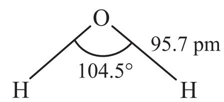
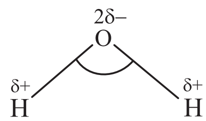
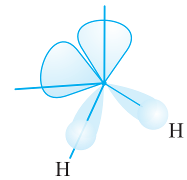
WATER Section - 3

In the gas phase water is a bent molecule with a bond angle of 104.5°, and O-H bond length of 95.7 pm. It is a highly polar molecule. Its orbital overlap is shown in figure below. In liquid phase, water molecules are associated together by hydrogen bonds. In ice each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.

(a)


(b)


(c)


Chemical Properties of Water :

Water reacts with a large number of substances. Some of the important reactions are given below.

1. **Amphoteric Nature :** It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Bronsted sense it acts as an acid with NH_3 and a base with H_2S.

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_2O(l) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

The auto-protolysis (self-ionization) of water takes place as follows :

$$\underset{\substack{\text{acid - 1} \\ \text{(acid)}}}{H_2O(l)} + \underset{\substack{\text{base - 2} \\ \text{(base)}}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{acid - 2} \\ \text{(conjugate acid)}}}{H_3O^+(aq)} + \underset{\substack{\text{base - 1} \\ \text{(conjugate base)}}}{OH^-(aq)}$$

2. **Redox Reactions Involving Water :** Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(l) + 2Na(s) \longrightarrow 2NaOH(aq) + H_2(g)$$

Water is oxidised to O_2 during photosynthesis.

$$6CO_2(g) + 12H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$$

With fluorine also it is oxidized to O_2.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

3. **Hydrolysis Reaction :** Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$$

$$N^{3-}(s) + 3H_2O(l) \longrightarrow NH_3(g) + 3OH^-(aq)$$

4. **Hydrates Formation :** From aqueous solutions many salts can be crystallised as hydrated salts. Water of hydration are water molecules attached to a compound that can be removed on heating. Such an association of water is of different types viz.,

   (i) Coordinated water e.g., $[Cr(H_2O)]^{3+}\,3Cl^-$

   (ii) Interstitial water e.g., $BaCl_2 . 2H_2O$

(iii) Hydrogen-bonded water e.g., $[Cu(H_2O)_4]^{2+}\ SO_4^{2-}\ .\ H_2O$ in $CuSO_4\ .\ 5\,H_2O$
Here in $CuSO_4.\ 5H_2O$, four water molecules of hydration are coordinate bonded and one is hydrogen bonded.

Note : You will learn more about hydrates later in Coordination Compounds.

*Hard and Soft Water :

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water 'hard'. Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called Soft water. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium strearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg strearate.

$$2RCOONa(aq) + M^{2+}(aq) \longrightarrow \underset{\text{Scum}}{(RCOO)_2M\downarrow} + 2Na^+(aq)\ ; \qquad M \text{ is } Ca/Mg$$

e.g., $$2C_{17}H_{35}COONa(aq) + Ca^{2+}(aq) \longrightarrow \underset{\text{Scum}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2Na^+(aq)$$

It is, therefore, unsuitable for laundry.

The hardness of water is of two types :

(i) Temporary hardness, and **(ii)** Permanent hardness.

Temporary Hardness :

Temporary hardness is due to the presence of magnesium and calcium hydrogen-carbonates. It can be easily removed by:

1. **Boiling :** During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ changed to insoluble $CaCO_3$. These precipitates can be removed by filteration.

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

2. **Clark's method :** In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

Note : Temporary hardness such as $Ca(HCO_3)_2$ can also be removed by adding Na_2CO_3.

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaHCO_3$$

Permanent Hardness :

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

1. Treatment with washing soda (Sodium carbonate) :

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl \qquad (M = Mg, Ca)$$

$$MSO_4 + \underset{\text{(Washing soda)}}{Na_2CO_3} \longrightarrow MCO_3\downarrow + Na_2SO_4$$

2. Calgon's method : Sodium hexametaphosphate ($Na_6P_6O_{18}$), commercially called 'Calgon' or 'Graham's salt', when added to hard water, the following reactions take place :

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}{}^{2-} \qquad (M = Mg, Ca)$$

$$M^{2+} + Na_4P_6O_{18}{}^{2-} \longrightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$$

The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

3. Ion-exchange method : This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate ($NaAlSiO_4$) can be written as NaZ. When this is added in hard water, exchange reactions take place.

$$2NaZ(s) + M^{2+}(aq) \longrightarrow MZ_2(s) + 2Na^+(aq) \qquad (M = Mg, Ca)$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

$$MZ_2(s) + 2NaCl(aq) \longrightarrow 2NaZ(s) + MCl_2(aq)$$

4. Synthetic Resins Methods : It is used in the production of deionised water and more efficient than the Zeolite process.

Water is passed through two different ion-exchange columns :

1st Column (Cation Exchange Column) :

The resin exchanges H^+ with Na^+, Ca^{2+} and Mg^{2+}

$$\underbrace{resin - SO_3H}_{\text{sulphonic acid resin}} + M^+ \longrightarrow resin - SO_3M + H^+$$

2nd Column (Anion Exchange Column) :

The resin exchanges OH^- with Cl^-, HCO_3^-, SO_4^{2-}

$$\underbrace{resin - NR_4^+OH^-}_{\text{resin with basic group}} + X^- \longrightarrow resin\ NR_4^+X^- + OH^-$$

When all reactive sites on resins have been used they can be regenerated by treating first one with dil.H_2SO_4 and second one with Na_2CO_3 solution.

Heavy Water, D_2O

It is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries. It is used for the preparation of other deuterium compounds, for example :

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

$$Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$$

DEGREE OF HARDNESS Section - 4

Concentration of Solute in Terms of Parts per Million (or ppm) :

Concentration of solute (*in ppm*) = mass of solute (in gms) in 10^6 mL solution

It is used in determining the hardness of water which is due to the presence of bicarbonates (temporary hardness), chlorides and sulphates (permanent hardness) of Calcium and Magnesium. Degree of Hardness is defined as the number of parts of $CaCO_3$ or equivalent to other calcium and magnesium salts present in a million (10^6) parts of water.

$$\text{Degree of Hardness} = \frac{\text{Mass of } CaCO_3}{\text{Mass of water}} \times 10^6 \text{ ppm}$$

Illustrating the Concept :

How to calculate degree of hardness in a water sample containing* 111 *ppm of $CaCl_2$?

$$E_{CaCO_3} = \frac{100}{2} = 50 \quad ; \quad E_{CaCl_2} = \frac{111}{2} = 55.5$$

which means 50 gm of $CaCO_3 \equiv 55.5$ gm $CaCl_2$

or 55.5 gm $CaCl_2 \equiv 50$ gm of $CaCO_3$

$\Rightarrow$ 111.0 gm $CaCl_2 \equiv 100$ gm of $CaCO_3 = 100$ ppm

Illustration - 1 ***Calculate the weight of CaO required to remove hardness of 10^6 L of water containing 1.62 gm of $Ca(HCO_3)_2$ in 1.0 litre.***

Solution :

Consider the reaction between CaO and $Ca(HCO_3)_2$.

$$CaO + Ca(HCO_3)_2 \longrightarrow 2\,CaCO_3 + H_2O$$

From stoichiometry, we have:

1 mole of $Ca(HCO_3)_2$ $\equiv$ 1 mole of CaO

$\equiv$ 2 moles of $CaCO_3$

Now moles of bicarbonate in 1.0 L of sample

$$= \frac{1.62}{162} = 0.01 \ [M_0 \text{ of } Ca(HCO_3)_2 = 162]$$

$\Rightarrow$ moles of CaO required for 1.0 L of sample

= 0.01 (from stoichiometry)

$\Rightarrow$ moles of CaO required for 10^6 L of water

$= 0.01 \times 10^6 = 10^4$ moles.

$\Rightarrow$ grams of CaO $= 10^4 \times 56 = 5.6 \times 10^5$ gm.