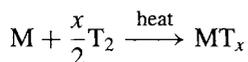
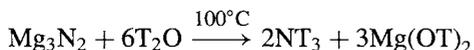
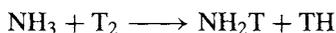
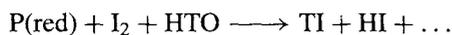
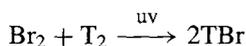
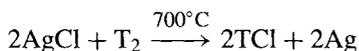
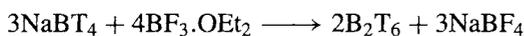
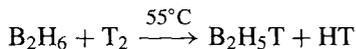
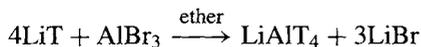
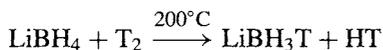
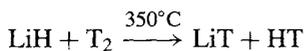


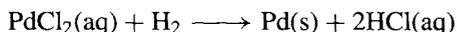
synthetic reagents are NaT, LiAlH<sub>3</sub>T, NaBH<sub>3</sub>T, NaBT<sub>4</sub>, B<sub>2</sub>T<sub>6</sub> and tritiated Grignard reagents. Typical preparations are as follows:



The preparation and use of LiEt<sub>3</sub>BT and LiAlT<sub>4</sub> at maximum specific activity (57.5 Ci mmol<sup>-1</sup>) has also been described.<sup>(16)</sup>

### 3.4 Chemical Properties and Trends

Hydrogen is a colourless, tasteless, odourless gas which has only low solubility in liquid solvents. It is comparatively unreactive at room temperature though it combines with fluorine even in the dark and readily reduces aqueous solutions of palladium(II) chloride:



This reaction can be used as a sensitive test for the presence of hydrogen. At higher temperatures hydrogen reacts vigorously, even explosively, with many metals and non-metals to give the corresponding hydrides. Activation can also be induced photolytically, by heterogeneous catalysts (Raney nickel, Pd, Pt, etc.), or by means of homogeneous hydrogenation catalysts. Industrially important processes include the hydrogenation of many organic compounds and the use of cobalt compounds as catalysts in the hydroformylation of olefins to aldehydes and alcohols at high temperatures and pressures (p. 1140):



An even more effective homogeneous hydrogenation catalyst is the complex [RhCl(PPh<sub>3</sub>)<sub>3</sub>] which permits rapid reduction of alkenes, alkynes and other unsaturated compounds in benzene solution at 25°C and 1 atm pressure (p. 1134). The Haber process, which uses iron metal catalysts for the direct synthesis of ammonia from nitrogen and hydrogen at high temperatures and pressures, is a further example (p. 421).

The hydrogen atom has a unique electronic configuration 1s<sup>1</sup>: accordingly it can gain an electron to give H<sup>-</sup> with the helium configuration 1s<sup>2</sup> or it can lose an electron to give the proton H<sup>+</sup> (p. 36). There are thus superficial resemblances both to the halogens which can gain an electron to give an inert-gas configuration ns<sup>2</sup>np<sup>6</sup>, and to the alkali metals which can lose an electron to give M<sup>+</sup> (ns<sup>2</sup>np<sup>6</sup>). However, because hydrogen has no other electrons in its structure there are sufficient differences from each of these two groups to justify placing hydrogen outside either. For example, the proton is so small (*r* ~ 1.5 × 10<sup>-3</sup> pm compared with normal atomic and ionic sizes of ~50–220 pm) that it cannot exist in condensed systems unless associated with other atoms or molecules. The transfer of protons between chemical species constitutes the basis of acid–base phenomena (see Section 3.5). The hydrogen atom is also frequently found in close association with 2

<sup>16</sup> H. ANDRES, H. MORIMOTO and P. G. WILLIAMS, *J. Chem. Soc., Chem. Commun.*, 627–8 (1990).

other atoms in linear array; this particularly important type of interaction is called hydrogen bonding (see Section 3.6). Again, the ability to penetrate metals to form nonstoichiometric metallic hydrides, though not unique to hydrogen, is one of its more characteristic properties as is its ability to form nonlinear hydrogen bridge bonds in many of its compounds. These properties will be further discussed during the general classification of the hydrides of the elements in section 3.7. The most important compound of hydrogen is, of course, water and a detailed discussion of this compound is given on pp. 620–33 in the chapter on oxygen.

### 3.4.1 The coordination chemistry of hydrogen

Perhaps the most exciting recent development in the chemistry of hydrogen is the discovery that, in transition metal polyhydrides, the molecule  $H_2$  can act as a dihapto ligand,  $\eta^2-H_2$  (see below). Even the H atom itself can form compounds in which its coordination number (CN) is not just 1 (as expected) but also 2, 3, 4, 5 or even 6. A rich and unexpectedly varied coordination chemistry is thus emerging. We shall deal with the H atom first and then with the  $H_2$  molecule.

By far the most common CN of hydrogen is 1, as in  $HCl$ ,  $H_2S$ ,  $PH_3$ ,  $CH_4$  and most other covalent hydrides and organic compounds. Bridging modes in which the H atom has a higher CN are shown schematically in the next column — in these structures M is typically a transition metal but, particularly in the  $\mu_2$ -mode and to some extent in the  $\mu_3$ -mode, one or more of the M can represent a main-group element such as B, Al; C, Si; N etc. Typical examples are in Table 3.3.<sup>(17–19)</sup> Fuller discussion and references, when appropriate, will be found in later chapters dealing with the individual elements concerned.

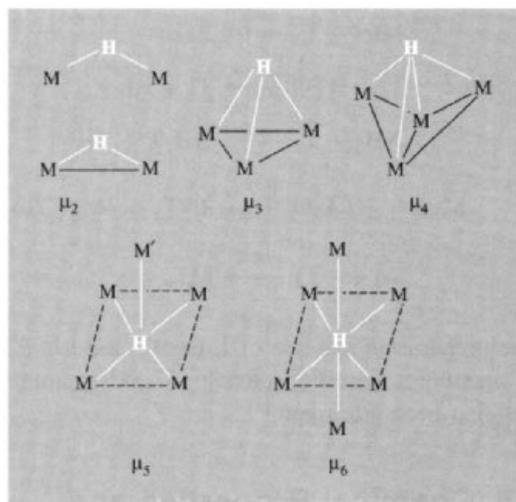
<sup>17</sup> D. S. MOORE and S. D. ROBINSON, *Chem. Soc. Revs.* **12**, 415–52 (1983).

<sup>18</sup> A. DEDIEU (ed.), *Transition Metal Hydrides*, VCH, Berlin, 1991, 416 pp.

<sup>19</sup> T. P. FEHLNER, *Polyhedron*, **9**, 1955–63 (1990).

**Table 3.3** Stereochemistry of hydrogen

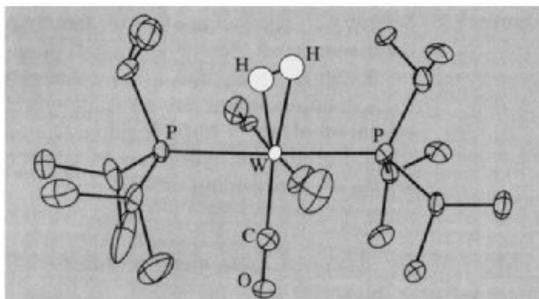
CN	Examples
1	$HCl$ , $H_2S$ , $PH_3$ , $NH_4^+$ , $BH_4^-$ , etc.; $[HMn(CO)_5]$ , $[H_2Fe(CO)_4]$ , $[H_3Ta(C_5H_5)_2]$ , $[H_4Cr(dmpe)_2]$ , $[CoH_5]^+$ , $[H_6W(PR_3)_3]$ , $\{[H_7Re(PR_3)_2]_2Ag\}^+$ , $[H_8Re(PR_3)]^-$ , $[ReH_9]^{2-}$
2	$B_2H_6$ , $[Me_2NAlH_2]_3$ , $[H_3BHCu(PMePh_3)_3]$ , <i>nido</i> - $Ir(B_5H_8)(CO)(PPh_3)_2$ , $[(CO)_5WHW(CO)_5]^-$ , $[(C_5Me_5)Ir(\mu_2-H)_3Ir(C_5Me_5)]$
3	<i>closo</i> - $B_6H_6(\mu_3-H)^-$ , $[(\mu_3-H)Rh_3(C_5H_5)_4]$ , $[(\mu_3-H)_4Co_4(C_5H_5)_4]$
4	$[(\mu_4-H)Ru_8(CO)_{21}H]^{2-}$
5	$\beta$ - $Mg_2NiH_4(d_4)$ (1 “covalent” Ni–D 149 pm plus 4 “ionic” Mg–D 230 pm)
6	$[HNb_6I_{11}]$ , $[HRu_6(CO)_{18}]^-$ , $[HCo_6(CO)_{15}]^-$ , $[(\mu_6-H)_2Ni_{12}(CO)_{21}]^{2-}$ , $[(\mu_6-H)Ni_{12}(CO)_{21}]^{3-}$



The crucial experiment suggesting that the  $H_2$  molecule might act as a dihapto ligand to transition metals was the dramatic observation<sup>(20)</sup> that toluene solutions of the deep purple coordinatively unsaturated 16-electron complexes  $[Mo(CO)_3(PCy_3)_2]$  and  $[W(CO)_3(PCy_3)_2]$  (where Cy = cyclohexyl) react readily and cleanly with  $H_2$  (1 atm) at low temperatures to precipitate yellow crystals of  $[M(CO)_3H_2(PCy_3)_2]$  in 85–95% yield. The

<sup>20</sup> G. J. KUBAS, *J. Chem. Soc., Chem. Commun.*, 61–2 (1980).

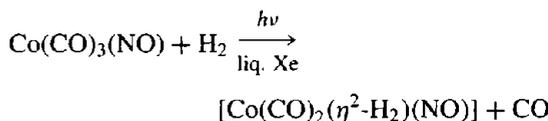
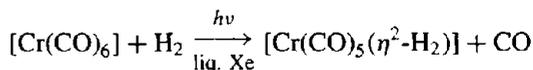
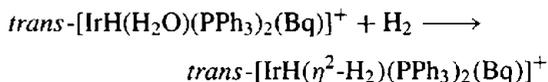
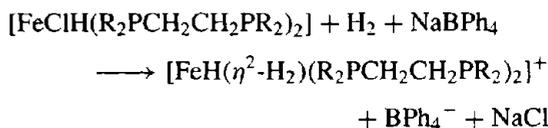
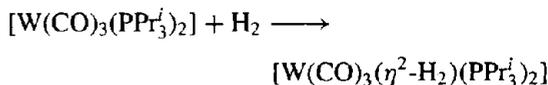
H<sub>2</sub> could be quantitatively removed at room temperature either by partial evacuation or by sparging the solution with argon. Definitive confirmation that the complexes did indeed contain  $\eta^2$ -H<sub>2</sub> came from X-ray and neutron diffraction studies on the bis(tri *i*-propylphosphine) analogue at -100°, which revealed the side-on coordination of H<sub>2</sub> as shown in Fig. 3.2.<sup>(21)</sup> During the past decade many other such compounds have been prepared and studied in great detail, and the field has been well reviewed.<sup>(22-24)</sup>



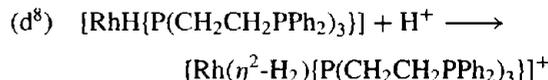
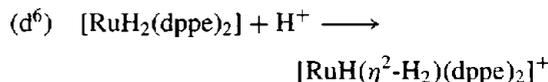
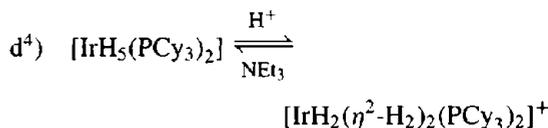
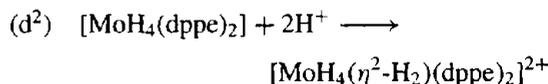
**Figure 3.2** The geometry of *mer-trans*-[W(CO)<sub>3</sub>-( $\eta^2$ -H<sub>2</sub>)(PPR<sub>3</sub>)<sub>2</sub>] from X-ray and neutron diffraction data:  $r(\text{H}-\text{H})$  84 pm (compared with 74.14 pm for free H<sub>2</sub>),  $r(\text{W}-\text{H})$  175 pm. Infrared vibration spectroscopy gives  $\nu(\text{H}-\text{H})$  2690 cm<sup>-1</sup> compared with 4159 cm<sup>-1</sup> (Raman) for free H<sub>2</sub>.

There are two general routes to  $\eta^2$ -H<sub>2</sub> complexes. The first involves direct addition of molecular H<sub>2</sub> either to an unoccupied coordination site in a 16-electron complex (as above) or by displacement of a ligand such as CO, Cl, H<sub>2</sub>O in the coordination sphere of an 18-electron complex; in this latter case ultraviolet irradiation may be required to assist in the

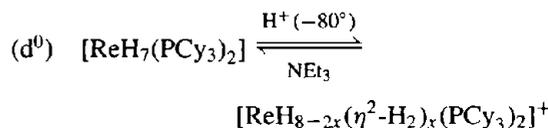
substitution reaction. Examples are:



The second general method involves the protonation of a polyhydrido complex using a strong acid such as HBF<sub>4</sub>·Et<sub>2</sub>O. Typical examples involving d<sup>2</sup>, d<sup>4</sup>, d<sup>6</sup> or d<sup>8</sup> metal centres are:



There is even a rare example involving a d<sup>0</sup> polyhydride:<sup>(25)</sup>



<sup>21</sup> G. J. KUBAS, R. R. RYAN, B. I. SWANSON, P. I. VERGAMINI and H. J. WASSERMAN, *J. Am. Chem. Soc.* **106**, 452-4 (1984).

<sup>22</sup> G. J. KUBAS, *Acc. Chem. Res.* **21**, 120-8 (1988).

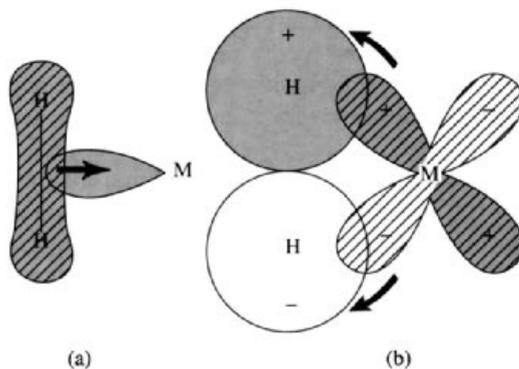
<sup>23</sup> R. H. CRABTREE and D. G. HAMILTON, *Adv. Organomet. Chem.* **28**, 299-338 (1988); R. H. CRABTREE, *Acc. Chem. Res.* **23**, 95-101 (1990).

<sup>24</sup> A. G. GINZBURG and A. A. BAGATUR'ANTS, *Organomet. Chem. in USSR* **2**, 111-26 (1989).

<sup>25</sup> X. L. R. FONTAINE, E. H. FOWLES and B. L. SHAW, *J. Chem. Soc., Chem. Commun.*, 482-3 (1988).

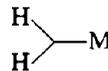
If deuterio acids are used then  $\eta^2$ -HD complexes are formed; these are particularly useful in establishing the retention of substantive H-H bonding in the coordinated ligand by observation of a 1:1:1 triplet in the proton nmr spectrum (the proton signal being split by coupling to deuterium with nuclear spin  $J = 1$ ).

The stability of  $\eta^2$ -H<sub>2</sub> complexes varies considerably, from those which can be observed only in low-temperature matrix-isolation experiments to those which are moderately robust even at room temperature and above. Stability depends on the electron configuration of the metal centre, the electronic and steric nature of the co-ligands, the overall charge on the complex, the state of aggregation and, of course, the temperature. Most  $\eta^2$ -H<sub>2</sub> complexes involve transition metals in Groups 6–8, in oxidation states having a formal d<sup>6</sup> electron configuration. No  $\eta^2$ -H<sub>2</sub> complexes are yet known for transition metals in Groups 3 or 4 of the periodic table, although examples involving Group 5 metals have recently been reported, e.g. the d<sup>4</sup> species [V( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>( $\eta^2$ -H<sub>2</sub>)]<sup>(26)</sup> and [Nb( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>( $\eta^2$ -H<sub>2</sub>)]<sup>(27)</sup>. Within a given Group, the first and second members more readily form  $\eta^2$ -H<sub>2</sub> complexes while the third member tends to form polyhydrido species, e.g. [Fe(H)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>3</sub>] and [Ru(H)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] but [Os(H)<sub>4</sub>(P(*o*-tol)<sub>3</sub>)<sub>3</sub>]<sup>(28)</sup>. Stability is also enhanced by an overall cationic charge on the complex (remember protonation as a route to  $\eta^2$ -H<sub>2</sub> complexes). In such cases, however, stability of the resulting compound depends on the presence of a non-coordinating anion such as BF<sub>4</sub><sup>-</sup>, otherwise there is a risk of decomposition by displacement of the more weakly coordinating ( $\eta^2$ -H<sub>2</sub>). Neutral complexes are also well known, but no examples of anionic  $\eta^2$ -H<sub>2</sub> complexes have been reported.



**Figure 3.3** Schematic representation of the two components of the  $\eta^2$ -H<sub>2</sub>-metal bond: (a) donation from the filled (hatched)  $\sigma$ -H<sub>2</sub> bonding orbital into a vacant hybrid orbital on M; (b)  $\pi$ -back donation from a filled d orbital (or hybrid) on M into the vacant  $\sigma^*$  antibonding orbital of H<sub>2</sub>.

Most of the observed facts can be understood in terms of a bonding scheme which envisages donation of electron density from the  $\sigma$  bond of H<sub>2</sub> into a vacant hybrid orbital on the metal, plus a certain amount of synergic back donation from an occupied d orbital on the metal into the  $\sigma^*$  antibonding orbital of H<sub>2</sub> (see Fig. 3.3). This is reminiscent of the bonding in the well known metal-alkene complexes (to be discussed in more detail on p. 931) but with two significant differences: (a) the electron density being donated from the H<sub>2</sub> ligand is in the single-bond  $\sigma$  orbital whereas for alkenes such as H<sub>2</sub>C=CH<sub>2</sub> it is in the  $\pi$  component of the double bond; and (b) the H<sub>2</sub> antibonding orbital involved in accepting back-donated electron density has  $\sigma^*$  symmetry rather than  $\pi^*$  as in alkenes. It is clear from this description that an overall positive charge on the metal centre encourages forward donation to form the 3-centre



bond, but diminishes the extent of back donation. By contrast, an overall negative charge might be expected to enhance back donation into the  $\sigma^*$  antibonding orbital and thus promote rupture of the H<sub>2</sub> single bond, with concomitant formation of two new hydrido M-H bonds.

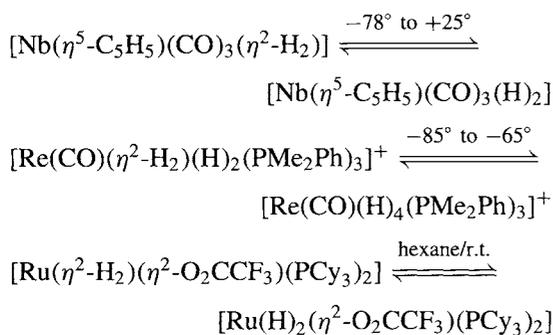
<sup>26</sup> M. T. HAWARD, M. W. GEORGE, S. M. HOWDLE and M. POLIAKOFF, *J. Chem. Soc., Chem. Commun.*, 913–5 (1990).

<sup>27</sup> M. T. HAWARD, M. W. GEORGE, P. HAMLEY and M. POLIAKOFF, *J. Chem. Soc., Chem. Commun.*, 1101–3 (1991).

<sup>28</sup> R. H. CRABTREE and D. G. HAMILTON, *J. Am. Chem. Soc.* **108** 3124–5 (1986).

The bonding scheme is also consistent with the observed lengthening of the H–H distance to about 84–90 pm in the  $\eta^2$ -H<sub>2</sub> complexes (as compared with 74 pm in free molecular H<sub>2</sub>), and with the lowering of the  $\nu$ (H–H) vibration frequency from 4159 cm<sup>-1</sup> in free H<sub>2</sub> to values typically in the range 2650–3250 cm<sup>-1</sup> in the complexes.

There is evidently a very fine balance between the two options {M( $\eta^2$ -H<sub>2</sub>)} and {M(H)<sub>2</sub>}; indeed, examples of an equilibrium between the two forms have recently been discovered:<sup>(27,29,30)</sup>



In the niobium system<sup>(27)</sup> the  $\eta^2$ -H<sub>2</sub> form is marginally the more stable, with  $\Delta H = 2.0 \text{ kJ mol}^{-1}$ , whereas in the rhenium system,<sup>(29)</sup> it is the tetrahydrido form which is the more stable, with  $-\Delta G_{208} = 2.5 \text{ kJ mol}^{-1}$  and  $-\Delta H = 4.6 \text{ kJ mol}^{-1}$ .

In a sense the formation of  $\eta^2$ -H<sub>2</sub> complexes can be thought of as an intermediate stage in the oxidative addition of H<sub>2</sub> to form two M–H bonds and, as such, the complexes might serve as a model for this process and for catalytic hydrogenation reactions by metal hydrides.<sup>(31)</sup> Indeed, intermediate cases between  $\eta^2$ -H<sub>2</sub> and ( $\sigma$ -H)<sub>2</sub> coordination are occasionally observed, as in [ReH<sub>7</sub>(P(*p*-tol)<sub>3</sub>)<sub>2</sub>], where neutron-diffraction

studies<sup>(32)</sup> have revealed one H···H contact of 137.7(7) pm whereas all other H···H distances in the complex are greater than 174 pm. (This distance of 137.7 pm is seen to be intermediate between values of *ca.* 80 pm typical of  $\eta^2$ -H<sub>2</sub> complexes and values greater than *ca.* 160 pm which are found in classical hydrido complexes.) Likewise, some trihydrogen complexes, such as [Ir( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)H<sub>3</sub>(PMe<sub>3</sub>)],<sup>(33)</sup> have nmr behaviour which suggests the presence of a bent (or possibly triangular)  $\eta^3$ -H<sub>3</sub> ligand which is bonded “side-on” rather like an allylic group (pp. 933–5).

The possibility of  $\eta^1$ -H<sub>2</sub> “end-on” coordination has also been mooted. For example, deposition of Pd atoms onto a krypton matrix doped with H<sub>2</sub> at 12 K apparently yields both Pd( $\eta^1$ -H<sub>2</sub>) and Pd( $\eta^2$ -H<sub>2</sub>) species, whereas with a Xe/H<sub>2</sub> matrix only Pd( $\eta^2$ -H<sub>2</sub>) was obtained.<sup>(34)</sup> Again, the complex [ReCl(H<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub>] appears to feature an asymmetrically-bonded H<sub>2</sub> ligand which may well be ( $\eta^1$ -H<sub>2</sub>).<sup>(35)</sup>

Nearly one hundred  $\eta^2$ -H<sub>2</sub> complexes have so far been prepared and the crystal and molecular structure of about half a dozen have been determined by X-ray/neutron diffraction. Some are dinuclear, such as the homobimetallic [(P–N)( $\eta^2$ -H<sub>2</sub>)Ru( $\mu$ -Cl)<sub>2</sub>( $\mu$ -H)Ru(H)(PPh<sub>3</sub>)<sub>2</sub>]<sup>(36)</sup> and the heterobimetallic [(PPh<sub>3</sub>)<sub>2</sub>HRe( $\mu$ -H)( $\mu$ -Cl)<sub>2</sub>( $\mu$ -CO)Ru( $\eta^2$ -H<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>(37)</sup>.

The coordination chemistry of hydrogen is still being intensively studied and new developments are continually being reported.

<sup>32</sup> L. BRAMMER, J. A. K. HOWARD, O. JOHNSON, T. F. KOETZLE, J. L. SPENCER and A. M. STRINGER, *J. Chem. Soc., Chem. Commun.*, 241–3 (1991).

<sup>33</sup> D. M. HEINEKEY, N. G. PAYNE and G. K. SCHULTE, *J. Am. Chem. Soc.* **110**, 2303–5 (1988).

<sup>34</sup> G. A. OZIN and J. GARCIA-PRIETO, *J. Am. Chem. Soc.* **108**, 3099–100 (1986).

<sup>35</sup> F. A. COTTON and R. L. LUCK, *Inorg. Chem.* **30**, 767–74 (1991).

<sup>36</sup> C. HAMPTON, W. R. CULLEN and B. R. JAMES, *J. Am. Chem. Soc.* **110**, 6918–9 (1988). In this compound, P–N is a complex substituted ferrocene ligand. See also A. M. JOSHI and B. R. JAMES, *J. Chem. Soc., Chem. Commun.*, 1785–6 (1989).

<sup>37</sup> M. CAZANOUE, Z. HE, D. NEILBECKER and R. MATHIEU, *J. Chem. Soc., Chem. Commun.*, 307–9 (1991).

<sup>29</sup> X.-L. LUO and R. H. CRABTREE, *J. Chem. Soc., Chem. Commun.*, 189–90 (1990).

<sup>30</sup> T. ANLIGUIE and B. CHAUDRET, *J. Chem. Soc., Chem. Commun.*, 155–7 (1989).

<sup>31</sup> C. BIANCHINI, C. MEALLI, A. MELI, M. PERUZZINI and F. ZANOBINI, *J. Am. Chem. Soc.* **110**, 8725–6 (1988). See also L. D. FIELD, A. V. GEORGE, E. Y. MALOUF and D. J. YOUNG, *Chem. Soc., Chem. Commun.*, 931–3 (1990).

### 3.5 Protonic acids and bases<sup>(38)</sup>

Many compounds that contain hydrogen can donate protons to a solvent such as water and so behave as acids. Water itself undergoes ionic dissociation to a small extent by means of autoprotolysis; the process is usually represented formally by the equilibrium



though it should be remembered that both ions are further solvated and that the time a proton spends in close association with any one water molecule is probably only about  $10^{-13}$  s. (See also pp. 630–2 for structural studies on  $[\text{H}(\text{OH}_2)_n]^+$   $n = 1-6$ .) Depending on what aspect of the process is being emphasized, the species  $\text{H}_3\text{O}^+(\text{aq})$  can be called an oxonium ion, a hydrogen ion, or simply a solvated (hydrated) proton. The equilibrium constant for autoprotolysis is

$$K_1 = [\text{H}_3\text{O}^+][\text{OH}^-]/[\text{H}_2\text{O}]^2$$

and, since the concentration of water is essentially constant, the ionic product of water can be written as

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \text{ mol}^2 \text{ l}^{-2}$$

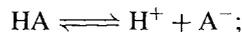
The value of  $K_w$  depends on the temperature, being  $0.69 \times 10^{-14} \text{ mol}^2 \text{ l}^{-2}$  at  $0^\circ\text{C}$ ,  $1.00 \times 10^{-14}$  at  $25^\circ\text{C}$  and  $47.6 \times 10^{-14}$  at  $100^\circ\text{C}$ . It follows that the hydrogen-ion concentration in pure water at  $25^\circ\text{C}$  is  $10^{-7} \text{ mol l}^{-1}$ . Acids increase this concentration by means of the reaction



$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

It is to be understood that all the species are in aqueous solution and the symbol HA implies only that the (aquated) species can act as a proton donor: it can be a neutral species (e.g.  $\text{H}_2\text{S}$ ), an anion (e.g.  $\text{H}_2\text{PO}_4^-$ ) or a cation such as

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . The hydrogen-ion concentration is usually expressed as pH (see Panel). In dilute solution the concentration of water molecules is constant at  $25^\circ\text{C}$  ( $55.345 \text{ mol l}^{-1}$ ), and the dissociation of the acid is often rewritten as



$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] \text{ mol l}^{-1}$$

The acid constant  $K_a$  can also be expressed by the relation

$$\text{p}K_a = -\log K_a. \quad \text{Hence, as } K_a = 55.345 K$$

$$\text{p}K_a = \text{p}K - 1.734$$

Further, as the free energy of dissociation is given by

$$\Delta G^\circ = -RT \ln K = -2.3026RT \log K,$$

the standard free energy of dissociation is

$$\begin{aligned} \Delta G_{298.15}^\circ &= 5.708 \text{ p}K \\ &= 5.708(\text{p}K_a + 1.734) \text{ kJ mol}^{-1} \end{aligned}$$

Textbooks of analytical chemistry should be consulted for further details concerning the ionization of weak acids and bases and the theory of indicators, buffer solutions, and acid-alkali titrations.<sup>(39-41)</sup>

Various trends have long been noted in the acid strengths of many binary hydrides and oxoacids.<sup>(38)</sup> Values for some simple hydrides are given in Table 3.4 from which it is clear that acid strength increases with atomic number both in any one horizontal period and in any

<sup>39</sup> A. I. VOGEL, *Quantitative Chemical Analysis*, 5th edn., Sections 2.12–2.27, pp. 31–60. Longman, London, 1989.

<sup>40</sup> A. HULANICKI, *Reactions of Acids and Bases in Analytical Chemistry*, Ellis Horwood (Wiley), Chichester, 1987, 308 pp.

<sup>41</sup> D. ROSENTHAL and P. ZUMAN, Acid-base equilibria, buffers and titrations in water, Chap. 18 in I. M. KOLTHOFF and P. J. ELVING (eds.), *Treatise on Analytical Chemistry*, 2nd edn., Vol. 2, Part 1, 1979, pp. 157–236. Succeeding chapters (pp. 237–440) deal with acid-base equilibria and titrations in non-aqueous solvents.

<sup>38</sup> R. P. BELL, *The Proton in Chemistry*, 2nd edn. Chapman & Hall, London, 1973, 223 pp.

## The Concept of pH

The now universally used measure of the hydrogen-ion concentration was introduced in 1909 by the Danish biochemist S. P. L. Sørensen during his work at the Carlsberg Breweries (*Biochem. Z.* 21, 131, 1909):

$$\text{pH} = -\log[\text{H}^+]$$

The symbol pH derives from the French *puissance d'hydrogène*, referring to the exponent or "power of ten" used to express the concentration. Thus a hydrogen-ion concentration of  $10^{-7} \text{ mol l}^{-1}$  is designated pH 7, whilst acid solutions with higher hydrogen-ion concentrations have a lower pH. For example, a strong acid of concentration  $1 \text{ mmol l}^{-1}$  has pH 3, whereas a strong alkali of the same concentration has pH 11 since  $[\text{H}_3\text{O}^+] = 10^{-14}/[\text{OH}^-] = 10^{-11}$ .

Unfortunately, it is far simpler to define pH than to measure it, despite the commercial availability of instruments that purport to do this. Most instruments use an electrochemical cell such as



Assuming that the glass electrode shows an ideal hydrogen electrode response, the emf of the cell still depends on the magnitude of the liquid junction potential  $E_j$  and the activity coefficients  $\gamma$  of the ionic species:

$$E = E^\circ - \frac{RT}{F} \ln \gamma_{\text{Cl}}[\text{Cl}^-] + E_j - \frac{RT}{F} \ln \gamma_{\text{H}}[\text{H}^+]$$

For this reason, the pH as measured by any of the existing national standards is an operational quantity which has no simple fundamental significance. It is defined by the equation

$$\text{pH}(\text{X}) = \text{pH}(\text{S}) + \frac{(E_x - E_s)F}{RT \ln 10}$$

where pH(S) is the *assigned* pH of a standard buffer solution such as those supplied with pH meters.

Only in the case of dilute aqueous solutions ( $< 0.1 \text{ mol l}^{-1}$ ) which are neither strongly acid or alkaline ( $2 < \text{pH} < 12$ ) is pH(X) such that

$$\text{pH}(\text{X}) = -\log[\text{H}^+] \gamma_{\pm} \pm 0.02$$

where  $\gamma_{\pm}$ , the mean ionic activity coefficient of a typical uni-univalent electrolyte, is given by

$$-\log \gamma_{\pm} = A I^{\frac{1}{2}} (1 + I)^{-\frac{1}{2}}$$

In this expression  $I$  is the ionic strength of the solution and  $A$  is a temperature-dependent constant ( $0.511^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}}$  at  $25^\circ\text{C}$ ;  $0.501^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}}$  at  $15^\circ\text{C}$ ). It is clearly unwise to associate a pH meter reading too closely with pH unless under very controlled conditions, and still less sensible to relate the reading to the actual hydrogen-ion concentration in solution. For further discussion of pH measurements, see *Pure Appl. Chem.* 57, 531–42 (1985): Definition of pH Scales, Standard Reference Values, Measurement of pH and Related Terminology. Also *C&E News*, Oct. 20, 1997, p. 6.

**Table 3.4** Approximate values of  $\text{p}K_a$  for simple hydrides

CH <sub>4</sub>	46	NH <sub>3</sub>	35	OH <sub>2</sub>	16	FH	3
		PH <sub>3</sub>	27	SH <sub>2</sub>	7	ClH	-7
				SeH <sub>2</sub>	4	BrH	-9
				TeH <sub>2</sub>	3	IH	-10

vertical group. Several attempts have been made to interpret these trends, at least qualitatively, but the situation is complex. The trend to increasing acidity from left to right in the

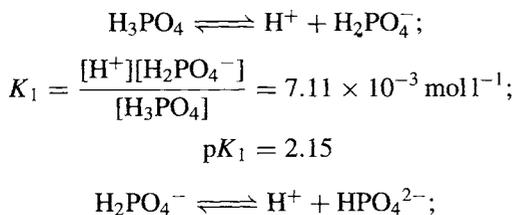
periodic table could be ascribed to the increasing electronegativity of the elements which would favour release of the proton, but this is clearly not the dominant effect within any one group since the trend there is in precisely the opposite direction. Within a group it is the diminution in bond strength with increasing atomic number that prevails, and entropies of solvation are also important. It should, perhaps, also be emphasized that thermodynamic computations do not "explain" the observed acid strengths; they merely allocate the overall values of  $\Delta G$ ,

$\Delta H$  and  $\Delta S$  to various notional subprocesses such as bond dissociation energies, ionization energies, electron affinities, heats and entropies of hydration, etc., which themselves have empirically observed values that are difficult to compute *ab initio*.

Regularities in the observed strengths of oxoacids have been formulated in terms of two rules by L. Pauling and others:

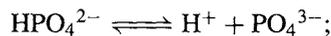
- (i) for polybasic mononuclear oxoacids, successive acid dissociation constants diminish approximately in the ratios  $1:10^{-5}:10^{-10}:\dots$ ;
- (ii) the value of the first ionization constant for acids of formula  $XO_m(OH)_n$  depends sensitively on  $m$  but is approximately independent of  $n$  and  $X$  for constant  $m$ , being  $\leq 10^{-8}$  for  $m = 0$ ,  $\sim 10^{-2}$  for  $m = 1$ ,  $\sim 10^3$  for  $m = 2$ , and  $> 10^8$  for  $m = 3$ .

Thus to illustrate the first rule:



$$K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.31 \times 10^{-8} \text{ mol l}^{-1};$$

$$pK_2 = 7.20$$



$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.22 \times 10^{-13} \text{ mol l}^{-1};$$

$$pK_3 = 12.37$$

Qualitatively, a reduction in  $pK_a$  for each successive stage of ionization is to be expected since the proton must separate from an anion of increasingly negative charge, though the approximately constant reduction factor of  $10^5$  is more difficult to rationalize quantitatively.

Acids which illustrate the second rule are summarized in Table 3.5. The qualitative explanation for this regularity is that, with increasing numbers of oxygen atoms the single negative charge on the anion can be spread more widely, thereby reducing the electrostatic energy attracting the proton and facilitating the ionization. On this basis one might expect an even more dramatic effect if the anion were monoatomic (e.g.  $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$ ) since the attraction of these dianions for protons will be very strong and the acid dissociation constant of  $SH^-$ ,  $SeH^-$  and  $TeH^-$  correspondingly small; this is indeed observed and the ratio of

**Table 3.5** Values of  $pK_a$  for some mononuclear oxoacids  $XO_m(OH)_n$  ( $pK_a \approx 8-5n$ )

$X(OH)_n$ (very weak)		$XO(OH)_n$ (weak)		$XO_2(OH)_n$ (strong)		$XO_3(OH)_n$ (very strong)	
Cl(OH)	7.2	NO(OH)	3.3	NO <sub>2</sub> (OH)	-1.4	ClO <sub>3</sub> (OH)	(-10)
Br(OH)	8.7	ClO(OH)	2.0	ClO <sub>2</sub> (OH)	-1	MnO <sub>3</sub> (OH)	—
I(OH)	10.0	CO(OH) <sub>2</sub>	3.9 <sup>(a)</sup>	IO <sub>2</sub> (OH)	0.8		
B(OH) <sub>3</sub>	9.2	SO(OH) <sub>2</sub>	1.9	SO <sub>2</sub> (OH) <sub>2</sub>	<0		
As(OH) <sub>3</sub>	9.2	SeO(OH) <sub>2</sub>	2.6	SeO <sub>2</sub> (OH) <sub>2</sub>	<0		
Sb(OH) <sub>3</sub>	11.0	TeO(OH) <sub>2</sub>	2.7				
Si(OH) <sub>4</sub>	10.0	PO(OH) <sub>3</sub>	2.1				
Ge(OH) <sub>4</sub>	8.6	AsO(OH) <sub>3</sub>	2.3				
Te(OH) <sub>6</sub>	8.8	IO(OH) <sub>5</sub>	1.6				
		HPO(OH) <sub>2</sub>	1.8 <sup>(b)</sup>				
		H <sub>2</sub> PO(OH)	2.0 <sup>(b)</sup>				

<sup>(a)</sup>Corrected for the fact that only 0.4% of dissolved CO<sub>2</sub> is in the form of H<sub>2</sub>CO<sub>3</sub>; the conventional value is  $pK_a$  6.5.

<sup>(b)</sup>Note that the value of  $pK_a$  for hypophosphorous acid H<sub>3</sub>PO<sub>3</sub> is consistent with its (correct) formulation as HPO(OH)<sub>2</sub> rather than as P(OH)<sub>3</sub>, which would be expected to have  $pK_a > 8$ . Similarly for H<sub>3</sub>PO<sub>2</sub>, which is H<sub>2</sub>PO(OH) rather than HP(OH)<sub>2</sub>.

**Table 3.6** First and second ionization constants for H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te

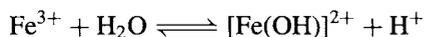
	p <i>K</i> <sub>1</sub>	p <i>K</i> <sub>2</sub>	Δp <i>K</i>
H <sub>2</sub> S	7	14	7
H <sub>2</sub> Se	4	12	8
H <sub>2</sub> Te	3	11	8

the first and second dissociation constants is  $\sim 10^8$  rather than  $10^5$  (Table 3.6).

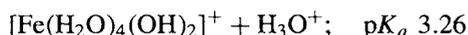
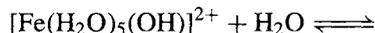
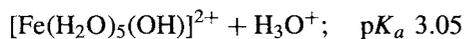
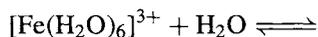
The results for dinuclear and polynuclear oxoacids are also consistent with this interpretation. Thus for phosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, the successive p*K*<sub>a</sub> values are 1.5, 2.4, 6.6 and 9.2; the  $\sim 10$ -fold decrease between p*K*<sub>1</sub> and p*K*<sub>2</sub> (instead of a decrease of  $10^5$ ) is related to the fact that ionization occurs from two different PO<sub>4</sub> units. The third stage ionization, however, is  $\sim 10^5$  less than the first stage and the difference between the mean of the first two and the last two ionization constants is  $\sim 5 \times 10^5$ .

Another phenomenon that is closely associated with acid–base equilibria is the so-called hydrolysis of metal cations in aqueous solution, which is probably better considered as the protolysis of hydrated cations, e.g.:

“hydrolysis”:



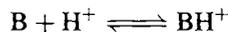
protolysis:



It is these reactions that impart the characteristic yellow to reddish-brown coloration of the hydroxoquo species to aqueous solutions of iron(III) salts, whereas the undissociated ion  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is pale mauve, as seen in crystals of iron(III) alum  $\{[\text{Fe}(\text{H}_2\text{O})_6][\text{K}(\text{H}_2\text{O})_6](\text{SO}_4)_2\}$  and iron(III) nitrate  $\{[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}\}$ . Such reactions may proceed to the stage where the diminished charge on the hydrated cation permits the formation of oxobridged,

or hydroxobridged polynuclear species that eventually precipitate as hydrous oxides (see discussion of the chemistry of many elements in later chapters). A useful summary is in Fig. 3.4. By contrast, extensive studies of the p*K*<sub>a</sub> values of hydrated metal ions in solution has generated a wealth of numerical data but no generalizations such as those just discussed for the hydrides and oxoacids of the non-metals.<sup>(42)</sup> Typical p*K*<sub>a</sub> values fall in the range 3–14 and, as expected, there is a general tendency for protolysis to be greater (p*K*<sub>a</sub> values to be lower) the higher the cationic charge. For example, aqueous solutions of iron(III) salts are more acidic than solutions of the corresponding iron(II) salts. However, it is difficult to discern any regularities in p*K*<sub>a</sub> for series of cations of the same ionic charge, and it is clear that specific “chemical” effects must also be considered.

Brønsted acidity is not confined to dilute aqueous solutions and the ideas developed in the preceding pages can be extended to proton donors in nonaqueous solutions.<sup>(43,44)</sup> In organic solvents and anhydrous protonic liquids the concepts of hydrogen-ion concentration and pH, if not actually meaningless, are certainly operationally inapplicable and acidity must be defined on some other scale. The one most frequently used is the Hammett acidity function *H*<sub>0</sub> which enables various acids to be compared in a given solvent and a given acid to be compared in various solvents. For the equilibrium between a base and its conjugate acid (frequently a coloured indicator)



the acidity function is defined as

$$H_0 = \text{p}K_{\text{BH}^+} - \log\{[\text{BH}^+]/[\text{B}]\}$$

In very dilute solutions

$$K_{\text{BH}^+} = [\text{B}][\text{H}^+]/[\text{BH}^+]$$

<sup>42</sup> L. G. SILLÉN, *Q. Rev. (London)* **13**, 146–68 (1969); *Pure Appl. Chem.* **17**, 55–78 (1968).

<sup>43</sup> C. H. ROCHESTER, *Acidity Functions*, Academic Press, London, 1970, 300 pp.

<sup>44</sup> G. A. OLAH, G. K. S. PRAKASH and J. SOMMER, *Superacids*, Wiley, New York, 1985, 371 pp.