

This material is for reference only. Points present in the slides are only for assistance and their elaboration are present in book. Examination questions will be in depth and can be solved by following text book only.



Natural Water Chemistry

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Water Quality Parameters

Temperature - Dissolved Oxygen (DO) - pH

Alkalinity - Hardness

Nitrates and Phosphates - Turbidity

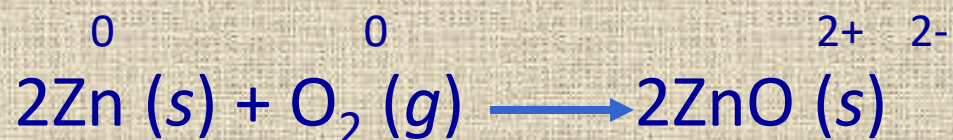
Conductivity



Oxidation Reduction chemistry of Natural water

Electrochemical processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



Terminology for Redox Reactions

- OXIDATION—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- **REDUCTION**—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- **OXIDIZING AGENT**—electron acceptor; species is reduced.
- **REDUCING AGENT**—electron donor; species is oxidized.

You can't have one... without the other!

- Reduction (gaining electrons) can't happen without an oxidation to provide the electrons.
- You can't have 2 oxidations or 2 reductions in the same equation. Reduction has to occur at the cost of oxidation

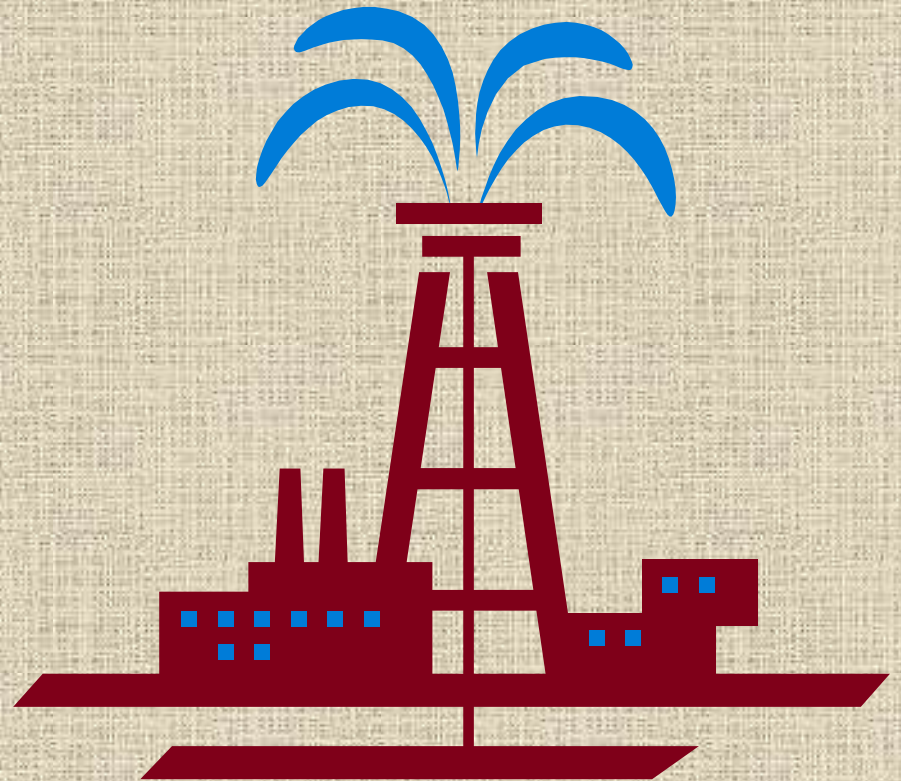
LEO the lion says GER!

GER!

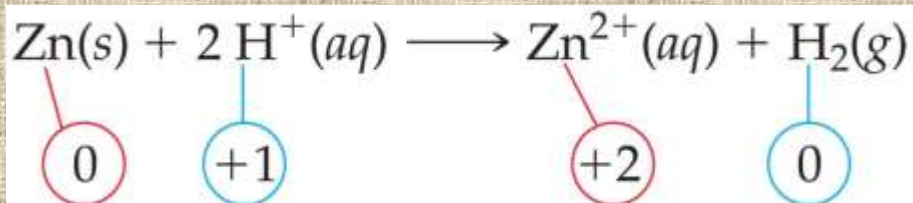


Another way to remember

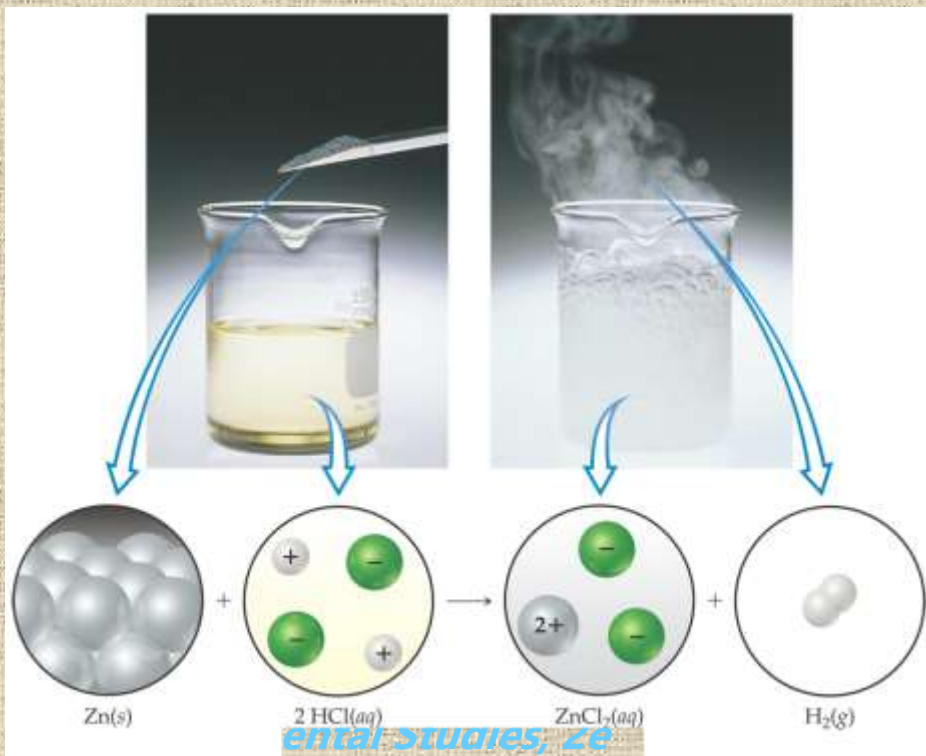
- OIL RIG



Oxidation Numbers



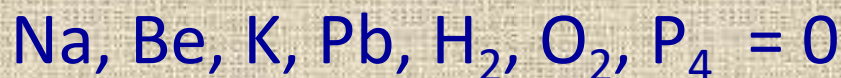
In order to keep track of what loses electrons and what gains them, we assign **oxidation numbers**.



Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.



2. In monatomic ions, the oxidation number is equal to the charge on the ion.



3. The oxidation number of oxygen is **usually** -2 . In H_2O_2 and O_2^{2-} it is -1 .

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is -1 .
5. Group IA metals are +1, IIA metals are +2 and fluorine is always -1 .
6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.



Oxidation numbers of all the atoms in HCO_3^- ?



$$\text{O} = -2 \quad \text{H} = +1$$

$$3 \times (-2) + 1 + ? = -1$$

$$\text{C} = +4$$

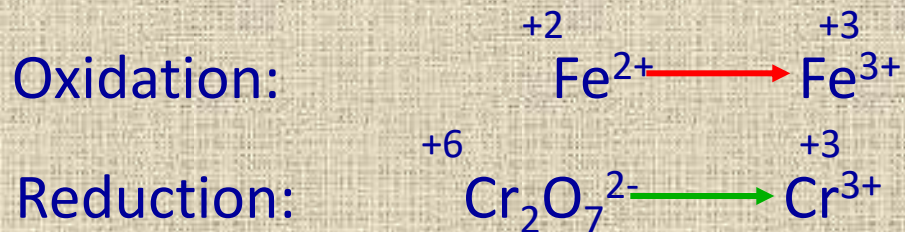
Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $\text{Cr}_2\text{O}_7^{2-}$ in acid solution?

1. Write the unbalanced equation for the reaction in ionic form.



2. Separate the equation into two half-reactions.

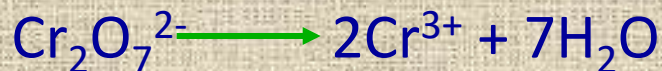


3. Balance the atoms other than O and H in each half-reaction.

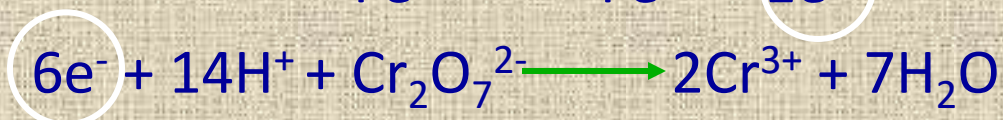


Balancing Redox Equations

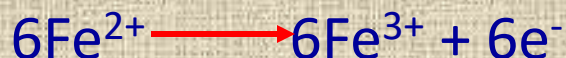
4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.



5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.



6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.



Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation:



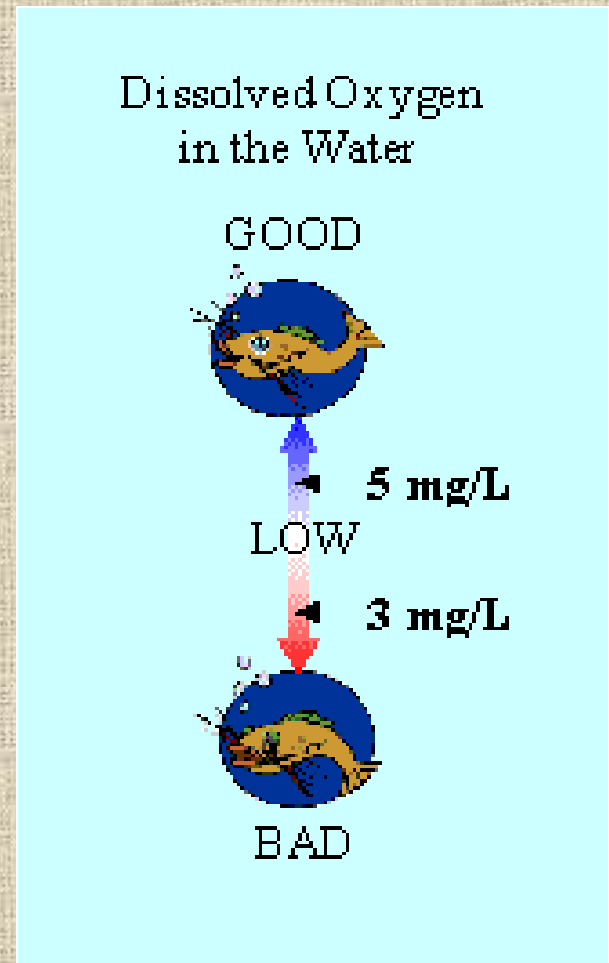
8. Verify that the number of atoms and the charges are balanced.

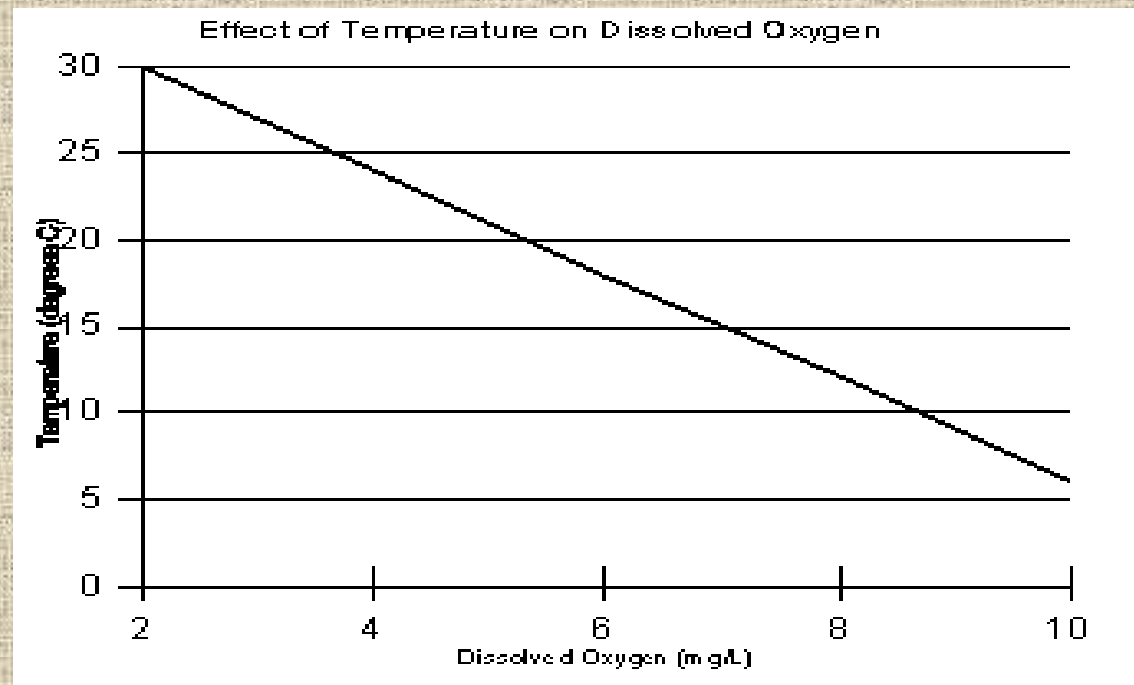
$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

Dissolved Oxygen (DO)

- DO is the measurement of oxygen dissolved in water and available for fish and other aquatic life.
- Indicates health of an aquatic system.
- Can range from 0-18 ppm.
- Most natural water systems require 5-6 ppm to support a diverse population.
- Varies with time of day, weather, temperature.





Thermal pollution can effect

Dissolved Oxygen (DO)

Increase in organic waste



Increase in algae/plant vegetation



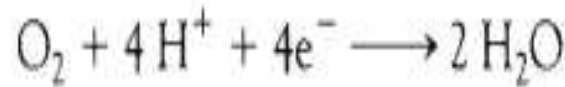
Decrease in DO available to organisms



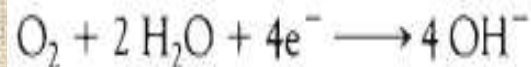
Leads to changes in ecosystem as organisms needing lots of DO are replaced by organisms needing little.



- O_2 is the most important oxidizing agent in natural water.
- The half reaction which occur in acidic solution is



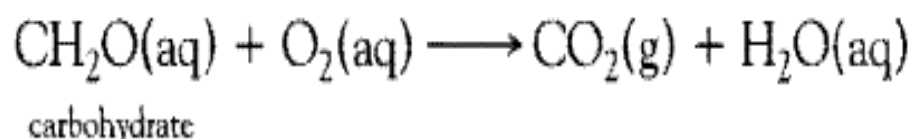
- And in basic aqueous solution is



- The concentration of DO is very small.

Oxygen Demand

The most common substance oxidized by dissolved oxygen in water is organic matter having a biological origin, such as dead plant matter and animal wastes. If, for the sake of simplicity, the organic matter is assumed to be entirely polymerized carbohydrate (e.g., plant fiber) with an approximate empirical formula of CH_2O , the oxidation reaction would be



Dissolved oxygen in water is also consumed by the oxidation of dissolved **ammonia**, NH_3 , and **ammonium ion**, NH_4^+ —substances that, like organic matter, are present in water as a result of biological activity—eventually to **nitrate ion**, NO_3^- (see Problem 13-4).

Show that 1 L of water saturated with oxygen at 25°C is capable of oxidizing 8.2 mg of polymeric CH_2O .

Biochemical Oxygen Demand (BOD)

Amount of oxygen used by microorganisms to decompose organic matter in a water.

OR

The capacity of the organic and biological matter in a sample of natural water to consume oxygen, a process catalyzed by bacteria present.

OR

The BOD equals the amount of oxygen consumed as a result of the oxidation of dissolved organic matter in the sample.

Theoretical BOD can be determined by balancing a chemical equation in which all organic matter is converted to CO_2

Problem:- Calculate the theoretical oxygen demand of 1.67×10^{-3} moles of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in mg/L:



$$1.67 \times 10^{-3} \text{ moles glucose/L} \times 6 \text{ moles O}_2 / \text{mole glucose} \times 32 \text{ g O}_2 / \text{mole O}_2$$

© Oxford University Press 2015 = 0.321 g O_2 /L = 321 mg O_2 /L All rights reserved

Low BOD
(few organics
to be degraded)

High BOD,
zone of
mixing (lots
of sewage)

Dilution and
recovery zone
(several
kilometers)



Effect of Organic Wastes on Dissolved Oxygen

Chemical Oxygen Demand

- The quantity of oxygen used in biological and non-biological oxidation of materials in water; a measure of water quality. Acid and heat are used to oxidize the sample.
- The determination of chemical oxygen demand (COD) is used in municipal and industrial laboratories to measure the overall level of organic contamination in wastewater. The contamination level is determined by measuring the equivalent amount of oxygen required to oxidize organic matter in the sample.
- BOD/COD ratio – the greater the ratio, the more oxidizable (biologically treatable) the waste. Ratios rarely exceed 0.8-0.9.

Acid Mine Drainage

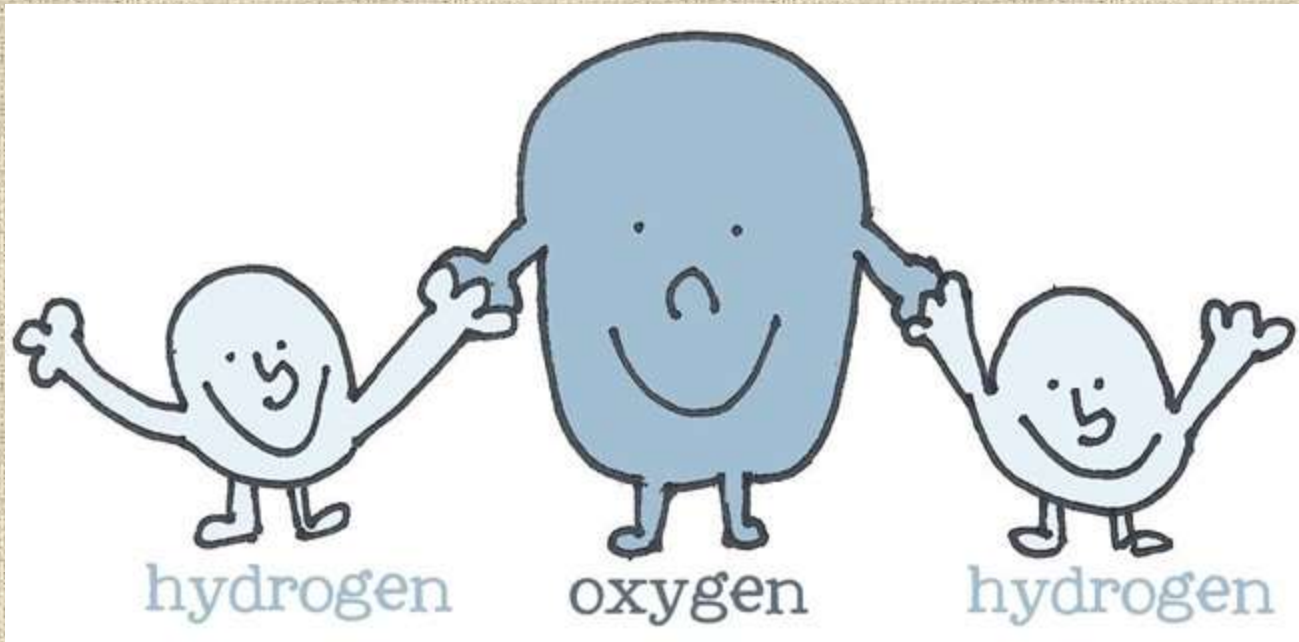
Acid mine drainage, acid and metalliferous drainage (AMD), or acid rock drainage (ARD) is the outflow of acidic water from metal mines or coal mines. Acid rock drainage occurs naturally within some environments as part of the rock weathering process but is exacerbated by large-scale earth disturbances characteristic of mining and other large construction activities, usually within rocks containing an abundance of sulfide minerals.

Effects of Acid mine drainage

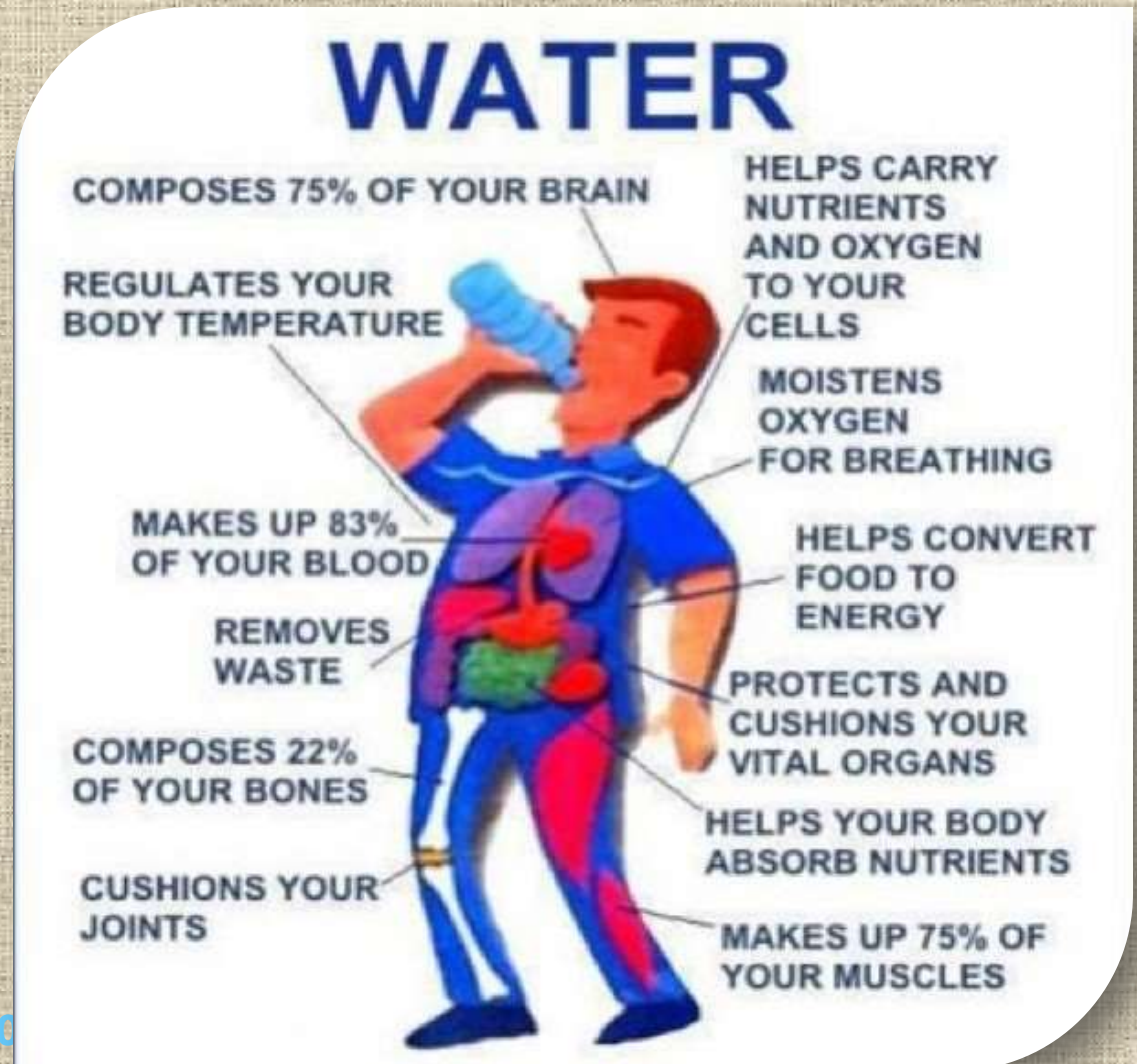
- Effects on pH
- Yellow boy
- Trace metal and semi-metal contamination
- Effects on aquatic wildlife

Unit 1

Water and its Treatment



Some facts about water



Sources of Water

Oceans and seas contain 96.5% water, and snow and groundwater hold 1.74% and 1.7%, respectively.

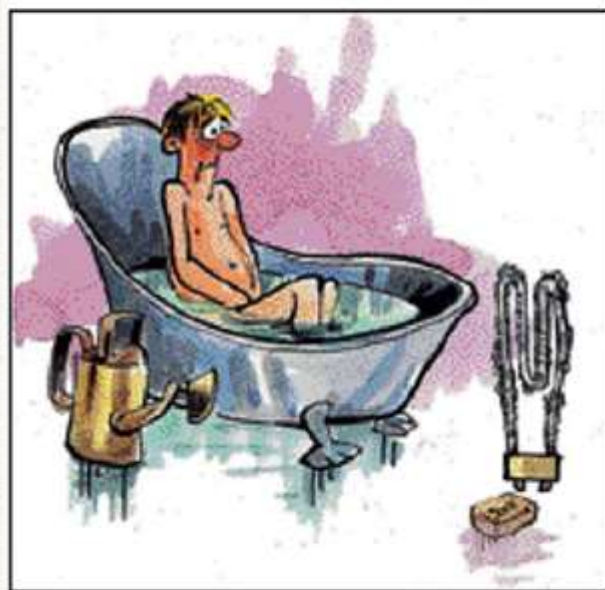
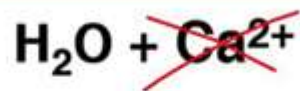
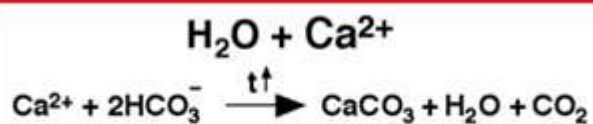


Types of Water

- Soft Water
- Hard Water



Hard Water





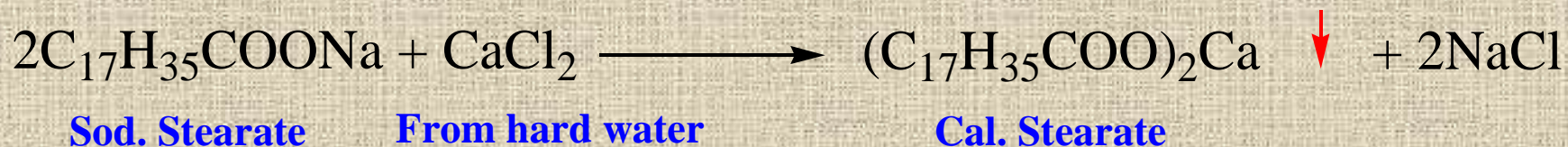
(a)

Soap in soft water — lather is formed.

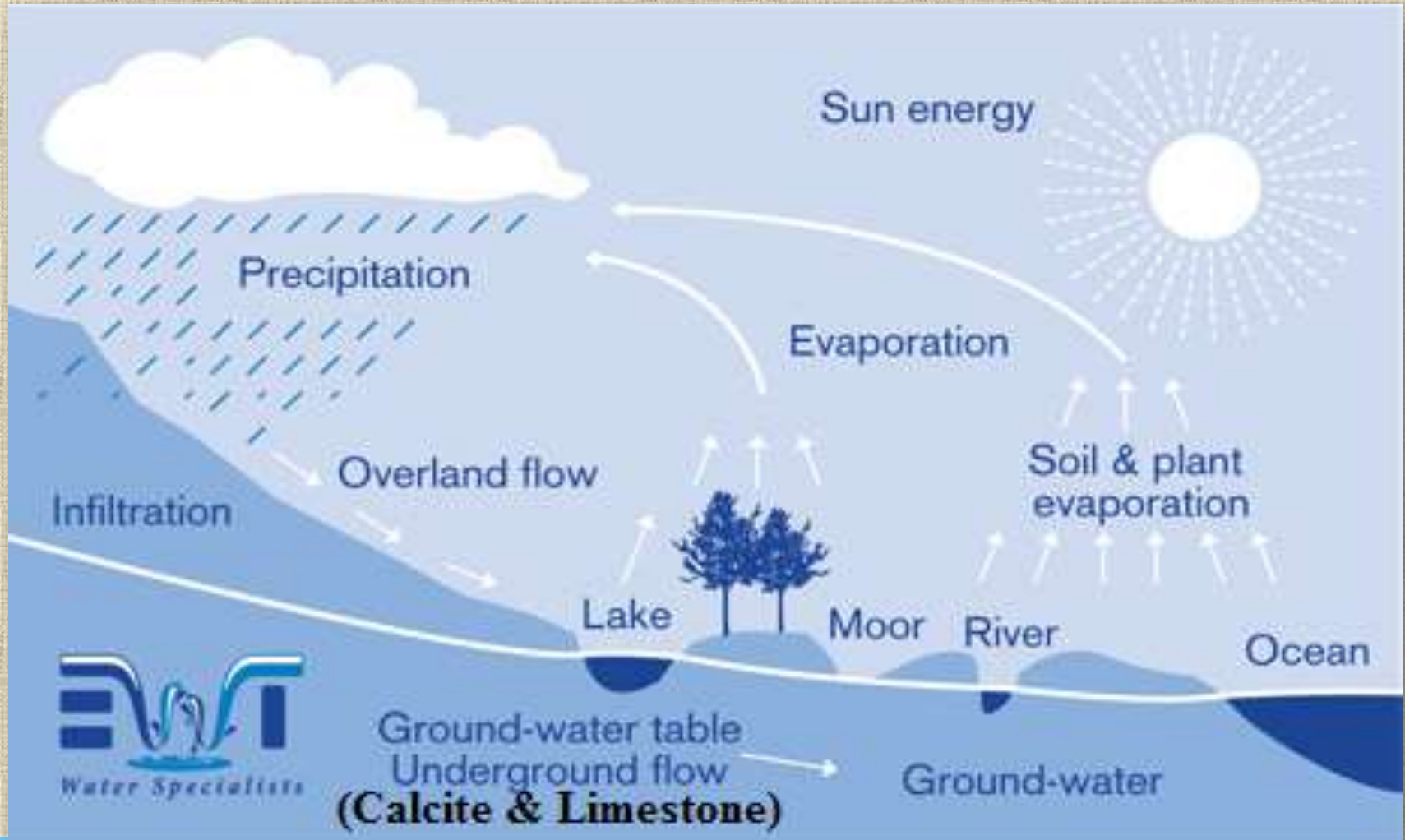


(b)

Soap in hard water — no lather is formed. Note the scum formed



Hard Water Formation



Hardness of Water

- **DEFINITION:**

" The property of water to form an insoluble curd with soap instead of lather. In other words hardness is the soap destroying property due to the presence of Bicarbonates, Sulphates and Chlorides of Calcium and Magnesium."

Using hard and soft water

Soft water forms a lather easily with soap.

Hard water needs more soap to form a lather, adding additional cost to cleaning processes.

This is because dissolved chemicals in the hard water react with soap to form a scum.



Hardness of water:

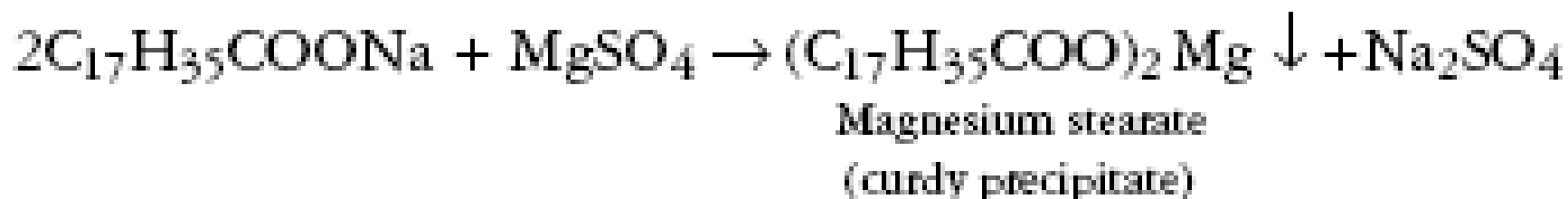
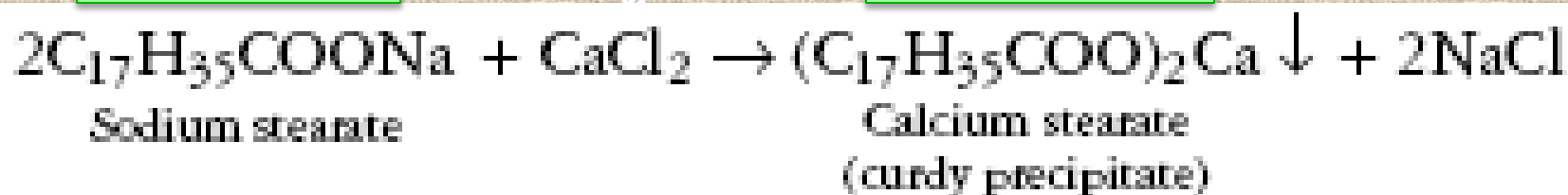
Presence of Ca^{+2} and Mg^{+2} ions in water and hard water prevents the formation of lather with soap.

In hard water the Ca^{+2} and Mg^{+2} ions replaces the Na^{+} ion from fatty acid salt (in the soap) and make water insoluble fatty acid salt, thus prevent the formation of foam.

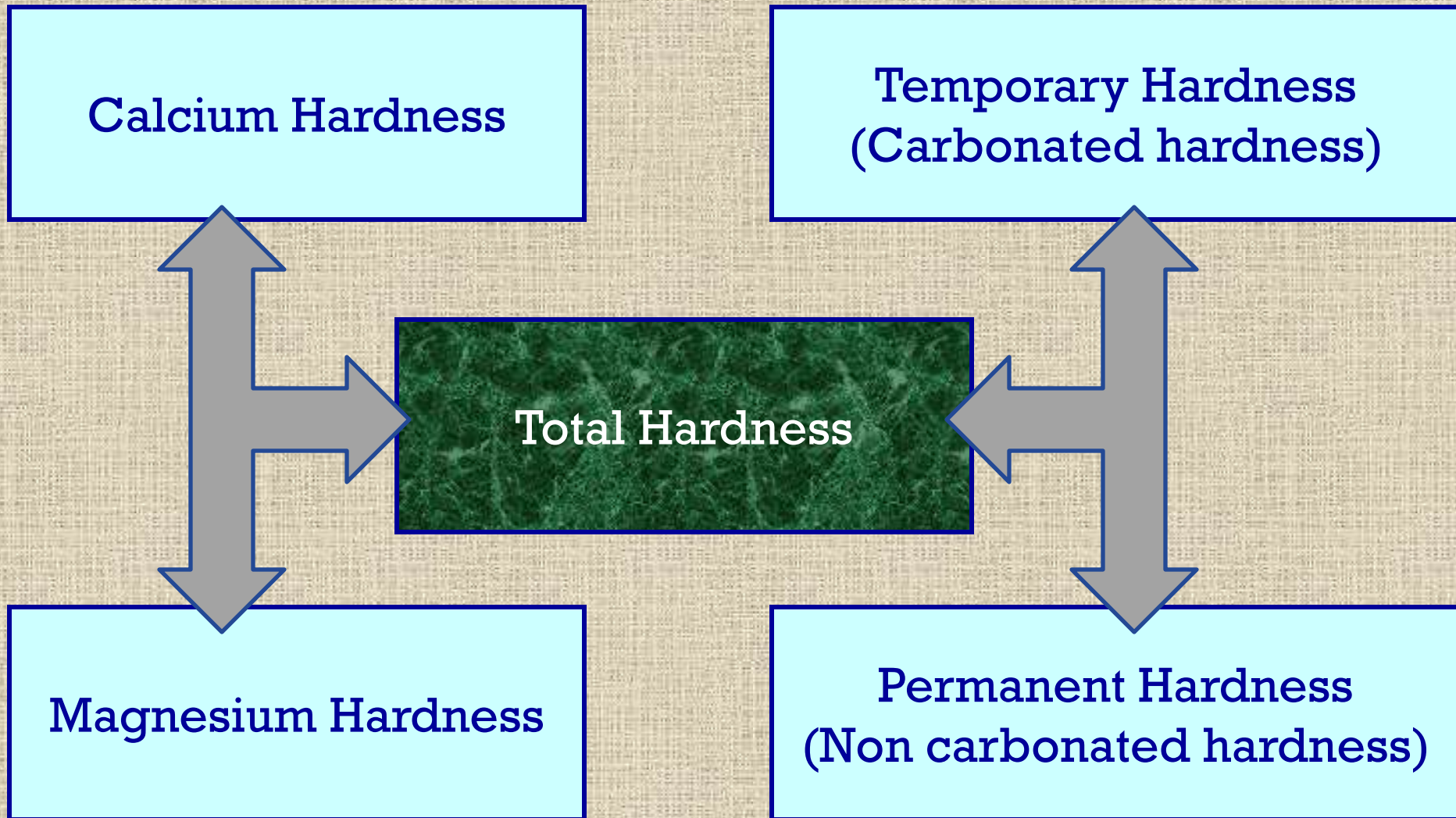
From soap
Water soluble

From hard water

Water insoluble



Types of hardness

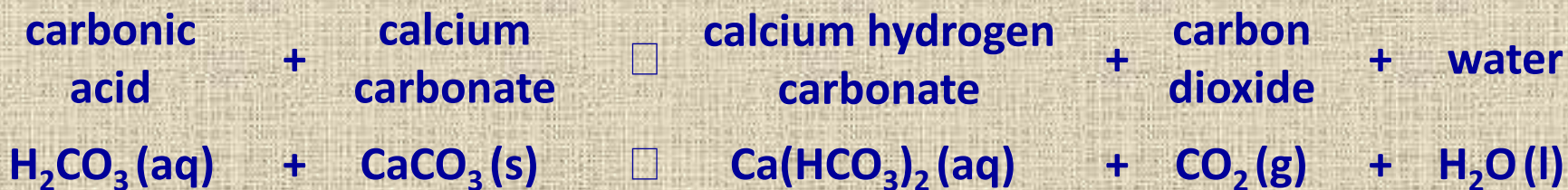


How can we divide water hardness??

- Carbonate hardness – also called temporary water hardness is caused by the presence of carbonates, hydrocarbonates of calcium and magnesium.
- Noncarbonate hardness – caused by the presence of Ca^{2+} , Mg^{2+} of other cations and anions like: Al^{3+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Cl^- , SO_4^{2-} , NO_3^- , which do not decompose and do not precipitate during boiling water.
- General water hardness – is the summary content of calcium, magnesium and other ions

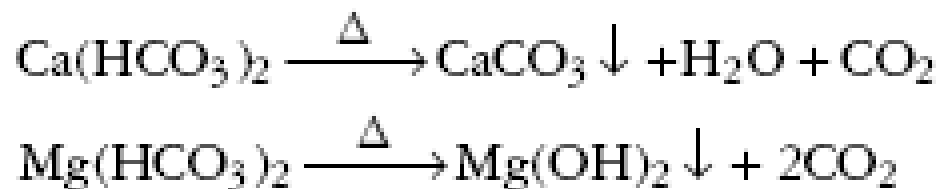
Temporary hardness

- Rainwater becomes slightly acidic as carbon dioxide from the air dissolves in it, forming carbonic acid.
- Limestone contains calcium carbonate. As the slightly acidic rainwater trickles through rocks, the calcium carbonate reacts to form soluble calcium hydrogen carbonate



Types of Hardness

Temporary hardness: due to presence of bicarbonates and carbonate of calcium and magnesium; can be Removed by boiling.



Permanent hardness: due to presence of chlorides and sulphates of calcium and Magnesium; cannot be removed by boiling; removed by softening agents.

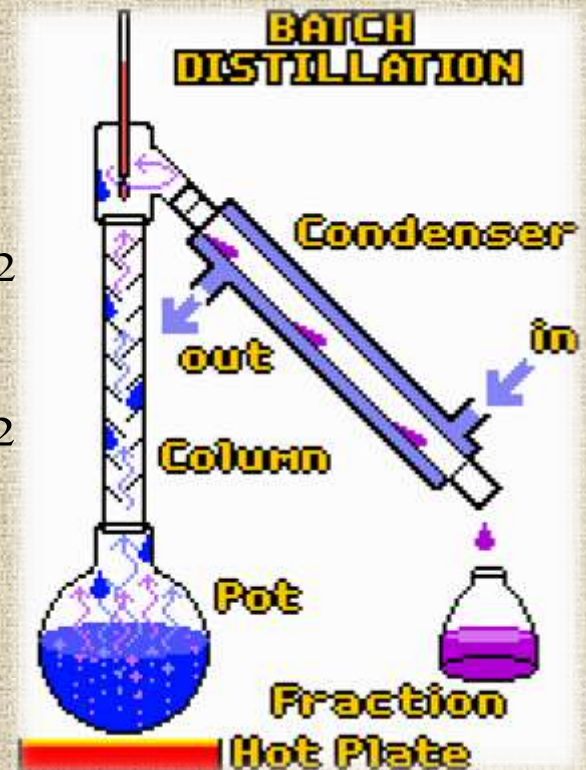
Temporary hardness of water (carbonate or alkaline hardness)

- due to presence of bicarbonates of Ca & Mg



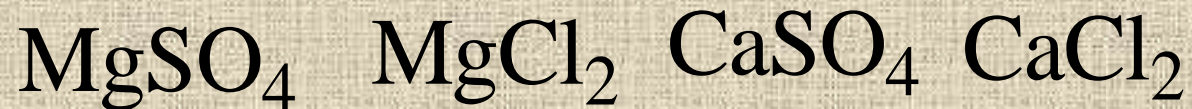
- removal of temporary hardness

Boiling



Permanent hardness of water

- due to presence of sulphates & chlorides Ca & Mg

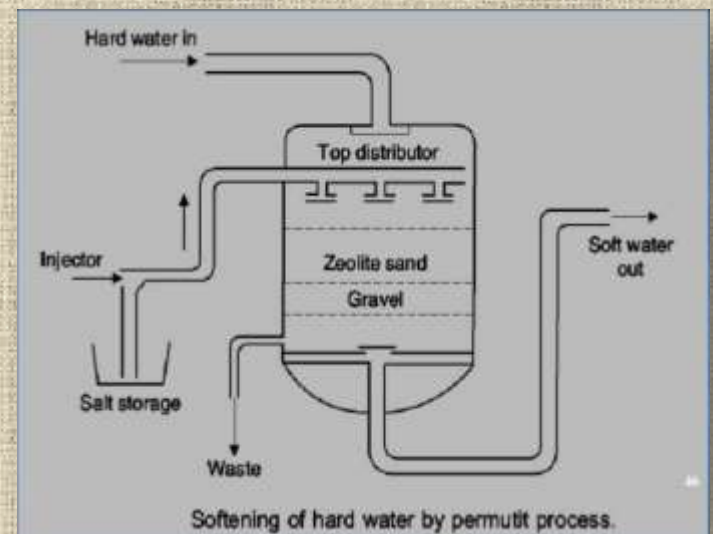


- removal of Permanent hardness

Use of Softening agents

Ion exchange method

Zeolite/Permutit method etc.





Harmful effects of hard water

- Hard water interferes with almost every cleaning task from laundering and dish washing to bathing and personal grooming.
- Clothes laundered in hard water may look dingy and feel harsh and scratchy.
- Dishes and glasses may be spotted when dry.
- Hard water may cause a film on glass shower doors, shower walls, bathtubs, sinks, faucets, etc.
- Hair washed in hard water may feel sticky and look dull.
- Water flow may be reduced by deposits in pipes.

Degree of hardness:

Expressed in terms of CaCO_3 equivalent (in mg/l)

Hardness of substance in terms of CaCO_3 = Strength of substance in mg/l * Chemical equivalents of CaCO_3 / Chemical equivalents of substance

Or

Hardness of substance in terms of CaCO_3 = Strength of substance in mg/l * Molar mass of CaCO_3 / Molar mass of substance

Degree Clarke ($^{\circ}\text{Cl}$) = It's number of equivalent of CaCO_3 present in 70,000 parts of water

Degree Feenck ($^{\circ}\text{F}$) = It's number of equivalent of CaCO_3 present in 10^5 parts of water

Relation

$$1 \text{ ppm} = 1 \text{ mg/l} = 0.1^{\circ}\text{F} = 0.07^{\circ}\text{Cl}$$

Degree hardness of water

$$\text{Equivalent of CaCO}_3 = \frac{\left[\text{Strength of substance producing hardness (mg/l)} \right] \times \left[\text{Chemical equivalent of CaCO}_3 \right]}{\text{Chemical equivalent of hardness producing substance}}$$

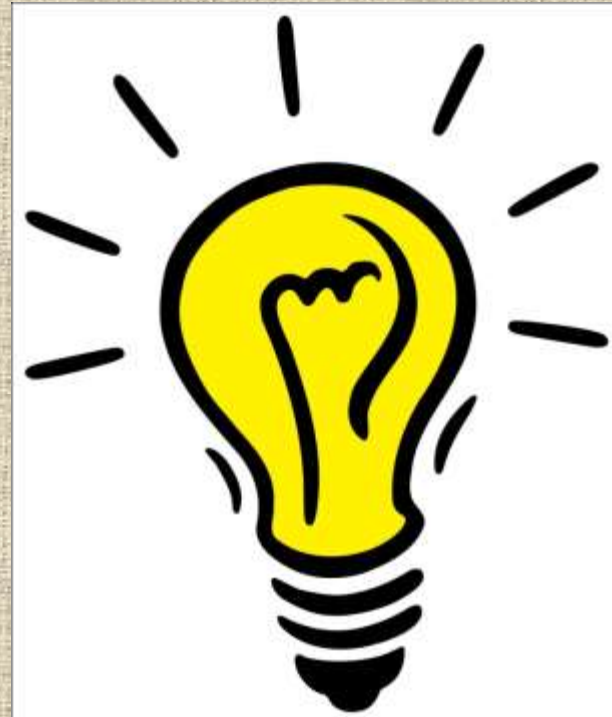
➤ Units of hardness

Parts Per million (ppm)

Milligrams per liter (mg/l)



Calculate the temporary hardness in terms of calcium carbonate equivalents in a water sample containing calcium bicarbonate (12.2 mg/l). Given that at. Wt. of Ca=40 amu, O=16 amu, C=12 amu, H=1 amu.



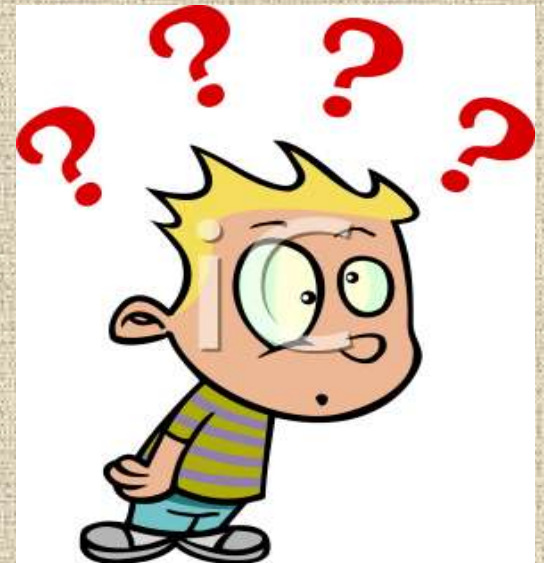
Q1 What is the temporary , permanent and total hardness of a 1L of water sample containing 12.2 mg of $\text{Ca}(\text{HCO}_3)_2$ and 5.6 mg of MgSO_4 (M.W=120)?

Q2 A water sample contains 200 mg of $\text{Ca}(\text{HCO}_3)_2$ per liter. Calculate the hardness in terms of CaCO_3 equivalents in mg/l, Degree clark and degree french?

Q3 How many grams of MgCl_2 (M.W.=95) dissolved in water will give hardness of 76ppm ?



Calculate the temporary hardness, permanent magnesium hardness, total permanent hardness & total hardness in terms of calcium carbonate equivalents in a water sample containing calcium bicarbonate (12.2 mg), magnesium bicarbonate (8.2 mg), magnesium sulphate (5.6 mg), magnesium chloride (6.2 mg), calcium sulphate (10.3 mg) & sodium sulphate (7.5 mg). Given that at. Wt. of $\text{Mg}=24$ amu, $\text{S}=32$ amu, $\text{Cl}=35.5$ amu, $\text{Ca}=40$ amu, $\text{O}=16$ amu, $\text{C}=12$ amu, $\text{H}=1$ amu.

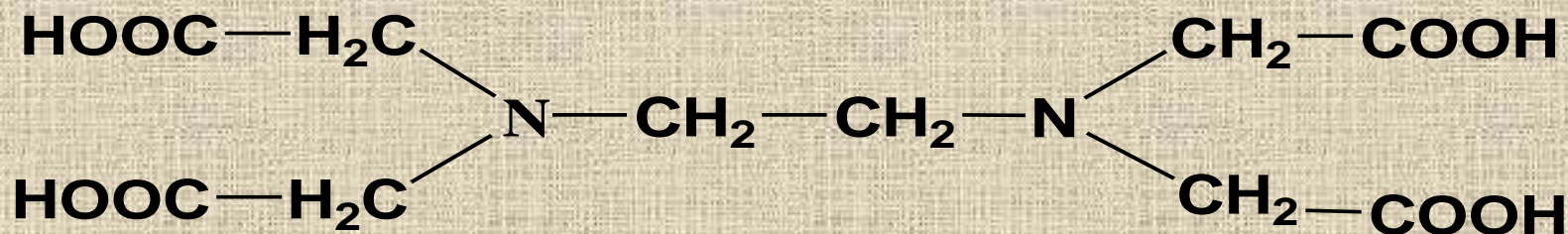


Lecture 3

Determination of hardness of EDTA method



Complexometric Titration



EDTA: Ethylenediamine tetraacetic acid

- Used for determining the conc. of hardness causing agents
- Form complexes with metal ions viz. Ca^{2+} , Mg^{2+}

How to determine hardness of water



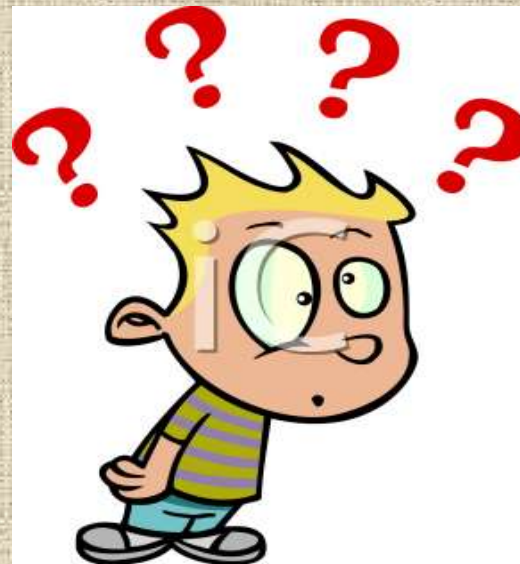
What we need ?

- EDTA solution
- Hard water (Temporary/Permanent)
- Erichrome black-T (Indicator-blue, org. dye)

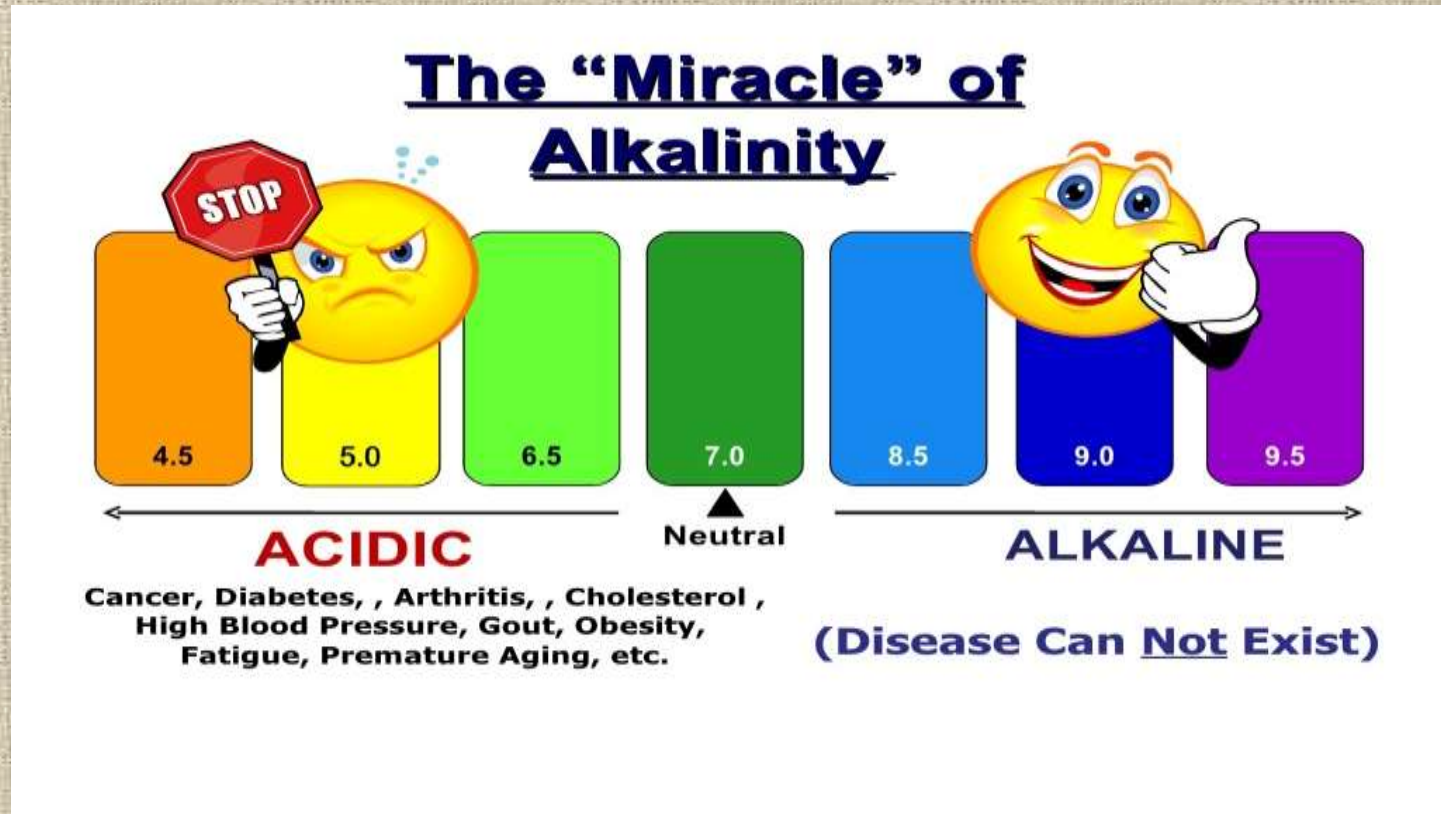
Procedure

- Take known quantity of hard water
- Add few drops of EBT indicator
- EDTA added

A 100 ml sample of water require 13.5 ml of 0.02 M EDTA for titration using EBT as indicator. Another 100 ml of water from the same source was boiled and precipitate removed by filtration, the filtrate requires 6 ml of 0.02 M EDTA for titration. Calculate the total hardness, permanent hardness & carbonate hardness of water sample.



Alkalinity of water



The Hardness Index for Natural Waters

Water is termed "hard" if it contains substantial concentrations of calcium and/or magnesium ions

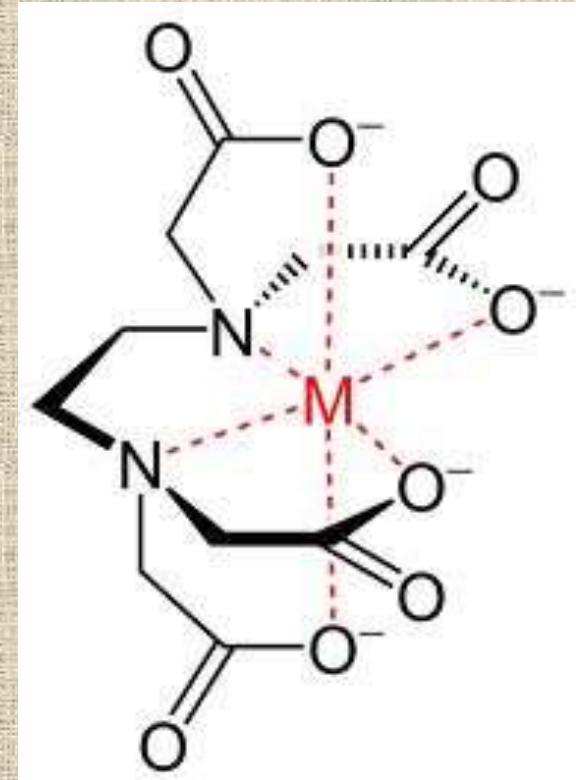
$$\text{hardness} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}]$$

Experimentally, hardness can be determined by titrating a water sample with ethylenediaminetetraacetic acid (EDTA)

Traditionally, hardness is expressed *in milligrams (per liter) of calcium carbonate that contains the same total number of dipositive ions.*

Source of calcium in water: CaCO_3 , CaSO_4

Source of Magnesium in water: $\text{CaMg}(\text{CO}_3)_2$

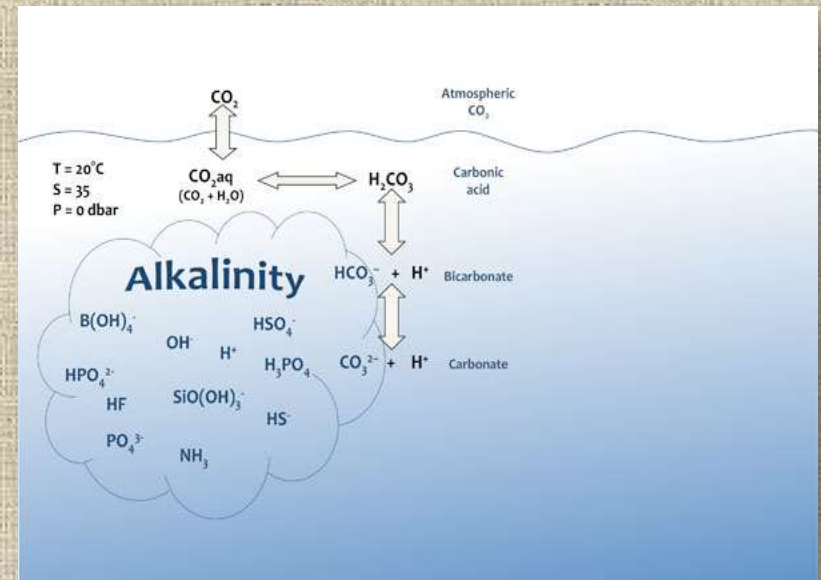


Alkalinity: ability of water to neutralize acids

Alkalinity of water is due to presence of carbonates, bicarbonates & hydroxides of sodium, potassium, magnesium & calcium, alone or in combination.

*

However hydroxide and bicarbonate doesn't exist together.



Types

CO_2 alkalinity: 4.2-4.5 pH

CO_2 & bicarbonate alkalinity: 4.2-4.5 & 8.2-8.4 pH

Bicarbonate & carbonate alkalinity: 8.2-8.4 & 9.6 pH

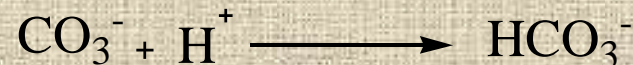
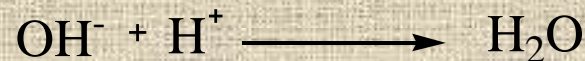
Hydroxyl alkalinity: above 9.6 pH

Significance:

- Lowers the acidity of water
- Its amount determines its suitability for irrigation processes or waste water treatment

Estimation of Alkalinity:

- titration against standard acid solution, in presence of suitable indicators.
- volume of acid used up to the phenolphthalein end point marks neutralization of HCO_3^- ions, P-alkalinity.
- volume of acid used up to methyl orange end point indicates OH^- ions neutralization, M-alkalinity.



Formula to calculate

The **table1** below shows the type and amount of alkalinity in water

S.No	Result of Titration	OH ⁻ ion	CO ₃ ²⁻	HCO ₃ ⁻
1	P=0	nil	nil	M
2	P=M	P or M	nil	nil
3	P=1/2M(V1=V2)	nil	2P	nil
4	P>1/2M(V1>V2)	2P-M	2(M-P)	nil
5	P<1/2M(V<V2)	nil	2P	M-2P

A 100 ml water sample required 25 ml of 0.05N Sulphuric acid for phenolphthalein end point and another 10 ml for methyl orange end point. Determine the nature and amount of alkalinity present in the water.



Effect and significance of Alkalinity

- Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes.
- Large amount of alkalinity imparts bitter taste in water.
- The resultant precipitate can corrode pipes and other accessories of water distribution systems.
- Alkalinity as carbonate and bicarbonate of saline water is very important in tertiary recovery processes for recovering petroleum.
- The alkalinity value is necessary in the calculation of carbonate scaling tendencies of saline waters.
- The alkalinity acts as a pH buffer in coagulation and lime-soda softening of water.
- In wastewater treatment, alkalinity is an important parameter in determining the amenability of wastes to the treatment process and control of processes such as anaerobic digestion.