ENVIRONMENTAL CHEMISTRY



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ENVIRONMENTAL

- Environmental chemistry is a science which deals with the study of various chemical reactions taking place in the environment and includes the study of sources and adverse effects of chemical substances produced either by natural source or by human activity on environment i.e. on air, water and soil.
- Environment segments: The environment may be considered to comprise of the following four segments viz. *lithosphere, hydrosphere*, *atmosphere* and *biosphere*. Out of these four segments the atmosphere is of special interest.



ATMOSPHERE

The region of air present on earth is called atmosphere. The air present in the atmosphere consists of a number of gases like N_2 , O_2 , CO_2 , Ar etc. and extends upto a height of about 500 km from the earth's surface. The weight of the atmosphere is approximately 4.5 to $5x10^{15}$ metric tons which is about one millonth of the total weight of the earth.

Composition of the present in the atmosphere:

We have said above the air of the atmosphere consists of a number of gases like N_2 . O_2 , CO_2 , Ar etc. The actual composition of clean dry air near sea-level is that which is shown in Table 1.



NATURAL ATMOSPHERE

Table : 1 Composition of clean dry air near sea-level

Components		Content	
		Per cent by volume	ррт
(a)	Major components		
	Nitrogen (N ₂)	78.09	780900
	Oxygen (O ₂)	20.94	209400
	Water vapour (H ₂ O)	0.15	1000-50000
(b)	Minor components		
	Argon (Ar)	0.934	9340
	Carbon dioxide (CO ₂)	0.032	320
(c)	Trace components		
	Neon (Ne)	0.00182	18.2
	Helium (He)	0.000524	5.24
	Methane (CH ₄)	0.00018	1.8
	Krypton oxide (Kr)	0.00011	1.1
	Nitrogen oxide (N ₂ O)	0.000025	0.25
	Hydrogen (H ₂)	0.0005	0.5
	Xenon (Xe)	0.0000087	0.087
	Sulphur dioxide (SO ₂)	0.0000002	0.002
	Nitrogen dioxide (NO ₂)	0.0000001	0.001
	Ammonia (NH ₃)	0.000001	0.01
	Carbon monoxide (CO)	0.000012	0.12
	Ozone (O ₃)	0.000002	0.02
	Iodine (I ₂)	Trace	Trace



Air Pollution





- The proportions of the various components of the atmosphere more or less remain constant upto a height of about 16 km from the earth's surface. Above this height, gravitational separation begins, although this becomes significant above 130 km.
- Relation between temperature of the atmosphere and the height above the earth's surface : Division of the atmosphere into four regions.

Name of the region	Height above the earth's surface, km	Temperature range °C	Major chemical species present
Troposphere	0-11	15 to -56	O ₂ , N ₂ , CO ₂ , H ₂ O
Stratosphere	11-50	-56 to -2	O ₃
Mesosphere	50-90	-2 to -92	0 ₂ ⁺ , NO ⁺
Thermosphere	90-500	-92 to 1200	0 ₂ ⁺ , 0 ⁺ , NO ⁺

POLLUTION AND POLLUTANTS

The contamination of air, water and soil with substances, which have adverse effect on human beings, animals and plants, is called pollution of air, water and soil respectively. The pollution of air, water and soil is also called environmental pollution. These substances, whose presence in air, water and soil makes them polluted, are called pollutants. Thus a pollutant can be defined as a substance whose contamination with air, water and soil makes them polluted and has adverse effect on living and non-living things.

TYPES OF POLLUTION

- Air pollution : Pollution of atmosphere.
- Water pollution : Pollution of river and sea water.
- Industrial pollution : This pollution is caused by the wastes from industry.
- Noise (sound) pollution : The adverse affects produced by the excessive noise on human beings is called pollution. Excessive noise reduces our hearing capacity.
- Thermal pollution : Excessive of heat affects our health adversely and increase in temperature results in the death of aquatic animals. This is called thermal pollution.
- Radioactive (Radiation) pollution : The radioactive wastes have adverse effect on water, earth and air. The pollution caused by radioactive wastes is called radio active pollution.
- Soil pollution : The contamination of soil with acid rain, excess of fertilizer etc. is called soil pollution.

AIR POLLUTION



- Chemical composition of atmosphere
 Particles
 - lons

- Radical
- Their formation
- Chemical and photochemical Reactions in atmosphere
- Smog formation
- Oxides of N, C, S, O and their effect
- Pollution by chemicals
- Petroleum
- Minerals
- Chlorofluorohydrocarbons

PARTICULATE POLLUTANTS

 Aerosols (Smoke and fog) : Aerosols are the fine particles of smoke and fog having diameter less than 100µ. The particles of aerosols are so small that they behave almost like gases. A detailed discussion of smoke has been given on the subsequent pages of this chapter. The word fog is used for tiny water droplets suspended in the air near the surface of the earth. Fog droplets are produced, when water vapour present in air gets condensed. The formation of fog droplets takes place in winter season. Fog helps in the formation of smog which is very harmful for human beings.

- Fly-ash: We know that when fossil fuels undergo combustion, they produce small ash particle and gases. These particles are carried into the air through these gases and form fly-ash. Coal ash coming out of the chimney of coal based thermal power station is an important example of fly-ash.
- Harmful effects of particulate pollutants present in air:
- The particulate pollutants produce various allergic reactions in our body and many diseases such as bronchial asthma, tuberculosis etc.

Smoke particles present in air combine with the droplets of fog containing poisonous gases discharged by the burning of fossil fuels in homes industries and automobiles and form smog. Smoke particles + Droplets of fog containing poisonous gases \longrightarrow Smog

Smog formed as above causes respiratory problems. Smoke particles also blacken the buildings and our clothes. TYPES OF AIR POLLUTANTS

- Gaseous pollutants : Examples of gaseous air pollutants are CO, CO₂, oxides of nitrogen (NO, NO₂), oxides of sulphur (SO₂, SO₃),O₃ etc.
- Particulate pollutants: These have already been discussed. Smoke and dust particles are the important examples of particulate pollutants.
- Smog and photochemical smog: These have been discussed on the subsequent of this chapter.
- Metallic pollutants: These have been discussed on subsequent pages of this chapter.

CARBON MONOXIDE, CO

Sources of CO: CO is produced by the incomplete combustion of all carbon-containing fuels (incomplete combustion is that which takes place in presence of insufficient quantity of O_2) used in automobile engines and defective furnaces Thus the smoke obtained by the incomplete combustion of petrol in the internal combustion engines of cars buses trucks scooters aeroplanes etc. (The engines used in these motor vehicles are called internal combustion engines, because the petrol which is used as fuel is burnt inside the engine and not separately) contains a lot of CO.



Traffic on road



 When coal, wood and oil are burnt, black smoke is produced. This smoke also contains CO.

 $2C+O_2 \rightarrow 2CO$

- Cigarette smoke also contains CO.
- Incomplete combustion of agricultural and slush matter produces CO.
- The reactions that take place at high temperature in industrial furnance like blast furnace, evolve CO.
- All the above mentioned sources of the production of CO come under human activities. CO is also generated by natural like forest fibres, volcanic eruptions, seed germination, electric discharge during storms etc.

HARMFUL EFFECTS OF CO

 We know that hemoglobin (Hb) present in our body acts as an oxygen-carrier, since it combines with O₂ reversibly to form oxy-hemoglobin, HbO₂.

 $Hb + O_2 \iff HbO_2 + H_2O$

If we breathe in air containing CO, O_2 present in HbO₂ is replaced by CO and carboxy-hemoglobin, HbCO is formed.

 $HbO_2 + CO \longrightarrow HbCO + O_2$

HbCO is a stable compound and its formation takes place, since Hb has more affinity for CO than for O₂. The formation of HbCO makes Hb unable to take up O₂ from the lungs. Thus the formation of HbCO results in that the quantity of O₂ available to the body cells gets reduced.

TREATMENT OF CO POISONING

The most effective treatment of CO poisoning is that the victim is exposed to 2 to 2.5 atm. O₂ under a higher pressure. This results in that CO present in HbCO is substituted by O₂. When HbO₂ comes in contact with the cells of muscles, O₂ is given up by it.

HbCO + $O_2 \longrightarrow$ HbO₂ + CO ; HbO₂ \longrightarrow Hb + O_2

 T monitoring of CO is done by means of nondispersive infrared spectrometer. This technique estimates CO upto a level of 150 ppm and is based on the principle that CO strongly absorbs infrared radiations at certain specific wavelengths.

CARBON DIOXIDE, CO₂

Although small quantity of CO_2 is not usually considered to be pollutant, its excess quantity in the atmosphere has an adverse effect on our climate and thus pollutes the air. Thus greater amount of CO_2 in the atmosphere acts as an air pollutant.



Major suppliers of CO₂ to the atmosphere

- Burning of fossil fuels: The fossil fuels, like coal, natural gas and petroleum, are carbon compounds. When these fuels are burnt, they produce CO₂ which is discharged into the atmosphere. The burning of fossil fuels is releasing about 6000 million tonnes of CO₂ in the atmosphere every year.
- Cultivation of soil: The cultivation of soil also releases large amount of CO₂ into the atmosphere, which is produced by bacteria. The cultivation of land release 2000 million tonnes of CO₂ into the air every year.

- Eruption of volcanoes. CO₂ is also given to the atmosphere through the eruption of volcanoes. This gas comes from the interior of the earth.
- Respiration of living organisms.
- Decay of dead organisms
- Major consumers of CO₂ from the atmosphere
- The green plants absorbs CO₂ gas from the atmosphere to prepare their food (carbohydrates) through the process of photosynthesis, while the oceans dissolve CO₂ gas to form carbonate rocks.



OXIDES OF NITROGEN (NO and NO₂)

- The smoke released by the automobile engines (engines of cars, buses, trucks etc.) contains NO and NO₂. This smoke results by the combustion of petrol or diesel in the engines.
- When coal, oil and natural gas undergo combustion, high temperature produced by the combustion makes N_2 and O_2 present in the atmosphere combine together to form NO and NO_2 . $+O_2, > 100^{\circ}C$ $+O_2$ $N_2 = 2NO = 2NO_2$
- Many chemical plants, like those which manufacture explosives and nitrogenous fertilizers, also produce NO₂. It is also present in tobacco smoke.

 Large amounts of SO₂ and nitrogen oxides are also emitted from power plants and many industrial processes. The mixture containing SO₂ and nitrogen oxides, thus obtained is called flue gases mixture.



Thermal & Nuclear Plants

Harmful effects of NO₂:

- Though NO and NO₂ both are toxic, the latter (i.e., NO₂) is by far more harmful. Some of the harmful effects of NO₂ on human beings, animals and vegetables are given below:
- Formation of nitric acid rain or acid snow and its harmful effects. NO₂ present in the air combines with rainy water or atmospheric moisture in presence of O₂ or O₃ of the air and forms HNO₃.

 $4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$ $2NO_2 + H_2O + O_3 \longrightarrow 2NHO_3 + O_2$

HNO₃ formed as above dissolves in rain water and falls on earth in the form of nitric acid rain or acid snow or acid rain. When this nitric acid rain falls over a historical monument, it gradually eats up the marble stone (CaCO₃) of the monument and corrodes it slowly.

 $CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + CO_2 + H_2O_3$ Nitrogen dioxide (NO₂) present in the air absorbs sunlight and undergoes photo chemical dissociation (photochemical reaction) to form nitric oxide (NO) and free O-atom. Sunlight (Photochemical dissociation NO_2 NO + O (Very reactive) O-atom formed at (a) very reactive and hence combines with another NO₂ molecule and forms free reactive nitrate radical (NO_3) . $O + NO_2 \longrightarrow NO_3$ (Reactive radical) Being reactive, NO_3 , radical combines with another NO_2 molecule to form nitrogen peroxide (N_2O_5) . $NO_3 + NO_2 \longrightarrow N_2O_5$ N₂O₅ combines with rainy wear or moisture present in the atmosphere to form nitric acid rain, HNO₃ $N_2O_5 + H_2O \longrightarrow 2HNO_3$ (Nitric acid rain)

- NO₂ causes extensive leaf-drop in the plants.
- Nitrogen oxides react with O₂ to produce another pollutant namely ozone.
- It has been shown that if monkeys inhale NO₂ of 15-30 ppm concentration for 2 hours, their lungs, heart, liver and kidneys are damaged.
- NO₂ is very corrosive and attacks skin.
- NO₂ helps in the formation of smog (which is combination of smoke and fog). Smog causes irritation in eyes due to the presence of O₃ in it.
- Oxides of nitrogen bring about corrosion of teeth and cause loss of appetite.
- We know that the atmosphere contains a layer of O₃ which absorbs harmful ultra-violet radiations coming from the sun and reaching the earth.

If these radiations reach the earth, they will cause skin cancer and will destroy the organic molecules necessary for life. O₃ layer prevents the ultra-violet radiations to come to the earth. NO and NO₂ present in the atmosphere decompose O₃ to O₂ and are generated again.

 $NO + O_3 \longrightarrow NO_2 + O_2$ $NO_2 + O_3 \longrightarrow NO + 2O_2$

Thus we see that NO and NO₂ both present in the atmosphere destroy O₃ layer. Greater is the amount of NO and NO₂ in the atmosphere, greater is the percentage of O₃ which is destroyed.



Chimneys of Industries

OXIDES OF SULPHUR (SO₂ AND SO₃)

Sources of Oxides: The common oxide of sulphur which is the most harmful gaseous pollutant is SO_2 . This oxide is released into the atmosphere by volcanic eruptions (normal activity). This oxide is also generated, when coal and oils are burnt in houses of industries. Coal always contains some sulphur as impurity. When coal is burnt, sulphur present in coal is converted into SO_2 . Oils also have some sulphur compounds, which give SO_2 on burning.

When sulphite ores, like iron pyrite (FeS₂), copper pyrites (CuS), copper glance (Cu₂S), zinc blende (ZnS), galena (PbS) etc. are roasted in air, SO₂ is produced.

•A part of SO₂ present in the atmosphere is oxidised to SO₃ by photolytic and catalytic oxidation processes. Thus SO₂ present in the atmosphere also contains SO₂, although the quantity of SO₃ is not high.



Tannery

Iron & Steel Industry

Effects of SO₂ and SO₃ on human beings, animals and plants

- We have shown above that SO₂ present in the atmosphere undergoes photolytic and catalytic oxidation to form SO₃. SO₃ thus produced reacts with rainy water or moisture and gives H₂SO₄ (SO₃ + H₂O H₂SO₄) which comes down the atmosphere in the form of sulphuric acid rain or acid snow or acid rain. This acid rain is a dangerous as nitric acid rain.
- The formation of sulphuric acid rain (H₂SO₄) can also be explained through the following steps :

Sunlight

→ SO (Sulhurmonoxide +O)

(Photochemical dissociation)

(a) SO_2

 $O + SO_2 \longrightarrow SO_3$ (sulphur trioxide)



Production of disposal of nitrogen dioxide

Production of disposal of sulphur dioxide

(c) $SO_3 + H_2O \longrightarrow H_2SO_4$ (sulphuric acid rain)

• When sulphuric acid rain (H_2SO_4) falls over a historical monument, it gradually eats up the marble stone (CaCO₃) of the monument and corrodes it slowly.

 $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$

- SO₂ irritates the respiratory system of animals and humans. It damages lungs.
- If plants are exposed to SO₂ of high concentration over short periods, brownish colour in the tips of pine needles gets declorised. If the plants are exposed to SO₂ of low concentration over longer periods, the production of chlorophyl in plants in hampered (Chlorosis) and hence green colour of the plants in lost.
- Due to corrosive nature of SO_2 and H_2SO_4 , these pollutants decolourise building materials like lime stone, marble, roof slate and mortar. The corrosion of most metals is accelerated by SO_2 .

OZONE (O₃)

Sources of O₃ : Some of O₃ is produced during various combustion processes taking place in the air around us. O₃ is also produced in the upper part of the atmosphere (stratosphere) by the action of sun rays on O₂.

sun rays

 $3O_2 \longrightarrow 2O_3$

Harmful effects of O₃ : Traces of O₃ in the air donot harm but O₃ of concentration more than 0.1 ppm is toxic and harmful to human beings. O₃ produces irritation in lungs, eyes and respiratory tract and accumulates fluid in lungs. These biochemical effects of O₃ mostly arise from the generation of free radicals which attack the – SH groups present in enzymes.

Protective role of ozone (O₃) layer present in stratosphere region of the atmosphere

- We know that air contains O_2 and at a height of 15 km from the earth's surface, this O_2 is converted into O_3 by the action of sun rays on it. $[3O_2 2O_3]$. O_3 thus produced forms a stable layer in stratosphere region (the region lying between 11 km and 50 km from the earth's surface) of the atmosphere. The thickest layer of O_3 exists at a height of 23 km from the earth's surface. This layer of O_3 is very useful for animals, human being and plants living on the earth.
- The radiations emitted by the sun and reaching on the earth also consist of ultra-violet radiations. These radiations are very harmful to the living organisms. These radiations are of short wavelength and hence penetrate deep into our body and cause skin cancer.

- These radiations also damage crop plants. Ozone layer present in the stratosphere region of the atmosphere absorbs harmful ultra-violet radiations coming from the sun and thus prevent these radiations from reaching earth. Thus we are saved from the harmful effects caused by ultra-violet radiations.
- Sources of destroying the ozone layer present in stratosphere
- In 1980 scientists showed that there is a hole in the O₃ layer. This hole was detected over the region of Antarctica. Due to the presence of this hole in of O₃ layer, the ultra-violet rays coming from the sun can pass through this hole and thus can reach the earth's surface.

- The presence of O₃ hole in the atmosphere is due to the fact that the amount of O₃ present in stratosphere is getting reduced day by day and thus the ozone layer is becoming thinner and thinner. The depletion of the ozone layer is due to the following:
- (i) Due to the formation of O_2 in the stratosphere. The oxides of nitrogen present in the atmosphere decomposes O_3 into O_2 and are themselves regenerated.

 $NO + O_3 \longrightarrow NO + O_2$ $NO + O \longrightarrow NO + O_2$

Thus we see that the presence of nitrogen oxides in the atmosphere destroys the ozone layer. These oxides destroy about 70% of O₃ found in the stratosphere. Greater is the amount of the oxides of nitrogen in the atmosphere, greater is the percentage of O₃ which is destroyed.

(ii) Due to the nuclear tests being conducted in various parts of the world. Nuclear tests being conducted in various parts of the world generate such a high temperature that N present in the atmosphere is oxidised to NO. NO thus formed decomposes O_3 to O_2 .

High temperature

 $N_2 + O_2 \longrightarrow 2NO$ $NO + O_3 \longrightarrow NO_2 + O_2$

• Thus O_3 layer is destroyed.

(iii) Due to the use of fluoro-chioro-carbons as acrosol spray propeliants. Fluorochloro carbons are the fluoro-chioro methanes like, Freon-I (CFCl₃) and Freon-12 (CF₂Cl₂).





Nuclear Power Plant

Super sonic jet



These are stable compounds. These are chemically inert and hence do not react with the substances. These are used as aerosol spray propellants, refrigerants, firefighting reagents and solvents for cleaning electronic components. When they enter stratosphere, they absorb ultra-violet solar radiations and get broken down into free atomic chlorine. This atomic chlorine decomposes O_3 into O_2 (NO also breaks O_3 into O_2).

 $CI + O_3 \longrightarrow CIO + O_2$ $CIO + O \longrightarrow CI + O_2$

Thus we find that the use of fluoro-chioro-carbons (e.g., Freon-11 and Freon-12) as aerosol spray propellants destroys the O₃ layer, as oxides of nitrogen do.

SMOKE

 Smoke contains unburnt carbon particles having diameter less than 100 m. These particles remain suspended in air.

Production of smoke particles in air

Smoke particles are emitted into the air during the process of burning (or combustion) of fuels like coal and oil in homes and factories. The quantity of smoke particles in air is variable.

Harmful effects of smoke

The smoke contains unburnt carbon particles which pollute the air. They spoil our clothes and blacken the buildings. Smoke damages our lungs. Due to cloud of smoke over big industries, the sun rays are not able to reach every corner of the city and hence infectious diseases in big cities are produced

How to control air pollution due to smoke

- The following two methods can be used for this purpose:
- (i) The pollution of air due to the presence of carbon particles (smoke particles) coming out of a chimney of a factory can be controlled by installation an electrostatic precipitator in the chimney.
- A high electric potential is applied across the chinmey. As the smoke particles (i.e., carbon particles) come up the chimney, they are attracted by the charged electrodes.
- The smoke particles cluster together to form soot, which gets deposited in the chimney. Thus the air is saved from being polluted by carbon particles. The soot can be removed by sweeping the chimney from time to time. -
- (ii) The pollution of air caused by carbon particles can also be prevented by using electrical energy, since these sources do not produce smoke or carbon particles.



Causes of Smoke





DUST PARTICLES

Production of dust particles in the air

 Dust particles are produced by heavy traffic on the roads and in some industrial operations. These particles remain suspended in the air.

Harmful effects of dust -

Dust in the air spoils our clothes and causes poor visibility. It provides allergic reactions and aggravates diseases like bronchitis. Dust is deposited on the leaves of plants and thus hinders the process of photo-synthesis taking place in plants. Dust in air reflects back some of the sun's heat rays and thus undue cooling of the earth takes place.

SMOG

What is smog or classic smog ?

The poisonous gases like SO₂ and NO₂ produced by the burning of fossil fuels (e.g., coal and petrol) in homes, industries and automobiles mix with the tiny droplets of fog (tiny water droplets) suspended in the air near the surface of earth (Fog is produced by the condensation of water vapour present in air). When the droplets of this fog which contains poisonous SO₂ and NO₂ gases get condensed on the solid particles of smoke or dust present in air; a colloidal dispersion is formed. This dispersion is called smog or classical smog. Tiny droplets of fog containing poisonous SO_2 and NO₂ gases condense on solid particles of smoke or dust present in air and produce collodial dispersion which is called .Smog or classical smog.



SMOG

- Thus smog is the combination of smoke particles with tiny droplets of fog containing poisonous gases like SO₂, NO₂ etc. discharged by the burning of fossil fuels (e.g., coal and petrol) in homes, industries and automobiles.
- Smog usually occurs during winter season. Smog present in the lower atmosphere is taken by men and animals during breathing and damages their health.
- In December 1952, a dense cloud of smog was formed over London city and remained there for five days. This smog produced respiratory problems in human beings and about 4000 people died. Many persons suffered from bronchitis and heart problems.

Harmful effects of smog

Various harmful effects of smog are

- Smog is harmful to all the human beings who breath in it. It produces bronchitis, asthama and heart problems.
- (ii) Smog creates irritation to the eyes, nose and throat.
- (iii) Smog has an adverse effect on the growth and development.
- (iv) Smog reduces the visibility and thus creates difficulties in road and air traffic.

The gases released by automobiles contain oxides of nitrogen (mainly NO₂ unburnt hydrocarbons, CO₂ and CO₂, NO₂ present in the auto-exhaust gases absorbs ultra-violet (U.V.) radiations of the sunlight and undergoes photolysis giving atomic oxygen (O). NO₂ + U.V. light \longrightarrow NO + O Atomic oxygen produced as above reacts with hydrocarbons (RH) to give a variety of free hydrocarbon radicals (e.g. RHO, RHO₂ and RHO₃), O₃, aldehydes, ketones, peroxy acetyl nitrate (CH₃CO.OO.NO₂ or PAN). All these substances are called photochemial pollutants.



PAN is harmful to human beings even in a concentration of 0.1 parts per million. PAN mixes with the fog and gets condensed in smoke or dust particles present in the air to form a smog which is called photochemical smog. Thus : Fog containing poisonous PAN + smoke or dust particles Photochemical smog.

Los Angeles is the name of a city situated in the U.S.A. Seven million people of this city have four million automobiles and consume 30 million litres of petrol every day. The smog formed in this city in photochemical smog. This Los Angeles smog is a photochemical smog.

Harmful effects of photochemical smog

- (i) Photochemical smog causes eye irritation and damages plants, since in the presence of this smog the leaves develop a metallic sheen.
- (ii) Rubber, on exposure to photochemical smog, loses its elasticity and becomes inflexible and brittle.
- (iii) Photochemical smog reduces the visibility and produces hindrance in the air and road traffic.

Comparison between classical smog and photochemical smog

Due to the presence of O_3 , NO_2 and other photochemical oxidants, photochemical smog is an oxidising smog whereas the classical smog formed by the combination of tiny droplets of fog containing poisonous gases viz., SO_2 and NO_2 and solid particles of smoke or dust is a reducing smog.

