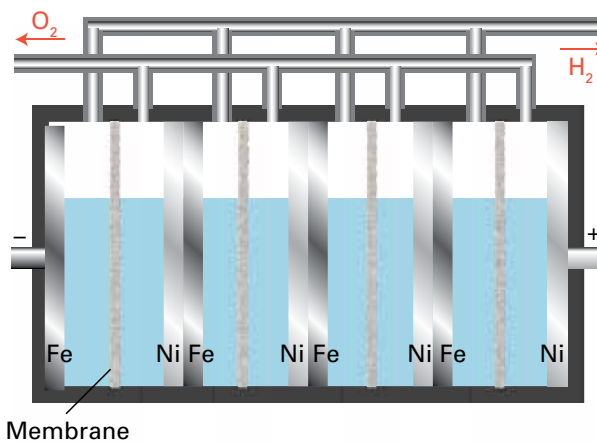


Figure 10.5 An industrial electrolysis cell for H₂ production using Ni anodes and Fe cathodes connected in series.

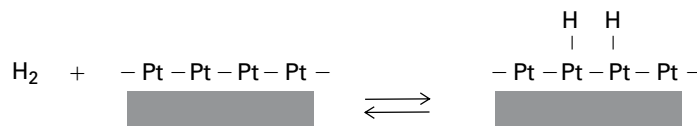
electron-chemistry) or biological processes (modified photosynthesis). The physical methods under investigation are outlined in Box 10.3. Biological production could take place in ‘hydrogen farms’ by nurturing photosynthetic microorganisms that have been modified to produce H₂ as well as organic molecules.

10.5 Reactions of dihydrogen

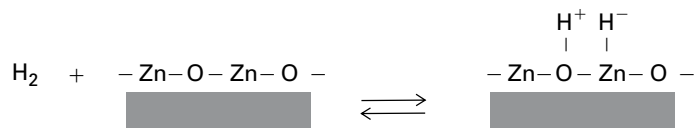
Key points: Molecular hydrogen is activated by homolytic or heterolytic dissociation on a metal or metal oxide surface or by coordination to a d-block metal. Reactions of hydrogen with O₂ and halogens involve a radical chain mechanism.

Although H₂ is quite an inert molecule, it reacts very rapidly under special conditions. Conditions for activating H₂ include:

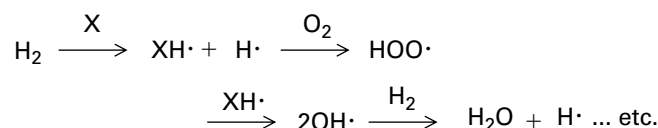
1. Homolytic dissociation into H atoms, induced by adsorption at certain metal surfaces:



2. Heterolytic dissociation into H⁺ and H⁻ ions induced by adsorption on a heteroatom surface, such as a metal oxide:



3. Initiation of a radical chain reaction:



(a) Homolytic dissociation

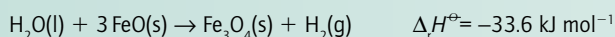
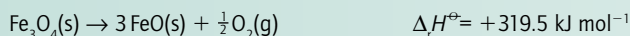
High temperatures are required to dissociate H₂ into atoms. An important example of homolytic dissociation at normal temperatures is the reaction of H₂ at finely divided Pt or Ni metal (Section 26.11).

BOX 10.3 Hydrogen from solar energy

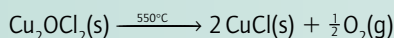
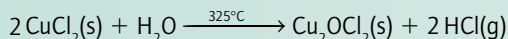
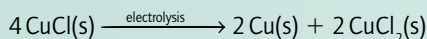
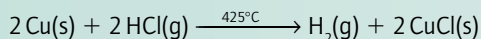
The Earth receives about 100 000 TW from the Sun, which is approximately 7000 times greater than the present global rate of energy consumption (15 TW). Solar energy is already harnessed in several familiar ways, such as wind turbines, photosynthesis (biomass), and photovoltaic cells but ultimately the use of solar energy to generate H₂ from water (water splitting) provides the greatest opportunity to end the world's dependence on fossil fuels and help curb global climate change. Two technologies under development are high-temperature solar H₂ production and solar photoelectrochemical H₂ production.

The so-called 'sunbelt' regions, which include Australia, southern Europe, the Sahara desert, and southwestern states of the USA, receive about 1 kW m⁻² of solar power. These regions are suitable sites for high-temperature solar H₂ production using solar concentrating systems that reflect and focus solar radiation onto a receiver furnace, producing temperatures in excess of 1500°C. The intense heat, which is also available in the mantle surrounding a nuclear reactor, can be used to drive a turbine for generating electricity or to split water into H₂ and O₂, so producing a fuel.

Direct, single-step thermolysis of water requires temperatures in excess of 4000°C, which is well above the threshold readily attainable in a solar concentrator or compatible with containment materials and engineering. By using a multi-step process, however, it is possible to produce H₂ at much lower temperatures. Many systems are under investigation and development, the simplest of which are two-stage processes involving metal oxides, such as the sequence

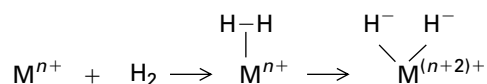


Dihydrogen production by this route still requires temperatures in excess of 2200°C. Water splitting at lower temperatures has been achieved with hybrid processes that combine thermochemical and electrochemical reactions, such as



This reaction, in which H₂ is dissociatively chemisorbed as H atoms, is used to catalyse the hydrogenation of alkenes and the reduction of aldehydes to alcohols. Platinum is also used as the electrocatalyst for H₂ oxidation in proton-exchange membrane fuel cells (Box 5.1). The facile chemisorption of H₂ at Pt anodes results in a minimal overpotential for H₂ oxidation and optimal performance.

Another example of homolytic cleavage involves the initial coordination of molecular H₂ as an η²-H₂ species in discrete metal complexes, which is described briefly in Section 10.6d and in more detail in Section 22.7. Dihydrogen complexes provide examples of species intermediate between molecular H₂ and a dihydrido complex. No dihydrogen complexes are known for the early d-block (Groups 3, 4, and 5), f-block, or p-block metals. If the metal is sufficiently electron rich, back donation of d electrons into the 1σ_u orbital splits the H–H bond, resulting in the formation of a *cis*-dihydrido complex in which the formal oxidation number of the metal has increased by 2:



Solar photoelectrochemical H₂ production operates on a principle similar to that used by plants for photosynthesis. To split water electrochemically a cell potential greater than 1.23 V is required, which in principle could be provided by light with a wavelength below 1000 nm. The principle of a photoelectrochemical water-splitting system based on light-sensitive particles is shown in Fig. B10.3, which represents water splitting in terms of two separate half-reactions. The essentials are (a) a mechanism for generating an excited electronic state by photon capture, (b) efficient transfer of electrons between the site of excitation and catalytic centres, (c) sites for the H₂ production half-reaction, and (d) sites for the O₂ production half-reaction. The excitation is produced at a photosensitive centre P, an organic molecule or metal complex attached to the particle. The sites for H₂ and O₂ production must be catalysts in order for these reactions to occur on timescales that are short compared to the lifetimes of the excited and oxidized states of P. For H₂, the catalyst can be Pt, although much cheaper alternatives are necessary in order to achieve a feasible industrial-scale system. The major challenge for photoelectrochemical water splitting is to achieve rapid and efficient production of O₂, and there are intense efforts to find substances that mimic the Mn catalyst used in plant photosynthesis (Section 27.10).

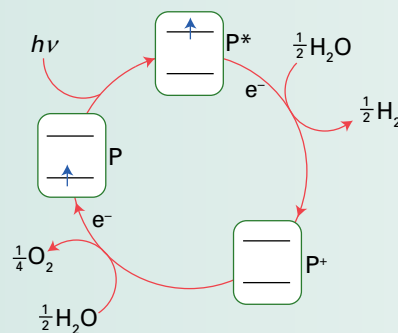
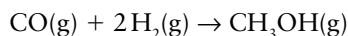


Figure B10.3 Schematic cycle for photoelectrochemical production of H₂ and O₂ by catalysts attached to particles of a conducting material such as doped TiO₂, to which a photosensitizer P is also attached. Excitation by visible light produces P*, a powerful reducing agent for producing H₂. Electron transfer from P* produces P+, a powerful oxidizing agent for producing O₂.

(b) Heterolytic dissociation

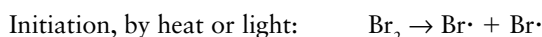
Heterolytic dissociation of H₂ depends on a metal ion (for hydride coordination) and a Brønsted base being in close proximity. Reaction of H₂ with a ZnO surface appears to produce a Zn(II)-bound hydride and an O-bound proton. This reaction is involved in the production of methanol by catalytic hydrogenation of carbon monoxide over Cu/ZnO/Al₂O₃.

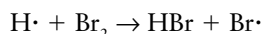
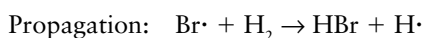


Another example in which H₂ is dissociated into a hydride and a proton is during its oxidation at the active site of metalloenzymes known as hydrogenases (Section 27.14).

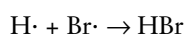
(c) Radical chain reactions

Radical chain mechanisms account for the thermally or photochemically initiated reactions between H₂ and the halogens in which atoms are generated that act as radical chain carriers in the propagation reaction:



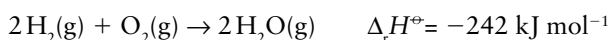


The activation energy for radical attack is low because a new bond is formed as one bond is lost, so once initiated the formation and consumption of radicals is self-sustaining and the production of HBr is very rapid. Chain termination occurs when the radicals recombine:



Termination becomes more important towards the end of the reaction when the concentrations of H_2 and Br_2 are low.

The highly exothermic reaction of H_2 with O_2 also occurs by a radical chain mechanism. Certain mixtures explode violently when detonated:



10.6 Compounds of hydrogen

Hydrogen forms compounds with most of the elements. These compounds are classified into molecular hydrides, saline hydrides (salts of the hydride anion), metallic hydrides (interstitial compounds of d-block elements), and discrete complexes of d-block elements in which hydride or dihydrogen are ligands.

(a) Molecular hydrides

Molecular hydrides are formed with p-block elements and Be. The bonding is covalent but variations in bond polarity (depending on the electronegativity of the atoms to which hydrogen is attached) result in a range of reaction types in which hydrogen is formally transferred as H^+ , H^- , or $\text{H}\cdot$.

(i) Nomenclature and classification

Key point: Molecular compounds of hydrogen are classified as electron-rich, electron-precise, or electron-deficient. Electron-deficient hydrides provide some of the most intriguing examples of molecular structure and bonding as their simplest units tend to associate via bridging hydrogen atoms to form dimers and higher polymers.

The systematic names of the molecular hydrogen compounds are formed from the name of the element and the suffix -ane, as in phosphane for PH_3 . The more traditional names, however, such as phosphine and hydrogen sulfide (H_2S , sulfane) are still widely used (Table 10.3). The common names ammonia and water are universally used rather than their systematic names azane and oxidane. Molecular compounds of hydrogen are divided further into three subcategories:

Electron-precise, in which all valence electrons of the central atom are engaged in bonds.

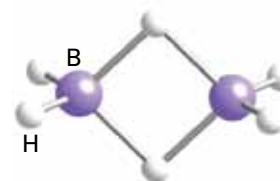
Electron-rich, in which there are more electron pairs on the central atom than are needed for bond formation (that is, there are lone pairs on the central atom).

Electron-deficient, in which there are too few electrons to be able to write a Lewis structure for the molecule.

Table 10.3 Some common molecular hydrogen compounds

Group	Formula	Traditional name	IUPAC name
13	B_2H_6	Diborane	Diborane(6)
14	CH_4	Methane	Methane
	SiH_4	Silane	Silane
	GeH_4	Germane	Germane
	SnH_4	Stannane	Stannane
15	NH_3	Ammonia	Azane
	PH_3	Phosphine	Phosphane
	AsH_3	Arsine	Arsane
	SbH_3	Stibine	Stibane
	H_2O	Water	Oxidane
16	H_2S	Hydrogen sulfide	Sulfane
	H_2Se	Hydrogen selenide	Sellane
	H_2Te	Hydrogen telluride	Tellane

Electron-precise molecular hydrogen compounds include hydrocarbons such as methane and ethane, and their heavier analogues silane, SiH_4 , and germane, GeH_4 (Chapter 14). All these molecules are characterized by the presence of two-centre, two-electron bonds ($2c,2e$ bonds) and the absence of lone pairs on the central atom. Electron-rich compounds are formed by the elements in Groups 15 to 17. Important examples include ammonia, water, and the hydrogen halides. Electron-deficient hydrogen compounds are common for boron and aluminium. The analogous simple hydride of boron, BH_3 , is not found. Instead it occurs as a dimer, B_2H_6 (diborane, **4**) in which the two B atoms are bridged by a pair of H atoms in two three-centre, two-electron bonds ($3c,2e$ bonds).



4 Diborane, B_2H_6

The shapes of the molecules of the electron-precise and electron-rich compounds can all be predicted by the VSEPR rules (Section 2.3). Thus, CH_4 is tetrahedral (1), NH_3 is trigonal pyramidal (2), H_2O is angular (3), and HF is (necessarily) linear.

Electron-deficient compounds provide some of the most interesting and unusual examples of structure and bonding. A Lewis structure for diborane, B_2H_6 , would require at least 14 valence electrons to bind the eight atoms together, but the molecule has only 12 valence electrons. The simple explanation of its structure is the presence of BHB three-centre, two-electron bonds ($3c,2e$; Section 2.11e) acting as bridges between the two B atoms, so two electrons contribute to binding three atoms. These bridging B–H bonds are longer and weaker than the terminal B–H bonds. Another way of viewing this structure is that each BH_3

moiety is a strong Lewis acid and gains the share of an electron pair from a B–H bond in the other BH₃ moiety. Being so small the H atoms pose little or no steric hindrance to dimer formation. The structures of boron hydrides are described more fully in Chapter 13.

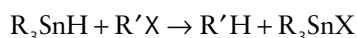
As expected, aluminium shows related behaviour that is modified by the larger atomic radius of this Period 3 element. The compound AlH₃ does not exist as a monomer but forms a polymer in which each relatively large Al atom is surrounded octahedrally by six H atoms. Beryllium, unlike its congeners, exhibits a diagonal relationship with Al and also forms a polymeric covalent hydride BeH₂. Although BH₃ and AlH₃ do not exist as monomers they do form important complex anions in combination with the hydride anion. The common reagents sodium tetrahydridoborate (NaBH₄) and lithium tetrahydridoaluminate (LiAlH₄) are examples of adduct formation between BH₃ or AlH₃, each a Lewis acid, and the Lewis base H[−].

(ii) Reactions of molecular hydrides

Key points: Homolytic dissociation of an E–H bond to produce a radical E· and hydrogen atom H occurs most readily for the hydrides of the heavy p-block elements. Hydrogen attached to an electronegative element has protic character and the compound is typically a Brønsted acid. Hydrogen attached to an electropositive element can be transferred to an acceptor as a hydride ion.

As was summarized briefly in Section 10.2 of Part A, the reactions of binary molecular hydrides are discussed in terms of their ability to undergo homolytic dissociation and, when the dissociation is heterolytic, in terms of their protic or hydridic character.

Homolytic dissociation occurs readily for the hydrogen compounds of some p-block elements, especially the heavier elements. For example, the use of a radical initiator greatly facilitates the reaction of trialkylstannanes, R₃SnH, with haloalkanes, RX, as a result of the formation of R₃Sn· radicals:

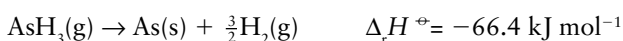


The tendency towards radical reactions increases towards the heavier elements in each group, and Sn–H compounds are in general more prone to radical reactions than are Si–H compounds. The ease of homolytic E–H bond cleavage correlates with the decrease in E–H bond strength down a group.

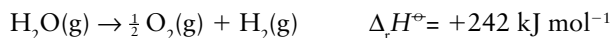
The order of reactivity for haloalkanes with trialkylstannanes is RF < RCl < RBr < RI

Thus fluoroalkanes do not react with R₃SnH, chloroalkanes require heat, photolysis, or chemical radical initiators, and bromoalkanes and iodoalkanes react spontaneously at room temperature. This trend indicates that the initiation step is halogen abstraction.

Thermal decomposition reactions of molecular hydrides yielding H₂ and the element occur by homolytic dissociation. Decomposition temperatures usually correlate with E–H bond energies and inversely with enthalpies of formation. For example, AsH₃ (As–H bond enthalpy 297 kJ mol^{−1}), which is an endothermic hydride, decomposes quantitatively at 250–300°C:



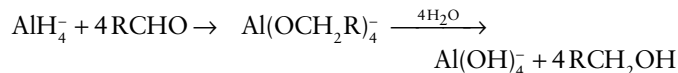
In contrast, water (O–H bond enthalpy 464 kJ mol^{−1}), which is a highly exothermic hydride, is only 4 per cent dissociated into H₂ and O₂ at 2200°C (Box 10.3):



Direct thermolysis of water is therefore not a practical solution for H₂ production.

As we saw in Section 10.2, compounds reacting by proton donation are said to show protic behaviour: in other words, they are Brønsted acids. We saw in Section 4.1 that Brønsted acid strength increases from left to right across a period in the p block (in the order of increasing electron affinity) and down a group (in the order of decreasing bond energy). One striking example of this trend is the increase in acidity from CH₄ to HF and then from HF to HI. Binary hydrogen compounds of elements on the right of the periodic table typically undergo these reactions.

Molecules in which hydrogen is bound to a more electropositive element can act as hydride ion donors. Important examples are the complex hydrido anions such as BH₄[−] and AlH₄[−], which are used to hydrogenate compounds containing a multiple bond.



EXAMPLE 10.1 Determining which hydrogen atoms in a molecule are the most acidic

Phosphorous acid, H₃PO₃, is a diprotic acid and is more helpfully written as OP(H)(OH)₂. Explain why the H atom bound to P is much less protonic than the two H atoms bound to O.

Answer We approach this problem by adapting the principles used to explain the Brønsted acidity of simple molecules. In Section 4.1 we saw that the Brønsted acidity of an acid EH depends upon the E–H bond enthalpy and electron affinity of B. In OP(H)(OH)₂ the P–H bond (bond enthalpy in PH₃ = 321 kJ mol^{−1}) is considerably weaker than an O–H bond (bond enthalpy in H₂O = 464 kJ mol^{−1}) and on this basis we would expect a P–H bond to be more protonic. But the determining factor is that O is much more electronegative than P and therefore better able to accommodate the negative charge left by the departing H⁺. Formic acid, HCO(OH), is another example of a molecule containing H atoms with very different protonic character.

Self-test 10.1 Which of the following, CH₄, SiH₄, or GeH₄, would you expect to be (a) the strongest Brønsted acid and (b) the strongest hydride donor?

(iii) Hydrogen bonding

Key points: Compounds and functionalities containing H atoms attached to electronegative elements with at least one lone pair often associate through hydrogen bonds.

An E–H bond between an electronegative element E and hydrogen is highly polar, ^{δ−}E–H^{δ+}, and the partially positively charged H atom can interact with a lone pair on the E atom of another molecule, forming a bridge that is known as a **hydrogen bond**. Striking evidence for hydrogen bonding is provided by the trends in normal boiling points, which are unusually high for the strongly hydrogen-bonded molecules water (in which there are O–H⋯O bonds), ammonia (containing N–H⋯N bonds), and

hydrogen fluoride (containing $F-H\cdots F$ bonds, Fig. 10.6). The relatively low boiling points of PH_3 , H_2S , HCl , and the heavier p-block molecular hydrides indicate that these molecules do not form strong hydrogen bonds. Although hydrogen bonds are usually much weaker than conventional bonds (Table 10.4), their collective action is responsible for stabilizing complex structures such as the open network structure of ice (Fig. 10.7). Collective hydrogen bonding interactions play a large part in maintaining the structure of protein molecules (Section 27.2). They are also responsible for the recognition between specific DNA bases, adenine/thymine and guanine/cytosine, that underlies gene replication (Fig. 10.8). Similarly, solid HF consists of chain structures that survive partially even in the vapour (5).

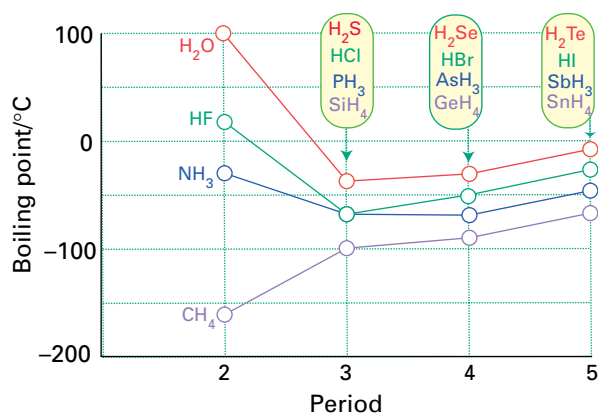


Figure 10.6 Normal boiling points of p-block binary hydrogen compounds.

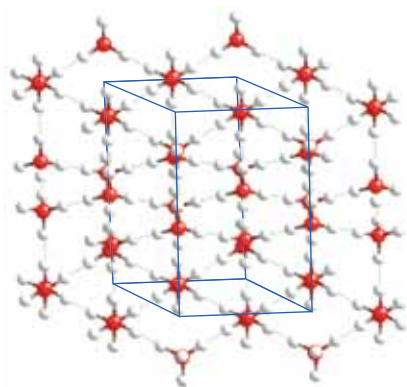


Figure 10.7 The structure of ice. The structure shows all possible atom positions, but only half are actually occupied.

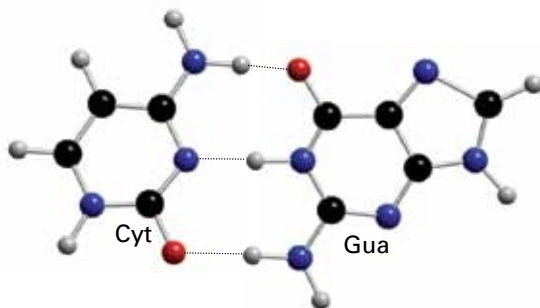
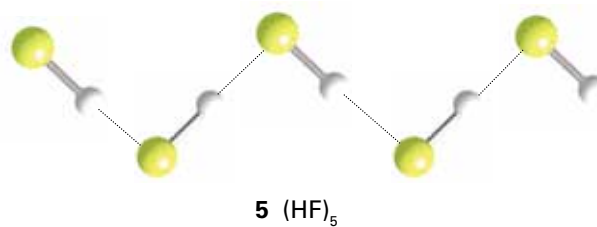


Figure 10.8 Base pairing in DNA. Cytosine recognizes guanine through the formation of three hydrogen bonds.

Table 10.4 Comparison of hydrogen bond enthalpies with the corresponding $E-H$ covalent bond enthalpies (kJ mol^{-1})

	Hydrogen bond		Covalent bond	
$HS-H\cdots SH_2$	7		$S-H$	363
$H_2N-H\cdots NH_3$	17		$N-H$	386
$HO-H\cdots OH_2$	22		$O-H$	464
$F-H\cdots FH$	29		$F-H$	574
$HO-H\cdots Cl^-$	55		$Cl-H$	428
$F-H\cdots F^-$	163			



Hydrogen bonding may be symmetrical or unsymmetrical. In unsymmetrical hydrogen bonding, the H atom is not midway between the two nuclei, even when the heavier linked atoms are identical. For example, the $[ClHCl]^-$ ion is linear but the H atom is not midway between the Cl atoms (Fig. 10.9). By contrast, in the bifluoride ion, $[FHF]^-$, the H atom lies midway between the F atoms; the $F-F$ separation (226 pm) is significantly less than twice the van der Waals radius of the F atom (2×135 pm).

Hydrogen bonding is readily detected by the shift to lower frequency and broadening of $E-H$ stretching bands in infrared spectra (Fig. 10.10) and by unusual proton chemical shifts in 1H -NMR. The structures of hydrogen-bonded complexes have been observed in the gas phase by microwave spectroscopy. The lone-pair orientation of electron-rich compounds implied by VSEPR theory (Section 2.3) shows good agreement with the HF orientation (Fig. 10.11). For example, HF is oriented along the threefold axis of NH_3 , collinear with HCN, out of the H_2O plane in its complex with H_2O , and off the HF axis in the HF dimer. X-ray single crystal structure determinations often show the same patterns, as, for example, in the structure of ice and in

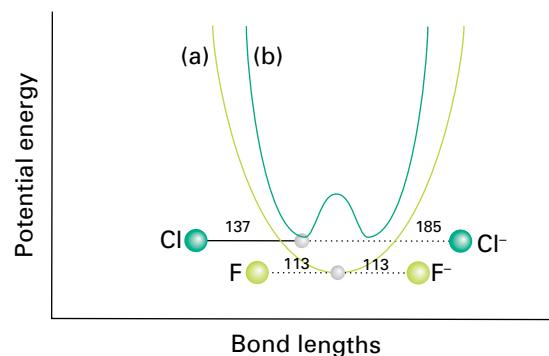


Figure 10.9 The variation of the potential energy with the position of the proton between two atoms in a hydrogen bond. (a) The single minimum potential characteristic of a strong hydrogen bond. (b) The double minimum potential characteristic of a weak hydrogen bond.

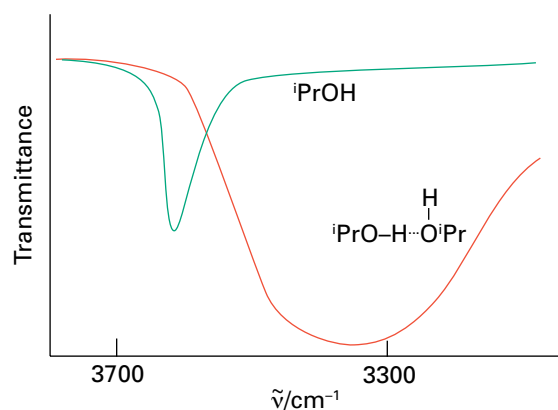


Figure 10.10 Infrared spectra of 2-propanol. In the upper curve, 2-propanol is present as unassociated molecules in dilute solution. In the lower curve, the pure alcohol is associated through hydrogen bonds. The association lowers the frequency and broadens the O–H stretching absorption band. (from N.B. Colthrup, L.H. Daly, and S.E. Wiberley, *Introduction to infrared and Raman spectroscopy*. Academic Press, New York (1975).)

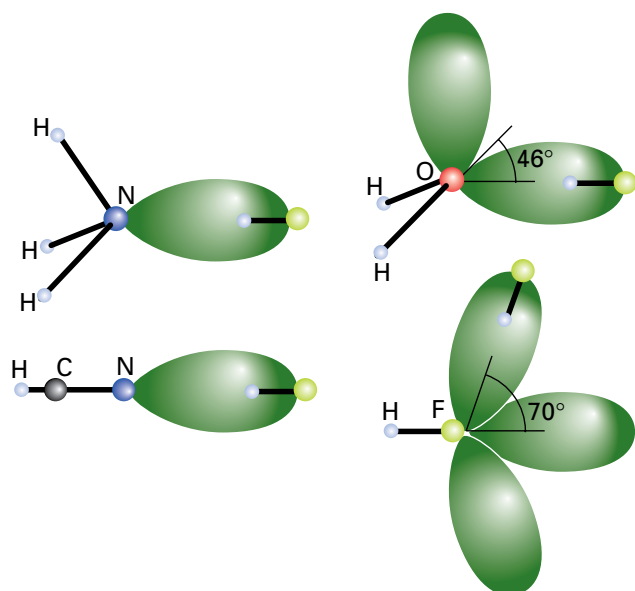


Figure 10.11 The orientation of lone pairs as indicated by VSEPR theory compared with the orientation of HF in the gas-phase hydrogen-bonded complex. The HF molecule is oriented along the threefold axis of NH_3 , collinear with HCN, out of the H_2O plane in its complex with H_2O , and off the HF axis in the HF dimer.

solid HF, but packing forces in solids may have a strong influence on the orientation of the relatively weak hydrogen bond.

One of the most interesting manifestations of hydrogen bonding is the structure of ice. There are at least ten different phases of ice but only one is stable under ordinary conditions. The familiar low-pressure phase of ice, ice-I, crystallizes in a hexagonal unit cell with each O atom surrounded tetrahedrally by four others (as shown in Fig. 10.7). These O atoms are held together by hydrogen bonds with $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}-\text{O}$ bonds largely randomly distributed through the solid. The resulting structure is quite open, which accounts for the density of ice being lower than that of water. When ice melts, the network of hydrogen bonds partially collapses.

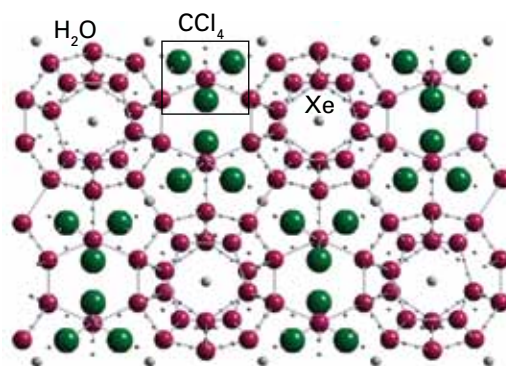
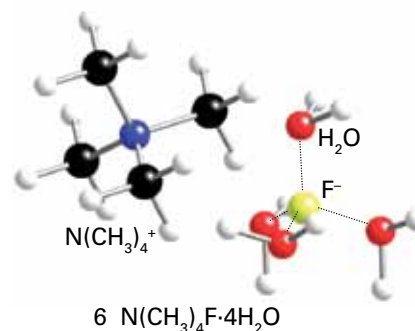


Figure 10.12 The cages of water molecules in clathrate hydrates; in this case $\text{Xe}_4(\text{CCl}_4)_8(\text{H}_2\text{O})_{68}$.

Water can also form **clathrate hydrates**, consisting of hydrogen-bonded cages of water molecules surrounding foreign molecules or ions. One example is the clathrate hydrate of composition $\text{Xe}_4(\text{CCl}_4)_8(\text{H}_2\text{O})_{68}$ (Fig. 10.12). In this structure, the cages with O atoms defining their corners consist of 14-faced and 12-faced polyhedra in the ratio 3:2. These O atoms are held together by hydrogen bonds and guest molecules occupy the interiors of the polyhedra. Aside from their interesting structures, which illustrate the organization that can be enforced by hydrogen bonding, clathrate hydrates are often used as models for the way in which water appears to become organized around nonpolar groups, such as those in proteins. Methane clathrate hydrates occur in the Earth at high pressures, and it is estimated that huge quantities of CH_4 are trapped in these formations (see Box 14.2).

Some ionic compounds form clathrate hydrates in which the anion is incorporated into the framework by hydrogen bonding. This type of clathrate is particularly common with the very strong hydrogen bond acceptors F^- and OH^- . One such example is $\text{N}(\text{CH}_3)_4\text{F}\cdot 4\text{H}_2\text{O}$ (6).



(b) Saline hydrides

Key points: Hydrogen compounds of the most electropositive metals may be regarded as ionic hydrides; they liberate H_2 in contact with Brønsted acids and transfer H^- to electrophiles. As direct hydride donors they react with halide compounds to form anionic hydride complexes.

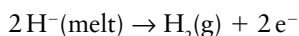
The saline hydrides are ionic solids containing discrete H^- ions and are analogous to corresponding halide salts. The ionic radius of H^- varies from 126 pm in LiH to 154 pm in CsH. This wide variability reflects the poor control that the single charge of the proton has on its two surrounding electrons and the resulting high compressibility and polarizability of H^- . Hydrides

of Group 1 and 2 elements, with the exception of Be, are ionic compounds. All Group 1 hydrides adopt the rock-salt structure. With the exception of MgH_2 , which has the rutile structure, the Group 2 hydrides adopt the PbCl_2 structure (Table 10.5).

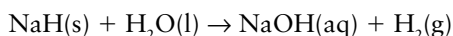
Table 10.5 Structures of s-block hydrides

Compound	Crystal structure
LiH, NaH, RbH, CsH	Rock salt
MgH_2	Rutile
CaH_2 , SrH_2 , BaH_2	Distorted PbCl_2

The saline hydrides are insoluble in common nonaqueous solvents but they do dissolve in molten alkali halides. Electrolysis of these molten-salt solutions produces hydrogen gas at the anode (the site of oxidation):



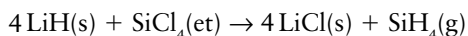
This reaction provides chemical evidence for the existence of H^- ions. The reaction of saline hydrides with water, as in



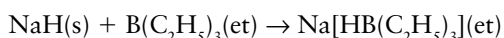
is dangerously vigorous.

Alkali metal hydrides are convenient reagents for making other hydride compounds because they are direct providers of H^- ions for the following synthetically useful reactions:

1. Metathesis with a halide, such as the reaction of finely divided lithium hydride with silicon tetrachloride in dry diethyl ether (et):

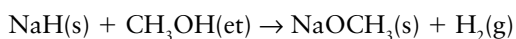


2. Addition to a Lewis acid, for example reaction with a trialkylboron compound yields a hydride complex that is a useful reducing agent and source of hydride ions in organic solvents:



where 'et' denotes solution in diethyl ether

3. Reaction with a proton source, to produce H_2 :



The absence of convenient solvents limits the use of saline hydrides as reagents, but this problem is partially overcome by the availability of commercial dispersions of finely divided NaH in oil. Even more finely divided and reactive alkali metal hydrides can be prepared from the metal alkyl and hydrogen.

Saline hydrides are pyrophoric; indeed, finely divided sodium hydride can ignite simply if it is left exposed to humid air. Such fires are difficult to extinguish because even carbon dioxide is reduced when it comes into contact with hot metal hydrides (water, of course, forms even more flammable hydrogen); they may, however, be blanketed with an inert solid, such as sand.

Magnesium dihydride, MgH_2 , is under investigation as a hydrogen storage medium for transport purposes, where lightness is important (Box 10.4). The amount of H atoms in a given

volume of MgH_2 is about 50 per cent higher than in the same volume of liquid H_2 . Calcium dihydride is used as a portable H_2 generator.

(c) Metallic hydrides

Key points: No stable binary metal hydrides are known for the metals in Groups 7 to 9; metallic hydrides have metallic conductivity and in many the hydrogen is very mobile.

Many of the d- and f-block elements react with H_2 to produce metallic hydrides. Most of these compounds (and the hydrides of alloys) have a metallic lustre and are electrically conducting (hence their name). They are less dense than the parent metal and are brittle. Most metallic hydrides have variable composition (they are nonstoichiometric). For example, at 550°C zirconium hydride exists over a composition range from $\text{ZrH}_{1.30}$ to $\text{ZrH}_{1.75}$; it has the fluorite structure (Fig. 3.38) with a variable number of anion sites unoccupied. The variable stoichiometry and metallic conductivity of these hydrides can be understood in terms of a model in which the band of delocalized orbitals responsible for the conductivity accommodates the electrons supplied by arriving H atoms. In this model, the H atoms as well as the metal atoms take up equilibrium positions in the electron sea. The conductivities of metallic hydrides typically vary with hydrogen content, and this variation can be correlated with the extent to which the conduction band is filled or emptied as hydrogen is added or removed. Thus, whereas CeH_{2-x} is a metallic conductor, CeH_3 (which has a full conduction band) is an insulator and is more like a saline hydride.

Metallic hydrides are formed by all the d-block elements of Groups 3, 4, and 5 and by almost all f-block elements (Fig. 10.13). However, the only hydride in Group 6 is CrH , and no hydrides are known for the unalloyed metals of Groups 7, 8, and 9. The region of the periodic table covered by Groups 7 through to 9 is sometimes referred to as the **hydride gap** because few, if any, stable binary metal–hydrogen compounds are formed by these elements. However, these metals are important as hydrogenation catalysts because they can activate hydrogen. Claims have been made, however, that hydrogen dissolves in iron at very high pressure and that iron hydride is abundant at the centre of the Earth.

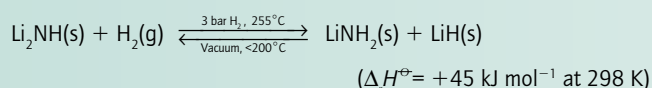
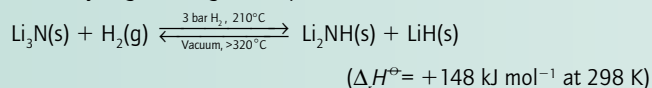
The Group 10 metals, especially Ni and Pt, are often used as hydrogenation catalysts in which surface hydride formation is thought to be involved (Chapter 26). However, somewhat surprisingly, at moderate pressures only Pd forms a stable bulk phase; its composition is PdH_x with $x < 1$. Nickel forms hydride phases at very high pressures but Pt does not form any at all. Apparently the Pt–H bond enthalpy is sufficiently great to disrupt the H–H bond but not strong enough to offset the loss of Pt–Pt bonding, which would occur on formation of a bulk platinum hydride. In agreement with this interpretation, the enthalpies of sublimation, which reflect M–M bond enthalpies, increase in the order Pd (378 kJ mol^{-1}) $<$ Ni (430 kJ mol^{-1}) $<$ Pt (565 kJ mol^{-1}). The M–H bond enthalpy is a crucial factor in the design of metal hydride batteries, which are described in Box 10.5.

Another striking property of many metallic hydrides is the high mobility of hydrogen within the material at slightly elevated temperatures. This mobility is used in the ultrapurification of H_2 by diffusion through a palladium/silver alloy tube (Fig. 10.14).

BOX 10.4 The quest for reversible H₂ storage materials

The need to develop practical systems for on-board hydrogen storage is considered to be a major obstacle to the future use of H₂ as an energy carrier in vehicles. The problem is only partly resolved by compression and liquefaction. Compression to high-pressure gaseous H₂ at 200 bar (energy density 0.53 kWh dm⁻³) then refrigeration to form liquid H₂ (energy density 2.37 kWh dm⁻³) requires considerable energy and containment costs, and these are particularly prohibitive for small private vehicles for which space and cost are also of prime concern. The challenge, therefore, is to identify and develop materials that can store H₂ in a fully reversible manner at high rates under reasonable temperatures and pressure conditions. One such material is LaNi₅H₆, which stores H₂ reversibly with a density of 2 per cent by mass, but for transport these materials also have to be lightweight. Materials under investigation include hydrides, borohydrides, and amides of the lightest metals. Examples of these compounds and their H₂ storage densities (as a percentage of hydrogen by mass) are MgH₂ (8 per cent), LiBH₄ (20 per cent), LiNH₂ (10 per cent), and Al(BH₄)₃ (17 per cent). The last is a liquid that melts at -65°C.

Some of the principles are illustrated by the LiNH₂ system, for which reversible hydrogen storage takes place in two reactions:



The second reaction is the thermodynamically more accessible.

Comparisons of the structures of Li₂NH and LiNH₂ suggest how the kinetics of absorption and desorption depend on ion mobility. The structure

of Li₂NH (antifluorite) is closely related to that of LiNH₂ (defect antifluorite structure with half the Li sites occupied in an ordered manner). The small Li⁺ ions can migrate within such a structure by a hopping mechanism involving transitory defect sites, so allowing H₂ uptake by protonation of NH²⁻ with corresponding expansion of the unit cell (Fig. B10.4) and coupled formation of a LiH phase. A problem that must be overcome with amides and other complex hydrides is their tendency to decompose to undesirable products, such as NH₃.

Liquid organic nitrogen-containing heterocyclic compounds that can take up H₂ reversibly are also under investigation. Compounds based on imidazole are easily handled and the discharged (dehydrogenated) product could simply be exchanged for hydrogenated fuel at a filling station. Another direction for reversible H₂ storage is as molecular clathrates, such as H₂(H₂O)₂. The H₂ molecule is held by weak van der Waals forces and is released by decreasing the pressure or increasing the temperature.

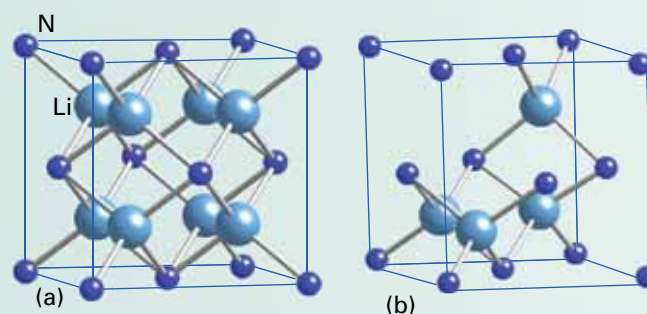


Figure B10.4 Structure relationship between Li₂NH and LiNH₂ which may facilitate transport of Li⁺ ions and reversible uptake of H₂.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				
MH														
MH ₂														
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd				
MH														
MH ₂														
MH ₃														
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg				
MH														
MH ₂														
MH ₃														
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
MH ₂														
MH ₃														
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
MH ₂														
MH ₃														

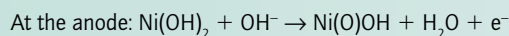
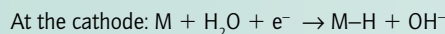
Th₄H₁₅
Np₄H₁₅

Figure 10.13 Hydrides formed by d- and f-block elements. The formulae are limiting stoichiometries based on the structure type.

BOX 10.5 Metal-hydride batteries

A nickel metal-hydride battery is a type of rechargeable battery similar to the widely used nickel-cadmium (NiCad) battery. The main advantages of metal-hydride over NiCad batteries are that they are more easily recycled and do not contain the very toxic element Cd. However, nickel metal-hydride batteries have a high self-discharge rate of approximately 30 per cent per month. This rate is higher than that of NiCad batteries, which is around 20 per cent per month. Despite this, nickel metal-hydride batteries are being investigated as possible power sources for electric vehicles. In contrast to vehicles powered by the internal combustion engine, electric vehicles are emission-free (if the generation of electricity elsewhere is ignored). In addition, the energy efficiency of generating electricity for vehicles is almost twice that of the internal combustion engine. Electric power also reduces society's reliance on oil and increases the opportunities for using renewable energy and also using coal and gas in such a way that the CO₂ can be captured (Box 14.4)

The attractive properties of nickel metal-hydride batteries include high power, long life, a wide range of operating temperatures, short recharging times, and sealed, maintenance-free operation. The cathode is made from a mixed metal alloy at which the metal hydrides are formed reversibly. The anode is made from nickel hydroxide. The electrolyte is a basic solution of 30 per cent by mass KOH. During charging the electrode reactions are



There is no net change in the electrolyte concentration over the charge-discharge cycle.

The strength of the M-H bond in the metal hydride is crucial to the operation of the battery. The ideal bond enthalpy falls in the range 25–50 kJ mol⁻¹. If the bond enthalpy is too low, the hydrogen does not react with the alloy and H₂ is evolved instead. If the bond enthalpy is too high, the reaction is not reversible. Other factors influence the choice of metal. For example, the alloy must not react with KOH solution, must be resistant to oxidation and corrosion, and must tolerate overcharge (during which O₂ is generated at the Ni(O)OH electrode) and overdischarge (during which H₂ is generated at the Ni(OH)₂ electrode). To satisfy these diverse requirements the alloys have disordered structures and use metals that would not be suitable if used alone, including Li, Mg, Al, Ca, V, Cr, Mn, Fe, Cu, and Zr. The number of H atoms per metal atom can be increased by using Mg, Ti, V, Zr, and Nb, and the M-H bond enthalpy can be adjusted by using V, Mn, and Zr. The charge and discharge reactions are catalysed by Al, Mn, Co, Fe, and Ni, and the corrosion resistance is improved by using Cr, Mo, and W. This wide range of properties allows nickel metal-hydride battery performance to be optimized for different applications.

The high mobility of the hydrogen they contain and their variable composition make the metallic hydrides potential hydrogen storage media. On cooling from red heat, palladium absorbs up to 900 times its own volume of H₂, which is given off again on heating. As a result, palladium is sometimes referred to as a 'hydrogen sponge'. The intermetallic compound LaNi₅ forms a hydride phase with a limiting composition LaNi₅H₆, and at this composition it contains a greater density of hydrogen than liquid H₂. A less expensive system with the composition FeTiH_x (x < 1.95) is now commercially available for low-pressure hydrogen storage and it has been tested as a fuel source in vehicle trials.

EXAMPLE 10.2 Correlating the classification and properties of hydrogen compounds

Classify the compounds PH₃, CsH, and B₂H₆ and discuss their probable physical properties. For the molecular compounds specify their subclassification (electron-deficient, electron-precise, or electron-rich).

Answer We need to consider the group to which the element E belongs. The compound CsH is a compound of a Group 1 element, and so it is expected to be a saline hydride, typical of the s-block metals. It is an electrical insulator with the rock-salt structure. As with the hydrogen compounds of other p-block elements, the hydrides PH₃ and B₂H₆ are molecular with low molar masses and high volatilities. They are in fact gases under normal conditions. The Lewis structure indicates that PH₃ has a lone pair on the phosphorus atom and that it is therefore an electron-rich molecular compound. On the other hand, diborane, B₂H₆, is an electron-deficient compound.

Self-test 10.2 Give balanced equations (or NR, for no reaction) for (a) Ca + H₂, (b) NH₃ + BF₃, (c) LiOH + H₂.

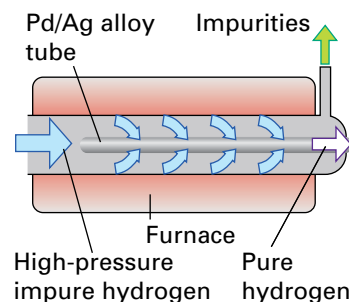
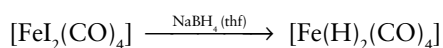
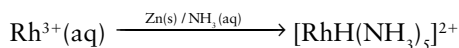


Figure 10.14 Schematic diagram of a hydrogen purifier. Because of a pressure differential and the mobility of H atoms in palladium, hydrogen diffuses through the palladium-silver alloy as H atoms but impurities do not.

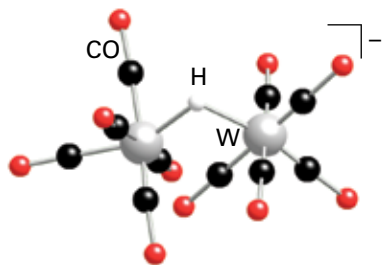
(d) Hydrido and dihydrogen complexes

Key points: A large number of d-block metals complexes are known in which the dihydrogen molecule or hydride anion are ligands. These complexes play important roles in catalysis and hydrogen activation.

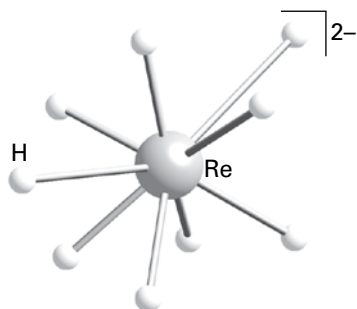
The H atom and the H₂ molecule play an important role in organometallic chemistry, particularly catalysis involving hydrogenation of alkenes and carbonyl groups (see Sections 22.7 and 26.4). An individual, bound H atom is usually regarded as a H⁻ (hydrido) ligand: H⁻ is highly polarizable and behaves as a soft, two-electron σ-donor (Section 22.3). There are a very large number of complexes of d-block and f-block elements containing one or more hydride ligands; these complexes include those of elements in the 'hydride gap' that do not form metallic hydrides. Hydrido complexes can be synthesized by many routes, such as the reaction of a metal ion or complex with a suitable hydrogen source (water) and (usually) a reducing agent.



As with binary compounds of the main group, the coordinated H ligand can be protonic or hydridic depending on the electron-withdrawing or electron-donating character of the metal atom, which in turn depends on the nature of the other ligands. Electron-withdrawing CO ligands in the coordination shell render the H atom protonic, and compounds such as $\text{Co}(\text{H})(\text{CO})_4$ are strong Brønsted acids. As with some main-group hydrides, an H atom can also occupy a bridging position (in a 3c,2e bond) between two metal atoms, usually in conjunction with a metal–metal bond. The complex $[(\mu\text{-H})\text{W}_2(\text{CO})_{10}]^-$ (7) provides a rare example of an H atom bridging two metal atoms that are not otherwise bonded.

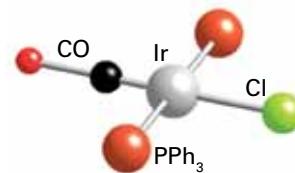
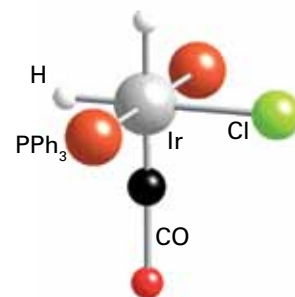
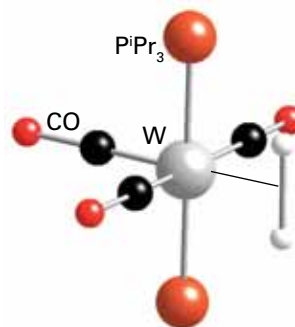
7 $[(\mu\text{-H})\text{W}_2(\text{CO})_{10}]^-$

A **homoleptic complex** is a complex that contains only one type of ligand. Examples of homoleptic hydrido metal complexes are provided by Fe, Rh, and Tc. The dark green compound Mg_2FeH_6 , which contains the octahedral $[\text{FeH}_6]^{4-}$ complex anion, is obtained by reacting the elements together under pressure. The complex anion $[\text{ReH}_9]^{2-}$ (8) is formed by reducing perrhenate, ReO_4^- , with K or Na in ethanol. In the solid state the H atoms form a tricapped trigonal prism around the Re, which is formally in the oxidation state +7. The TcH_9^{2-} complex has the same structure.

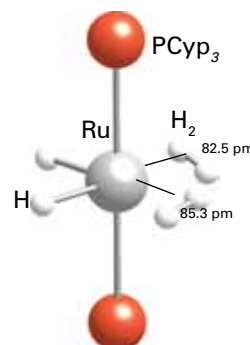
8 $[\text{ReH}_9]^{2-}$

The H_2 molecule can also coordinate, intact, using the $1\sigma_g$ orbital to donate an electron pair and the $1\sigma_u$ orbital to accept an electron pair back from the metal, in what is known as **π -back donation** or **synergic bonding** (Section 22.7). If the metal is electron-rich and in a sufficiently low oxidation state the π -back donation results in homolytic cleavage of the H–H bond and the two H atoms are formally reduced to H^- with concomitant oxidation of the metal. This process is known as **oxidative**

addition and is discussed in more detail in Section 22.22. Oxidative addition of H_2 is exemplified with the so-called ‘Vaska’s compound’ $[\text{IrClCO}(\text{PPh}_3)_2]$ (9). In the product (10), the two H atoms are regarded as hydrido (H^-) ligands and the formal oxidation number of Ir has increased by 2. Many d-block complexes have been isolated that contain a relatively stable, intact H_2 ligand. The first such compound to be identified was $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$ (11), where ^iPr denotes isopropyl, $\text{CH}(\text{CH}_3)_2$.

9 $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, $\text{Ph} = \text{C}_6\text{H}_5$ 10 $[\text{IrCl}(\text{H})_2\text{CO}(\text{PPh}_3)_2]$ 11 $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$

Both H atoms and H_2 molecules may be coordinated as ligands to the same metal atom. The complex $[\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{PCyp}_3)_2]$ (12) contains six H atoms in the inner coordination sphere: the two kinds of ligand, H^- and H_2 , can be distinguished by neutron diffraction.

12 $[\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{PCyp}_3)_2]$, $\text{Cyp} = \text{cyclo-C}_5\text{H}_9$

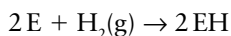
10.7 General methods for synthesis

Key points: The general routes to binary hydrogen compounds are direct reaction of H₂ and the element, protonation of nonmetal anions, and metathesis between a hydride source and a halide or pseudohalide.

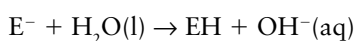
A negative Gibbs energy of formation is a clue that the direct combination of hydrogen and an element may be the preferred synthetic route for a hydrogen compound. When a compound is thermodynamically unstable with respect to its elements, an indirect synthetic route from other compounds can often be found, but each step in the indirect route must be thermodynamically favourable.

There are three common methods for synthesizing binary hydrogen compounds:

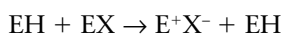
1. Direct combination of the elements (hydrogenolysis):



2. Protonation of a Brønsted basic anion:



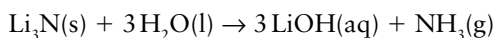
3. Reaction of an ionic hydride or hydride donor with a halide (metathesis):



In such general equations, the symbol E can also denote an element with higher valence, with corresponding changes of detail in the formulas and stoichiometric coefficients.

Direct combination is used commercially for the synthesis of compounds that have negative Gibbs energies of formation, including NH₃ and the hydrides of lithium, sodium, and calcium. However, in some cases high pressure, high temperature, and a catalyst are necessary to overcome unfavourable kinetic barriers. The high temperature used for the lithium reaction is an example: it melts the metal and hence helps to break up the surface layer of hydride that would otherwise passivate it. This inconvenience is avoided in many laboratory preparations by adopting one of the alternative synthesis routes, which may also be used to prepare compounds with positive Gibbs energies of formation.

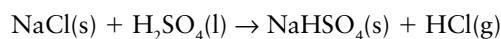
An example of protonation of a Brønsted base, such as a nitride ion, is



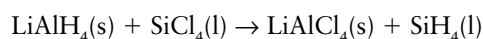
FURTHER READING

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- J. S. Rigden, *Hydrogen: the essential element*. Harvard University Press (2002).
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Lithium nitride is too expensive for the reaction to be suitable for the commercial production of ammonia, but it is very useful in the laboratory for the preparation of ND₃ (by using D₂O in place of H₂O). The success of the reaction depends on the Brønsted acid being a better proton donor than the conjugate acid of the N³⁻ anion (NH₃ in this case). Water is a sufficiently strong acid to protonate the very strong base N³⁻, but a stronger acid, such as H₂SO₄, is required to protonate the weak base Cl⁻:



An example of synthesis by metathesis is the preparation of silane

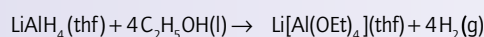


This reaction involves (at least formally) the exchange of Cl⁻ ions for H⁻ ions in the coordination sphere of the Si atom. Hydrides of the more electropositive elements (LiH, NaH, and the AlH₄⁻ anion) are the most active H⁻ sources. The favoured sources are often the AlH₄⁻ and BH₄⁻ ions in salts such as LiAlH₄ and NaBH₄, which are soluble in ether solvents that solvate the alkali metal ion. Of these two anion complexes, AlH₄⁻ is much the stronger hydride donor.

EXAMPLE 10.3 Using hydrogen compounds in synthesis

Suggest a procedure for synthesizing lithium tetraethoxyaluminate, Li[Al(OEt)₄], from LiAlH₄ and reagents and solvents of your choice.

Answer We need to note that AlH₄⁻ is a H⁻ donor. Because H⁻ is an even stronger Brønsted base than ethoxide (CH₃CH₂O⁻ = EtO⁻) it should react with ethanol to produce H₂ and yield EtO⁻, which will thus replace H⁻. The reaction of the slightly acidic compound ethanol with the strongly hydridic lithium tetrahydroaluminatoaluminate should yield the desired alkoxide and hydrogen. The reaction might be carried out by dissolving LiAlH₄ in tetrahydrofuran and dropping ethanol into this solution slowly:



This type of reaction should be carried out slowly under a stream of inert gas (N₂ or Ar) to dilute the H₂, which is explosively flammable.

Self-test 10.3 Suggest a way of making triethylmethylstannane, MeEt₃Sn, from triethylstannane, Et₃SnH, and a reagent of your choice.

- G.W. Crabtree, M.S. Dresselhaus, and M.V. Buchanan. The hydrogen economy. *Physics Today*, 2004, **57**, 39.
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EXERCISES

- 10.1** It has been suggested that hydrogen could be placed in Group 1, Group 14, or Group 17 of the periodic table. Give arguments for and against each of these positions.
- 10.2** Explain the relatively low reactivity of hydrogen.
- 10.3** Assign oxidation numbers to the elements in (a) H_2S , (b) KH , (c) $[\text{ReH}_9]^{2-}$, (d) H_2SO_4 , (e) $\text{H}_2\text{PO}(\text{OH})$.
- 10.4** Write balanced chemical equations for three major industrial preparations of hydrogen gas. Propose two different reactions that would be convenient for the preparation of hydrogen in the laboratory.
- 10.5** Preferably without consulting reference material, construct the periodic table, identify the elements, and (a) indicate positions of salt-like, metallic, and molecular hydrides, (b) add arrows to indicate trends in $\Delta_f G^\ominus$ for the hydrogen compounds of the p-block elements, and (c) identify the areas where the molecular hydrides are electron-deficient, electron-precise, and electron-rich.
- 10.6** Describe the expected physical properties of water in the absence of hydrogen bonding.
- 10.7** Which hydrogen bond would you expect to be stronger, $\text{S}-\text{H}\cdots\text{O}$ or $\text{O}-\text{H}\cdots\text{S}$? Why?
- 10.8** Name and classify the following hydrogen compounds: (a) BaH_2 , (b) SiH_4 , (c) NH_3 , (d) AsH_3 , (e) $\text{PdH}_{0.9}$, (f) HI .
- 10.9** Identify the compounds from Exercise 10.8 that provide the most pronounced example of the following chemical characteristics and give a balanced equation that illustrates each of the characteristics: (a) hydridic character, (b) Brønsted acidity, (c) variable composition, (d) Lewis basicity.
- 10.10** Divide the compounds in Exercise 10.8 into those that are solids, liquids, or gases at room temperature and pressure. Which of the solids are likely to be good electrical conductors?
- 10.11** Use Lewis structures and VSEPR theory to predict the shapes of H_2Se , P_2H_4 , and H_3O^+ and to assign point groups. Assume a skew structure for P_2H_4 .

- 10.12** Identify the reaction that is most likely to give the highest proportion of HD and give your reasoning: (a) $\text{H}_2 + \text{D}_2$ equilibrated over a platinum surface, (b) $\text{D}_2\text{O} + \text{NaH}$, (c) electrolysis of HDO.
- 10.13** Identify the compound in the following list that is most likely to undergo radical reactions with alkyl halides and describe the reason for your choice: H_2O , NH_3 , $(\text{CH}_3)_3\text{SiH}$, $(\text{CH}_3)_3\text{SnH}$.
- 10.14** Arrange H_2O , H_2S , and H_2Se in order of (a) increasing acidity and (b) increasing basicity towards a hard acid such as the proton.
- 10.15** Describe the three different common methods for the synthesis of binary hydrogen compounds and illustrate each one with a balanced chemical equation.
- 10.16** What is the trend in hydridic character of BH_4^- , AlH_4^- , and GaH_4^- ? Which is the strongest reducing agent? Give the equations for the reaction of GaH_4^- with excess 1 M $\text{HCl}(\text{aq})$.
- 10.17** Describe the important physical differences and a chemical difference between each of the hydrogen compounds of the p-block elements in Period 2 with their counterparts in Period 3.
- 10.18** Stibane, SbH_3 ($\Delta_f H^\ominus = +145.1 \text{ kJ mol}^{-1}$) decomposes above -45°C . Assess the difficulty in preparing a sample of BiH_3 ($\Delta_f H^\ominus = +277.8 \text{ kJ mol}^{-1}$) and suggest a method for its preparation.
- 10.19** What type of substance is formed by the interaction of water and krypton at low temperatures and elevated krypton pressure? Describe the structure in general terms.
- 10.20** Sketch the approximate potential energy surfaces for the hydrogen bond between H_2O and the Cl^- ion, and contrast this with the potential energy surface for the hydrogen bond in $[\text{FHF}]^-$.
- 10.21** Dihydrogen is a familiar reducing agent, but it is also an oxidizing agent. Explain this statement, giving examples.

PROBLEMS

- 10.1** What is the expected infrared stretching wavenumber of gaseous $^3\text{H}^{35}\text{Cl}$ given that the corresponding value for $^1\text{H}^{35}\text{Cl}$ is 2991 cm^{-1} ?
- 10.2** Consult Chapter 8 and then sketch the qualitative splitting pattern and relative intensities within each set for the ^1H - and ^{31}P -NMR spectra of PH_3 .
- 10.3** In his paper 'The proper place for hydrogen' (*J. Chem. Educ.*, 2003, 80, 947), M.W. Cronyn argues that hydrogen should be placed at the head of Group 14 immediately above carbon. Summarize his reasoning.
- 10.4** (a) Sketch a qualitative molecular orbital energy level diagram for the HeH^+ molecule ion and indicate the correlation of the molecular orbital levels with the atomic energy levels. The ionization energy of H is 13.6 eV and the first ionization energy of He is 24.6 eV. (b) Estimate the relative contribution of $\text{H}1s$ and $\text{He}1s$ orbitals to the bonding orbital and predict the location of the partial positive charge of the polar molecule. (c) Why do you suppose that HeH^+ is unstable on contact with common solvents and surfaces?
- 10.5** Spectroscopic evidence has been obtained for the existence of $[\text{Ir}(\text{C}_5\text{H}_5)(\text{H}_3)(\text{PR}_3)]^+$, a complex in which one ligand is formally H_3^+ . Devise a plausible molecular orbital scheme for the bonding in the complex, assuming that an angular H_3 unit occupies one coordination

site and interacts with the e_g and t_{2g} orbitals of the metal. An alternative formulation of the structure of the complex, however, is as a trihydro species with very large coupling constants (see *J. Am. Chem. Soc.*, 1991, 113, 6074 and the references therein, and especially *J. Am. Chem. Soc.*, 1990, 112, 909 and 920). Review the evidence for this alternative formulation.

- 10.6** Correct the faulty statements in the following description of hydrogen compounds. 'Hydrogen, the lightest element, forms thermodynamically stable compounds with all of the nonmetals and most metals. The isotopes of hydrogen have mass numbers of 1, 2, and 3, and the isotope of mass number 2 is radioactive. The structures of the hydrides of the Group 1 and 2 elements are typical of ionic compounds because the H^- ion is compact and has a well-defined radius. The structures of the hydrogen compounds of the nonmetals are adequately described by VSEPR theory. The compound NaBH_4 is a versatile reagent because it has greater hydridic character than the simple Group 1 hydrides such as NaH . Heavy element hydrides such as the tin hydrides frequently undergo radical reactions, in part because of the low E-H bond energy. The boron hydrides are called electron-deficient compounds because they are easily reduced by hydrogen.'