THE CHEMISTRY OF THE ELEMENTS

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- A progression through the periodic table concentrating on group trends

Hydrogen: inert , tasteless, colourless **gas** at room temperature

As a gas: **London forces** exist between **molecules**. These are instantaneous electric dipoles and give rise to the fact that H_2 is less dense than air and low boiling

Three **isotopes** exist :

	mm g/mol	Abundance
Hydrogen (H^1)	1.008	99.88%
Deuterium (H^2)	2.014	0.02%
Tritium (H^3)	3.016	radioactive β-emitter**,** half life 12.4 years

Deuterium

- obtained by fractional distillation or electrolysis of H_2O.

Often used as a moderator in nuclear reactors.

Chemical reactions of isotopes are identical but the **rate** of reaction is different

e.g C-H bond cleavage occurs 5-8 times faster than C-D bond cleavage

Preparation of hydrogen:

In laboratory , hydrogen can be obtained by reduction of H^+.

e.g **Zn** + $2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Or by the oxidation of H^-:

e.g $CaH_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + 2H_{2(g)}$

[Remember: Hydride (H^-) oxidation number = -1 (H in the presence of an electropositive metal atom)**]**

Formation of *atomic* hydrogen requires electric arcs, discharge tubes or UV irradiation

Atomic hydrogen is used in welding as the reformation of H_2 generates heat :

$$2H \rightarrow H_2 \quad \Delta H = -436\ kJmol^{-1}$$

Preparation of Hydrogen in industry:

Petroleum industry – **cracking** e.g $C_{12}H_{26(g)} \rightarrow C_5H_{10(g)} + C_4H_{8(g)} + C_3H_{6\,(g)} + H_{2(g)}$

Shift reaction two-step process :

1). **Reforming** reaction : $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$

2). **Shift** reaction : $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = -42kJmol^{-1}$

The carbon dioxide can be removed by "scrubbing" (K_2CO_3)

Uses of Hydrogen .

(i) Haber- Bosch Process : Synthesis of ammonia: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_3$

(ii) Formation of methanol - a starting material for plastics and synthetic fibres .

$2H_{2(g)} + CO_{(aq)} \rightarrow CH_3OH_{(l)}$

(iii) Hydrogenation - addition of H_2 to C=C bond generating a solid-fat from an unsaturated oil.

Binary compounds of hydrogen

Three main categories exist;

1. **Non-stoichiometric compounds**: Interstitial/metallic hydrides

   e.g $2Cu_{(s)} + H_{2(g)} \rightarrow 2\,CuH_{(s)}$ (Black powdery solid).

   Metallic hydrides can be thought of as hydrogen atoms occupying interstitial holes in metal lattices

2. **Molecular compounds** : Consist of discrete molecules e.g

SnH_4 (metal), SiH_4 (metalloid), NH_3, HF, (non-metals), B_2H_6 (diborane)

Preparation of molecular hydrides:

<u>direct</u> e.g $H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -286$ kJ/mol

<u>proton transfer</u> (from Bronsted acid) e.g $CaF_{2(g)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)}$

Hydrogen bonding - An important characteristic of molecular compounds.

$X^{\delta-} — H^{\delta+}$ ---------- $X^{\delta-} — H^{\delta+}$

___Covalent bond $\Delta H = 200$ kJmol^{-1} ------- Hydrogen bond ΔH =20-30 kJmol^{-1}

Responsible for H_2O being more dense than ice and raising surface tension of water.

It is also responsible for **hydrates** (solid containing a compound and water), **clathrates** (solid in which one component crystallises in an open structure into which a second small component can be trapped e.g $[R_4N]\ [C_6H_5CO_2].39.5H_2O$. **In cellulose** H–bonding gives cross-linking between glucose-like chains. **In DNA** protein structures of peptides held together by H bonds .

3. Saline Hydrides (Salt like)

Consist of the most electropositive metals e.g S-block, and hydrogen, as M^+ and H^- ions e.g $2K + H_{2(aq)} \rightarrow 2KH_{(s)}$

Evidence for presence of H^-

just above Mp. these materials conduct electricity

-when molten H_2 released at anode .

Structures are like NaCl – H^- radius in-between that of F^- and Cl^- .

Good reducing agents : readily lose e^- :

e.g $H_{2(g)} + 2e^- \rightarrow 2H^-_{(aq)}$ $E^o = - 2.25V$

they will reduce water

e.g. $NaH_{(s)} + H_2O_{(l)} \rightarrow NaOH + H_2$

-1 +1 0

(See " Atkins and Beran " table 17.3 for a list of reduction potentials .)

Group 1 Alkali Metals :

Li , Na, K, Rb, Cs, Fr.- all the elements are **soft**, silvery metals which give basic (alkali) solutions.

M-M bonding is weak and involves the delocalisation of e^- around a 'sea' of cations.

Preparation of the elements

Na - electrolysis of the molten salt (NaCl) (Down's Process). Chlorine gas is given off at the graphite anode (chlorine would react with steel) and molten sodium collects at the steel cathode .

(See fig 17.26 "Atkins and Beran ").$CaCl_2$ is added to the NaCl to lower the melting point from 800 to about 630°C .

K - more volatile metal (melt reaction)

$$KCl_{(l)} + Na_{(s)} \rightarrow NaCl_{(s)} + K_{(g)}$$

Uses :

1 . They readily from M^+ ions (low 1st ionisation energies) -

good reducing agents.

$$TiCl_{4(g)} + 4Na_{(l)} \rightarrow 4NaCl_{(s)} + Ti_{(s)}$$

2**. Alloys** of Na and K (mixture of the elements) are used in nuclear reactors as coolants. The packing of atoms with different metallic radii is poor so these alloys are liquids.

2. **Biological** -

Francium –Radioactive tracer experiments

Na^+, K^+ - physiological importance

Li^+ - used in treatment of bipolar disorder (manic depression).