

Chapter 10

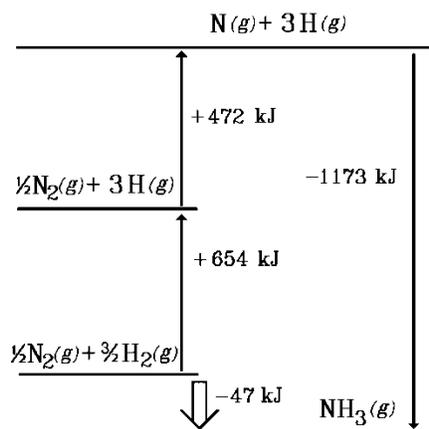
HYDROGEN

Exercises

- 10.1 (a) A hydrogen atom bridging two (or more) other atoms in a covalent bond in which the hydrogen is less electronegative than the atoms to which it is bonded.
(b) A hydrogen atom bridging two (or more) other atoms in a covalent bond in which the hydrogen is more electronegative than the atoms to which it is bonded.
- 10.3 The ice cube consists of “heavy” water, deuterium oxide, which has a higher density than normal water and will therefore sink in normal water.
- 10.5 The difference in absorption frequency is very small, about 10^{-6} of the signal itself. Thus ppm is a convenient unit.
- 10.7 Unlike the halogens, hydrogen rarely forms a negative ion, nor is it highly reactive like the halogens.
- 10.9 Enthalpy driven. The chemical equation is
$$\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$$

There is a decrease in the number of gas molecules, and hence a decrease in entropy. Thus for the reaction to be spontaneous, the reaction has to be exothermic.
- 10.11 (a) $2 \text{KHCO}_3(s) \rightarrow \text{K}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)$
(b) $\text{HC}\equiv\text{CH}(g) + 2 \text{H}_2(g) \rightarrow \text{H}_3\text{C}-\text{CH}_3(g)$
(c) $\text{PbO}_2(s) + 2 \text{H}_2(g) \rightarrow \text{Pb}(s) + 2 \text{H}_2\text{O}(g)$
(d) $\text{CaH}_2(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(aq) + \text{H}_2(g)$

- 10.13 See the diagram. The much lesser enthalpy of formation of ammonia compared to water can be explained in terms of the much greater bond energy of dinitrogen ($945 \text{ kJ}\cdot\text{mol}^{-1}$) compared with that of dioxygen ($498 \text{ kJ}\cdot\text{mol}^{-1}$).

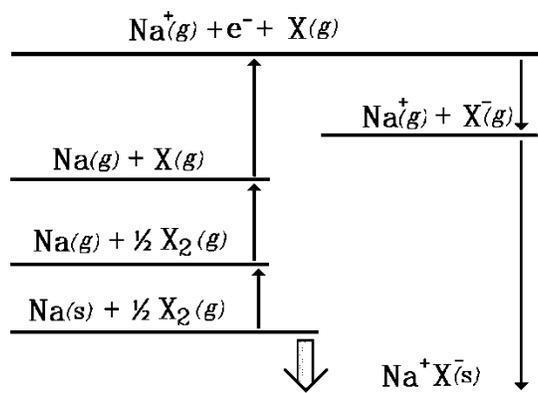


- 10.15 There are three categories of covalent hydrides: those in which the hydrogen is nearly neutral; those in which it is quite positive, and those in which it is negative. Most covalent hydrides belong in the first category; these are the low-polarity hydrides with low boiling points (except the long-chain hydrocarbons, where the dispersion forces become very significant). The second category consists of ammonia, water, and hydrogen fluoride, where hydrogen bonding (a protonic bridge) raises the melting and boiling points above those of the first category. Finally, there are the electron-deficient compounds of boron, where hydridic bridges form part of the molecular structure.
- 10.17 KH (m.p. 417°C); CaH_2 (m.p. 816°C), GaH_3 (m.p. -15°C), GeH_4 (m.p. -165°C), AsH_3 (m.p. -116°C), H_2Se (m.p. -86°C), HBr (m.p. -89°C). The trend is to increase by one H until germanium, then a stepwise decrease by one H to hydrogen bromide. The first two members of the series can be categorized as ionic on the basis of their (comparatively) high melting points [while GeH_4 through HBr are small molecule covalent and GaH_3 is polymeric in the solid, forming a dimer in the gas]. See for similar series Chapter 9, Table 9.9.

- 10.19 (a) Gas. It is a covalent hydride but not one of the three elements exhibiting strong hydrogen bonding (nitrogen, oxygen, fluorine).
 (b) Solid. This is an ionic hydride.
- 10.21 The closeness of the electronegativities of hydrogen and carbon (thus making the C–H bond of low polarity), and the ability to hydrogen bond.

Beyond the Basics

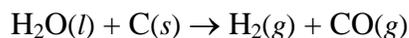
- 10.23 (a) Yes, liquid; (b) no, gas; (c) yes, liquid; (d) no, gas.
- 10.25. Looking at a generic Born-Haber cycle, where X = H or Cl, we see that there are two features that differ, depending upon X—the bond energy and the electron affinity.



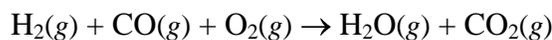
	Hydrogen	Chlorine
Bond energy	432 kJ·mol ⁻¹	240 kJ·mol ⁻¹
Electron affinity	-79 kJ·mol ⁻¹	-349 kJ·mol ⁻¹

Thus the difference results from the H–H bond being much stronger than the Cl–Cl bond, while the electron affinity of chlorine is much greater than that of hydrogen.

- 10.27 Hydrogen and carbon monoxide.



The combustion reaction would therefore be:



$$\Delta H = [(1 \text{ mol})(-242) + (1 \text{ mol})(-394) - (1 \text{ mol})(-111)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -525 \text{ kJ}$$

Per mole, this is $-525/2 \text{ kJ}\cdot\text{mol}^{-1} = -262 \text{ kJ}\cdot\text{mol}^{-1}$, compared with $-242 \text{ kJ}\cdot\text{mol}^{-1}$ for the combustion of pure dihydrogen. So there is about an 8 percent higher energy availability provided, and we consider the water to be produced in the gas phase (assuming the synthesis does produce the precise stoichiometric mixture).