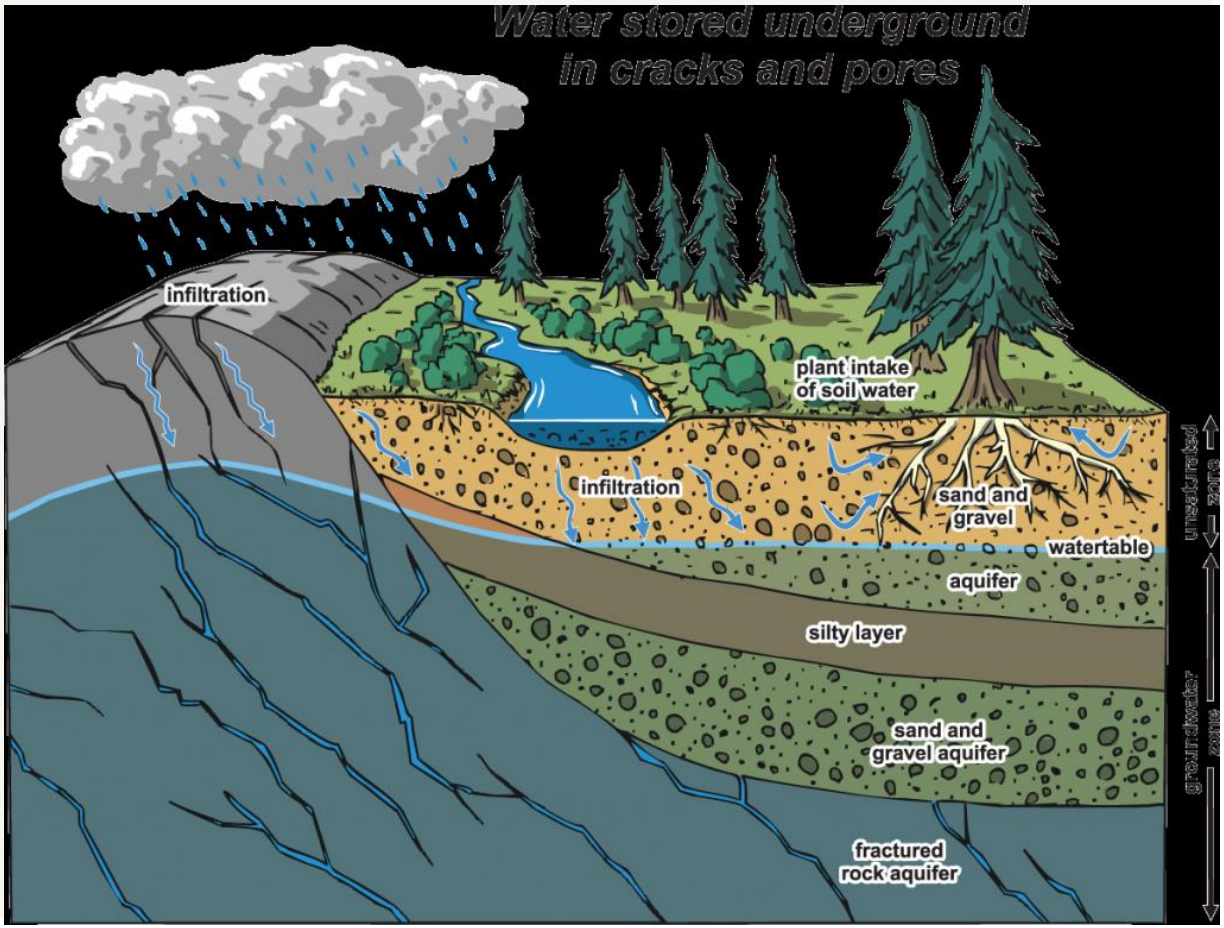
HYYROLOGIC CYCLE:

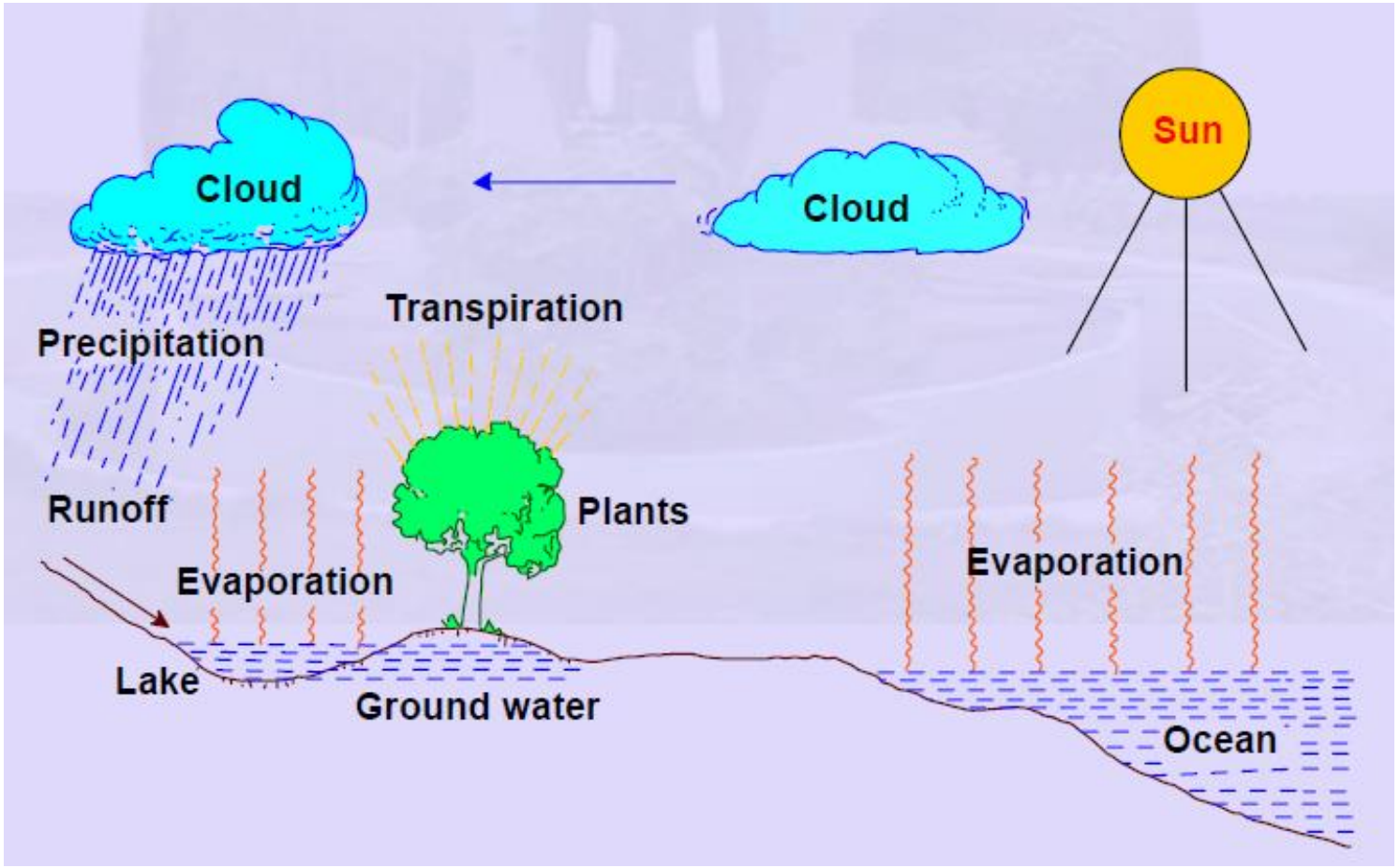
Water from the oceans, rivers, and lakes evaporates to become water vapor. Warm air is able to hold more water vapor than cool air so as convection in the troposphere moves air upward, the water vapor will condense at the cooler altitudes. The cloud droplets will grow as they pick up more water vapor. Eventually, the cloud droplets grow so large that the cooler air cannot hold them anymore and they fall to the surface. The rainwater runs downhill starting out as streams that flow into small rivers that in turn flow into large river down to the oceans. Water also percolates into the soil to become part of the groundwater that totals approximately 10% of the mass of the oceans. Some of the groundwater collects in reservoirs underground called *aquifers*. Groundwater can remain in aquifers for a million years or more. Some aquifer water can reach the surface and flow out to the oceans. Water that falls as snow can also store water for long periods of time as ice sheets and glaciers near the poles or a high elevations.



Water stored underground is called groundwater.

Groundwater is found within underground aquifers (in the "zone of saturation“). A zone of saturation is located where water fills in all of the spaces that are in the lower layers of soil. An aquifer is the area underground where spaces between gravel, sand, clay, or rock fill with water.

- there is more evaporation than precipitation and over the land, there is more precipitation than evapotranspiration
- About $4 \times 10^{13}\ m^3$ more water falls on land as precipitation than evaporates from it (the difference between evapotranspiration and precipitation on land) and this is the water that is returned to the oceans through stream flow



INVOLVEMENT OF BIOSHPERE IN WATER CYCLE

Plants

Of all living organisms, plants contribute the most to the water cycle.

❖ To produce their energy, plants perform photosynthesis, in which plants draw water from the surface and/or from under ground with their roots.

❖ A great deal of evaporates from the surface of the leaves. This type of plant-water evaporation is called transpiration. Transpiration from the tree canopies in forests plays a huge part in the water cycle; in fact, about 10 percent of all water vapor cycled back into the atmosphere is from plant transpiration.

Animals

❖ Both plants and animals produce water as a byproduct of respiration.

During breathing out water vapors are released to the atmosphere.

❖ Some of the water is excreted out (through urination and sweating) and the rest of water is released when the organism dies.

A 70-kg man is made up of about 42L of total water.

AQUATIC CHEMISTRY

THE CHARACTERISTICS OF BODIES OF WATER

A. Thermal Stratification:

B. Physical properties:

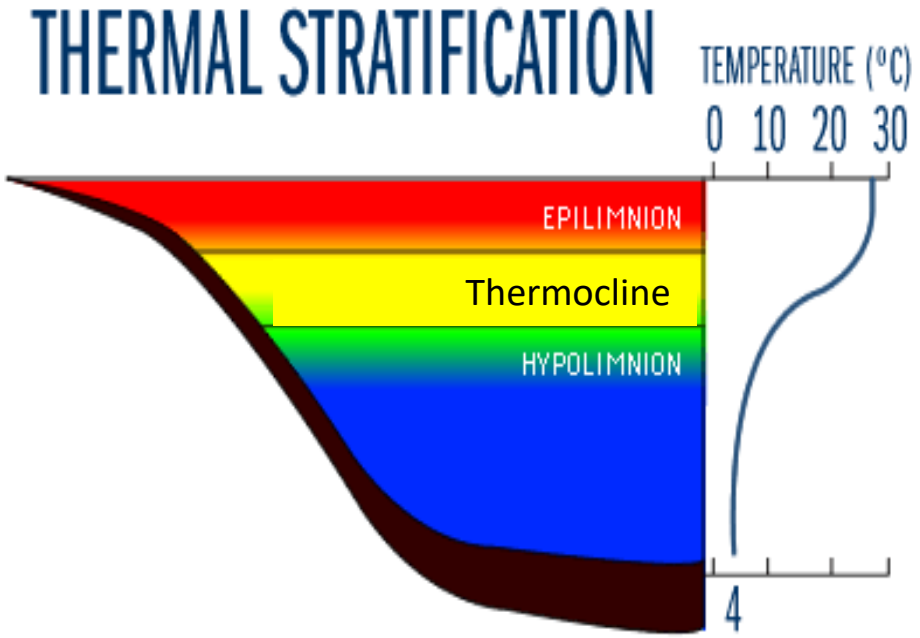
C. AQUATIC LIFE:

D. GASES IN WATER

E. SURFACE WATER QUALITY

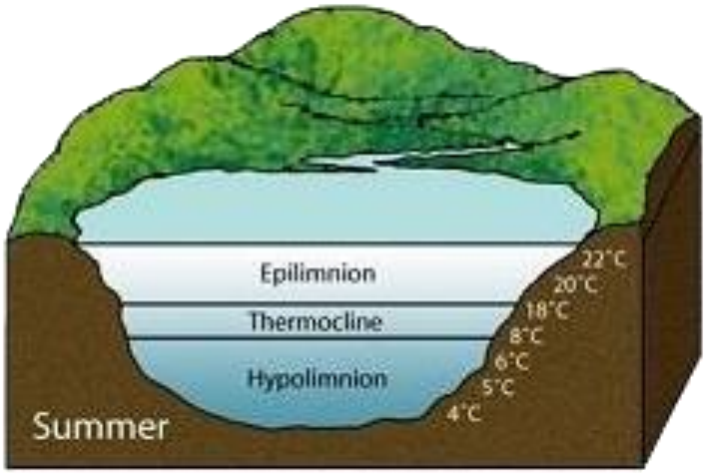
A. Thermal stratification

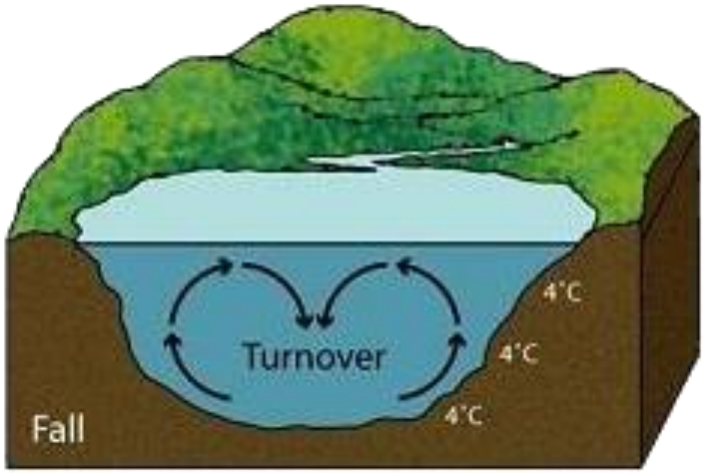
- During summer, the water separates into layers of distinctly different density caused by differences in temperature. This process is called thermal stratification.
- The sun warms the surface water, but the bottom of the lake remains cold. You can feel this difference when diving into a lake.
- Surface layer is known as epilimnion and bottom layer is known as hypolimnion. The layer between epilimnion and hypolimnion is called the thermocline.
- Once the stratification develops, it tends to persist until the air temperature cools again in autumn.
- Because the layers don't mix, as if surface layer floats upon the bottom layer, and they develop different physical and chemical characteristics.
- In autumn, the stratification is lost and the wind can turbulently mix the two water masses together because their densities are so similar and the resultant mixing is known as overturn.
- A similar process also may occur during the spring as colder surface waters warm to the temperature of bottom waters and the lake mixes (spring turnover).

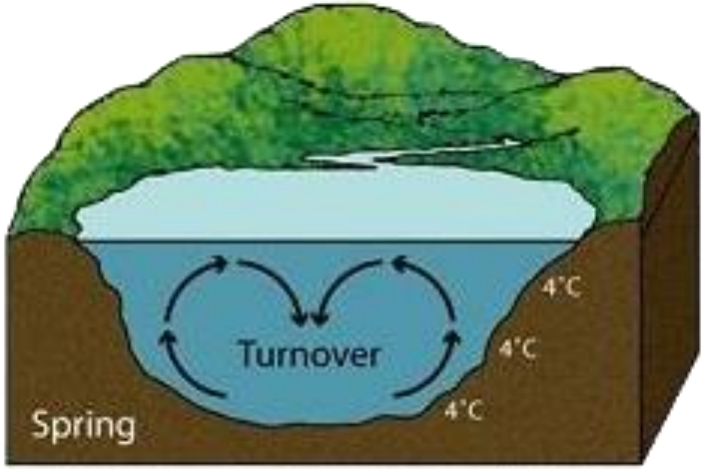


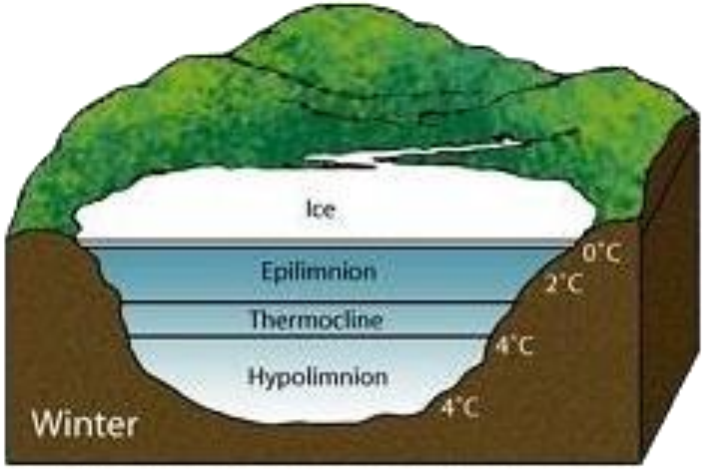
Since, the epilimnion is exposed to light, there is a heavy growth of algae in this layer. As a result of exposure to the atmosphere and because of the photosynthetic activity of algae during daylight hours, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic.

In the hypolimnion, biodegradable organic materials are broken down by the action of bacteria and this process needs consumption of dissolved oxygen. Thus water becomes anaerobic (lacking dissolved oxygen). As a result of this, in the hypolimnion, chemical species exist in a relatively reduced form.


Epilimnion
Thermocline
Hypolimnion
22°C
20°C
18°C
8°C
6°C
5°C
4°C
Summer


Turnover
4°C
4°C
4°C
Fall


Turnover
4°C
4°C
4°C
Spring


Ice
Epilimnion
Thermocline
Hypolimnion
0°C
2°C
4°C
4°C
Winter

B. Physical Properties:

(i) Temperature :

(a) Biodegradation of organic material in water and sediments is accelerated with increased temperatures, increasing the demand of DO.

(b) The solubility of gases decreases with increasing temperature, this can be expressed by the **Clausius-Clapeyron** equation,

$$\log\frac{C_2}{C_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

C. AQUATIC LIFE:

The living organisms are called **biota.**
All living things need food. In an aquatic ecosystem living organisms may be classified as either autotrophs or heterotrophs.

Autotrophic organisms are an organism that is able to produce their own food. Autotrophic organisms utilize solar or chemical energy to convert simple, non-living inorganic material into complex life molecules by photosynthesis or CHEMOSYNTHESIS.

There are main two types of autotrophic organisms: Photosynthetic organisms and chemosynthetic organisms.

In most cases, primary food production occurs in a process called photosynthesis, which is powered by sunlight example: cyanobacteria (often called "blue-green algae"). Cyanobacteria are not plants and are prokaryotes, while green algae are plants and are eukaryotes. Cyanobacteria are bacteria, are quite small and usually unicellular, they often grow in colonies large enough to see

In a few environments, primary production happens though a process called chemosynthesis, which runs on chemical energy. Together, photosynthesis and chemosynthesis fuel all life on Earth.

2 main types of autotrophs

- One type gets energy from the sun ⇨ by photosynthesis,
- Example: plants, cyanobacteria
- Oxygen is produced
- Another type gets energy without light ⇨ by chemosynthesis,
- Example : DEEPWATER ORGANISMs LIKE BACTERIA.
- Oxygen not evolved

❑ Both photosynthesis and chemosynthesis result in food for the organisms
❑ Both processes need carbon dioxide to produce the carbohydrates.
❑ Both processes also need an energy source to fuel the reactions.

Whereas there is only one basic reaction for photosynthesis, there are several ways for chemosynthesis, depending on the environment. At these hydrothermal vents, vent bacteria oxidize (use) hydrogen sulfide, add carbon dioxide and oxygen, and produce sugar, sulfur, and water:

$CO_2 + H_2O + 4H_2S$ ---------> $CH_20 + 3H_2SO_4$.

carbon dioxide + water + Inorganic substances

D. GASES IN WATER

Two most imported gases which are dissolved in water are CO_2 and O_2. Water supersaturated with N_2 can cause death of fish from bubbles of nitrogen formed in the blood. Now we will learn sources and uses of these gases.

Oxygen: O_2 is 20.95% by volume of dry air
The concentration of oxygen in water at 25°C in equilibrium with air at atmospheric pressure is only 8.32 mg/L.

CO_2 : Carbon dioxide is only about 0.037% by volume of normal dry air.
At 25°C, water in equilibrium with-unpolluted air has a $CO_2(aq)$ concentration of 1.146×10^{-5} M. CO_2 in water produces H_2CO_3.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H$$

Solubility of CO_2 in water has great impact in nature. CO_2 dissolved in water is the cause of LIMESTONE CAVE.

$$CaCO_3(s) + CO_2(aq) + H_2O \longleftrightarrow Ca^{2+} + 2HCO_3^-$$

The importance of oxygen in atmospheric chemistry, geo chemical transformation and life processes is as follows :

• Atmospheric oxygen participate in energy producing reactions such as burning of fossil fuels, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ .....*(1)*

• Atmospheric oxygen is utilized by aerobic organism in the degradation of organic material

$$[CH_2O] + O_2 \xrightarrow{\text{Organism}} CO_2 + H_2O \text{ .....(2)}$$

• Oxygen is consumed by some oxidative weathering processes of minerals

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \text{ .....(3)}$$

• Photosynthesis by plants return the oxygen to the atmosphere.

$$CO_2 + H_2O \xrightarrow[h\upsilon]{\text{plants}} CH_2O + O_2 \text{ .....(4)}$$

• A form of oxygen containing species O_3 occurring in the stratosphere absorbs harmful UV radiation and serves as radiation shield.

• All the molecular oxygen now in atmosphere is thought to have originated through the action of photosynthetic organisms, which shows the importance of photosynthesis in the oxygen balance of atmosphere.

ALKALINITY

- The capacity of water to accept H^+ ions is called alkalinity
- Generally, the main species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Henry's Law

At a constant temperature, the solubility of a gas in a liquid is proportional to the partial pressure of that gas in contact with the liquid.

$[X(aq)] = K P_X$ (P_X is the partial pressure of the gas).

The solubility of any gas increases as the external pressure is increased

E. SURFACE WATER QUALITY

(a) Biochemical oxygen demand, BOD refers to the amount of oxygen needed to degrade the organic matter biologically in a given volume of water.

- ✓ A sample of waste water is to be kept in a BOD bottle and water will be saturated with air (containing a known amount of oxygen)
- ✓ We will measure"initial dissolved oxygen" (DO_i)
- ✓ Then the bottle will be sealed and left for five days at 20°C in the dark.
- ✓ The oxygen content will be measured again after 5 days.
- ✓ The difference in DO divided by the volume of waste would be the five-day BOD (BOD_5)

The BOD bottle should be kept at dark to prevent photosynthesis

(b) CHEMICAL OXYGEN DEMAND (COD) measures he concentration of organic substances that can be oxidized by acidified dichromate at 100°C.

$$3\,CH_2O + 16\,H_3O^+ + 2\,Cr_2O_7^{2-} \rightarrow 4\,Cr^{3+} + 3\,CO_2 + 27\,H_2O$$

dichromate is the acting as an oxidizing agent

$$\mathbf{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O}$$

HARD WATER

Temporary Hardness

– Temporary Hardness is caused by the presence of dissolved bicarbonate of calcium and magnesium.

It is mostly destroyed by more boiling of water, when bicarbonates are decomposed yielding insoluble carbonates.

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

Calcium bicarbonate — Calcium Carbonate

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

Magnesium Bicarbonate — Magnesium hydroxide

– Calcium/Magnesium Carbonates thus formed being almost insoluble, are deposited as a scale at the bottom of vessel, while carbon dioxide escapes out.

Permanent Hardness

–Hardness which is due to the presence of dissolved sulfate or chloride of calcium and magnesium which cannot be removed by boiling is known as permanent hardness.