

3.3 Preparation, Production and Uses^(5,6)

3.3.1 Hydrogen

Hydrogen can be prepared by the reaction of water or dilute acids on electropositive metals such as the alkali metals, alkaline earth metals, the metals of Groups 3, 4 and the lanthanoids. The reaction can be explosively violent. Convenient laboratory methods employ sodium amalgam or calcium with water, or zinc with hydrochloric acid. The reaction of aluminium or ferrosilicon with aqueous sodium hydroxide has also been used. For small-scale preparations the hydrolysis of metal hydrides is convenient, and this generates twice the amount of hydrogen as contained in the hydride, e.g.:

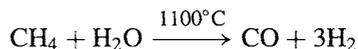


Electrolysis of acidified water using platinum electrodes is a convenient source of hydrogen (and oxygen) and, on a larger scale, very pure hydrogen (>99.95%) can be obtained from the electrolysis of warm aqueous solutions of barium hydroxide between nickel electrodes. The method is expensive but becomes economical

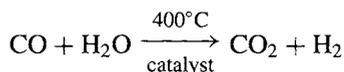
⁵ T. A. CZUPPON, S. A. KNEZ and D. S. NEWSOME, Hydrogen, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 13, Wiley, New York, 1995, pp. 838–94.

⁶ P. HÄUSSINGER R. LOHMÜLLER and A. M. WATSON, Hydrogen, in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edn., Vol. A13, VCH, Weinheim, 1989, pp. 297–442.

on an industrial scale when integrated with the chloralkali industry (p. 798). Other bulk processes involve the (endothermic) reaction of steam on hydrocarbons or coke:

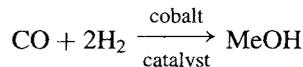


In both processes the CO can be converted to CO₂ by passing the gases and steam over an iron oxide or cobalt oxide catalyst at 400°C, thereby generating more hydrogen:



This is the so-called water-gas shift reaction ($-\Delta G_{298}^\circ 19.9 \text{ kJ mol}^{-1}$) and it can also be effected by low-temperature homogeneous catalysts in aqueous acid solutions.⁽⁷⁾ The extent of subsequent purification of the hydrogen depends on the use to which it will be put.

The industrial production of hydrogen is considered in more detail in the Panel. The largest single use of hydrogen is in ammonia synthesis (p. 421) but other major applications are in the catalytic hydrogenation of unsaturated liquid vegetable oils to solid, edible fats (margarine), and in the manufacture of bulk organic chemicals, particularly methanol (by the “oxo” or hydroformylation process):

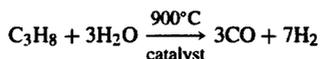


Direct reaction of hydrogen with chlorine is a major source of hydrogen chloride (p. 811), and a smaller, though still substantial use is in the manufacture of metal hydrides and complex metal hydrides (p. 64). Hydrogen is used in metallurgy to reduce oxides to metals (e.g. Mo, W) and to produce a reducing atmosphere. Direct reduction of iron ores in steelmaking is also now becoming technically and economically feasible.

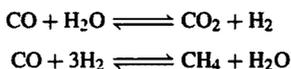
⁷ C.-H. CHENG and R. EISENBERG, *J. Am. Chem. Soc.* **100**, 5969–70 (1978).

Industrial Production of Hydrogen

Many reactions are available for the preparation of hydrogen and the one chosen depends on the amount needed, the purity required, and the availability of raw materials. Most (~97%) of the hydrogen produced in industry is consumed in integrated plants on site (e.g. ammonia synthesis, petrochemical works, etc.). Even so, vast amounts of the gas are produced for the general market, e.g. $\sim 6.5 \times 10^{10} \text{ m}^3$ or 5.4 million tonnes yearly in the USA alone. Small generators may have a capacity of $100\text{--}4000 \text{ m}^3 \text{ h}^{-1}$, medium-sized plants $4000\text{--}10\,000 \text{ m}^3 \text{ h}^{-1}$, and large plants can produce $10^4\text{--}10^5 \text{ m}^3 \text{ h}^{-1}$. The dominant large-scale process in integrated plants is the catalytic steam-hydrocarbon reforming process using natural gas or oil-refinery feedstock. After desulfurization (to protect catalysts) the feedstock is mixed with process steam and passed over a nickel-based catalyst at $700\text{--}1000^\circ\text{C}$ to convert it irreversibly to CO and H_2 , e.g.



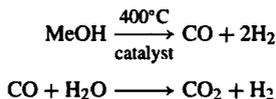
Two reversible reactions also occur to give an equilibrium mixture of H_2 , CO, CO_2 and H_2O :



The mixture is cooled to $\sim 350^\circ\text{C}$ before entering a high-temperature shift convertor where the major portion of the CO is catalytically and exothermically converted to CO_2 and hydrogen by reaction with H_2O . The issuing gas is further cooled to 200° before entering the low-temperature shift convertor which reduces the CO content to 0.2 vol%. The product is further cooled and CO_2 absorbed in a liquid contactor. Further removal of residual CO and CO_2 can be effected by methanation at 350°C to a maximum of 10 ppm. Provided that the feedstock contains no nitrogen the product purity is about 98%. Alternatively the low-temperature shift process and methanation stage can be replaced by a single pressure-swing absorption (PSA) system in which the hydrogen is purified by molecular sieves. The sieves are regenerated by adiabatic depressurization at ambient temperature (hence the name) and the product has a purity of $\geq 99.9\%$.

At present about 77% of the industrial hydrogen produced is from petrochemicals, 18% from coal, 4% by electrolysis of aqueous solutions and at most 1% from other sources. Thus, hydrogen is produced as a byproduct of the brine electrolysis process for the manufacture of chlorine and sodium hydroxide (p. 798). The ratio of $\text{H}_2:\text{Cl}_2:\text{NaOH}$ is, of course, fixed by stoichiometry and this is an economic determinant since bulk transport of the byproduct hydrogen is expensive. To illustrate the scale of the problem: the total world chlorine production capacity is about 38 million tonnes per year which corresponds to 105 000 tonnes of hydrogen ($1.3 \times 10^{10} \text{ m}^3$). Plants designed specifically for the electrolytic manufacture of hydrogen as the main product, use steel cells and aqueous potassium hydroxide as electrolyte. The cells may be operated at atmospheric pressure (Knowles cells) or at 30 atm (Lonza cells).

When relatively small amounts of hydrogen are required, perhaps in remote locations such as weather stations, then small transportable generators can be used which can produce $1\text{--}17 \text{ m}^3 \text{ h}^{-1}$. During production a 1:1 molar mixture of hydrogen and water is vaporized and passed over a "base-metal chromite" type catalyst at 400°C where it is cracked into hydrogen and carbon monoxide; subsequently steam reacts with the carbon monoxide to produce the dioxide and more hydrogen:



All the gases are then passed through a diffuser separator comprising a large number of small-diameter thin-walled tubes of palladium-silver alloy tightly packed in a stainless steel case. The solubility of hydrogen in palladium is well known (p. 1150) and the alloy with silver is used to prolong the life of the diffuser by avoiding troublesome changes in dimensions during the passage of hydrogen. The hydrogen which emerges is cool, pure, dry and ready for use via a metering device.

Another medium-scale use is in oxyhydrogen torches and atomic hydrogen torches for welding and cutting. Liquid hydrogen is used in bubble chambers for studying high-energy particles and as a rocket fuel (with oxygen) in the space programme. Hydrogen gas is potentially a large-scale fuel for use in internal combustion engines

and fuel cells if the notional "hydrogen economy" (see Panel on p. 40) is ever developed.

3.3.2 Deuterium

Deuterium is invariably prepared from heavy water, D_2O , which is itself now manufactured

The Hydrogen Economy^(6,8-11)

The growing recognition during the past decades that world reserves of coal and oil are finite and that nuclear power cannot supply all our energy requirements, particularly for small mobile units such as cars, has prompted an active search for alternatives. One solution which has many attractive features is the "hydrogen economy" whereby energy is transported and stored in the form of liquid or gaseous hydrogen. Enthusiasts point out that such a major change in the source of energy, though apparently dramatic, is not unprecedented and has in fact occurred twice during the past 100 y. In 1880 wood was overtaken by coal as the main world supplier of energy and now it accounts for only about 2% of the total. Likewise in 1960 coal was itself overtaken by oil and now accounts for only 15% of the total. (Note, however, that this does not imply a decrease in the total amount of coal used: in 1930 this was 14.5×10^6 barrels per day of oil equivalent and was 75% of the then total energy supply whereas in 1975 coal had increased in absolute terms by 11% to 16.2×10^6 b/d oe, but this was only 18% of the total energy supply which had itself increased 4.6-fold in the interim.) Another change may well be in the offing since nuclear power, which was effectively non-existent as an industrial source of energy in 1950, now accounts for 16% of the world supply of electricity; it has already overtaken coal as a source of energy and may well overtake oil during the next century. The aim of the "hydrogen economy" is to transmit this energy, not as electric power but in the form of hydrogen; this overcomes the great problem of electricity — that it cannot be stored — and also reduces the costs of power transmission.

The technology already exists for producing hydrogen electrically and storing it in bulk. For example huge quantities of liquid hydrogen are routinely stored in vacuum insulated cryogenic tanks for the US space programme, one such tank alone holding over 3400 m^3 (900 000 US gallons). Liquid hydrogen can be transported by road or by rail tankers of 75.7 m^3 capacity (20 000 US gallons). Underground storage of the type currently used for hydrogen — natural gas mixtures and transmission through large pipes is also feasible, and pipelines carrying hydrogen up to 80 km in the USA and South Africa and 200 km in Europe have been in operation for many years. Smaller storage units based on metal alloy systems have also been suggested, e.g. LaNi_5 can absorb up to 7 moles of H atoms per mole of LaNi_5 at room temperature and 2.5 atm, the density of contained hydrogen being twice that in the liquid element itself. Other systems include Mg-MgH_2 , $\text{Mg}_2\text{Ni-Mg}_2\text{NiH}_4$, Ti-TiH_2 and $\text{TiFe-TiFeH}_{1.95}$.

The advantages claimed for hydrogen as an automobile fuel are the greater energy release per unit weight of fuel and the absence of polluting emissions such as CO , CO_2 , NO_x , SO_2 , hydrocarbons, aldehydes and lead compounds. The product of combustion is water with only traces of nitrogen oxides. Several conventional internal-combustion petrol engines have already been simply and effectively modified to run on hydrogen. Fuel cells for the regeneration of electric power have also been successfully operated commercially with a conversion efficiency of 70%, and test cells at higher pressures have achieved 85% efficiency.

Non-electrolytic sources of hydrogen have also been studied. The chemical problem is how to transfer the correct amount of free energy to a water molecule in order to decompose it. In the last few years about 10 000 such thermochemical water-splitting cycles have been identified, most of them with the help of computers, though it is significant that the most promising ones were discovered first by the intuition of chemists.

The stage is thus set, and further work to establish safe and economically viable sources of hydrogen for general energy usage seems destined to flourish as an active area of research for some while.

on the multitonne scale by the electrolytic enrichment of normal water.^(12,13) The enrichment is expressed as a separation factor between the gaseous and liquid phases:

$$s = (\text{H/D})_g / (\text{H/D})_l$$

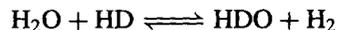
⁸ D. P. GREGORY, *The hydrogen economy*, Chap. 23 in *Chemistry in the Environment*, Readings from *Scientific American*, 1973, pp. 219-27.

⁹ L. B. MCGOWN and J. O'M. BOCKRIS, *How to Obtain Abundant Clean Energy*, Plenum, New York, 1980, 275 pp. L. O. WILLIAMS, *Hydrogen Power*, Pergamon Press, Oxford, 1980, 158 pp.

¹⁰ C. J. WINTER and J. NITSCH (eds.), *Hydrogen as an Energy Carrier*, Springer Verlag, Berlin, 1988, 377 pp.

¹¹ B. BOGDANOVIĆ, *Angew. Chem. Int. Edn. Engl.* **24**, 262-73 (1985).

The equilibrium constant for the exchange reaction



is about 3 at room temperature and this would lead to a value of $s = 3$ if this were the only effect. However, the choice of the metal used for the electrodes can also affect the various electrode processes, and this increases the separation still further. Using alkaline solutions s values in

¹² G. VASARU, D. URSU, A. MIHAILĂ and P. SZENT-GYÖRGYI, *Deuterium and Heavy Water*, Elsevier, Amsterdam, 1975, 404 pp.

¹³ H. K. RAE (ed.), *Separation of Hydrogen Isotopes*, ACS Symposium Series No. 68, 1978, 184 pp.

the range 5–7.6 are obtained for many metals, rising to 13.9 for platinum cathodes and even higher for gold. By operating a large number of cells in cascade, and burning the evolved H₂/D₂ mixture to replenish the electrolyte of earlier cells in the sequence, any desired degree of enrichment can ultimately be attained. Thus, starting with normal water (0.0156% of hydrogen as deuterium) and a separation factor of 5, the deuterium content rises to 10% after the original volume has been reduced by a factor of 2400. Reduction by 66 000 is required for 90% deuterium and by 130 000 for 99% deuterium. If, however, the separation factor is 10, then 99% deuterium can be obtained by a volume reduction on electrolysis of 22 000. Prior enrichment of the electrolyte to 15% deuterium can be achieved by a chemical exchange between H₂S and H₂O after which a fortyfold volume reduction produces heavy water with 99% deuterium content. Other enrichment processes are now rarely used but include fractional distillation of water (which also enriches ¹⁸O), thermal diffusion of gaseous hydrogen, and diffusion of H₂/D₂ through palladium metal.

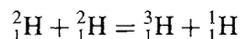
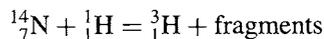
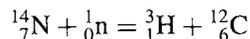
Many methods have been used to determine the deuterium content of hydrogen gas or water. For H₂/D₂ mixtures mass spectroscopy and thermal conductivity can be used together with gas chromatography (alumina activated with manganese chloride at 77 K). For heavy water the deuterium content can be determined by density measurements, refractive index change, or infrared spectroscopy.

The main uses of deuterium are in tracer studies to follow reaction paths and in kinetic studies to determine isotope effects.⁽¹⁴⁾ A good discussion with appropriate references is in *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 99–116. The use of deuterated solvents is widespread in proton nmr studies to avoid interference from solvent hydrogen atoms, and deuterated compounds are also valuable in structural studies involving neutron diffraction techniques.

¹⁴ L. MELANDER and W. H. SAUNDERS, *Reaction Rates of Isotopic Molecules*, Wiley, New York, 1980, 331 pp.

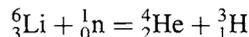
3.3.3 Tritium⁽¹⁵⁾

Tritium differs from the other two isotopes of hydrogen in being radioactive and this immediately indicates its potential uses and its method of detection. Tritium occurs naturally to the extent of about 1 atom per 10¹⁸ hydrogen atoms as a result of nuclear reactions induced by cosmic rays in the upper atmosphere:



The concentration of tritium increased by over a hundredfold when thermonuclear weapon testing began on Bikini Atoll in March 1954 but has now subsided as a result of the ban on atmospheric weapon testing and the natural radioactivity of the isotope ($t_{1/2}$ 12.33 y).

Numerous reactions are available for the artificial production of tritium and it is now made on a large scale by neutron irradiation of enriched ⁶Li in a nuclear reactor:



The lithium is in the form of an alloy with magnesium or aluminium which retains much of the tritium until it is released by treatment with acid. Alternatively the tritium can be produced by neutron irradiation of enriched LiF at 450° in a vacuum and then recovered from the gaseous products by diffusion through a palladium barrier. As a result of the massive production of tritium for thermonuclear devices and research into energy production by fusion reactions, tritium is available cheaply on the megacurie scale for peaceful purposes.[†] The most convenient way of storing the gas is to react it with finely divided uranium

¹⁵ E. A. EVANS, *Tritium and its Compounds*, 2nd edn., Butterworths, London, 1974, 840 pp. E. A. EVANS, D. C. WARRELL, J. A. ELVIDGE and J. R. JONES, *Handbook of Tritium NMR Spectroscopy and Applications*, Wiley, Chichester, 1985, 249 pp.

[†] See also p. 18 for the influence on the atomic weight of commercially available lithium in some countries.

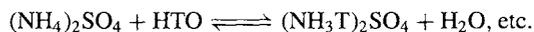
to give UT_3 from which it can be released by heating above 400°C .

Besides being one of the least expensive radioisotopes, tritium has certain unique advantages as a tracer. Like ^{14}C it is a pure low-energy β^- emitter with no associated γ -rays. The radiation is stopped by $\sim 6\text{ mm}$ of air or $\sim 6\ \mu\text{m}$ of material of density $1\ \text{g cm}^{-3}$ (e.g. water). As the range is inversely proportional to the density, this is reduced to only $\sim 1\ \mu\text{m}$ in photographic emulsion ($\rho \sim 3.5\ \text{g cm}^{-3}$) thus making tritium ideal for high-resolution autoradiography. Moreover, tritium has a high specific activity. The weight of tritium equal to an activity of 1 Ci is 0.103 mg and 1 mmol T_2 has an activity of 58.25 Ci. [Note: 1 Ci (curie) = 3.7×10^{10} Bq (becquerel); 1 Bq = $1\ \text{s}^{-1}$.] Tritium is one of the least toxic of radioisotopes and shielding is unnecessary; however, precautions must be taken against ingestion, and no work should be carried out without appropriate statutory authorization and adequate radiochemical facilities.

Tritium has been used extensively in hydrological studies to follow the movement of ground waters and to determine the age of various bodies of water. It has also been used to study the adsorption of hydrogen and the hydrogenation of ethylene on a nickel catalyst and to study the absorption of hydrogen in metals. Autoradiography has been used extensively to study the distribution of tritium in multiphase alloys, though care must be taken to correct for the photographic darkening caused by emanated tritium gas. Increasing use is also being made of tritium as a tracer for hydrogen in the study of reaction mechanisms and kinetics and in work on homogeneous catalysis.

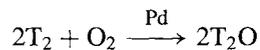
The production of tritium-labelled organic compounds was enormously facilitated by K. E. Wilzbach's discovery in 1956 that tritium could be introduced merely by storing a compound under tritium gas for a few days or weeks: the β^- radiation induces exchange reactions between the hydrogen atoms in the compound and the tritium gas. The excess of gas is recovered for further use and the tritiated compound is purified chromatographically. Another widely used method of

general applicability is catalytic exchange in solution using either a tritiated solution or tritium gas. This is valuable for the routine production of tritium compounds in high radiochemical yield and at high specific activity ($> 50\ \text{mCi mmol}^{-1}$). For example, although ammonium ions exchange relatively slowly with D_2O , tritium exchange equilibria are established virtually instantaneously: tritiated ammonium salts can therefore be readily prepared by dissolving the salt in tritiated water and then removing the water by evaporation:



For exchange of non-labile organic hydrogen atoms, acid-base catalysis (or some other catalytic hydrogen-transfer agent such as palladium or platinum) is required. The method routinely gives tritiated products having a specific activity almost 1000 times that obtained by the Wilzbach method; shorter times are required (2–12 h) and subsequent purification is easier.

When specifically labelled compounds are required, direct chemical synthesis may be necessary. The standard techniques of preparative chemistry are used, suitably modified for small-scale work with radioactive materials. The starting material is tritium gas which can be obtained at greater than 98% isotopic abundance. Tritiated water can be made either by catalytic oxidation over palladium or by reduction of a metal oxide:



Note, however, that pure tritiated water is virtually never used since 1 ml would contain 2650 Ci; it is self-luminescent, irradiates itself at the rate of $6 \times 10^{17}\ \text{eV ml}^{-1}\ \text{s}^{-1}$ ($\sim 10^9$ rad day^{-1}), undergoes rapid self-radiolysis, and also causes considerable radiation damage to dissolved species. In chemical syntheses or exchange reactions tritiated water of 1% tritium abundance ($580\ \text{mCi mmol}^{-1}$) is usually sufficient to produce compounds having a specific activity of at least $100\ \text{mCi mmol}^{-1}$. Other useful