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Hydrogen

25.1 Elemental hydrogen

- Hydrogen does not occur native on Earth as H_2 gas. Hydrogen generally occurs bonded to oxygen in water, or bonded to carbon in organic compounds.
- The major industrial source of H_2 is from the reaction of hydrocarbons with steam (steam reforming), but in the future production from the electrolysis of water is likely to become more important.
- Hydrogen gas is used industrially to make ammonia and methanol, and in the reduction of unsaturated organic compounds and metal ions.

25.2 Compounds of hydrogen

- Hydrogen forms binary hydrides with most of the elements.
- The electronegativity of hydrogen has an intermediate value (2.20), so the nature of a binary hydride XH_n depends on the electronegativity of the element X.
- Compounds with elements of lower electronegativity than hydrogen are hydridic and often ionic, whereas compounds with elements of higher electronegativity than hydrogen are protic and form covalent structures.
- Group 1 and 2 hydrides are mostly ionic, and react with water to give H_2.
- Group 13 hydrides are electron deficient and contain bridging hydrogen atoms. 3-centre 2-electron bonding is required to explain their structures. The most important compound for this group is diborane (B_2H_6).
- Group 14–17 hydrides are covalent compounds containing ‘normal’ 2-centre 2-electron bonds. In addition to the simple hydrides XH_n, hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) are important compounds. These compounds are electron precise (Group 14) or electron rich (Groups 15–17).

- For Groups 13–17, the stability of the hydrides decreases going down a group. This is caused by weakening of the X–H bonds, which is due to reduced orbital overlap as X gets larger.
- For Groups 15–17, the hydrides become more acidic as each group is descended. This is due to the weakening of the X–H bonds and the increasing size of the resulting anions, which weakens the attraction between X^- and H_3O^+.

25.3 Hydrogen bonding

- Most hydrogen bonds are electrostatic interactions between a hydrogen atom bound to an electronegative atom ($D^{\delta-}$–$H^{\delta+}$) and another atom that is also electronegative ($A^{\delta-}$) and has one or more lone pairs enabling it to act as a base.
- A typical hydrogen bond has an enthalpy of approximately 30 kJ mol^{-1}, which is approximately one-tenth the strength of a typical covalent bond.
- Strong hydrogen bonding leads to an increase in the melting point and boiling point. In the absence of hydrogen bonding water would be a gas at room temperature.

25.4 Isotope effects

- Bonds to deuterium are stronger than those to normal hydrogen because X–D bonds have lower zero point energies than X–H bonds.
- Deuterium labelling is useful in the assignment of infrared spectra. Large isotopic shifts are observed in infrared spectra due to the greater mass of ^{2}D over ^{1}H.

Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe the means of production and the main uses of hydrogen gas.
- Understand why binary hydrides can be protic or hydridic, and predict the character of a particular hydride.

- Predict whether the bonding in a binary hydride is covalent or ionic, and whether a covalent hydride is likely to contain bridging hydrogen atoms.
- Describe how the reactivity of hydride compounds changes across the Periodic Table and down each group.
- Explain why the hydrogen halides increase in acidity from HF to HI.
- Explain how hydrogen bonds are formed and why very strong hydrogen bonds can be described as covalent interactions.
- Predict the effect of hydrogen bonding on melting points, boiling points, and infrared spectra.
- Calculate the effects of replacing hydrogen by deuterium on infrared stretching frequencies.