

APPLIED CHEMISTRY-I

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(An ISO 9001:2008 Certified Company)

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Applied Chemistry–I

Copyright ©VAYU EDUCATION OF INDIA

ISBN: 978-93-83137-15-2

First Edition: 2013

Price: ₹ 70/-

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Printed & bounded in India

Published by:

(An ISO 9001:2008 Certified Company)

VAYU EDUCATION OF INDIA

2/25, Ansari Road, Darya Ganj, New Delhi-110 002

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Chapter-1

Acids-Bases, Catalysis

1.1 THEORY OF ACIDS AND BASES

The term Lewis acid refers to a definition of acid published by Gilbert N. Lewis in 1923, specifically: An acid substance is one which can employ an electron lone pair from another molecule in completing the stable group of one of its own atoms. Thus, H_3O^+ is a Lewis acid, since it can accept a lone pair, completing its stable form, which requires two electrons.

A Lewis base, then, is any species that donates a pair of electrons to a Lewis acid to form a Lewis adduct. For example, OH^- and NH_3 are Lewis bases, because they can donate a lone pair of electrons.

Some compounds, such as H_2O , are both Lewis acids and Lewis bases, because they can either accept a pair of electrons or donate a pair of electrons, depending upon the reaction.

Reformulation of Lewis Theory

Lewis had suggested in 1916 that two atoms are held together in a chemical bond by sharing a pair of electrons. When each atom contributed one electron to the bond it was called a covalent bond. When both electrons come from one of the atoms it was called a dative covalent bond or coordinate bond. The distinction is not very clear-cut. For example, in the formation of an ammonium ion from ammonia and hydrogen the ammonia molecule donates a pair of electrons to the proton the identity of the electrons is lost in the ammonium ion that is formed. Nevertheless, Lewis suggested that an electron-pair donor be classified as a base and an electron-pair acceptor be classified as acid.

A more modern definition of a Lewis acid is an atomic or molecular species with a localized empty atomic or molecular orbital of low energy. This lowest energy molecular orbital (LUMO) can accommodate a pair of electrons.

1.2 CATALYSIS

A catalyst is defined as a substance which increases the rate of a chemical reaction without being consumed in the process.

The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as catalysis.



Presence of certain substances in exceedingly small amounts often considerably affects the activity of catalyst.

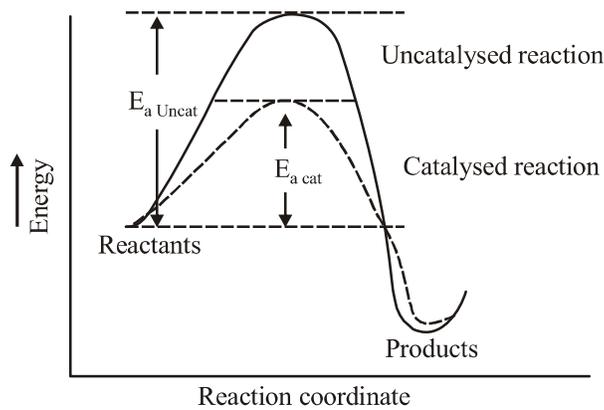


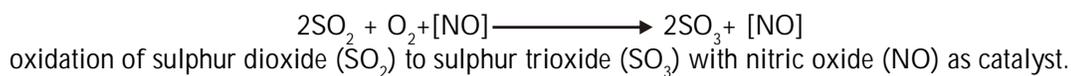
Fig.

'A catalyst lowers the activation energy, E_a of a reaction there by increasing the rate of reaction' There is no doubt that usually a catalyst accelerates a reaction but a number of case are now known where the catalyst definitely retard the rate of reaction.

Thus a catalyst is now-a-days defined as a substance which alters the rate of a chemical reaction itself remaining chemically unchanged at the end of the reaction. A catalyst may increase or decrease the rate of chemical reaction. Thus a catalyst which enhances the rate of reaction is called a **positive catalyst** and a catalyst which retards the rate of a reaction is called a **negative catalyst**.

Examples:

Positive catalyst:



Negative Catalyst:



The decomposition of hydrogen peroxide is retarded by the presence of dilute acids or glycerol.

Substances which increases the activity of catalyst are known as **promoters** and substance which inhibit catalytic activity are called, **poisons**.

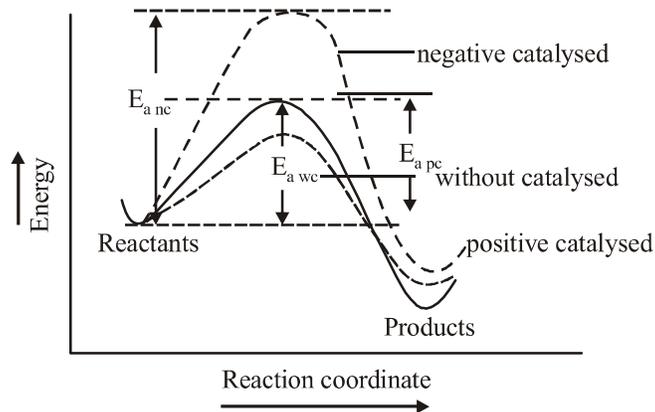


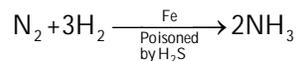
Fig.

Examples of Promoters and Poisons

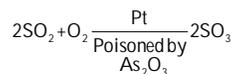
- (i) Molybdenum (Mo) or aluminum oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.



- (ii) The iron catalyst used in the synthetic of ammonia (Haber process) is poisoned by H_2S



- (iii) The platinum catalyst used in the oxidation of sulphur dioxide (contact process) is poisoned by arsenic oxide (As_2O_3)



Type of Catalysis

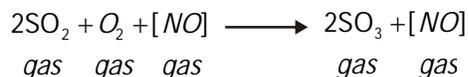
There are two main types of catalysis

- Homogeneous Catalysis
- Heterogeneous Catalysis
- Enzyme Catalysis

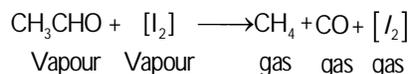
(a) Homogeneous Catalysis: The catalytic reaction where in all reactants, products, and the catalyst itself are in the same phase is called homogeneous catalysis.

Examples of Homogeneous catalysis:

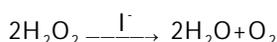
- Oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) with nitric oxide (NO) as catalyst



- (ii) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst.



- (iii) Decomposition of hydrogen peroxide (H_2O_2) in the presence of iodide ion (I^-) as catalyst

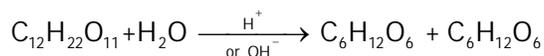


Acid-Base Catalysis

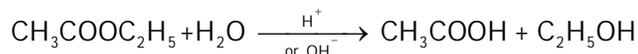
A number of homogeneous catalytic reactions are known which are catalysed by acids or bases or both acids and bases

Examples:

- (i) Inversion of cane sugar: (Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst)



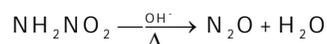
- (ii) Hydrolysis of an ester in the presence of acid or alkali



- (iii) Decomposition of diacetone alcohol in presence of OH^- to form acetone



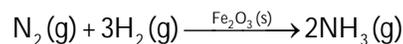
- (iv) Decomposition of nitroamide.



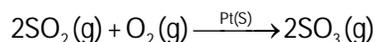
- (b) **Heterogeneous Catalysis:** The catalysis in which the catalyst is in a different physical phase from the reactant is termed Heterogeneous catalysis.

Examples:

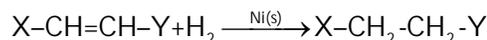
- (i) Formation of ammonia from nitrogen and hydrogen under the catalytic influence of iron oxide.



- (ii) Oxidation of sulphur dioxide to sulphur trioxide in the presence of finely divided platinum



- (iii) Hydrogenation of unsaturated compounds in the presence of nickel



(c) Enzyme Catalysis:

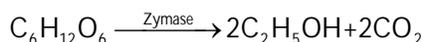
The catalysis brought about by enzymes is known as enzyme catalysis.

Example:

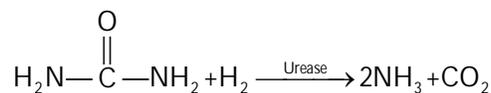
1. Inversion of cane sugar ($C_{12}H_{22}O_{11}$) by invertase present in yeast.



2. Conversion of glucose into ethanol by zymase present in yeast.



3. Hydrolysis of urea (NH_2CONH_2) by urease present in soybean.



- The rate of enzyme catalysed reaction is increased with rise of temperature but up to a certain point.

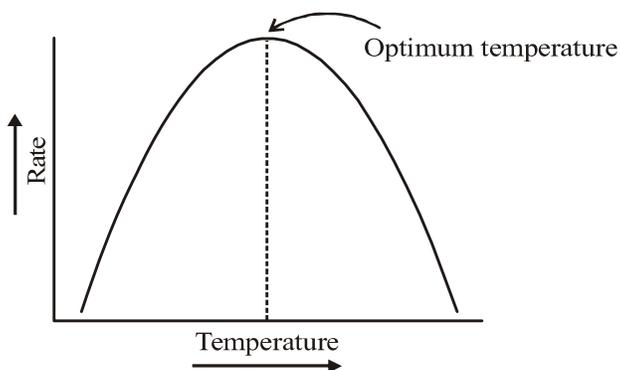


Fig.

The optimum temperature of enzyme reaction occurring in human body is 37°C (98.6°F) much higher temperatures, all physiological reaction will cease due to loss of enzymatic activity.

- Rate of an enzyme catalysed reaction varies with pH of the system.

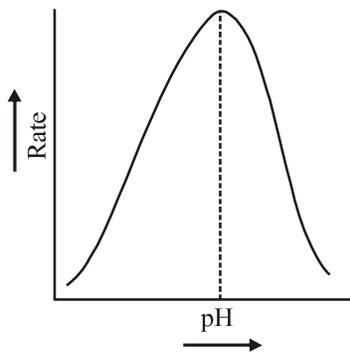


Fig.

Note: The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4 i.e the pH of the blood and body fluids.

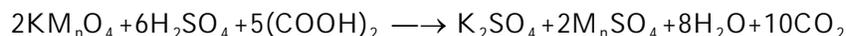
1.3 CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of reactions.

- (i) The catalyst remains unchanged in amount and chemical composition at the end of reactions
- (ii) Only a small quantity of the catalyst is generally needed to produce almost unlimited reaction. For example, one ten millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.
- (iii) **A catalyst is specific in its action.** While a particular catalyst work for one reaction, it will not necessarily work for another reaction.
For example manganese dioxide (MnO_2) can catalyze the decomposition of potassium chlorate but not that of potassium nitrate or potassium perchlorate. Thus manganese dioxide is specific in its action.
- (iv) **The catalyst does not initiate the reaction.** The reaction is already occurring through extremely slowly in the absence of a catalyst The function of the catalyst seems to be only to speed up the reaction considerably. The reaction in the presence of a catalyst takes place through some alternative path which requires much lower energy of activation. Hence it is speed up.
- (v) **The catalyst cannot alter the nature of the products of the reaction.**
The combination of nitrogen and hydrogen for example under suitable conditions, results invariably in the formation of ammonia whether a catalyst is added or not.
- (vi) **A catalyst is poisoned by certain substances.**
It has been found that impurities of any type even if present in small amounts inhibit or retard the rate of catalyzed reactivity to a large extent. These impurities are called catalytic poisons. For example, the rate combination of sulphur dioxide and oxygen is slowed down, considerably if some arsenic components are present even in traces.

Auto Catalysis

In certain reactions, one of the products act as a catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate represented as



Increases in velocity as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed in the reaction.

This type of phenomenon in which one of the products itself acts as a catalyst is known as **auto catalysis**.

Theories of Catalysis

There are two main theories of catalysis

- (i) Intermediate compound formation theory.
- (ii) The adsorption theory.

In general, the Intermediate compound formation theory applies to **homogenous catalytic reaction** and the adsorption theory applies to **heterogeneous catalytic reactions**.

(i) **Intermediate Compound Formation Theory:** As already discussed a catalyst function by providing a new pathway of lower activation energy. In homogeneous catalysis, it does not so by forming an intermediate compound with one of the reactants. The highly reactive compound then reacts with the second reactant to yield the product, releasing the catalyst. Let us illustrate it by taking the general reaction.



Where C acts a catalyst. The reaction proceeds through the reaction



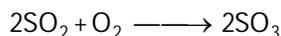
Intermediate



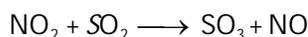
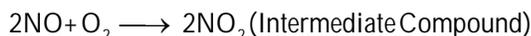
The activation energies of the reactions (2) and (3) are lower than that of the reaction (1) Hence the involvement of the catalyst in the formation of the intermediate compound and its subsequent decomposition, accelerates the rate of the reaction 1 which was originally very slow.

Examples-1: Catalytic oxidation of sulphur dioxide (SO_2) in the presence of nitric oxide (NO) as catalyst.

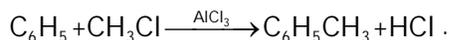
(process for sulphuric acid)



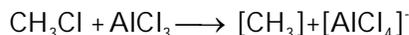
Mechanism:



Example-2: formation of methylbenzene, $C_6H_5CH_3$ by reaction between benzene, C_6H_6 and methyl chloride, CH_3Cl , using aluminium chloride, $AlCl_3$ as catalyst Friedel-Crafts reaction.



Mechanism:



Intermediate compound

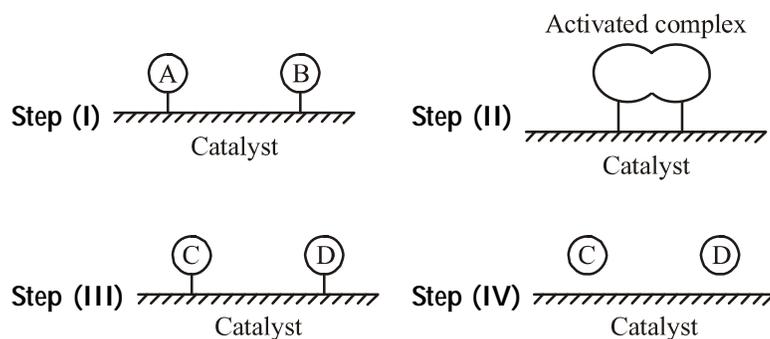


It may be noted that the actual isolation of intermediate compounds which would prove their existence is very difficult. In general, the intermediate compounds suggested as being formed are usually plausible rather than proved.

(ii) **Adsorption theory:** This theory explains the a reaction between two gases catalysed by a heterogeneous mechanism. Here the catalyst function by adsorption of the reacting molecules on its surface.

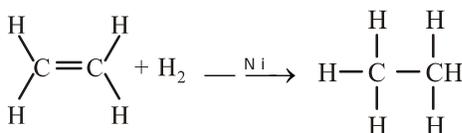


- **Adsorption of reactant molecules:** The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak vander Waal's forces or partial chemical bonds.
- **Formation of activated complex:** The particles of the reactants adjacent to one another join to form an intermediate complex (A-B). The activated complex is unstable.
- **Decomposition of activated complex:** The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.
- **Desorption of products:** The particles of the products are desorped or released from the surface. They are stable and can lead an in dependent existence.

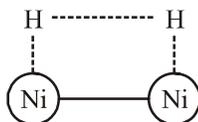


For Example:

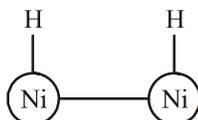
Hydrogenation of ethene in presence of Nickel



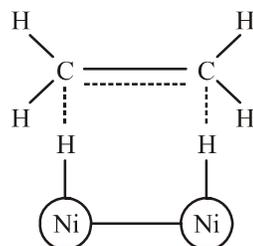
Adsorption of Hydrogen molecules



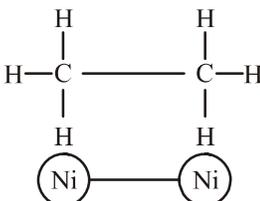
H - H bonds are broken



Formation of activated complex



Decomposition of activated complex



1.4 INDUSTRIALLY IMPORTANT CATALYTIC REACTION OR INDUSTRIAL APPLICATION OF CATALYSTS.

Catalyst find extensive use in the chemical Industry. They are used in gaseous, liquids or solid forms. A few examples of catalyst that are of major importance in chemical industry are as follows:

- (i) Ziegler- Natta polymerization of olefins and dienes to yield stereo regular polymers uses a mixture of titanium (III) compounds and aluminum alkyls as catalyst.
- (ii) Ni, Fe and Pt are used to accelerate reactions in which hydrogen is added to another atom or compound.
- (iii) Pt, V_2O_5 and MnO_2 are used to catalyse the union of O_2 and SO_2 in the manufacture of H_2SO_4 .
- (iv) Chromium oxide may be used to convert a hydrocarbon such as heptane into toluene used for making TNT.
- (v) Carbonylation of methanol to manufacture of acetic acid is catalysed by rhodium catalysts $[Rh_2 CO_2]_2$?
- (vi) Wacker process involves the use of organometallic catalyst of Pd for the selective oxidation of ethylene to yield acetaldehyde
- (vii) Olefin hydrogenation to yield alkenes is catalyzed by Wilkinson catalyst $RhCl(pPPH_3)_3$
- (viii) Manufacture of L-dopa, achiral amino acid used in the treatment of Parkinson's disease is obtained by asymmetric hydrogenation of acetamidocinnamic acid derived by-rhodium catalyst to give L-dopa.

Table given below includes some catalytic processes of technical importance.

Table. Catalytic Processes of Technical Importance

S.No.	Types of reaction	Important examples	Common Catalysts
1.	Oxidation	1. Oxidation of NH_3 to HNO_3 2. Oxidation of SO_2 to SO_3 3. Preparation of ethylene oxide from ethylene	Spongy Pt, MnO_2 , rare earth oxides. Pt, V_2O_5 Ag_2O

		4. Preparation of HCHO from CH ₄ 5. Oxidation of alcohols to aldehydes.	Fe ₂ O ₃ , Cr ₂ O ₃ Cu, Ag and their oxides
2.	Hydrogenation	1. Synthesis of NH ₃ catalysts. 2. Hydrogenation of fats and oils 3. Hydrogenation of coal, coaltar	Promoted Fe, Ni Sulphides and oxalates of Sn Mo, W etc.
3.	Dehydrogenation	1. Preparation of styrene from ethyl benzene.	Cr ₂ O ₃ -Al ₂ O ₃
4.	Dehydration	1. Preparation of olefines from alcohols. 2. Preparation of amines from amides. 3. Preparation of HCN from CO+NH ₃	Al ₂ O ₃ , SiO ₂ H ₃ PO ₄ , H ₂ SO ₄ Oxide of Al, Th, Ce, Fe,
5.	Hydration	1. Preparation of CH ₃ CHO from C ₂ H ₂	Hg salts
6.	Halogenation	1. Preparation of vinyl chloride 2. Preparation of tetrachloromethane.	FeCl ₃
7.	Isomerization	1. The Preparation of isopentane, iso-octane and other branched aliphatic hydrocarbons.	Supported Ni and Pt, AlCl ₃
8.	Polymerisation	1. The Preparation of synthetic rubber from butadiene, isoprene, styrene etc. 2. Preparation of plastics from ethylene, propylene, vinyl compound acrylates, phcnols, aldehydes, polybasic acids.	NaK, Li-AIH Oxides of transition metals and also Cu ₂ Cl ₂ , H ₃ PO ₄ , BF ₃ , AlCl ₃ etc.
9.	Alkylation	1. Preparation of ethyl benzene	SiO ₂ -Al ₂ O ₃ , AlCl ₃
10.	Decomposition	1. Cracking of high boiling petroleum hydrocarbons to the gasoline fractions, ethylene, butane-butene etc.	Different type of clays, AlCl ₃ , SiO ₂ etc.
11.	Miscellaneous Catalytic reaction	1. Synthesis of methonal. 2. Higher alcohol synthesis, 3. Preparation of branched hydrocarbons.	ZnO, Cr ₂ O ₃ ZnO, Cr ₂ O ₂ ThO ₂ , SnO ₂ , Al ₂ O ₃

The suitability of a catalyst for chemical industry is determined by considerations of activity and durability. The catalyst must be able to bring about the desired reaction at acceptable rate under conditions of temperature and pressure that are practicable. It must also be able to sustain the desired reaction over prolonged periods. Desirable characteristics of an industrial catalyst are:

1. High surface area and porosity.
2. High thermal stability and mechanical strength.
3. Freedom from any constituent which may impair the catalyst activity.
4. Long life.
5. Possibility of easy regeneration or reactivation.

Chapter-2

Pollution

2.1 ENVIRONMENTAL POLLUTION

Introduction

The increase in human activities like industrialisation and the release of industrial wastes into the environment; have been of serious concern in recent years in view of environmental pollution. Serious degradation and depletion is caused through excessive use, misuse and mismanagement of resources to meet the human needs and greed. The situation poses major threat to the survival of all life-forms.

Environmental Pollution (Definition and Scope)

It includes the study of sources and effects of some specific chemical species, called pollutants, on air, water and soil. Pollutant is a material produced either by a natural source or by human activity, which has an adverse effect on the environment, that is, which causes environmental pollution. It can be defined as an alteration of the environment that results from human activity and that adversely affects something of value. People generally fail to correlate interrelationships between humans, other life forms, and the physical environment. Pollution, therefore, is viewed as any deviation from the normal in the natural composition of the environment that adversely affects the life in general.

Environmental pollution, deforestation and population explosion, are endangering the existence of life on the earth. The environmental pollution is interesting to the scientists engaged in scientific and engineering activities as well as the persons involved in research, resource planning and material handling management. It is increasingly realized that future development activity must be viewed in the light of their long-term environmental impact. This situation can be improved by **environmental education** and awareness among masses.

It is defined in various ways as: It may be defined as “an undesirable change in the physical, chemical or biological characteristics of our air, water and land that may harmfully affect human life, other life-forms, industrial processes, living conditions, cultural assets, or our raw material resources”.

It may also be defined as “an addition or excessive addition of certain materials to the physical environment (water, air and lands), making it less fit or unfit for life”.

Environmental pollution can affect humans, animals, plants and materials. It may cause health problems or death in case of humans and animals. It may retard the growth of plants and in some cases injuries. The effect on materials includes corrosion of metals and marble as well as discoloring of paints.

2.2 POLLUTANTS

Pollutants are predominantly the materials or factors, which cause adverse effect on the natural quality of any component of the environment. Common pollutants are the waste products either of human biology, like domestic sewage, the residues and waste of industrial and agricultural processes, automobile exhausts, chemicals from factories, radioactive materials from nuclear plants, etc. However, all pollutants are not waste materials, nitrogen and phosphorus is used to increase soil fertility, but their excess amount may cause water pollution. Many potential pollutants, like CO and ozone, are present as normal constituents of various parts of environment, but in most cases, they are kept at harmless levels by natural processes.

Classification of Pollutants

Pollutants are classified as follows:

- (I) According to the form in which they persist after getting released into the environment, the pollutants may be primary or secondary.
 - (a) **Primary pollutants:** Those pollutants that are emitted directly from the identifiable sources and are found in the atmosphere in the same form in which they were emitted are called **primary pollutants** *e.g.*, DDT, plastic.
 - (b) **Secondary pollutants or derived pollutants:** These are formed by interaction of the primary pollutants. For example, peroxy-acetyl nitrate (PAN) is formed by the reaction of primary pollutants like nitrogen oxides and hydrocarbons during sunlight.
- (II) According to their existence in nature, the pollutants may be quantitative or qualitative.
 - (a) **Quantitative pollutants:** These are the materials, which occur in nature but become pollutant when their concentration reaches beyond a threshold value in the environment. *e.g.*, carbon dioxide, nitrogen oxide.
 - (b) **Qualitative pollutants:** These are the materials that do not occur in the environment but are passed into it through human activities *e.g.*, spraying of herbicides, fungicides, DDT etc.
- (III) According to their disposal by natural means, the pollutants may be biodegradable and nondegradable.
 - (a) **Biodegradable (degradable) pollutants:** These are waste products, which gets slowly degraded by microbes. They cause pollution, if their production exceeds the capacity to degrade them *e.g.*, sewage.
 - (b) **Non-degradable (non-biodegradable) pollutants:** These pollutants could not be decomposed or are decomposed very slowly. They include wastes (*e.g.*, plastics, glass, plastic bottles, polythene bags, used soft drink cans etc.) or poisonous materials (*e.g.*, pesticides like DDT, radioactive materials, heavy metal salts, etc.). The non-biodegradable pollutants are difficult to manage and in there is no treatment process.
- (IV) According to their origin, they may be natural and anthropogenic.
 - (a) **Natural:** Natural pollution is caused by volcanic eruptions, emission of natural gases, soil erosion, cosmic rays, UV rays, etc. Volcanic eruptions add huge masses of toxic gases and particulate matter in the environment.
 - (b) **Anthropogenic:** Pollution is mostly man made; it includes industrial pollution, agricultural pollution, etc.

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Publisher : **Vayu Education**

ISBN : 9789383137152

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