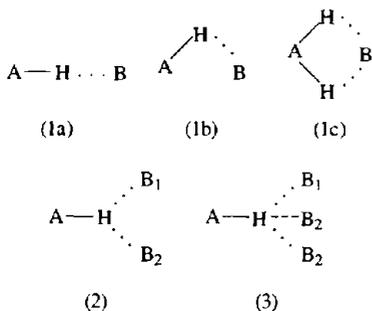


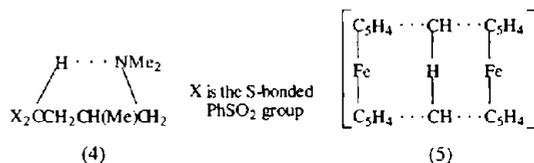
Figure 3.5 Some examples of branched H bonds: (a) the bifurcated bond in 1,3-dioxanol-5⁽⁴⁹⁾; and trifurcated bonds in (b) *N,N*-bis(2-hydroxyethyl)glycine⁽⁵⁰⁾ and (c) the nitrilotriacetate dianion.⁽⁵¹⁾

as $A-H \cdots B$ and usually occurs when A is sufficiently electronegative to enhance the acidic nature of H (proton donor) and where the acceptor B has a region of high electron density (such as a lone pair of electrons) which can interact strongly with the acidic hydrogen. In fact, the H bond in $A-H \cdots B$ can be either linear as in schematic structure (1) or significantly non-linear as in structures (1b) and (1c). H-bonds can also join three adjacent atoms (bifurcated) as in structure (2) or even four atoms (trifurcated) as in structure (3).



Thus, in a recent survey of 1509 $N-H \cdots O=C$ hydrogen bonds in organic carbonyls or carbonylates, nearly 80% (1199) were unbranched, some 20% (304) were bifurcated, but only 0.4% (6) were trifurcated.⁽⁴⁸⁾ Some examples are in Fig. 3.5.

It will be convenient first to indicate the range of phenomena which are influenced by H bonding and then to discuss more specifically the nature of the bond itself according to current theories. The experimental evidence suggests that strong H bonds can be formed when A is F, O or N; weaker H bonds are sometimes formed when A is C or a second row element, P, S, Cl or even Br, I. Strong H bonds are favoured when the atom B is F, O or N; the other halogens Cl, Br, I are less effective unless negatively charged and the atoms C, S and P can also sometimes act as B in weak H bonds. Recent examples of $C-H \cdots N$ and $C-H \cdots C$ bonds are in bis(phenylsulfonyl)trimethylbutylamine (4)⁽⁵²⁾ and the carbanion of [1.1]ferrocenophane (5).⁽⁵³⁾



3.6.1 Influence on properties

It is well known that the mps and bps of NH_3 , H_2O and HF are anomalously high when compared with the mps and bps of the hydrides of other elements in Groups 15, 16 and 17, and the

⁴⁸ R. TAYLOR, O. KENNARD and W. VERICHEL, *J. Am. Chem. Soc.* **106**, 244-8 (1984).

⁴⁹ J. L. ALONSO and E. B. WILSON, *J. Am. Chem. Soc.* **102**, 1248-51 (1980).

⁵⁰ V. CODY, J. HAZEL and D. LANGS, *Acta Crystallogr.* **B33**, 905-7 (1977).

⁵¹ S. H. WHITLOW, *Acta Crystallogr.* **B28**, 1914-9 (1972).

⁵² R. L. HARLOW, C. LI and M. P. SAMMES, *J. Chem. Soc., Chem. Commun.*, 818-9 (1984).

⁵³ P. AHLBERG and O. DAVIDSSON, *J. Chem. Soc., Chem. Commun.*, 623-4 (1987).

same effect is noted for the heats of vaporization, as shown in Fig. 3.6. The explanation normally given is that there is some residual interaction (H bonding) between the molecules of NH_3 , H_2O and HF which is absent for methane, and either absent or much weaker for heavier hydrides. This argument is probably correct in outline but is deceptively oversimplified since it depends on the assumption that only some of the H bonds in solid HF (for example) are broken during the melting process and that others are broken on vaporization, though not all, since HF is known to be substantially polymerized even in the gas phase. The mp is the temperature at which there is zero

free-energy change on passing from the solid to the liquid phase:

$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0;$$

hence
$$T_m = \Delta H_m / \Delta S_m$$

It can be seen that a high mp implies either a high enthalpy of melting, or a low entropy of melting, or both. Similar arguments apply to vaporization and the bp, and indicate the difficulties in quantifying the discussion.

Other properties that are influenced by H bonding are solubility and miscibility, heats of mixing, phase-partitioning properties, the

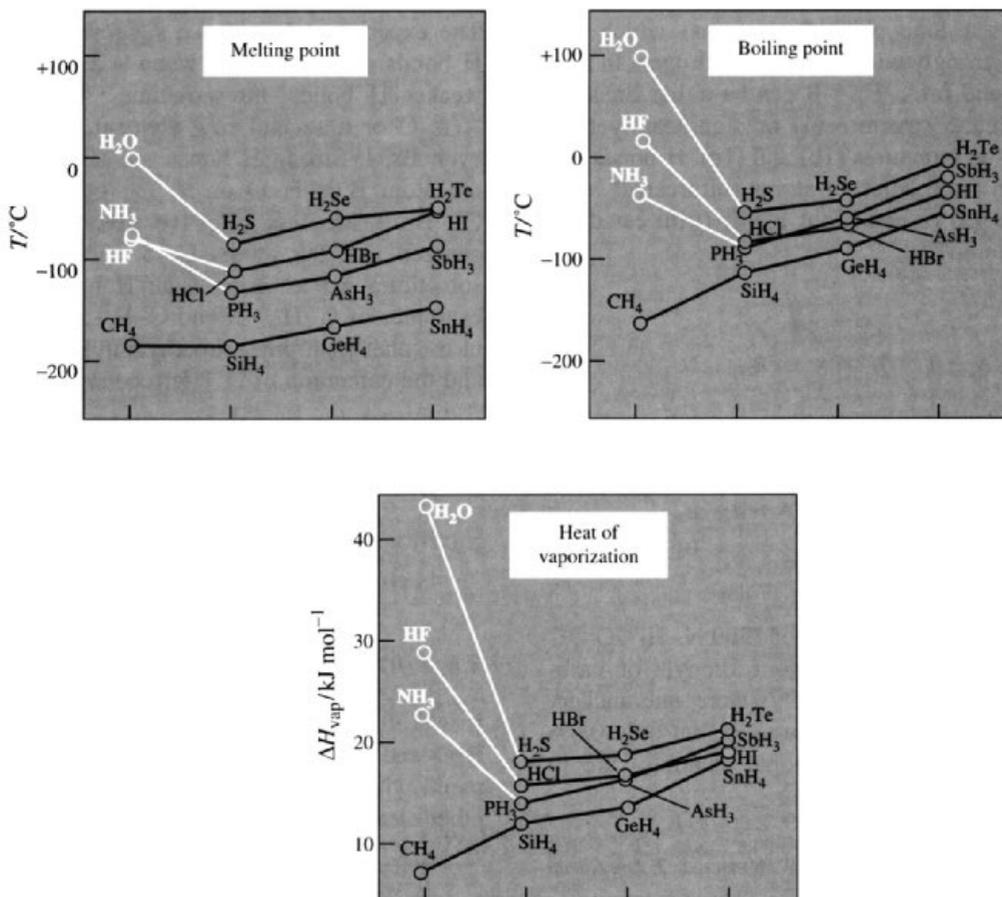


Figure 3.6 Plots showing the high values of mp, bp and heat of vaporization of NH_3 , H_2O and HF when compared with other hydrides. Note also that the mp of CH_4 (-182.5°C) is slightly higher than that of SiH_4 (-185°C).

existence of azeotropes, and the sensitivity of chromatographic separation. Liquid crystals (or mesophases) which can be regarded as “partly melted” solids also frequently involve molecules that have H-bonded groups (e.g. cholesterol, polypeptides, etc.). Again, H bonding frequently results in liquids having a higher density and lower molar volume than would otherwise have been expected, and viscosity is also affected (e.g. glycerol, anhydrous H_2SO_4 , H_3PO_4 , etc.).

Electrical properties of liquids and solids are sometimes crucially influenced by H bonding. The ionic mobility and conductance of H_3O^+ and OH^- in aqueous solutions are substantially greater than those of other univalent ions due to a proton-switch mechanism in the H-bonded associated solvent, water. For example, at 25°C the conductance of H_3O^+ and OH^- are 350 and $192 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, whereas for other (viscosity-controlled) ions the values fall

mainly in the range $50\text{--}75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. (To convert to mobility, $\nu \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, divide by 96485 C mol^{-1} .) It is also notable that the dielectric constant is not linearly related to molecular dipole moments for H-bonded liquids being much higher due to the orientating effect of the H bonds: large domains are able to align in an applied electric field so that the molecular dipoles reinforce one another rather than cancelling each other due to random thermal motion. Some examples are given in Fig. 3.7, which also illustrates the substantial influence of temperature on the dielectric constant of H-bonded liquids presumably due to the progressive thermal dissociation of the H bonds. Even more dramatic are the properties of ferroelectric crystals where there is a stable permanent electric polarization (see Fig. 3.8). Hydrogen bonding is one of the important ordering mechanisms

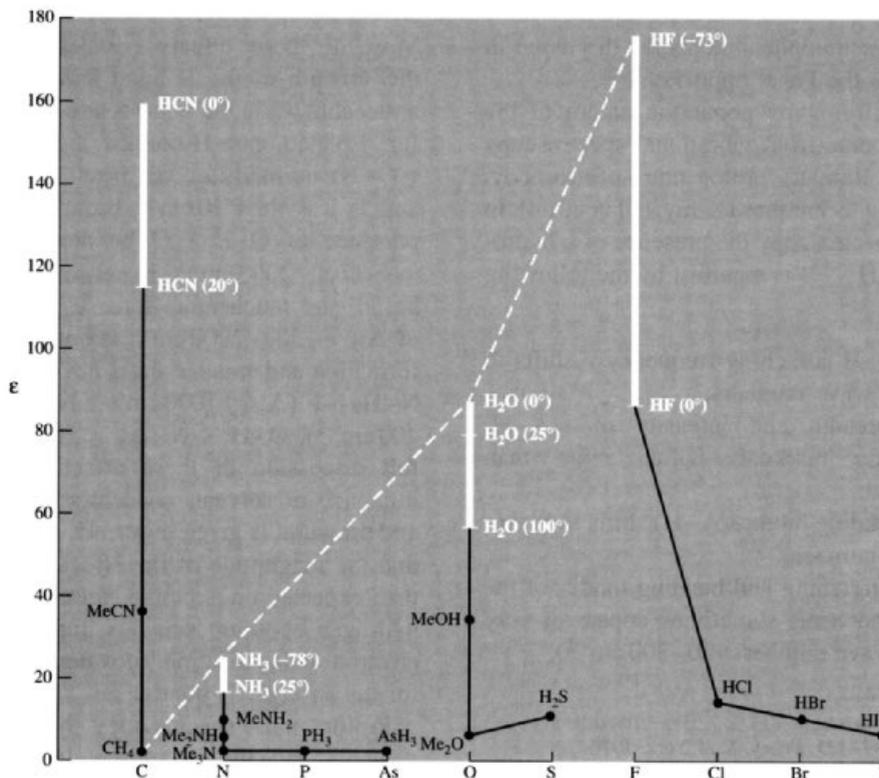


Figure 3.7 Dielectric constant of selected liquids.

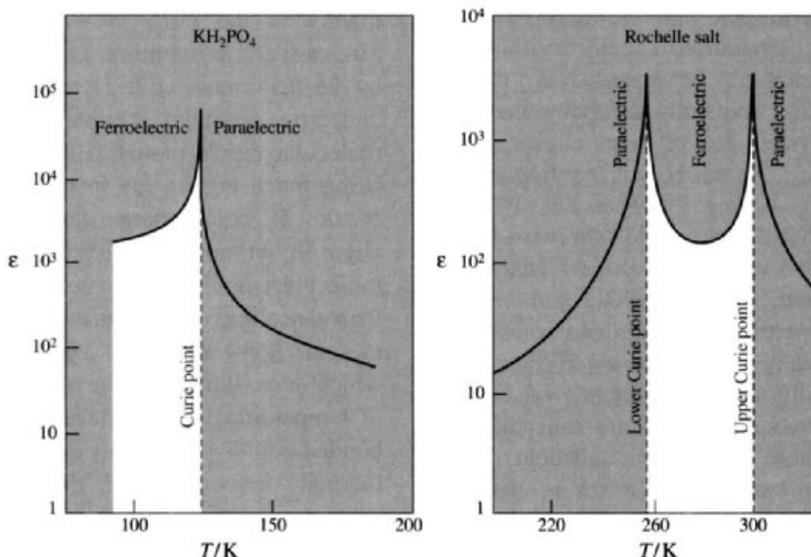


Figure 3.8 Anomalous temperature dependence of relative dielectric constant of ferroelectric crystals at the transition temperature (Curie point).

responsible for this phenomenon as discussed in more detail in the Panel opposite.^(54,55)

Intimate information about the nature of the H bond has come from vibrational spectroscopy (infrared and Raman), proton nmr spectroscopy, and diffraction techniques (X-ray and neutron). In vibrational spectroscopy the presence of a hydrogen bond $A-H \cdots B$ is manifest by the following effects:

- (i) the $A-H$ stretching frequency ν shifts to lower wave numbers;
- (ii) the breadth and intensity of $\nu(A-H)$ increase markedly, often more than tenfold;
- (iii) the bending mode $\delta(A-H)$ shifts to higher wave numbers;
- (iv) new stretching and bending modes of the H bond itself sometimes appear at very low wave numbers ($20-200 \text{ cm}^{-1}$).

⁵⁴ C. KITTEL, *Introduction to Solid State Physics*, 5th edn., Chap. 13, pp. 399-431. Wiley, New York, 1976.

⁵⁵ H.-G. UNRUH, *Ferroelectrics in Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A10, VCH, Weinheim, 1987, pp. 309-21, and references cited therein.

Most of these effects correlate roughly with the strength of the H bond and are particularly noticeable when the bond is strong. For example, for isolated non-H-bonded hydrogen groups, $\nu(O-H)$ normally occurs near $3500-3600 \text{ cm}^{-1}$ and is less than 10 cm^{-1} broad whereas in the presence of $O-H \cdots O$ bonding ν_{antisym} drops to $\sim 1700-2000 \text{ cm}^{-1}$, is several hundred cm^{-1} broad, and much more intense. A similar effect of $\Delta\nu \sim 1500-2000 \text{ cm}^{-1}$ is noted on $F-H \cdots F$ formation and smaller shifts have been found for $N-H \cdots F$ ($\Delta\nu \leq 1000 \text{ cm}^{-1}$), $N-H \cdots O$ ($\Delta\nu \leq 400 \text{ cm}^{-1}$), $O-H \cdots N$ ($\Delta\nu \leq 100 \text{ cm}^{-1}$), etc. A full discussion of these effects, including the influence of solvent, concentration, temperature and pressure, is given in ref. 45. Suffice it to note that the magnitude of the effect is much greater than expected on a simple electrostatic theory of hydrogen bonding, and this implies appreciable electron delocalization (covalency) particularly for the stronger H bonds.

Proton nmr spectroscopy has also proved valuable in studying H-bonded systems. As might be expected, substantial chemical shifts are observed and information can be obtained

Ferroelectric Crystals^(54,55)

A ferroelectric crystal is one that has an electric dipole moment even in the absence of an external electric field. This arises because the centre of positive charge in the crystal does not coincide with the centre of negative charge. The phenomenon was discovered in 1920 by J. Valasek in Rochelle salt, which is the H-bonded hydrated d-tartrate $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. In such compounds the dielectric constant can rise to enormous values of 10^3 or more due to presence of a stable permanent electric polarization. Before considering the effect further, it will be helpful to recall various definitions and SI units:

$$\text{electric polarization } P = D - \epsilon_0 E (\text{C m}^{-2})$$

where D is the electric displacement (C m^{-2})

E is the electric field strength (V m^{-1})

ϵ_0 is the permittivity of vacuum ($\text{F m}^{-1} = \text{A s V}^{-1} \text{m}^{-1}$)

$$\text{dielectric constant } \epsilon = \frac{\epsilon_0 E + P}{\epsilon_0 E} = 1 + \chi \text{ (dimensionless)}$$

where $\chi = \epsilon - 1 = P/\epsilon_0 E$ is the dielectric susceptibility.

There are two main types of ferroelectric crystal:

- those in which the polarization arises from an ordering process typically by H bonding;
- those in which the polarization arises by a displacement of one sublattice with respect to another, as in perovskite-type structures like barium titanate (p. 963).

The ferroelectricity usually disappears above a certain transition temperature (often called a Curie temperature) above which the crystal is said to be paraelectric; this is because thermal motion has destroyed the ferroelectric order. Occasionally the crystal melts or decomposes before the paraelectric state is reached. There are thus some analogies to ferromagnetic and paramagnetic compounds though it should be noted that there is no iron in ferroelectric compounds. Some typical examples, together with their transition temperatures and spontaneous permanent electric polarization P_s , are given in the Table.

Table Properties of some ferroelectric compounds

Compound	T_c/K	$P_s/\mu\text{C cm}^{-2(a)}$	(at T/K)
KH_2PO_4	123	5.3	(96)
KD_2PO_4	213	4.5	—
KH_2AsO_4	96	3.0	(80)
KD_2AsO_4	162		
RbH_2PO_4	147	5.6	(90)
$(\text{NH}_2\text{CH}_2\text{CO}_2\text{H})_3 \cdot \text{H}_2\text{SO}_4^{(b)}$	322	2.8	(293)
$(\text{NH}_2\text{CH}_2\text{CO}_2\text{H})_3 \cdot \text{H}_2\text{SeO}_4^{(b)}$	295	3.2	(273)
BaTiO_3	393	26.0	(296)
KNbO_3	712	30.0	(523)
PbTiO_3	763	>50.0	(300)
LiTaO_3	890	23.0	(720)
LiNbO_3	1470	300.0	—

^(a)To convert to the basic SI unit of C m^{-2} divide the tabulated values of P_s by 10^2 ; to convert to the CGS unit of esu cm^{-2} multiply by 3×10^3 . For a full compilation see E. C. Subbarao, *Ferroelectrics* 5, 267 (1973).

^(b)Triglycinesulfate and selenate.

In KH_2PO_4 and related compounds each tetrahedral $[\text{PO}_2(\text{OH})_2]^-$ group is joined by H bonds to neighbouring $[\text{PO}_2(\text{OH})_2]^-$ groups; below the transition temperature all the short O–H bonds are ordered on the same side of the PO_4 units, and by appropriate application of an electric field, the polarization of the H bonds can be reversed. The dramatic effect of deuterium substitution in raising the transition temperature of such compounds can be seen from the Table: this has been ascribed to a quantum-mechanical effect involving the mass dependence of the de Broglie wavelength of hydrogen. Other examples of H-bonded ferroelectrics are $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)\text{H}_2\text{AsO}_4$, $\text{Ag}_2\text{H}_3\text{IO}_6$, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$. Rochelle salt is unusual in having both an upper and a lower critical temperature between which the compound is ferroelectric.

Panel continues

The closely related phenomenon of antiferroelectric behaviour is also known, in which there is an ordered, self-cancelling arrangement of permanent electric dipole moments below a certain transition temperature; H bonding is again implicated in the ordering mechanism for several ammonium salts of this type, e.g. $(\text{NH}_4)\text{H}_2\text{PO}_4$ 148 K, $(\text{NH}_4)\text{D}_2\text{PO}_4$ 242 K, $(\text{NH}_4)\text{H}_2\text{AsO}_4$ 216 K, $(\text{NH}_4)\text{D}_2\text{AsO}_4$ 304 K and $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ 254 K. As with ferroelectrics, antiferroelectrics can also arise by a displacive mechanism in perovskite-type structures, and typical examples, with their transition temperatures, are:

PbZrO_3 506 K, PbHfO_3 488 K, NaNbO_3 793, 911 K, WO_3 1010 K.

Ferroelectrics have many practical applications: they can be used as miniature ceramic capacitors because of their large capacitance, and their electro-optical characteristics enable them to modulate and deflect laser beams. The temperature dependence of spontaneous polarization induces a strong pyroelectric effect which can be exploited in thermal and infrared detection. Many applications depend on the fact that all ferroelectrics are also piezoelectrics. Piezoelectricity is the property of acquiring (or altering) an electric polarization P under external mechanical stress, or conversely, the property of changing size (or shape) when subjected to an external electric field E . Thus ferroelectrics have been used as transducers to convert mechanical pulses into electrical ones and vice versa, and find extensive application in ultrasonic generators, microphones, and gramophone pickups; they can also be used as frequency controllers, electric filters, modulating devices, frequency multipliers, and as switches, counters and other bistable elements in computer circuits. A further ingenious application is in delay lines by means of which an electric signal is transformed piezoelectrically into an acoustic signal which passes down the piezoelectric rod at the velocity of sound until, at the other end, it is reconverted into a (delayed) electric signal.

It should be noted that, whereas ferroelectrics are necessarily piezoelectrics, the converse need not apply. The necessary condition for a crystal to be piezoelectric is that it must lack a centre of inversion symmetry. Of the 32 point groups, 20 qualify for piezoelectricity on this criterion, but for ferroelectric behaviour a further criterion is required (the possession of a single non-equivalent direction) and only 10 space groups meet this additional requirement. An example of a crystal that is piezoelectric but not ferroelectric is quartz, and indeed this is a particularly important example since the use of quartz for oscillator stabilization has permitted the development of extremely accurate clocks (1 in 10^8) and has also made possible the whole of modern radio and television broadcasting including mobile radio communications with aircraft and ground vehicles.

concerning H-bond dissociation, proton exchange times, and other relaxation processes. The chemical shift always occurs to low field and some typical values are tabulated below for the shifts which occur between the gas and liquid phases or on dilution in an inert solvent:

Compound	CH_4	C_2H_6	CHCl_3	HCN	NH_3	PH_3
δ ppm	0	0	0.30	1.65	1.05	0.78
Compound	H_2O	H_2S	HF	HCl	HBr	HI
δ ppm	4.58	1.50	6.65	2.05	1.78	2.55

The low-field shift is generally interpreted, at least qualitatively, in terms of a decrease in diamagnetic shielding of the proton: the formation of $\text{A-H}\cdots\text{B}$ tends to draw H towards B and to repel the bonding electrons in A-H towards A thus reducing the electron density about H and reducing the shielding. The strong electric field due to B also inhibits the diamagnetic circulation within the H atom and this further reduces the shielding. In addition,

there is a magnetic anisotropy effect due to B; this will be positive (upfield shift) if the principal symmetry axis of B is towards the H bond, but the effect is presumably small since the overall shift is always downfield.

Ultraviolet and visible spectra are also influenced by H bonding, but the effects are more difficult to quantify and have been rather less used than ir and nmr. It has been found that the $n \rightarrow \pi^*$ transition of the base B always moves to high frequency (blue shift) on H-bond formation, the magnitude of $\Delta\nu$ being $\sim 300\text{--}4000\text{ cm}^{-1}$ for bands in the region $15\,000\text{--}35\,000\text{ cm}^{-1}$. By contrast $\pi \rightarrow \pi^*$ transitions on the base B usually move to lower frequencies (red shift) and shifts are in the range -500 to -2300 cm^{-1} for bands in the region $30\,000\text{--}47\,000\text{ cm}^{-1}$. Detailed interpretations of these data are somewhat complex and obscure, but it will be noted that the shifts are approximately of the same magnitude as the enthalpy of formation of many H bonds (83.59 cm^{-1} per atom $\equiv 1\text{ kJ mol}^{-1}$).

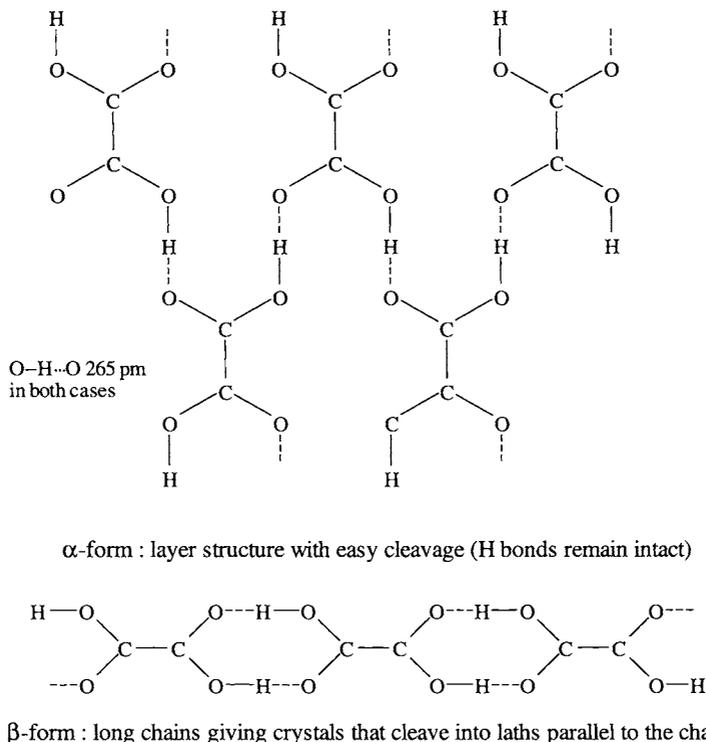


Figure 3.9 Schematic representation of the two forms of oxalic acid, $(-\text{CO}_2\text{H})_2$.

3.6.2 Influence on structure^(56,57)

The crystal structure of many compounds is dominated by the effect of H bonds, and numerous examples will emerge in ensuing chapters. Ice (p. 624) is perhaps the classic example, but the layer lattice structure of $\text{B}(\text{OH})_3$ (p. 203) and the striking difference between the α - and β -forms of oxalic and other dicarboxylic acids is notable (Fig. 3.9). The more subtle distortions that lead to ferroelectric phenomena in KH_2PO_4 and other crystals have already been noted (p. 57). Hydrogen bonds between fluorine atoms result in the formation of infinite zigzag chains in crystalline hydrogen fluoride

with $\text{F}-\text{H}\cdots\text{F}$ distance 249 pm and the angle HFH 120.1° . Likewise, the crystal structure of NH_4HF_2 is completely determined by H bonds, each nitrogen atom being surrounded by 8 fluorines, 4 in tetrahedral array at 280 pm due to the formation of $\text{N}-\text{H}\cdots\text{F}$ bonds, and 4 further away at about 310 pm; the two sets of fluorine atoms are themselves bonded pairwise at 232 pm by $\text{F}-\text{H}-\text{F}$ interactions. Ammonium azide NH_4N_3 has the same structure as NH_4HF_2 , with $\text{N}-\text{H}\cdots\text{N}$ 298 pm. Hydrogen bonding also leads NH_4F to crystallize with a structure different from that of the other ammonium (and alkali) halides: NH_4Cl , NH_4Br and NH_4I each have a low-temperature CsCl-type structure and a high-temperature NaCl-type structure, but NH_4F adopts the wurtzite (ZnS) structure in which each NH_4^+ group is surrounded tetrahedrally by 4 F to which it is bonded by 4 $\text{N}-\text{H}\cdots\text{F}$ bonds at 271 pm. This is very similar to the structure

⁵⁶ L. PAULING, *The Nature of the Chemical Bond*, 3rd edn., Chap. 12, Cornell University Press, Ithaca, 1960.

⁵⁷ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1984, 1382 pp.

Table 3.8 Length of typical H bonds^(46,57)

Bond	Length/pm	Σ /pm ^(a)	Examples
F-H-F	227	(270)	NaHF ₂ , KHF ₂
F-H...F	245-249	(270)	KH ₄ F ₅ , HF
O-H...F	265-287	(275)	CuF ₂ ·2H ₂ O, FeSiF ₆ ·6H ₂ O
O-H...Cl	295-310	(320)	HCl·H ₂ O, (NH ₃ OH)Cl, CuCl ₂ ·2H ₂ O
O-H...Br	320-340	(335)	NaBr·2H ₂ O, HBr·4H ₂ O
O-H-O	240-263	(280)	Ni dimethylglyoxime, KH maleate, HCrO ₂ Na ₃ H(CO ₃) ₂ ·2H ₂ O
O-H...O	248-290	(280)	KH ₂ PO ₄ , NH ₄ H ₂ PO ₄ , KH ₂ AsO ₄ , AlOOH, α -HIO ₃ , numerous hydrated metal sulfates and nitrates
O-H...S	310-340	(325)	MgS ₂ O ₃ ·6H ₂ O
O-H...N	268-279	(290)	N ₂ H ₄ ·4MeOH, N ₂ H ₄ ·H ₂ O
N-H...F	262-296	(285)	NH ₄ F, N ₂ H ₆ F ₂ , (N ₂ H ₆)SiF ₆
N-H...Cl	300-320	(330)	Me ₃ NHCl, Me ₂ NH ₂ Cl, (NH ₃ OH)Cl
N-H...I	346	(365)	Me ₃ NHI
N-H...O	281-304	(290)	HSO ₃ NH ₂ , (NH ₄) ₂ SO ₄ , NH ₄ OOCH, CO(NH ₂) ₂
N-H...S	323, 329	(335)	N ₂ H ₅ (HS)
N-H...N	294-315	(300)	NH ₄ N ₃ , NCNC(NH ₂) ₂ (i.e. dicyandiamide)
P-H...I	424	(405)	PH ₄ I

^(a) Σ = sum of van der Waals' radii (in pm) of A and B (ignoring H which has a value of ~120 pm) and using the values F 135, Cl 180, Br 195, I 215; O 140, S 185; N 150, P 190.

of ordinary ice. Typical values of A-H...B distances found in crystals are given in Table 3.8.

The precise position of the H atom in crystalline compounds containing H bonds has excited considerable experimental and theoretical interest. In situations where a symmetric H bond is possible in principle, it is frequently difficult to decide whether the proton is vibrating with a large amplitude about a single potential minimum or whether it is vibrating with a smaller amplitude but is also statistically disordered between two close sites, the potential energy barrier between the two sites being small.^(46,47) It now seems well established that the F-H-F bond is symmetrical in NaHF₂ and KHF₂, and that the O-H-O bond is symmetrical in HCrO₂. Other examples are the intra-molecular H bonds in potassium hydrogen maleate, K⁺[*cis*- $\overline{\text{C}}\text{H}=\overline{\text{C}}\text{H}\text{C}(\text{O})\text{O}-\text{H}-\overline{\text{O}}\text{C}(\text{O})$]⁻ and its monochloro derivative: Numerous other examples of H bonding will be found in later chapters.

In summary, we can see that H bonding influences crystal structure by linking atoms or groups

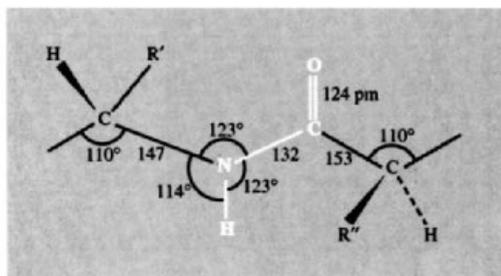
into larger structural units. These may be:

- finite groups: HF₂⁻; [O₂CO-H...OCO₂]³⁻ in Na₃H(CO₃)₂·2H₂O dimers of carboxylic acids, etc.;
- infinite chains: HF, HCN, HCO₃⁻, HSO₄⁻, etc.;
- infinite layers: N₂H₆F₂, B(OH)₃, B₃O₃(OH)₃, H₂SO₄, etc.;
- three-dimensional nets: NH₄F, H₂O, H₂O₂, Te(OH)₆, H₂PO₄⁻ in KH₂PO₄, etc.

H bonding also vitally influences the conformation and detailed structure of the polypeptide chains of protein molecules and the complementary intertwined polynucleotide chains which form the double helix in nucleic acids.^(56,58) Thus, proteins are built up from polypeptide chains of the type shown at the top of the next column.

These chains are coiled in a precise way which is determined to a large extent by N-H...O hydrogen bonds of length 279 ±

⁵⁸ G. A. JEFFREY and W. SAENGER, *Hydrogen Bonding in Biological Structures*, Springer Verlag, Berlin, 1991, 567 pp.



12 pm depending on the amino-acid residue involved. Each amide group is attached by such a hydrogen bond to the third amide group from it in both directions along the chain, resulting in an α -helix of pitch (total rise of helix per turn) of about 538 pm, corresponding to 3.60 amino-acid residues per turn. These helical chains can, in turn, become stretched and form hydrogen bonds with neighbouring chains to generate either parallel-chain pleated sheets (repeat distances 650 pm) or antiparallel-chain pleated sheets (700 pm).

Nucleic acids, which control the synthesis of proteins in the cells of living organisms and which transfer heredity information via genes, are also dominated by H bonding. Their structure involves two polynucleotide chains intertwined to form a double helix. The complementarity in the structure of the two chains is ascribed to the formation of H bonds between the pyrimidine residue (thymine or cytosine) in one chain and the purine residue (adenine or guanine) in the other as illustrated in Fig. 3.10. Whilst there is still some uncertainty as to the precise configuration of the $N-H \cdots O$ and $N-H \cdots N$ hydrogen bonds in particular cases, the extraordinary fruitfulness of these basic ideas has led to a profusion

of developments of fundamental importance in biochemistry.⁽⁵⁸⁾

3.6.3 Strength of hydrogen bonds and theoretical description⁽⁵⁹⁾

Measurement of the properties of H-bonded systems over a range of temperatures leads to experimental values of ΔG , ΔH and ΔS for H-bond formation, and these data have been supplemented in recent years by increasingly reliable *ab initio* quantum-mechanical calculations.⁽⁶⁰⁾ Some typical values for the enthalpy of dissociation of H-bonded pairs in the gas phase are in Table 3.9.

The uncertainty in these values varies between ± 1 and ± 6 kJ mol⁻¹. In general, H bonds of energy < 25 kJ mol⁻¹ are classified as weak; those in the range 25–40 kJ mol⁻¹ are medium; and those having $\Delta H > 40$ kJ mol⁻¹ are strong. Until recently, it was thought that the strongest H bond was that in the hydrogendifluoride ion $[F-H-F]^-$; this is difficult to determine experimentally and values in the range 150–250 kJ mol⁻¹ have been reported. A recent theoretically computed value is 169 kJ mol⁻¹ which agrees well with the value of 163 ± 4 kJ mol⁻¹ from ion cyclotron resonance studies.⁽⁶¹⁾ In fact, it now seems that the H bond between formic acid and the fluoride ion,

⁵⁹ A. C. LEGON and D. J. MILLEN, *Chem. Soc. Revs.* **21**, 71–8 (1992).

⁶⁰ P. A. KOLLMAN, Chap. 3 in H. F. SCHAEFFER (ed.), *Applications of Electronic Structure Theory*, Plenum Press, New York, 1977.

⁶¹ J. EMSLEY, *Polyhedron* **4**, 489–90 (1985).

Table 3.9 Enthalpy of dissociation of H-bonded pairs in the gas phase, $\Delta H_{298}(A-H \cdots B)/\text{kJ mol}^{-1}$

Weak		Medium		Strong	
HSH \cdots SH ₂	7	FH \cdots FH	29	HOH \cdots Cl ⁻	55
NCH \cdots NCH	16	ClH \cdots OMe ₂	30	HCONH ₂ \cdots OCHNH ₂	59
H ₂ NH \cdots NH ₃	17	FH \cdots OH ₂	38	HCOOH \cdots OCHOH	59
MeOH \cdots OHMe	19			HOH \cdots F ⁻	98
HOH \cdots OH ₂	22			H ₂ OH ⁺ \cdots OH ₂	151
				FH \cdots F ⁻	169
				HCO ₂ H \cdots F ⁻	~200

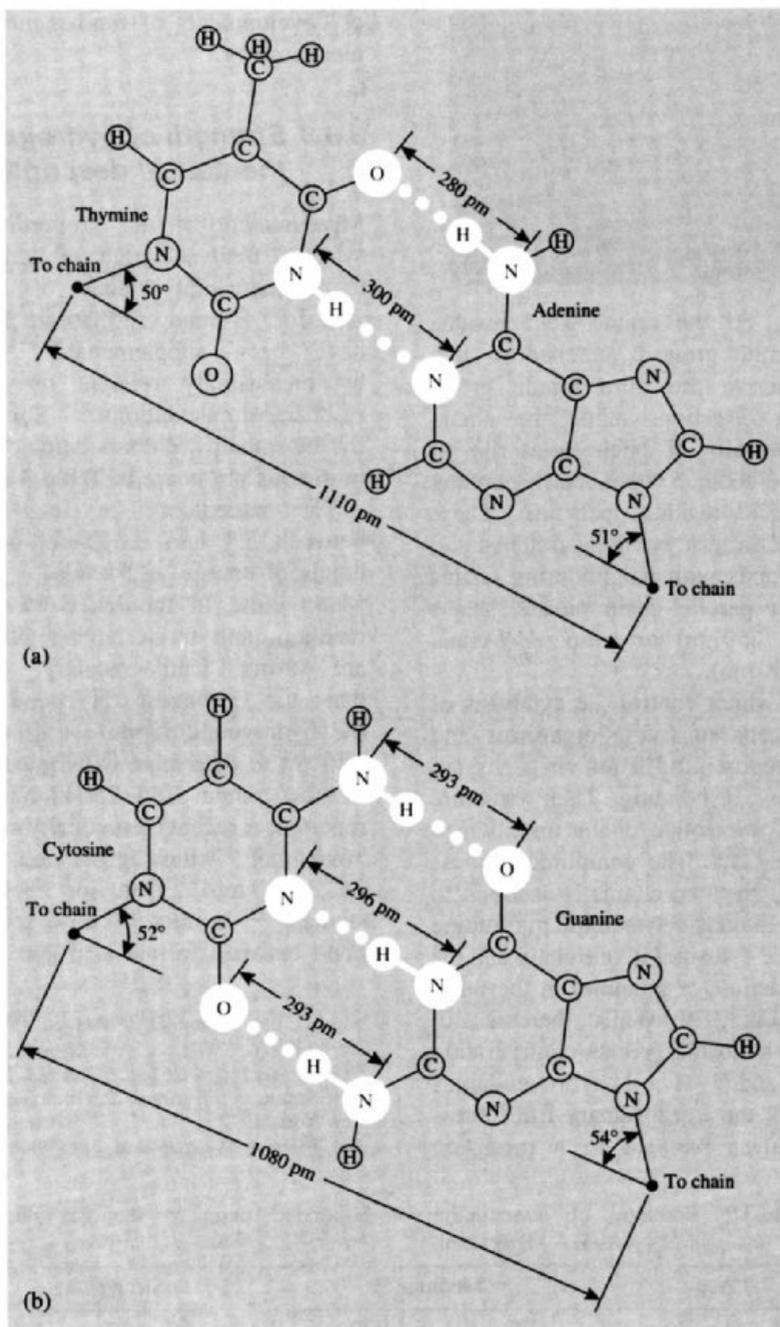


Figure 3.10 Structural details of the bridging units between pairs of bases in separate strands of the double helix of DNA: (a) the thymine-adenine pair (b) the cytosine-guanine pair.

[HCO₂H...F⁻], is some 30 kJ mol⁻¹ stronger than that calculated on the same basis for HF₂⁻.⁽⁶²⁾

Early discussions on the nature of the hydrogen bond tended to adopt an electrostatic approach in order to avoid the implication of a covalency greater than one for hydrogen. Indeed, such calculations can reproduce the experimental H-bond energies and dipole moments, but this is not a particularly severe test because of the parametric freedom in positioning the charges. However, the purely electrostatic theory is unable to account for the substantial increase in intensity of the stretching vibration $\nu(\text{A-H})$ on H bonding or for the lowered intensity of the bending mode $\delta(\text{A-H})$. More seriously, such a theory does not account for the absence of correlation between H-bond strength and dipole moment of the base, and it leaves the frequency shifts in the electronic transitions unexplained. Nonlinear A-H...B bonds would also be unexpected, though numerous examples of angles in the range 150–180° are known.⁽⁴⁶⁾

Valence-bond descriptions envisage up to five contributions to the total bond wave function,⁽⁴⁵⁾ but these are now considered to be merely computational devices for approximating to the true wave function. Perturbation theory has also been employed and apportions the resultant bond energy between (1) the electrostatic energy of interaction between the fixed nuclei and the electron distribution of the component molecules, (2) Pauli exchange repulsion energy between electrons of like spin, (3) polarization energy resulting from the attraction between the polarizable charge cloud of one molecule and the permanent multipoles of the other molecule, (4) quantum-mechanical charge-transfer energy, and (5) dispersion energy, resulting from second-order induced dipole-induced dipole attraction. The results suggest that electrostatic effects predominate, particularly for weak bonds, but that covalency effects increase in importance as the strength of the bond increases. It is also

possible to apportion the energy obtained from *ab initio* SCF-MO calculations in this way.⁽⁶³⁾ For example, in one particular calculation for the water dimer HOH...OH₂, the five energy terms enumerated above were calculated to be: $E_{\text{elec stat}} - 26.5$, $E_{\text{Pauli}} + 18$, $E_{\text{polar}} - 2$, $E_{\text{ch tr}} - 7.5$, $E_{\text{disp}} 0 \text{ kJ mol}^{-1}$. There was also a coupling interaction $E_{\text{mix}} - 0.5$, making in all a total attractive force $\Delta E_0 = E_{\text{dimer}} - E_{\text{monomers}} = -18.5 \text{ kJ mol}^{-1}$. To calculate the enthalpy change ΔH_{298} as listed on p. 61, it is also necessary to consider the work of expansion and the various spectroscopic degrees of freedom:

$$\Delta H_{298} = E_0 + \Delta(PV) + \Delta E_{\text{trans}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$$

Such calculations can also give an indication of the influence of H-bond formation on the detailed electron distribution within the interacting components. There is general agreement that in the system X-A-H...B-Y as compared with the isolated species XAH and BY, there is a net gain of electron density by X, A and B and a net loss of electrons by H and Y. There is also a small transfer of electronic charge (~0.05 electrons) from BY to XAH in moderately strong H bonds (20–40 kJ mol⁻¹). In virtually all neutral dimers, the increase in the A-H bond length on H-bond formation is quite small (<5 pm), the one exception so far studied theoretically being ClH...NH₃, where the proton position in the H bond is half-way between completely transferred to NH₃ and completely fixed on HCl.

It follows from the preceding discussion that the unbranched H bond can be regarded as a 3-centre 4-electron bond A-H...B in which the 2 pairs of electrons involved are the bond pair in A-H and the lone pair on B. The degree of charge separation on bond formation will depend on the nature of the proton-donor group AH and the Lewis base B. The relation between this 3-centre bond formalism and the 3-centre bond descriptions frequently used for boranes, polyhalides and compounds of xenon is particularly instructive and is elaborated in

⁶² J. EMSLEY, O. P. A. HOYTE and R. E. OVERILL, *J. Chem. Soc., Chem. Commun.*, 225 (1977).

⁶³ H. UMEYAMA and K. MOROKUMA, *J. Am. Chem. Soc.* **99**, 1316–32 (1977).

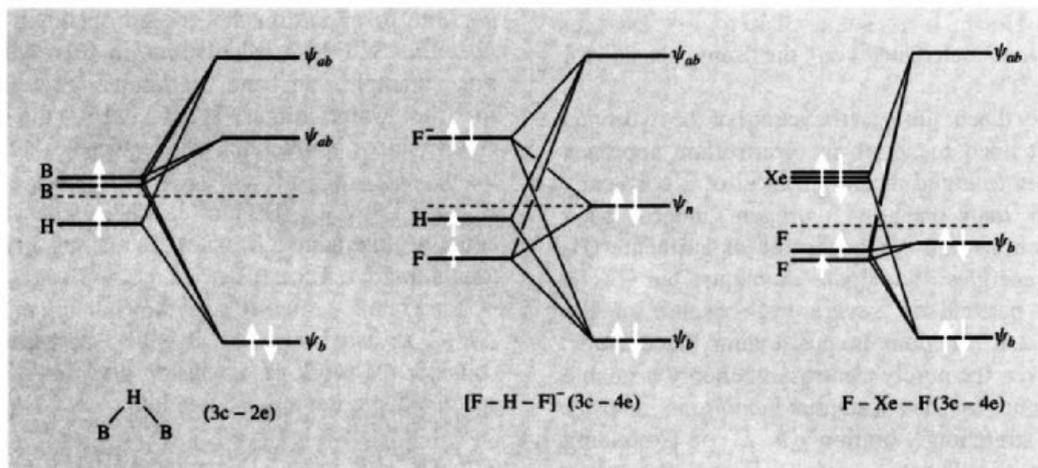


Figure 3.11 Schematic representation of the energy levels in various types of 3-centre bond. The B-H-B (“electron deficient”) bond is non-linear, the (“electron excess”) F-Xe-F bond is linear, and the A-H...B hydrogen bond can be either linear or non-linear depending on the compound.

Fig. 3.11. Numerous examples are also known in which hydrogen acts as a bridge between metallic elements in binary and more complex hydrides, and some of these will be mentioned in the following section which considers the general question of the hydrides of the elements.

3.7 Hydrides of the Elements⁽⁶⁴⁻⁶⁾

Hydrogen combines with many elements to form binary hydrides MH_x (or M_mH_n). All the main-group elements except the noble gases and perhaps indium and thallium form hydrides, as do all the lanthanoids and actinoids that have been studied. Hydrides are also formed by the more electropositive transition elements, notably Sc, Y, La, Ac; Ti, Zr, Hf; and to a lesser

extent V, Nb, Ta; Cr; Cu; and Zn. Hydrides of other transition elements are either non-existent or poorly characterized, with the spectacular exception of palladium which has been more studied than any other metal hydride system.⁽⁶⁷⁾ The situation is summarized in Fig. 3.12; this indicates the idealized formulae of the known hydrides though many of the d-block and f-block elements form phases of variable compositions.

It has been customary to group the binary hydrides of the elements into various classes according to the presumed nature of their bonding: ionic, metallic, covalent, polymeric, and “intermediate” or “borderline”. However, this is unsatisfactory because the nature of the bonding is but poorly understood in many cases and the classification obscures the important point that there is an almost continuous gradation in properties — and bond types(?) — between members of the various classes. It is also somewhat misleading in implying that the various bond types are mutually exclusive whereas it seems likely that more than one type of bonding is present in many cases. The situation is not unique to hydrides but is also well known for

⁶⁴ K. M. MACKAY, *Hydrogen Compounds of the Metallic Elements*, E. and F. N. Spon, London, 1966, 168 pp.; Hydrides, *Comprehensive Inorganic Chemistry*, Vol. 1, Chap. 2, Pergamon Press, Oxford, 1973.

⁶⁵ E. WIBERG and E. AMBERGER, *Hydrides of the Elements of Main Groups I-IV*, Elsevier, Amsterdam, 1971, 785 pp.

⁶⁶ W. M. MUELLER, J. P. BLACKLEDGE and G. G. LIBOWITZ (eds.), *Metal Hydrides*, Academic Press, New York, 1968, 791 pp.

⁶⁷ F. A. LEWIS, *The Palladium-Hydrogen System*, Academic Press, London, 1967, 178 pp.

		H ₂		He																	
LiH	BeH ₂															~40 boranes B _n H _n	lanthanide C _m H _m hydrides Si _n H _{2n+2} etc. n = 1-8(+)	NH ₃ N ₂ H ₄ N ₃ H	OH ₂ O ₂ H ₂	FH	Ne
NaH	MgH ₂															AlH ₃	etc.	P _n H _{m-2} n = 1-9 etc.	S _n H ₂ n = 1-8(+)	CH	Ar
KH	CaH ₂	ScH ₂	TiH ₂	VH VH ₂	CrH	Mn	Fe	Co	(NiH)	CuH	ZnH ₂	GaH ₃	(Gr _m H _{2n+2}) n = 1-8(+)	AsH ₃	SeH ₂	BrH	Kr				
RbH	SrH ₂	YH ₂ YH ₃	ZrH ₂	NbH NbH ₂	Mo	Tc	Ru	Rh	PdH<1	Ag	(CdH ₂) ?	(InH ₃) ?	SnH ₄ Sn ₂ H ₆	SbH ₃	TeH ₂	Hl	Xc				
CsH	BaH ₂	LaH ₂ LaH ₃	HfH ₂	TaH	W	Re	Os	Ir	Pt	Au	(HgH ₂) ?	(TlH ₃) ?	PbH ₄	BiH ₃	(PoH ₂) ?	AtH	Rn				
Fr	Ra	AcH ₂																			
			CeH ₂ CeH ₃	PrH ₂ PrH ₃	NdH ₂ NdH ₃	Pm	SmH ₂ SmH ₃	EuH ₂	GdH ₂ GdH ₃	TbH ₂ TbH ₃	DyH ₂ DyH ₃	HoH ₂ HoH ₃	ErH ₂ ErH ₃	TmH ₂ TmH ₃	YbH ₂ YbH _{2.5}	LuH ₂ LuH ₃					
			ThH ₂ Th ₄ H ₁₅	PaH ₃	UH ₃	NpH ₂ NpH ₃	PuH ₂ PuH ₃	AmH ₂ AmH ₃	CmH ₂	Bk	Cf	Es	Fm	Md	No	Lr					

Figure 3.12 The hydrides of the elements.

binary halides, oxides, sulfides, etc.: this serves to remind us that the various bond models represent grossly oversimplified limiting cases and that in most actual systems the position is more complex. For example, oxides might be classed as ionic (MgO), metallic (TiO, ReO₃), covalent (CO₂), polymeric (SiO₂), or as intermediate between these various classes, though any adequate bonding theory would recognize the arbitrary nature of these distinctions which merely emphasize particular features of the overall assembly of molecular orbitals and electron populations.

The metals in Groups 1 and 2 of the periodic table react directly with hydrogen to form white, crystalline, stoichiometric hydrides of formula MX and MX₂ respectively. The salt-like character of these compounds was recognized by G. N. Lewis in 1916 and he suggested that they contained the hydride ion H⁻. Shortly thereafter

(1920) K. Moers showed that electrolysis of molten LiH (mp 692°C) gave the appropriate amount of hydrogen at the anode; the other hydrides tended to decompose before they could be melted. As expected, the ionic-bond model is most satisfactory for the later (larger) members of each group, and the tendency towards covalency becomes more marked for the smaller elements LiH, MgH₂, and particularly BeH₂, which is best described in terms of polymeric covalent bridge bonds. X-ray and neutron diffraction studies show that the alkali metal hydrides adopt the cubic NaCl structure (p. 242) whereas MgH₂ has the tetragonal TiO₂ (rutile type) structure (p. 961) and CaH₂, SrH₂ and BaH₂ adopt the orthorhombic PbCl₂-type structure (p. 382). The implied radius of the hydride ion H⁻ (1s²) varies considerably with the nature of the metal because of the ready deformability of the pair of electrons surrounding a single proton. Typical values are

given below and these can be compared with $r(\text{F}^-) \sim 133$ pm and $r(\text{Cl}^-) \sim 184$ pm.

Compound	MgH ₂	LiH	NaH	KH	RbH	CsH	Free H ⁻ (calculated)
$r(\text{H}^-)/\text{pm}$	130	137	146	152	154	152	208

The closest M–M approach in these compounds is often less than for the metal itself: this should occasion no surprise since this is a common feature of many compounds in which there is substantial separation of charge. For example, the shortest Ca–Ca interatomic distance is 393 pm in calcium metal, 360 pm in CaH₂, 380 pm in CaF₂, and only 340 pm in CaO (why?).

The thermal stability of the alkali metal hydrides decreases from lithium to caesium, the temperature at which the reversible dissociation pressure of hydrogen reaches 10 mmHg being $\sim 550^\circ\text{C}$ for LiH, $\sim 210^\circ\text{C}$ for NaH and KH, and $\sim 170^\circ\text{C}$ for RbH and CsH. The corresponding figures for the alkaline earth metal hydrides are CaH₂ 885°C , SrH₂ 585°C and BaH₂ 230°C , though for MgH₂ it is only 85°C . Chemical reactivity depends markedly on both the purity and the state of subdivision but increases from lithium to caesium and from calcium to barium with CaH₂ being rather less reactive than LiH. The reaction of water with these latter two compounds forms a convenient portable source of hydrogen, but with NaH the reaction is more violent than with sodium itself. RbH and CsH actually ignite spontaneously in dry air.

Turning next to Group 3, Fig. 3.12 indicates that hydrides of limiting stoichiometry MH₂ are also formed by Sc, Y, La, Ac and by most of the lanthanoids and actinoids. In the special case of EuH₂ (Eu^{II} 4f⁷) and YbH₂ (Yb^{II} 4f¹⁴) the hydrides are isostructural with CaH₂ and the ionic bonding model gives a reasonable description of the observed properties; however, YbH₂ can absorb more hydrogen up to about YbH_{2.5}. The other hydrides adopt the fluorite (CaF₂) crystal structure (p. 118) and the supernumerary valence electron is delocalized, thereby conferring considerable metallic conductivity. For example, LaH₂ is a dark-coloured, brittle compound with a conductivity of about $10 \text{ ohm}^{-1} \text{ cm}^{-1}$ ($\sim 1\%$ of

that of La metal). Further uptake of hydrogen progressively diminishes this conductivity to $< 10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ for the cubic phase LaH₃ (cf. $\sim 3 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ for YbH₂). The other Group 3 elements and the lanthanoids and actinoids are similar.

There is a lively controversy concerning the interpretation of these and other properties, and cogent arguments have been advanced both for the presence of hydride ions H⁻ and for the presence of protons H⁺ in the d-block and f-block hydride phases.^(64,66) These difficulties emphasize again the problems attending any classification based on presumed bond type, and a phenomenological approach which describes the observed properties is a sounder initial basis for discussion. Thus the predominantly ionic nature of a phase cannot safely be inferred either from crystal structure or from calculated lattice energies since many metallic alloys adopt the NaCl-type or CsCl-type structures (e.g. LaBi, β -brass) and enthalpy calculations are notoriously insensitive to bond type.

The hydrides of limiting composition MH₃ have complex structures and there is evidence that the third hydrogen is sometimes less strongly bound in the crystal. For the earlier (larger) lanthanoids La, Ce, Pr and Nd, hydrogen enters octahedral sites and LnH₃ has the cubic Li₃Bi structure.⁽⁵⁷⁾ For Y and the smaller lanthanoids Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu, as well as for the actinoids Np, Pu and Am, the hexagonal HoH₃ structure is adopted. This is a rather complex structure based on an extended unit cell containing 6 Ho and 18 H atoms.⁽⁶⁸⁾ The idealized structure has hcp Ho atoms with 12 tetrahedrally coordinated H atoms and 6 octahedrally coordinated H atoms; however, to make room for the bulky Ho atoms, close pairs of tetrahedral H atoms are slightly displaced and there is a more substantial movement of the "octahedral" H atoms towards the planes of the Ho atoms so that 2 of the H atoms are actually in the Ho planes and are trigonal 3-coordinate. The

⁶⁸ M. MANSMANN and W. E. WALLACE *J. de Physique* **25**, 454–9 (1964).

hydrogen atoms are thus of three types having respectively 14, 11, and 9 H neighbours for the distorted trigonal, octahedral and tetrahedral sites. Each H atom has 3 Ho neighbours at either 210 or 217 or 224–299 pm respectively, and each Ho has 11 hydrogen neighbours, 9 at 210–229 pm and 2 somewhat further away at 248 pm. The 3-coordinate hydrogen is most unusual, the only other hydride in which it occurs being the complex cubic phase Th_4H_{15} .

Uranium forms two hydrides of stoichiometric composition UH_3 . The normal β -form has a complex cubic structure and is the only one formed when the preparation is carried out above 200°C. Below this temperature increasing amounts of the slightly denser cubic α -form occur and this can be transformed to the β -phase by warming to 250°C. Both phases have ferromagnetic and metallic properties. Uranium hydride is commonly used as a starting material for the preparation of uranium compounds as it is finely powdered and extremely reactive. It is also used for purifying and regenerating hydrogen (or deuterium) gas.

The hydrides of Ti, Zr and Hf are characterized by considerable variability in composition and structure. When pure, the limiting phases MH_2 form massive, metallic crystals of fluorite structure (TiH_2) or body-centred tetragonal structure (ZrH_2 , HfH_2 , ThH_2), but there are also several hydrogen-deficient phases of variable composition and complex structure in which several M–H distances occur.^(57,64,66) These phases (and others based on Y, Ce and Nb) have been extensively investigated in recent years because of their potential applications as moderators, reflectors, or shield components for high-temperature, mobile nuclear reactors.

Other hydrides with interstitial or metallic properties are formed by V, Nb and Ta; they are, however, very much less stable than the compounds we have been considering and have extensive ranges of composition. Chromium also forms a hydride, CrH , though this must be prepared electrolytically rather than by direct reaction of the metal with hydrogen. It has the anti-NiAs structure (p. 555). Most other elements

in this area of the periodic table have little or no affinity for hydrogen and this has given rise to the phrase “hydrogen gap”. The notable exception is the palladium–hydrogen system which is discussed on p. 1150.

The hydrides of the later main-group elements present few problems of classification and are best discussed during the detailed treatment of the individual elements. Many of these hydrides are covalent, molecular species, though association via H bonding sometimes occurs, as already noted (p. 53). Catenation flourishes in Group 14 and the complexities of the boron hydrides merit special attention (p. 151). The hydrides of aluminium, gallium, zinc (and beryllium) tend to be more extensively associated via M–H–M bonds, but their characterization and detailed structural elucidation has proved extremely difficult.

Two further important groups of hydride compounds should be mentioned and will receive detailed attention in later chapters. One is the group of complex metal hydrides of which notable examples are LiBH_4 , NaBH_4 , LiAlH_4 , $\text{Al}(\text{BH}_4)_3$, etc.⁽⁶⁹⁾ The other is the growing number of compounds in which the hydrogen atom is a monodentate or bidentate (bridging) ligand to a transition element.^(70–73) these date from the early 1930s when W. Hieber discovered $[\text{Fe}(\text{CO})_4\text{H}_2]$ and $[\text{Co}(\text{CO})_4\text{H}]$ and now cover an astonishing variety of structural types. The modest steric requirements of the H atom enable complexes such as $[\text{ReH}_9]^{2-}$ to be synthesized, and bridged complexes such as the linear $[\text{Cr}_2(\text{CO})_{10}\text{H}]^-$ and bent $[\text{W}_2(\text{CO})_9\text{H}(\text{NO})]$, are known. For $\eta^2\text{-H}_2$ complexes see pp. 44–7. The role of hydrido complexes in homogeneous catalysis is also exciting considerable attention.

⁶⁹ A. HAJOS, *Complex Hydrides*, Elsevier, Amsterdam, 1979, 398 pp.

⁷⁰ J. C. GREEN and M. L. H. GREEN, *Comprehensive Inorganic Chemistry*, Vol. 4, Chap. 48, Pergamon Press, Oxford, 1973.

⁷¹ H. D. KAESZ and R. B. SAILLANT, *Chem. Rev.* **72**, 231–81 (1972).

⁷² A. P. HUMPHRIES and H. D. KAESZ, *Progr. Inorg. Chem.* **25**, 145–222 (1979).

⁷³ G. L. GEOFFROY, *Progr. Inorg. Chem.* **27**, 123–51 (1980).