COMPREHENSIVE INORGANIC CHEMISTRY

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PERGAMON PRESS
OXFORD · NEW YORK · TORONTO
SYDNEY · BRAUNSCHWEIG

Pergamon Press Ltd., Headington Hill Hall, Oxford
Pergamon Press (Aust.) Pty. Ltd., 19a Boundary Street,
Rushcutters Bay, N.S.W. 2011, Australia
Vieweg & Sohn GmbH, Burgplatz 1, Braunschweig

First edition 1973

Library of Congress Cataloging in Publication Data

Main entry under title:
Comprehensive inorganic chemistry.
1. Chemistry, Inorganic. I. Bailar, John
Christian, 1904– ed. II. Trotman-Dickenson, A. F., ed.
[DNLM: 1. Chemistry. QD 151.2 C737 1973]
QD151.2.C64 547 77–189736
ISBN 0–08–017275–X

Exclusive distributors in the Western Hemisphere
Compendium Publishers
Fairview Park, Elmsford, New York 10523

Printed in Great Britain by A. Wheaton & Co., Exeter
ISBN 0 08 015655 X

PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters on the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

CONTENTS

1. THE ELEMENT HYDROGEN, ORTHO- AND PARA-HYDROGEN, ATOMIC HYDROGEN

K. M. MACKAY
University of Waikato

1. INTRODUCTION

In this article, the properties of elemental hydrogen are detailed, together with those of its various forms. The heavier isotopes, and species containing them such as HD, are treated in Chapter 2, and hydrogen compounds are reviewed in Chapter 3. More detailed accounts of individual hydrides are given under each element and major sections are devoted to boron hydrides and related compounds and to hydrido-complexes of the transition elements. The proton, protonic acids, and the hydrogen bond are treated later.

The first record of hydrogen probably dates back to Paracelsus in the sixteenth century who observed an "air" formed by the action of acids on iron which was inflammable. Observations on this air were made by a number of seventeenth-century chemists, including Boyle and de Mayerne, but the first isolation of pure hydrogen was not achieved until 1766 by Cavendish, who distinguished it from other inflammable gases. In later work (1784), Cavendish showed that hydrogen burned in oxygen to form water, and the decomposition of water into hydrogen and oxygen by an electric current was demonstrated a few years later. The name *hydrogen* was given by Lavoisier, who demonstrated the formation from steam by the action of red hot iron.

Combined hydrogen is abundant on earth and it is estimated to form just under 1% by weight, or 15·4% by atoms, of the outermost kilometre of the earth's crust (including the oceans and atmosphere). In the Universe, hydrogen is of course the most abundant element and the source of all others by fusion processes in the stars. The common forms of combined hydrogen are water and hydroxyl, and as organic compounds. Much smaller amounts occur combined with nitrogen, sulphur or the halogens, and these mainly in special cases such as volcanic gases and juvenile water.

Free hydrogen is rare, forming about one part in 10^7 of the atmosphere. It is produced in volcanic gases and is also found in inclusions in minerals, in natural gas, and as a product of a few anaerobic fermentation processes such as that of starch by *B. subtilis*. However, its lightness leads to a high mean velocity of 1·84 km $\sec^{-1}$, which is a sufficiently large fraction of the escape velocity of 11·2 km $\sec^{-1}$ to mean that hydrogen is rapidly lost from the atmosphere.

Hydrogen is important to the chemist in many ways. It is the simplest element, combines with every other element except the rare gases and one or two of the heavier radioactive elements, and is found in a larger number of compounds than any other element. This simplicity and ubiquity combine to present a major challenge to theoretician and experimentalist alike. It is found in electrovalent, covalent, and metallic bonding, delocalized polycentred sigma bonds were first invoked to account for a hydride, B_2H_6, and the hydrogen bond in all its varieties adds further to its range of behaviour.

The most detailed modern account of the properties of hydrogen is that given by Pascal[1], though the data should be used with caution. More abbreviated discussions are given in the slightly older textbooks of inorganic chemistry, especially by Remy and Emeléus and Anderson[2], but the modern successors give little on the element itself. The books on hydrides by Shaw[3] and Mackay[4] give brief accounts of the element.

2. PREPARATION AND PRODUCTION

Hydrogen is readily available commercially and laboratory preparations are now rarely used except for demonstration purposes. Methods used divide essentially into reductions of the solvated proton (action of metals on water or acid, action of carbon on steam), oxidations of hydride or complex hydride ions, and thermal decomposition of hydrogen compounds (hydrocarbons, water). The more convenient laboratory preparations are as follows.

Active Metal + Water

Use of sodium, as the amalgam for greater control, or calcium is preferred.

Metal + Acid

For the metal, zinc is most convenient and iron is the classic choice. Hydrochloric acid is preferred, but sulphuric acid may be used provided it is sufficiently dilute (or SO_2 is formed). Impurities in the metal give rise to phosphine, arsine, and sometimes hydrogen sulphide.

In the first two preparations many other metals may be used under appropriate conditions. Magnesium and hot water react rapidly and this may be a useful route in special cases.

Metal + Alkali

The most convenient choices are aluminium or silicon (as ferrosilicon) used with caustic soda. Other amphoteric metals may be substituted.

Hydride + Water

LiH, CaH_2 or $LiAlH_4$ may all be used and react in a controllable manner with water. This is an expensive method, but it does give a comparatively pure product and, as half the hydrogen comes from the water, it gives a large amount of hydrogen for unit weight of reagent. This has advantages in the field, for example in filling balloons used for meteorological observations.

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[1] *Nouveau Traité de Chimie Minerale*, Vol. I, p. 565, Masson et Cie, Paris (1956).

[2] H. Remy, *Treatise on Inorganic Chemistry* (translated by J. S. Anderson), Vol. I, p. 21. Elsevier (1956); H. J. Emeléus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, 3rd ed., p. 383, Routledge & Kegan Paul, London (1960).

[3] B. L. Shaw, *Inorganic Hydrides*, Pergamon (1967).

[4] K. M. Mackay. *Hydrogen Compounds of the Metallic Elements*, E. & F. N. Spon, London (1966).

Electrolysis of Water

Electrolysis of acidified water at platinum electrodes is commonly used to demonstrate the composition of water, and is a small-scale source of hydrogen or oxygen. Very pure hydrogen is formed when warm concentrated barium hydroxide solution is electrolysed between nickel electrodes.

Large-scale production of hydrogen is at present mainly by:

(I) *Electrolysis.* As a by-product, hydrogen is formed in substantial quantities during the electrolytic preparations of chlorine and of sodium hydroxide. The direct electrolytic manufacture uses dilute sodium or potassium hydroxide electrolysed with iron or nickel electrodes. As electrolytic hydrogen is very pure it is used in hardening of fats and for other catalytic hydrogenations. It is, however, expensive to use this route.

(II) *From hydrocarbons.* Hydrocarbons nowadays provide a major share of manufactured hydrogen. The cracking of hydrocarbons thermally is an important part of petroleum refining and produces much hydrogen. Methane, from natural gas, may also be thermally decomposed to hydrogen and carbon, but the reaction with steam at 1100°C

$$CH_4+H_2O = CO+3H_2$$

is preferable. This reaction is endothermic by 48·9 kcal, and the heat is most simply provided by allowing some of the methane to burn in oxygen or air to CO_2 plus H_2O (exothermic by 191·8 kcal per mole CH_4). The gas mixture is purified as for water gas.

(III) *From coke.* Steam passed over coke above 1000°C gives the well-known *water gas* reaction,

$$H_2O+C = CO+H_2$$

This is endothermic, and is commonly run in alternation with the passage of air, which yields CO_2 plus N_2 (*producer gas*).

Water gas, or the methane-steam gases, may be subject to *CO conversion* by passing the gases and steam over an iron or cobalt oxide catalyst at 400°C,

$$CO+H_2O = H_2+CO_2$$

The CO_2 is removed by washing with water under pressure and CO by washing with ammoniacal cuprous chloride. The hydrogen, which is mixed with nitrogen in the water gas–producer gas process, is used mainly for preparation of ammonia by the Haber process.

Pure hydrogen may be obtained from the water gas process by washing out CO_2 and then removing nitrogen by cooling with liquid air. This also takes out most of the CO and the last traces are removed by reaction with heated soda lime to give sodium formate. The hydrogen thus formed is suitable for treatment of fats.

Coke oven gas has also been processed to yield hydrogen by fractional liquefaction.

The purification of hydrogen by the methods indicated, combined with drying and dust extraction, is usually sufficient. A high degree of purity may be obtained by diffusion through palladium or by formation and subsequent decomposition of a suitable hydride. The use of palladium is discussed in detail by Lewis[5] and is of importance, not only in purification, but also as the hydrogen electrode in fuel cells. Industrial scale applications have been studied in the last few years. The temperature of the palladium needs to be raised, usually above 200°, to obtain an adequate rate of equilibration of hydrogen gas with hydrogen in the metal. Temperature cycling is usually involved, and this leads to distortion

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[5] F. A. Lewis, *The Palladium/Hydrogen System*, Academic Press (1967).

of the palladium particularly when the system goes through the α (solution) to β (palladium hydride) transition. When alloys of palladium (especially with silver, although nickel and platinum have also been studied) are used, distortion is greatly reduced and this has opened the way to industrial application. Similarly, such alloys are of advantage in fuel cell electrodes. Diffusion through other metals is also possible though less efficient, and nickel has been studied because of its cost advantage, again especially in fuel cells.

Instead of diffusion through palladium the metal may be allowed to cool in a hydrogen atmosphere when large volumes are taken up. Impurities are pumped away in the residual gas and pure hydrogen is evolved on reheating. Palladium has an extensive solution region with hydrogen (see Chapter 2, Hydrides) and this hydrogen absorption may involve both the solution and hydride phases. For other metals, a similar purification by way of hydride formation and decomposition is used

$$U+\tfrac{3}{2}H_2 = UH_3 \xrightarrow{\text{heat}} U+\tfrac{3}{2}H_2$$

Uranium and titanium are the most convenient metals and here the main uptake of hydrogen is in forming the hydride phase, as the solution phase is more restricted. Hydrogen is taken up to form the hydride at temperatures around 250°, impurities are pumped off, and the hydride is decomposed by heating 200–300° higher. As the hydride is of different structure from the metal, the metal becomes finely divided after a few hydriding–dehydriding cycles and is then in a condition where hydrogen is very readily combined, even at lower temperatures. Uranium is particularly useful in this application, as there is a large change in U–U spacing between the metal and hydride. This purification route, via the metal hydrides, is particularly used in studies of hydride formation.

The largest use of hydrogen is in ammonia synthesis, and other important outlets are in the preparation of alcohols by the OXO process

$$RCH{=}CH_2+CO+2H_2 = RCH_2CH_2CH_2OH$$

using a cobalt catalyst, in the synthesis of methanol by reaction with CO, in the hydrogenation of vegetable oils in margarine manufacture, in the reaction with Cl_2 to give HCl, and in the preparation of metal hydrides. Other catalytic hydrogenations of unsaturated bonds and the oxy-hydrogen torch provide minor uses and its employment in rocket engines is of topical interest.

3. PHYSICAL PROPERTIES

Naturally occurring hydrogen is mainly the lightest isotope, ^1H, with only 0·015% ^2H content, so that the properties treated here are essentially those of the light isotope. The heavier isotopes are discussed in Chapter 2, and some of the atomic properties are included in a later section.

Hydrogen is a colourless, odourless gas with a density of 0·069, which is one-fourteenth that of air. The gas may be liquefied by cooling with liquid air and then allowing the compressed gas to expand. It is solidified by boiling under reduced pressure. The solubility in common solvents is low, some typical values being (in cc gas per litre at 25°C) 19·9 for water, 89·4 for ethanol, 76·4 for acetone, and 75·6 for benzene. The gas is also taken up by most metals in a form which does not alter the metal structure (as opposed to the formation of binary hydrides with distinct structures which are discussed in Chapter 3). This

TABLE 1. PHYSICAL PROPERTIES OF HYDROGEN

Melting point	−259·23°C = 13·957°K at 54 mm pressure (triple point)
Heat of fusion	28·0 cal mole^{-1} at triple point
Entropy of fusion	2·0 cal deg^{-1} mole^{-1}: C_p change = 1·94 cal deg^{-1} mole^{-1}
Boiling point	−252·77°C = 20·39°K
Heat of vaporization	216 cal mole^{-1}
Entropy of vaporization	10·6 cal deg^{-1} mole^{-1}
Heat of sublimation	245·8 cal mole^{-1} at 13·96°K
Vapour pressure: liquid[a]	$\log p$ (atm) = $-56{\cdot}605/T+3{\cdot}8015-0{\cdot}10458T+0{\cdot}003321T^2-0{\cdot}000032197T^3$ (up to critical point) [The best simple form is $\log p$ (atm) = $2{\cdot}872-58{\cdot}59/T$]
solid	$\log p$ (mm) = $4{\cdot}56488-47{\cdot}2059/T+0{\cdot}03939T$
Critical point	T_c = 33·19°K, P_c = 12·98 atm, V_c = 66·95 cm^3 mole^{-1}
Critical density	335, $P_cV_c/(RT_c)$ = 0·3191
Density: gas	0·06952 (air = 1) or 0·062893 (oxygen = 1)
liquid	0·0700 at boiling point
solid	0·0763 at 13°K

	H_2 (gas)	H (gas)	H^+ (gas)	H^- (gas)	H_2^+ (gas)
Heat of formation (kcal mole^{-1}): at 0°K	0·000	51·620	365·138	35·066	355·67
at 25°C	0·000	52·089	367·088	34·054	357·15
Free energy of formation at 25°C (kcal mole^{-1})	0·000	48·575			
Equilibrium constant at 25°C	0·0000	−35·6048 ($\log_{10} K_f$)			
$S°$ at 25°C (cal deg^{-1} mole^{-1})	31·210	27·392			
$C_p°$ at 25°C (cal deg^{-1} mole^{-1})	6·892	4·9680			

Thus, for H atom, ionization potential 13·54 V

H—H bond: energy	104·2 kcal (see p. 7)
length	0·7414 Å
force constant	5·73 dyne cm^{-1} × 10^5
Electron affinity of H	0·715 eV
Virial coefficient, B	150 (at 20°K), −3 (at 123°K), −14 (at 273°K) cm^3 mole^{-1}

Solubility (H_2 pressure = 760 mm)	temp. (°C)	0	10	20	50
	cm^3 H_2 at N.T.P.	0·0214	0·0195	0·0182	0·0161

Electronegativity	2·1 (Pauling's scale: most other scales are adjusted to the same base)
Dielectric constant, ε	
gas	1·000265 at 20° and 1 atm: 1·00500 at 20 atm
liquid	1·225 at 20·33°; 1·241 at 14·64°
solid	1·2188 at 14·0°; 1·224 at 13·5°
Magnetic susceptibility	−1·97 × 10^{-6} c.g.s.

Viscosity of gas, η

temp. (°K)	η (poise)
10	5·10 × 10^{-6}
20	1·093 × 10^{-5}
50	2·489 × 10^{-5}
100	4·211 × 10^{-5}
200	6·814 × 10^{-5}
300	8·960 × 10^{-5}
500	1·264 × 10^{-4}
1000	2·013 × 10^{-4}

Empirically, $\eta = \dfrac{85{\cdot}558\times10^{-7}T^{\frac{3}{2}}}{T+19{\cdot}55}\times\dfrac{T+650{\cdot}39}{T+1175{\cdot}9}$ poise

[*continued overleaf*]

Table 1—*cont.*

	temp. (°K)	conductivity (cal cm^{-1} sec^{-1} deg^{-1})
Thermal conductivity	10	$1{\cdot}43 \times 10^{-5}$
	20	$3{\cdot}46 \times 10^{-5}$
	100	$1{\cdot}613 \times 10^{-4}$
	200	$3{\cdot}154 \times 10^{-4}$
	273·16	$4{\cdot}12 \times 10^{-4}$
	300	$4{\cdot}463 \times 10^{-4}$

Empirically, $k = [1{\cdot}8341 - 0{\cdot}004458T + (1{\cdot}1308 + 0{\cdot}0008973T)C_p^\circ]\eta/M\left(\frac{1}{1+3{\cdot}2/T}\right)$

where C_p° is in cal mole^{-1} deg^{-1}, T in °K, η in poise, and M = mol. wt.

[a] See also Table 3.

Properties apply to H_2 of normal isotopic composition and ratio of ortho- to para-forms in equilibrium at room temperature. For comparative properties of ortho- and para-ratios typical of other temperatures, see Table 4.

Data are from refs. 6 and 7 supplemented from refs. 1 to 4.

Table 2. Thermodynamic Functions of Normal Hydrogen

T (°K)	S° (cal mole^{-1} deg^{-1})	$H^\circ - E_0^\circ$ (cal mole^{-1})	$-(F^\circ - E\ )/T$ (cal mole^{-1} deg^{-1})	C_p° (cal deg^{-1})
10	15·607	303·67	−14·760	4·968
20	19·050	353·34	1·382	4·968
20·39	19·146	355·28	1·721	4·968
50	23·063	502·43	13·554	4·978
100	27·142	758·92	19·55	5·393
200	31·275	1361·6	24·45	6·518
298·16	33·963	2028·3	27·18	6·891
500	37·561	3429·5	30·70	6·993
1000	42·455	6966·2	35·49	7·219

See ref. 6 for a much more extensive listing. The values for S° and $-(F^\circ - E_0^\circ)/T$ include nuclear spin contributions.

region of the phase diagram is labelled the α or solution phase. In many cases only a fraction of a percent of hydrogen is held in the α-phase, presumably almost entirely on the surface, but a much more extensive solution region is sometimes observed, for example up to a composition $TaH_{0{\cdot}15}$ at room temperature and as the only phase above 200°C for all the vanadium group metals and above 300°C for palladium. At such temperatures, the hydrogen content may rise to over 50 at.%. In studies on liquid metals, the alkali metals have been shown to dissolve small amounts of hydrogen. The solubility is very low, but rises rapidly with temperature, for example from 0·00042 at 250°C to 0·02 at 450°C expressed as weight percent hydrogen dissolved in liquid sodium.

The physical properties of hydrogen, of natural composition, are listed in Table 1. Values for ortho- and para-hydrogen are discussed in a later section. A useful and extensive compilation of thermal properties of hydrogen, including heavier isotopes, is given by Woolley[6] and his colleagues. The thermal conductivity of hydrogen is five times that of air and is the highest of all common gases.

[6] H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Res. Nat. Bur. Standards*, 41 (1948) 379.

[7] *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 600, Washington (1952).

The basic physical properties of hydrogen have been known with precision for some time, but the simple nature of the molecule has led to more extensive studies in which it has been used as a model for detailed calculation, often accompanied by a wide range of measurements of suitable properties. Only a selection of recent studies of this type are cited. The contributions made by various terms to the magnetic susceptibility of hydrogen have been calculated in detail[8] and compared with experimental values. Similar studies of densities[9] and of the effect of organic vapours on the viscosity[10] are reported. The refractive indices of gaseous and liquid hydrogen (including para-hydrogen) have been compared[11] with the Lorentz–Lorenz function. Various dissociation paths of H_2 are considered[12]. Electron impact cross-sections of H_2 [13] and ionization of hydrogen by H and hydride ion[14] are reported. The action of atomic hydrogen on hydride ion gives an electron and excited H_2 [15], and resonant charge exchange in such collisions is discussed[16].

The structure of solid hydrogen has been the subject of some study. H_2 usually freezes in the hexagonal close-packed form, with $a_0 = 3{\cdot}761$ Å, $c_0 = 6{\cdot}105$ Å, but can be formed in a cubic close-packed modification in the presence of gold foil with a cube texture[17]. In the same study, it was shown that D_2 and para-H_2 behave similarly. When hydrogen was plastically deformed at about 3°K, cubic reflections were added to the hcp diffraction pattern, suggesting that normal hydrogen is metastable in the hexagonal form at this temperature.

Laser action was observed in flash photolysed H_2+Cl_2 explosions in 1965 [18] and since then a number of laser systems involving hydrogen have been studied[19]. The laser action arises from HX molecules formed from H_2 and halogen atoms from various sources such as X_2, UF_6 or halocarbons. Apart from their technical interest, such lasers provide unique chemical information on the energy distribution in the initial steps of the hydrogen–halogen atom reaction.

4. CHEMICAL PROPERTIES

The dissociation energy of the H–H bond is high for a single bond (compare 57·2 kcal mole^{-1} for Cl_2) and much more comparable with the double-bond dissociation energy of 117 kcal mole^{-1} for oxygen. As a result, molecular hydrogen is relatively inert at ordinary temperatures. It combines with fluorine, even in the dark, or with liquid or solid fluorine at

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[8] B. M. Ludwig and J. Voitlander, *Z. Naturforsch.* **24A** (1969) 471.

[9] R. D. Goodwin, D. E. Diller, H. M. Roder and L. A. Weber, *J. Res. Nat. Bur. Standards*, **67A** (1963) 173.

[10] N. Dyson and A. B. Littlewood, *Trans. Faraday Soc.* **63** (1967) 1895.

[11] D. E. Diller, *J. Chem. Phys.* **49** (1968) 3096.

[12] F. J. Comes, B. Schmitz, H. O. Wellern and U. Wenning, *Ber. Bunsengesellschaft Phys. Chem.* **72** (1968) 986 (photo dissociation); S. E. Nielsen and R. S. Berry, *Chem. Phys. Letters*, **2** (1968) 503 (vibronic); K. Lauckner, *Diss. Abs.* **29B** (1968) 1132 (calculation).

[13] G. M. Prok, C. F. Monnin and H. J. Hettel, *J. Quant. Spectroscopy Radiative Transfer*, **9** (1969) 361; S. Trajmar, D. C. Cartwright, J. K. Rice, R. T. Brinkmann and A. Kupperman, *J. Chem. Phys.* **49** (1969) 5464.

[14] W. C. Keever, G. J. Lockwood, H. F. Helbig and E. Everhart, *Phys. Rev.* **166** (1968) 68; J. F. Williams, *Phys. Rev.* **154** (1967) 9.

[15] J. C. Y. Chen and J. L. Peacher, *Phys. Rev.* **168** (1968) 56.

[16] R. K. Yanev, *Vestnik Leningr. Univ. Ser. Fiz. i Khim.* **22** (1968) 61.

[17] C. S. Barrett, L. Meyer and J. Wasserman, *J. Chem. Phys.* **45** (1966) 834.

[18] J. V. V. Kasper and G. C. Pimental, *Phys. Rev. Letters*, **14** (1965) 352; P. H. Corneil and G. C. Pimental, *J. Chem. Phys.* **49** (1968) 1379.

[19] T. F. Deutsch, *Appl. Phys. Letters*, **11** (1967) 18; *ibid.* **10** (1967) 234; K. L. Kompa, J. H. Parker and G. C. Pimental, *J. Chem. Phys.* **49** (1968) 4257.

temperatures down to −250°, but there is no reaction in the cold with the other halogens nor with oxygen. Only a few compounds are reduced by hydrogen at room temperature, one example being palladous chloride

$$PdCl_2 + H_2 = Pd + 2HCl$$

This reaction, using a 1 % solution of $PdCl_2$, acts as a sensitive test for the presence of hydrogen and may be used quantitatively.

Certain highly purified and finely divided metals will also react with hydrogen at room temperature. Maeland[20] reports that vanadium powder, prepared by decomposing the powdered hydride in a vacuum, reacts exothermically with hydrogen at room temperature and atmospheric pressure to form the VH hydride phase. The essential requirement is presumably a surface free of any film of oxide or other compound. The adsorption of hydrogen on the surface probably is the source of the activation of the H–H bond.

Apart from these cases, hydrogen needs to be activated by heating, by irradiation, by radical formation or similar means, before it reacts. As most hydrides are formed exothermically, it is then found that activated hydrogen reacts vigorously with a wide variety of substrates. Most solid hydrides, either the ionic species formed by the *s* elements or the metallic hydrides of the transition elements, are formed by direct combination of the heated metal and hydrogen gas, usually at pressures less than one atmosphere (see Chapter 2, Hydrides).

On ignition or photolysis, mixtures of hydrogen and the halogens or oxygen combine vigorously. The reactions are strongly exothermic (22·0 kcal mole^{-1} for HCl_{gas} or 68·35 kcal mole^{-1} for H_2O_{liquid} at 25°) and explosive at certain concentrations and temperatures. A mixture of hydrogen and oxygen in exact 2:1 proportions detonates violently when ignited and hydrogen/air mixtures explode over a wide range of compositions from about 6 to 67 vol. % hydrogen. In the dark, hydrogen and chlorine or bromine combine above about 400°C, and iodine or oxygen mixtures with hydrogen need to be heated to 500° or above. The halogens react much more readily in the light and hydrogen/chlorine mixtures explode under strong illumination at room temperature. The reactions are all complex, but are basically chain reactions propagated via hydrogen atoms and halogen, or OH, radicals. As the combinations of hydrogen with oxygen or halogens are catalysed by many materials, explosions of these gas mixtures may occur at much lower temperatures than those indicated. Once combination starts, the gases are rapidly heated to ignition temperature by the exothermic reaction.

Hydrogen burns in oxygen or air with a very hot flame, the temperature reaching 3000°C in the near neighbourhood. On rapid cooling, H, O, OH, and H_2O_2 are found in addition to hydrogen, oxygen and water. This is, of course, used in the oxy-hydrogen torch.

The reaction of hydrogen with sulphur or selenium takes place at 250°, but direct combination at elevated temperatures does not occur for the other non-metallic and semi-metallic elements. Other routes to these hydrides are discussed in Chapter 2, Hydrides. Hydrogen combines with nitrogen only on catalysis (Haber process) or in an electric arc or discharge, and hydrocarbons are formed when an arc is struck between graphite electrodes in a hydrogen atmosphere.

The kinetics and mechanisms of many of these reactions of gaseous hydrogen with non-metallic elements have been studied—systems such as $H_2 + O_2$ and $H_2 + X_2$ in great

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[20] A. J. Maeland, *J. Chem. Phys.* 48 (1964) 219.

detail. The reaction of hydrogen and chlorine is initiated by the photochemical or thermal formation of chlorine atoms, and proceeds by a chain of atom displacements

$$\begin{aligned} Cl_2 &= 2Cl \\ Cl+H_2 &= HCl+H \\ H+Cl_2 &= HCl+Cl \end{aligned}$$

The chains are very long as shown by the quantum yield of 10^6 in the photochemical reaction. As a result, the chain termination processes are impossible to distinguish, but probably involve atom recombination on the walls or reaction with impurities. Such very long-chain sequences make the reaction characteristics very sensitive to impurities. For Br_2, a similar chain is possible but, in contrast to the chlorine chain, the step

$$Br+H_2 = HBr+H$$

is endothermic, by nearly 17 kcal, so that the chains are much shorter. This feature of a possible chain in the H_2+I_2 system is even more important, with $I+H_2 = HI+H$ endothermic by 35 kcal. Thus, although I–I is weak so that the concentration of I atoms at a given temperature is much greater than that of Br or Cl, the stepwise chain mechanism plays no part in the H_2/I_2 system. A bimolecular reaction was always postulated, but recent work suggests a termolecular step H_2+I+I. The H_2+F_2 reaction presents difficult experimental problems but is now the subject of a number of studies[21].

The reaction between hydrogen and oxygen differs in that chain-branching is possible, as in the step $H+O_2 = HO+O$. Thus one atom gives rise to two chain carriers and the reaction propagates as an explosion. At very low pressures, reaction of the carriers at the walls terminates the chains before the explosion builds up, and at high pressures chain carriers are destroyed by termolecular processes in the gas phase. The explosion region thus has upper and lower pressure limits. A system such as this is difficult to study, particularly in the explosion region[21a], and a great deal of work has been published. These studies are reviewed in a number of places, for example refs. 1 and 22.

In its reaction with compounds, hydrogen follows the pattern of the reactions with elements. Few reactions occur without heating, but once started most reductions by hydrogen are exothermic and proceed readily. Most oxides or halides yield the element or the binary hydride when heated in hydrogen

$$GeO_2+2H_2 = Ge+2H_2O \text{ at } 500°$$

Catalysts, especially nickel, palladium and platinum in finely divided forms, activate hydrogen to allow reduction of many compounds at moderate temperatures. The prime examples here are the wide variety of hydrogenations of organic compounds[23]. In industrially important hydrogenations, similar catalysts are important such as cobalt in the OXO alcohol synthesis and iron in the Haber process. In general, elements towards the right of the transition series are most useful as heterogeneous hydrogenation catalysts.

The extensive studies of the hydrido-complexes of the transition metals have led to the more extensive understanding of the catalytic action of these elements and to the

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[21a] D. H. Edwards and D. J. Parry, *Trans. Faraday Soc.* **63** (1967) 1992.

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development of homogeneous hydrogenation catalysts which often act under mild conditions. For example, the active species in the OXO process has been shown to be $HCo(CO)_4$ and this can be isolated and studied. The process is the conversion of an olefin to an aldehyde by the action of H_2 and CO under pressure in presence of cobalt and the sequence of reactions involves

(a) Addition of H–Co to the double bond, e.g.

$$C_2H_4 + HCo(CO)_4 = EtCo(CO)_4$$

(b) CO insertion into C–CO

$$CO + EtCo(CO)_4 = EtCOCo(CO)_4 = EtCOCo(CO)_3 + CO$$

(c) Hydrogenolysis of the acyl–cobalt complex, probably the tricarbonyl

$$H_2 + EtCOCo(CO)_3 = EtCHO + HCo(CO)_3$$

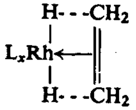
(d) The tricarbonyl then acts with CO to form $HCo(CO)_4$.

Alternative pathways are possible involving di-cobalt species, but the main feature of the hydrogen chemistry is the action of molecular hydrogen on the reactive cobalt–acyl bond.

Molecular hydrogen also adds to low valency complexes in an oxidative addition under mild conditions as in

$$IrCl(CO)(PPh_3)_2 + H_2 = IrCl(H)_2CO(PPh_3)_2$$

which occurs at 25°C. The iridium is oxidized from +I to +III. A similar step is postulated in olefin hydrogenation, for example by solvated $(Ph_3P)_2RhCl$ where the postulated intermediate, the dihydride, may also be isolated. Addition to the olefin involves a five-membered cyclic intermediate involving *cis* hydrogens and an



olefin–rhodium π-bond. This is supported by the observation that D_2 gives CH_2DCH_2D with no scrambling of the deuterium. Many studies of such hydrogenations are currently being reported, for example hydrogen activation by the complexes of the Group VIII elements[24, 25]. This work, which is almost entirely of recent development, has led to the situation where the high bond energy of hydrogen is overcome by allowing it to react with active transition metal species to give smooth reaction of hydrogen under mild, homogeneous conditions. It is to be expected that more selective reactions will be developed and catalysts will be tailored for particular applications.

Analytical

The use of $PdCl_2$ in the analysis of hydrogen is referred to above. Hydrogen is commonly determined by conversion to water over heated copper oxide, but the presence of volatile hydrides has first to be excluded. Hydrogen may usually be separated from hydrides by fractional condensation. Alternatively, silver oxide may be used which is reduced by hydrogen but not by, for example, hydrocarbons under mild heating. In absence of combustible gases, hydrogen is measured eudiometrically in presence of a large excess of oxygen.

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5. ORTHO-HYDROGEN AND PARA-HYDROGEN

The rotational bands in the vibration–rotation spectrum of hydrogen were early observed to show a weak, strong, weak, strong alternation in intensity. This led Mecke to propose that two varieties of hydrogen exist, one where only odd rotational quanta were allowed and one with only even values. Dennison made a similar postulate to account for the anomalous variation with temperature of the specific heat of hydrogen. These ideas were rationalized by Heisenberg and by Hund in terms of the possible combinations of the nuclear spins in the H_2 molecule. If the two proton spins are antiparallel, the resultant nuclear spin is zero and the state is non-degenerate. This form is termed *para-hydrogen* and the rotational quantum number *J* is limited to even values. When the proton spins are parallel, the resultant nuclear spin is 1, the state is three-fold degenerate, and only odd values of *J* are allowed. This species is *ortho-hydrogen*. As the ortho–para conversion involves the forbidden triplet–singlet transition in the nuclear spin state, spontaneous transformation is very slow. Thus samples of hydrogen which have been cooled show the proportion of the two forms which corresponds to the equilibrium composition at room temperature. This is a high temperature, relative to the energy difference between the two spin states, so that the room temperature composition of H_2 is essentially the statistically weighted one arising from the difference in the degeneracies of the two nuclear spin states, i.e. 3 parts ortho to 1 part para. Hydrogen of this composition is often termed *normal* and all data for molecular hydrogen given in Tables 1 and 2 apply to normal hydrogen. It is the 3:1 ratio of the two forms which accounts for the intensity alternation observed in the rotational spectrum.

TABLE 3. EQUILIBRIUM COMPOSITION OF HYDROGEN AT VARIOUS TEMPERATURES

Temperature (°K)	Percentage para-hydrogen	Temperature (°K)	Percentage para-hydrogen
0	100·00	95	40·48
20	99·82	100	38·51
25	99·01	105	36·82
30	96·98	110	35·30
35	93·45	115	34·00
40	88·61	120	32·87
45	82·91	130	31·03
50	76·89	140	29·62
55	70·96	150	28·54
60	65·39	170	27·09
65	60·33	190	26·23
70	55·83	210	25·72
75	51·86	230	25·42
80	48·39	250	25·24
85	45·37	273	25·13
90	42·75	∞	25·00

Values from ref. 26 which agree closely with those calculated in ref. 27. For example, the latter gives 51·776% at 75°K and 76·798% at 50°K.

At 0°K, on the other hand, all the molecules must be in the rotational ground state at equilibrium, that is hydrogen in equilibrium at absolute zero would be entirely para, where