WATER

Water stands as one of the abundantly accessible compounds, functioning as the oxide of hydrogen. It holds a critical role as a fundamental component within all living organisms. In the human body, water comprises approximately 65% of the total composition, while in plants, it constitutes an even more significant proportion at 95%. This pervasive presence underscores its vital importance for sustaining life.

The remarkable attribute of water lies in its capacity to dissolve a wide array of substances, rendering it a compound of immense significance in various biological and chemical processes. Notably, nearly three-fourths of the Earth's surface is covered by water, emphasizing the widespread and foundational role it plays in shaping the planet's landscape and supporting diverse ecosystems.

Properties of Pure Water

Physical properties

(i) Pure water is transparent, lacking in flavor and scent. In thicker quantities, it exhibits a faint bluish hue.

(ii) Water freezes at 0°C and boils at 100°C.

(iii) At 4°C, its density reaches a maximum value of 1.00.

(iv) Water possesses a polar nature, featuring a V-shaped molecular structure with a bond angle of 104.5°.

(v) It exhibits a high dielectric constant, which is attributed to its polar characteristics, making it an effective solvent for polar and ionic substances.

(vi) Water is a poor conductor of electricity.

(vii) Water demonstrates a propensity for association. In its liquid state, it does not exist as isolated H_2O molecules but as associated molecules connected through hydrogen bonding.

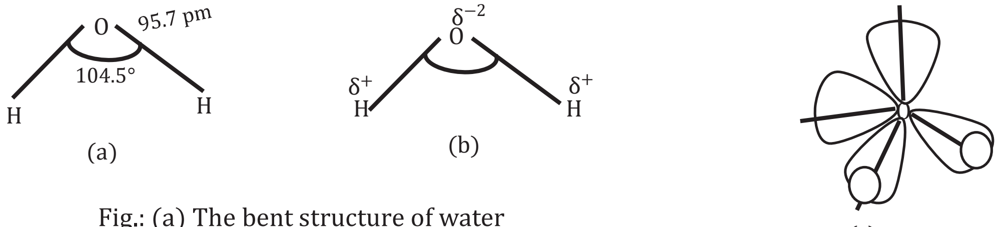
The presence of hydrogen bonding accounts for the elevated specific heat, latent heat of fusion, and latent heat of vaporization values observed in water.

Structure of Water

The investigation into the structure of water encompasses its three distinct phases.

(1) Gas Phase:

When water transitions into its gaseous phase, it manifests as discrete molecules. The presence of two lone pairs contributes to the distortion of water's geometry, resulting in a bent molecular structure with a bond angle measuring 104.5° and an O-H bond length of 95.7 picometers. Each O-H bond within the water molecule is polar, a characteristic attributed to the high electronegativity of oxygen in contrast to that of hydrogen. This distinctive arrangement and polarity in the gas phase play a pivotal role in understanding the behavior and properties of water molecules in this state.



(a) (b) (c)

Fig.: (a) The bent structure of water
(b) the water molecule as a dipole
(c) the orbital overlap picture in water molecule

(2) Liquid Phase:
When transitioning into the liquid phase, water molecules exhibit a unique association, forming an extensive network through hydrogen bonds. In this state, a multitude of water molecules are linked together through these intermolecular forces, specifically hydrogen bonding. The cohesive nature of these hydrogen bonds is a defining feature of the liquid phase of water, influencing its properties and behavior in this state. Understanding the dynamics of water molecules in the liquid phase is crucial for unraveling various aspects of the substance's behavior and its significance in diverse contexts.

(3) Solid Phase:
The solid state of water, commonly recognized as ice, showcases distinctive characteristics. Under atmospheric pressure, ice crystallizes in a hexagonal structure. However, at extremely low temperatures, it undergoes a transition and condenses into a cubic form. This transition between hexagonal and cubic structures represents a noteworthy feature of ice in its solid phase, highlighting the influence of temperature and pressure on the arrangement of water molecules in the crystalline lattice. Understanding these structural variations is essential for comprehending the diverse physical properties exhibited by ice under different conditions.

Structure of Ice

In the context of ice, each oxygen atom is arranged tetrahedrally, with four other oxygen atoms surrounding it at a distance of 276 picometers. Furthermore, each oxygen atom is connected to four hydrogen atoms – two through covalent bonds and two through hydrogen bonds. The prevalence of hydrogen bonding in ice leads to the formation of an open, cage-like structure characterized by numerous empty spaces. Consequently, the structure of ice exhibits a highly organized three-dimensional arrangement due to the intricate network of hydrogen bonds, emphasizing the unique and ordered nature of its molecular configuration.

Ice exhibits a lower density compared to water due to its distinctive open cage-like structure, creating vacant spaces that result in a reduced packing of molecules per milliliter. The process of melting ice involves the disruption of hydrogen bonds, causing the molecules to approach each other more closely in the liquid state than they were in the solid state. Consequently, the density of ice is lower than that of water.

This characteristic holds considerable ecological importance. Ice formed on the surface of lakes, being less dense, does not sink to the bottom. Instead, it remains afloat, providing thermal insulation for the water beneath. This insulation contributes to the survival of aquatic life, ensuring a more stable and habitable environment by preventing extreme temperature fluctuations in the underlying water.

The peak density of water occurs at 4°C, a phenomenon influenced by two key factors.

(i) Breaking of Hydrogen Bonds: The density of water is intricately linked to the breaking of hydrogen bonds within its molecular structure. As temperature rises, ice melts, causing the disruption of hydrogen bonds. This event leads to a closer-packed molecular arrangement, reducing the volume and consequently increasing the density until reaching 4°C.

(ii) Thermal Expansion: As temperature continues to increase beyond 4°C, the kinetic energy of water molecules intensifies. This heightened energy prompts the molecules to move away from each other, causing an expansion in volume and a subsequent decrease in density.

At the critical temperature of 4°C, these two opposing effects—thermal expansion and the breaking of hydrogen bonds—reach a delicate equilibrium. The result is that water attains its maximum density at this specific temperature. Understanding this balance is essential for comprehending the unique behavior of water in terms of density fluctuations with temperature variations.

Chemical Properties

(i) Water is neutral in nature. pH of the pure water is 7. It is a weak electrolyte and feebly ionises into H^+ and OH^- ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

In pure water $[H^+] = [OH^-] = 10^{-7}$ at 25°C.

(ii) With Metals: it reacts with active metals and evolves hydrogen. The reaction is exothermic in the case of alkali and alkaline earth metals.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

(iii) Reaction With Non-Metals: Chlorine decomposes cold water forming HCl and HClO.

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\text{(Hypochlorous acid)}}{HClO}$$

When steam is passed over red-hot coke (1000°C), water gas is formed.

$$C + H_2O \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

(iv) Action On Nonmetallic Oxides: Acidic oxides combine with water to form acids.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad \text{(Carbonic acid)}$$

$$SO_2 + H_2O \longrightarrow H_2SO_3 \quad \text{(Sulphureous acid)}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(Sulphuric acid)

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad \text{(Orthophosphoric acid)}$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad \text{(Nitric acid)}$$

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4 \quad \text{(Perchloric acid)}$$

(v) Action on Metallic Oxides: basic oxides combine with water to form alkalis.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

(vi) Action On Hydrides, Carbides, Nitrides, Phosphides: Water decomposes these compounds with liberation of hydrogen, acetylene (or methane), ammonia, phosphine respectively.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(vii) Hydrolysis: Many salts specially the salts of strong bases with weak acids, weak bases with strong acids and weak bases with weak acids undergo hydrolysis with water.

$$CH_3COONa + H_2O \longrightarrow CH_3COOH + NaOH$$

$$CH_3COONH_4 + H_2O \longrightarrow CH_3COOH + NH_4OH$$

Halides of nonmetals are decomposed by water.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$
$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

Hard And Soft Water

When we classify water as "soft water," it means that it can generate an ample lather when mixed with soap. On the other hand, we label water as "hard" if it tends to create an unsightly, insoluble scum before producing a lather with soap. The hardness of naturally occurring water typically results from the presence of bicarbonates, chlorides, and sulfates of calcium and magnesium. However, it's important to note that the true source of water hardness lies in soluble salts that lead to the formation of this problematic scum when soap is introduced.

$$Ca^{2+}(aq) + 2C_{17}H_{35}COO^{-}(aq) \longrightarrow (C_{17}H_{35}COO)_2Ca$$

$$Mg^{2+}(aq) + \underset{\text{Anion of soap}}{2C_{17}H_{35}COO^{-}(aq)} \longrightarrow \underset{\text{Inso luble precipitates}}{(C_{17}H_{35}COO)_2Mg}$$

Soap fails to create a lather in water until all the calcium and magnesium ions have been removed through precipitation. Consequently, hard water is not efficient in facilitating the action of soap and, as a result, it leads to soap wastage.

Effects of Hard Water

1. **Inappropriate for washing purposes:**
Soaps, composed of sodium or potassium salts derived from long-chain fatty acids, undergo a chemical reaction when exposed to hard water. Specifically, soap that contains sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to generate insoluble precipitates known as scum.

$$\underset{\text{(Originating from hard water)}}{M^{2+}} + \underset{\text{Sodium stearate (Soap)}}{2C_{17}H_{35}COONa} \rightarrow \underset{\text{Metal stearate (precipitate)}}{(C_{17}H_{35}COO)_2M\downarrow} + 2Na^{+}$$

Where $M^{2+} = Ca^{2+}$ or Mg^{2+}

Consequently, the formation of scum results in the absence of lather until all calcium and magnesium ions are precipitated. Additionally, this process leads to the wasteful use of a significant amount of soap.

2. **Detrimental to boiler systems:**
Water is employed in the steam production process. When hard water is utilized for steam generation in boilers, it diminishes the efficiency of the boilers due to the substantial deposition of salts in the form of scale within the boiler system.

Types of Hardness

(a) Temporary hardness
(b) Permanent hardness

Temporary Hardness

This situation arises from the existence of calcium and magnesium bicarbonates. Temporary water hardness can be readily eliminated through boiling, as the bicarbonates decompose readily, causing the formation of insoluble carbonates that precipitate out of the water.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(In so lub le)}}{CaCO_3} + H_2O + CO_2$$

$$Mg\ (HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(In so lub le)}}{Mgco_3} + H_2O + CO_2$$

Temporary hardness can also be removed by Clark's process which involves the addition of slaked lime $[Ca(OH)_2]$.

$$Ca\ (HCO_3)_2 + Ca\ (OH)_2 \longrightarrow \underset{\text{(In so lub le)}}{2CaCO} + 2H_2O$$

It is essential to add only the calculated amount of $Ca(OH)_2$ because excess will cause artificial hardness.

Softening of Water

Water softening is the procedure undertaken to eliminate hardness from water.

(i) Removal of temporary hardness:

Temporary hardness can be eradicated through various methods:

(a) Boiling:

Temporary hardness in water can be effectively removed through the process of boiling, particularly when dealing with large quantities of water in boilers. Boiling induces a chemical transformation where soluble $Mg(HCO_3)_2$ is converted into $Mg(OH)_2$ instead of $MgCO_3$. This is because $Mg(OH)_2$ readily precipitates, while Ca $(HCO_3)_2$ is transformed into insoluble $CaCO_3$, leading to its precipitation. The resulting precipitates can be separated through a filtration process, yielding softened water.

Chemical reactions involved:

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

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

(b) Clark's method:

In this approach, a calculated quantity of lime is introduced into hard water containing bicarbonates of calcium and magnesium. The lime addition initiates the precipitation of calcium carbonate and magnesium hydroxide. Subsequently, these precipitates are separated through filtration, resulting in the acquisition of soft water.

Chemical reactions involved:

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

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

Permanent Hardness

In detail, permanent hardness is incurred when water traverses over geological formations that contain significant amounts of calcium and magnesium sulfates or chlorides. Unlike temporary hardness, this form of hardness cannot be alleviated through the process of boiling, nor can it be mitigated by adding slaked lime. It persists in the water and poses a challenge for various industrial and domestic applications.

Consequently, various methods are employed to address and remove permanent hardness.

(i) Washing soda:

In a more detailed explanation, the process eliminates both temporary and permanent hardness by converting soluble compounds of calcium and magnesium into insoluble carbonates. This transformation helps precipitate these insoluble carbonates out of the water, effectively addressing and remedying the issue of hardness.

$$CaCl_2 + Na_2CO_3 \quad = \quad CaCO_3 + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \quad = \quad CaCO_3 + Na_2SO_4$$

$$Ca\ (HCO_3)_2 + Na_2CO_3 \quad = \quad + \underset{\text{(In soluble)}}{CaCO} + \underset{\text{(soluble)}}{2NaHCO3}$$

In place of sodium carbonate, caustic soda or sodium phosphate can also be used.

$$3MgSO_4 + 2Na_3PO_4 \longrightarrow \quad + 3Na_2SO_4$$

$$MgCl_2 + 2NaOH \longrightarrow \underset{\text{(In soluble)}}{Mg\ (OH)_2} + 2NaCl$$

(ii) Calgon:

The complex salt of metaphosphoric acid, sodium hexametaphosphate $(NaPO_3)_6$, is known as Calgon. It is represented as $Na_2[Na_4(PO_3)_6]$. Calcium and magnesium salts present in hard water react with Calgon to give complex salts.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + 2Na_2SO_4$$

Degree of Hardness

It is quantified in parts per million (ppm) and is defined as the quantity of $CaCO_3$ or equivalents of various calcium and magnesium salts present in 10^6 parts of water by mass.

For instance, In a 1000 mL water sample containing 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$, the total hardness in terms of $CaCO_3$ is determined as follows:

111g of $CaCl_2$ is equivalent to 100 g of $CaCO_3$,

and 95 g of $MgCl_2$ is equivalent to 100 g of $CaCO_3$.

Therefore,

(1 mg $CaCl_2$) + (1 mg $MgCl_2$) is equal to $\frac{100}{111} + \frac{100}{95}$ mg of $CaCO_3$, resulting in 1.95 mg of $CaCO_3$.

Considering that 1 liter (10^3 parts) of water contains 1.95 mg of $CaCO_3$, it follows that 10^6 parts of water would contain 1.95 g.

Consequently, the degree of hardness is determined to be 1.95 ppm.

In the dissociation of protium water H_2O and heavy water D_2O,

where $H - O - H \rightleftharpoons H^+ + OH^-$ with $K_{H_2O} = 1.0 \times 10^{-14}$ (at 298 K)

and $D - O - D \rightleftharpoons D^+ + OD^-$ with $KD_2O = 1.3 \times 10^{-15}$ (at 298 K)

it is observed that protium water dissociates to a higher extent than heavy water.

This difference in dissociation is attributed to the fact that protium bonds are more readily broken than deuterium bonds.