Thermodynamics & Thermochemistry

By
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Oxidation Number Concept

Oxidation Number is defined as **actual charge of atom**

Decrease in oxidation number is called reduction

And increase in oxidation number is oxidation

It is not same as valency. Valency represents charge in whole numbers with no plus or minus sign

Basics For Calculation of Oxidation Number

1. Electron shared between two unlike atoms are counted to be with more electronegative atom

2. Oxidation number of an atom in an element in its uncombined state is always zero

Oxidation & Reduction

Oxidation

- ✓ the gain of oxygen, $2Fe(s) + O_2(g) \rightarrow Fe_2O_3(s)$
- ✓ the loss of hydrogen, $C_2H_2(g) + O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$
- ✓ the loss of electrons (de-electronation), $Zn(s) \rightarrow Zn^{++} + 2e^-$

Reduction

- ✓ The loss of oxygen $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l)$
- ✓ The gain of hydrogen $CH_3COCH_3 \xrightarrow{LiAlH_4} CH_3 - CH(OH)CH_3$
- ✓ The gain of electron $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

Oxidation Number For Some Element

1. Oxidation number of H in a compound is = +1

   Except in metal hydrides Where it is $= -1$

2. For O in compounds oxidation number $= -2$

   Except in peroxides where it is $= -1$

   in OF_2 it is = +2

   in superoxide it is $= \frac{-1}{2}$

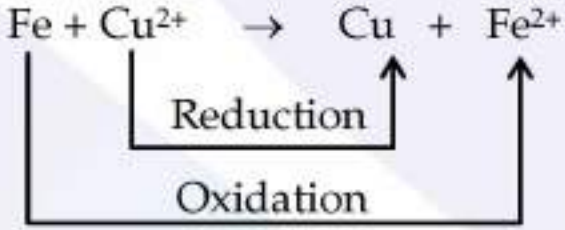
Fluorine is more electronegative than oxygen

3. Fluorine has oxidation number of -1 in all of its compound

Redox Reaction

Complete reaction showing oxidation and reduction together

1



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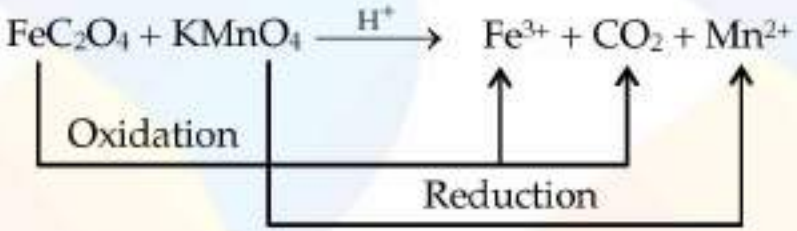

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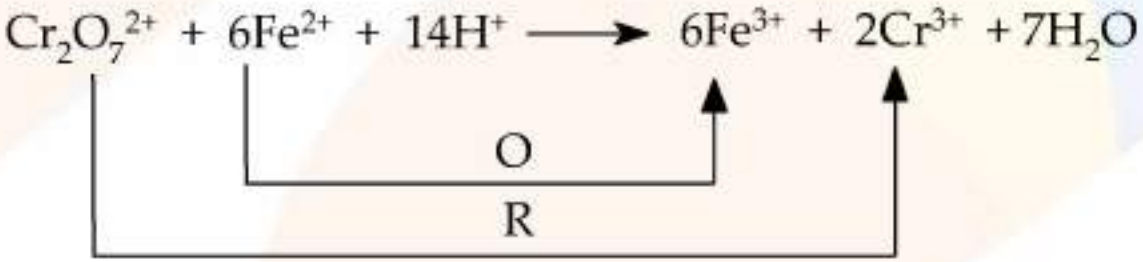
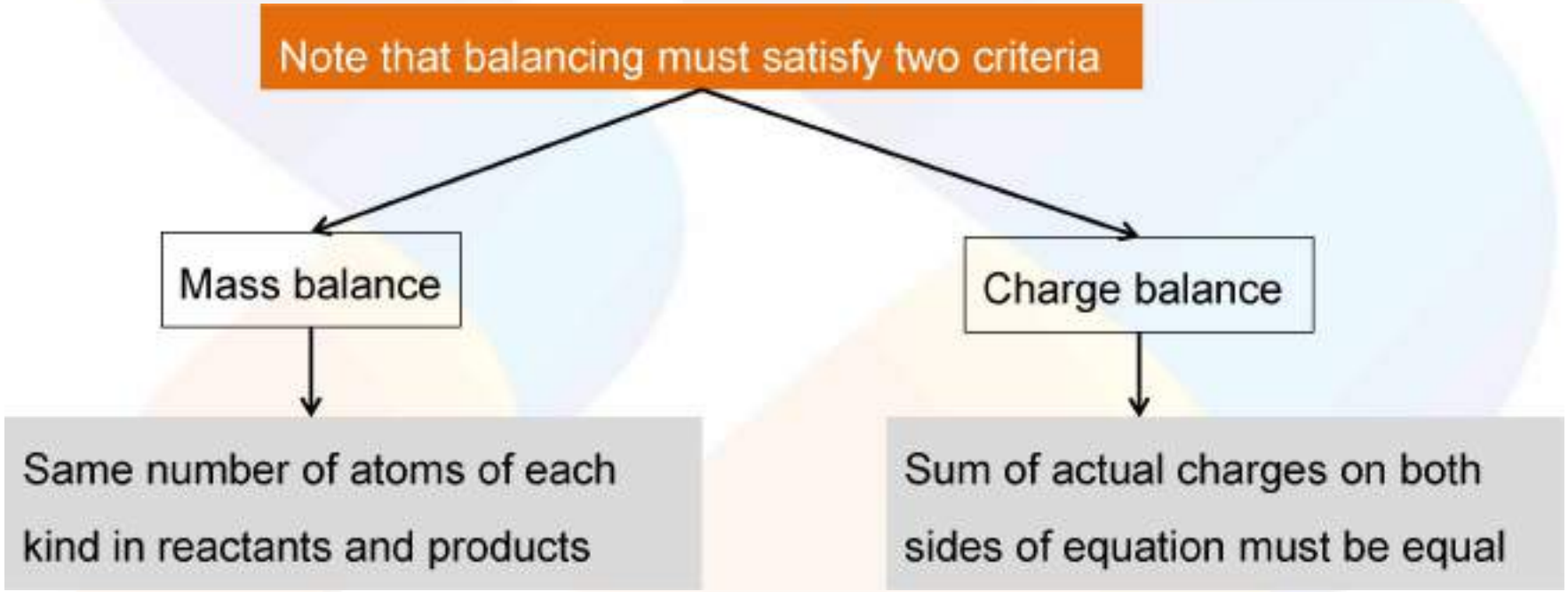


Balancing of Redox Reactions

Total increase in oxidation numbers must equal to the total decrease in oxidation numbers



Half–Reaction Method to Balance Reactions

2 equations describing oxidation and reduction in redox are separated and completely balanced

Note that use of half – reaction permits us to balance equations using only the principle of atom and charge conservation

The number of electrons gained and lost in each half-reaction are equalized and finally half-reactions are added to get overall balanced equation

Half–Reaction Method: Balancing Reaction

$$NO_3^- + H_2S \xrightarrow[\text{acidic medium}]{H^+} HSO_4^- + NH_4^+$$

Balancing the Above Reaction

1. $N^{5+} + 8e \rightarrow N^{3-}$
2. $S^{2-} \rightarrow S^{6+} + 8e$
3. $NO_3^- + H_2S \rightarrow NH_4^+ + HSO_4^-$
4. No other atom (except H and O) is unbalanced
5. Balancing O atom. This is made by using H_2O and H^+ ions. Add desired molecules of H_2O on the side deficient in O atom and double H^+ on opposite side

$$NO_3^- + H_2S + H_2O \longrightarrow NH_4^+ + HSO_4^- + 2H^+$$

6. Balancing charge by H^+

$$NO_3^- + H_2S + H_2O + 3H^+ \longrightarrow NH_4^+ + HSO_4^- + 2H^+$$

Balanced equation is

$$NO_3^- + H_2S + H_2O + H^+ \longrightarrow NH_4^+ + HSO_4^-$$

Oxidation Number Change Method

Note that the method is based on the fact that total increase in oxidation number is equal to total decrease in oxidation number

Assign oxidation number to elements undergoing changes in oxidation numbers AND first balance atoms of these elements only

Connect atoms of element undergoing changes in oxidation number

Insert coefficients to make total increase and decrease in oxidation numbers equal

Balance atoms of other elements

Balancing H And O Atoms In Aqueous Solutions

Acidic medium

- For one excess O add one H_2O on **other side**
- And add $2H^+$ on same side

Basic medium

- For one excess O add one H_2O on **same side**
- And Add two OH^- on other side
- In case H-atoms are unbalanced

For one excess H-atom

- Add one OH^- on same side
- one H_2O on other side

In some cases both H & O atoms are balanced together by adding H_2O only

Environmental Chemistry

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Environmental Chemistry

It is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings.

A substance, which causes pollution, is known as **pollutant.**

Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and produced due to human activities or due to natural happenings.

Pollutants can be degradable, like discarded vegetables which rapidly break down by natural processes.

Pollutants which are slowly degradable, remain in environment in an unchanged form for many decades. For example, substances such as dichlorodiphenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc.

Atmospheric Pollution

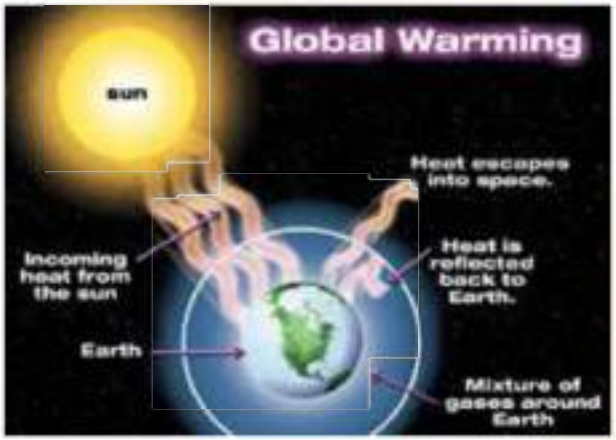
- Lowest region of atmosphere in which human beings along with other organisms live is called troposphere.
- It extends up to the height of ~ 10 km from sea level.
- It is a turbulent, dusty zone containing air, much water vapour and clouds.
- Above troposphere, between 10 and 50 km above sea level lies stratosphere.

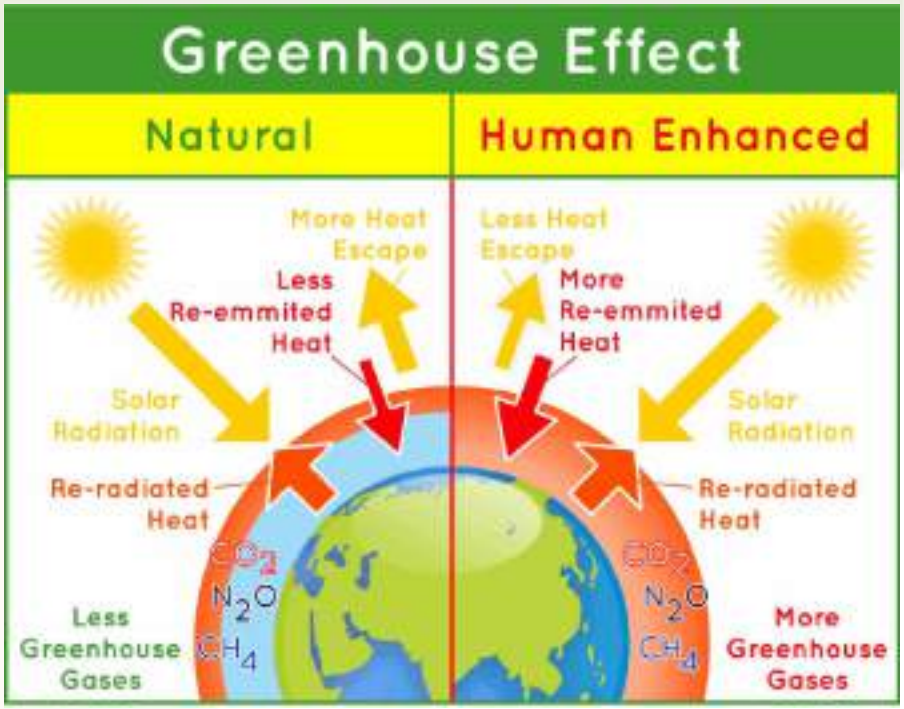
It contains dinitrogen, dioxygen, ozone and little water vapour .

Greenhouse Gasses and Global Warming

The dominant gases of the atmosphere (nitrogen and oxygen) are transparent to infrared, the so-called **Greenhouse Gasses**, primarily water vapour (H_2O), CO_2, and methane (CH_4), absorb some of the infrared radiation. They collect this heat energy and hold it in the atmosphere, delaying its passage back out of the atmosphere.

Global Warming is the increase of Earth's average surface temperature due to effect of greenhouse gases, such as carbon dioxide emissions from burning fossil fuels or from deforestation, which trap heat that would otherwise escape from Earth e.g. CFCs.





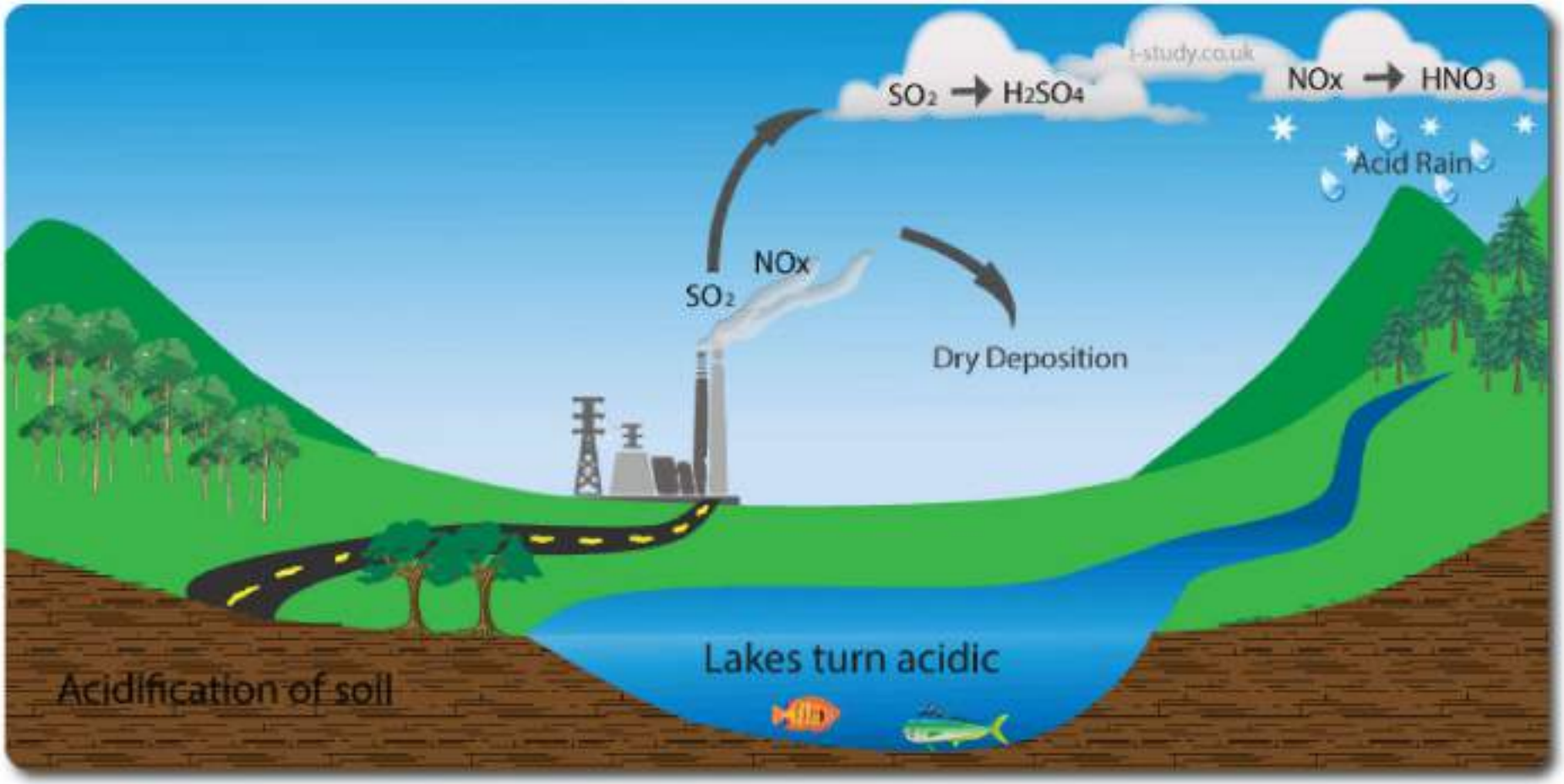
Causes of Global Warming

- Besides CO_2, other greenhouse gases are CH_4, water vapour, nitrous oxide, CFCs and ozone.
- Methane is produced when vegetation is burnt, digested or rotted in absence of oxygen
- Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels.
- Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning etc. and damages the ozone layer.
- Nitrous oxide have increased due to use of chemical fertilizers and burning of fossil fuels

Average global temperature will increase and may lead to melting of polar ice caps and flooding of low lying areas all over the earth.

Increase in temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

Acid Rain Deposition



Causes of Acid Rain

The chemicals in acid rain can cause paint to peel, corrosion of steel structures, and erosion of stone statues.

➢Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth.

➢It affects plants and animal life in aquatic ecosystem.

2. Particulate Pollutants

➢Particulates pollutants are minute solid particles or liquid droplets in air.

➢Present in vehicle emissions, smoke particles, dust particles and ash from industries.

Viable particulates e.g., bacteria, fungi, moulds, algae etc., are minute living organisms dispersed in atmosphere.

Ozone Hole

- In summers, nitrogen dioxide and methane react with chlorine monoxide and chlorine atoms forming chlorine sinks, preventing ozone depletion, whereas in winter, polar stratospheric clouds are formed over Antarctica.

- Chlorine radicals thus formed, initiate the chain reaction for ozone depletion.

$$ClO^{\cdot} + NO_2 \longrightarrow ClONO_2$$

$$Cl^{\cdot} + CH_4 \longrightarrow CH_3^{\cdot} + HCl$$

$$ClONO_2 + H_2O \longrightarrow HOCl + HNO_3$$

$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3$$

$$HOCl \xrightarrow{UV} {\cdot}OH + Cl$$

$$Cl_2 \xrightarrow{UV} 2Cl^{\cdot}$$

Effects of Depletion of the Ozone Layer

Effects of Depletion of the Ozone Layer

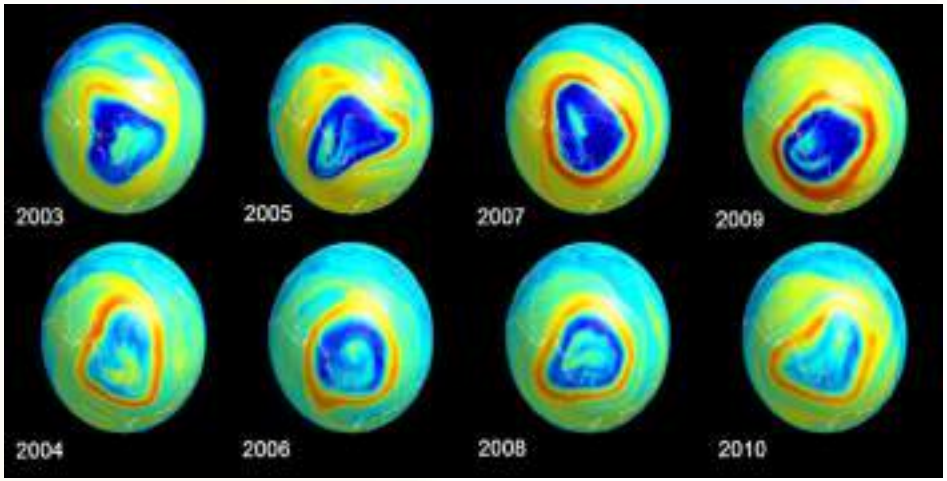
➢With depletion of ozone layer, more UV radiation filters into troposphere.

➢UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc.

➢Plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells.

➢It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil.

➢Increase in UV radiations damage paints and fibres, causing them to fade faster.



Water Pollution

- Pollution of water originates from human activities.
- Through different paths, pollution reaches surface or ground water.
- Non point sources of pollution are those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc.

Causes of Water Pollution

(i) Pathogens:

- Most serious water pollutants are disease causing agents called pathogens.
- Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta.
- Human excreta contain bacteria such as Escherichia coli and Streptococcus faecalis which cause gastrointestinal diseases.

Water Pollution-2

(ii) Organic wastes:

- amount of oxygen required by bacteria to break down the organic matter is called Biochemical Oxygen Demand (BOD).
- Amount of BOD in water is a measure of amount of organic material in the water.
- Clean water have BOD less than 5 ppm whereas highly polluted water have BOD value of 17 ppm or more.

(iii) Chemical Pollutants:

- Water soluble inorganic chemicals include heavy metals such as cadmium, mercury, nickel etcconstitute an important class of pollutants.
- All these metals are dangerous to humans because our body cannot excrete them.
- These metals can damage kidneys, central nervous system, liver etc.
- Acids (like sulphuric acid) from mine drainage and salts such as raw salt used to melt snow and ice in colder climates (sodium and calcium chloride) are water soluble chemical pollutants

Eutrophication

The enrichment of a water body with nutrients, usually with an excess amount of nutrients. This process induces growth of plants and algae and due to the biomass load, may result in oxygen depletion of the water body.

One example is the "bloom" or great increase of phytoplankton in a water body as a response to increased levels of nutrients. Eutrophication is almost always induced by the discharge of phosphate-containing detergents, fertilizers, or sewage, into an aquatic system.

- Organic chemicals are another group of substances found in polluted water
- Petroleum products pollute many sources of water e.g., major oil spills in oceans.
- Bloom-infested water inhibits growth of other living organisms in water body.