

Classroom



In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. “Classroom” is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

G Nagendrappa
Department of Chemistry
Central College Campus
Bangalore University
Bangalore 560 001, India.
Email:nagendrappa@vsnl.net

An Appreciation of Free Radical Chemistry Part 4. Free Radicals in Atmospheric Chemistry

¹ Note: Some chemical species such as NO, NO₂, O₂ that occur naturally as stable free radicals in the atmosphere are not marked so in the article. However, they are free radicals nevertheless and should be treated so.

The earth is unique in having a blanket of atmosphere, which has helped evolution and sustenance of life. For a layman, the atmosphere seems a simple, just some air that we breathe, with clouds and rain at times. But actually what is atmosphere and what happens within it in chemical terms is unimaginably complex. Even small changes in its composition can greatly affect the life processes. Though different kinds of chemical reactions take place in the atmosphere, the most dominant ones involve free radicals. In this part, we shall take a brief look at this aspect.

The Atmosphere

Let us first of all familiarise ourselves with brief background information about the atmosphere. Air is a mixture of gases and suspended particulate matter. *Table 1* shows the percentage composition of the gases present. Industrialisation and related human activities have infused into the environment increasing quantities of pollutants that have changed atmospheric chemistry noticeably in recent times.

Keywords

Atmosphere, ozone hole, CFCs, atmospheric chemistry, acid rain.



Table 1. Composition of atmospheric air.

Name of gas	Symbol	Percentage by Volume
Nitrogen	N ₂	78.0840000
Oxygen	O ₂	20.9476000
Argon	Ar	00.9340000
Carbon Dioxide	CO ₂	00.0310000
Neon	Ne	00.0018180
Krypton	Kr	00.0011400
Helium	He	00.0005240
Methane	CH ₄	00.0002000
Hydrogen	H ₂	00.0000500
Xenon	Xe	00.0000087

In addition to those in *Table 1*, other gases such as hydrogen sulphide (H₂S), carbonyl sulphide (COS) and nitrous oxide (N₂O) emanated from the earth and the biosphere are also found in trace amounts. Other oxides of nitrogen (NO, NO₂, NO₃, etc., collectively denoted as NO_x), oxides of sulphur (SO₂, SO₃), water vapour (H₂O), volatile organic compounds (VOCs) and dust particles are other notable components of air. The presence of ozone (O₃) at higher altitudes is as important as that of oxygen for life processes, though in a totally different way.

The Division of the Atmosphere

The atmosphere extends from the surface of the earth to hundreds of kilometres above the ground. However, much of it is confined to less than 100 km altitude as the density of air decreases rapidly with increasing altitude.

An interesting aspect of atmospheric temperature is that it does not increase or decrease continuously, but undergoes slow fluctuations till about an altitude of 100 km, and then rises progressively. Based on this, the atmosphere is divided into temperature dependant segments called troposphere, stratosphere, mesosphere, and thermosphere. Beyond that is known as exosphere.

The boundaries called tropopause, stratopause and mesopause between these divisions are not sharp and the contents move and mix freely.



The changes in temperature at different altitudes involve various phenomena. The solar radiation reaching the earth through the atmosphere is absorbed by sea, land and vegetation. Much of it is radiated back into the atmosphere as infrared (heat) radiation and is absorbed by air, so that it is warmer near the earth's surface. Then cooling starts and continues till the temperature drops to about -63°C . This is the boundary between troposphere and stratosphere.

In the stratosphere, exothermic reactions – mainly ozone forming and destroying (see later) – occur, and the atmosphere gets heated up again till the temperature rises to about 15°C . Moving further upwards, the ozone concentration declines, and the absorption of radiation drops off rapidly. This results in atmospheric cooling for the second time until the temperature reaches -88°C at about 88 km altitude (mesosphere). Beyond this boundary also the atmosphere does not end suddenly, but extends to hundreds of kilometres in extremely thin form. The temperature in this stratum rises steadily due to absorption of radiation of $\lambda < 200\text{ nm}$ (very high energy radiation) by a little oxygen, nitrogen, ionic and atomic species present there. Figure 1a and 1b depict this in graphical form and as a pictorial diagram, respectively.

Solar Radiation Initiates Chemical Reactions

Though the chemical composition of the atmosphere is far too simple and most of its components, except nitrogen and oxygen, occur only in trace amounts compared to the enormous chemical

Figure 1a. Graph showing the division of the atmosphere.

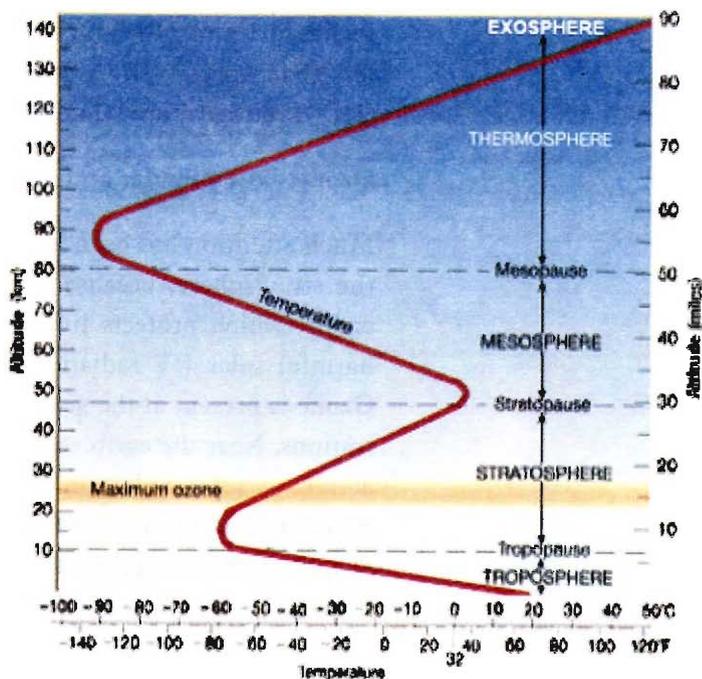
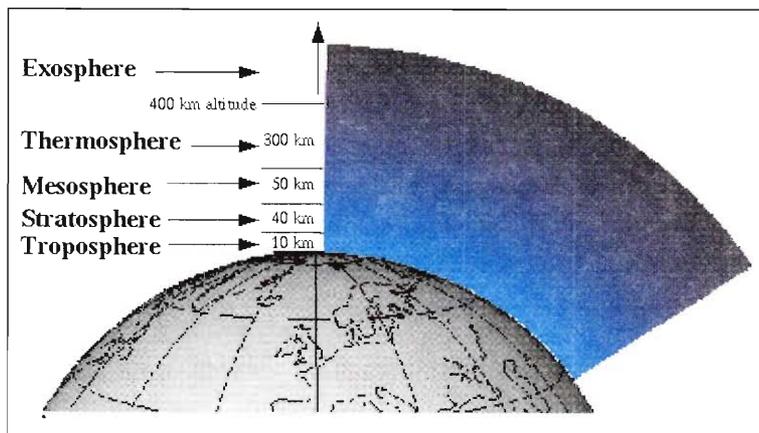


Figure 1b. Schematic diagram of the earth and its atmosphere.

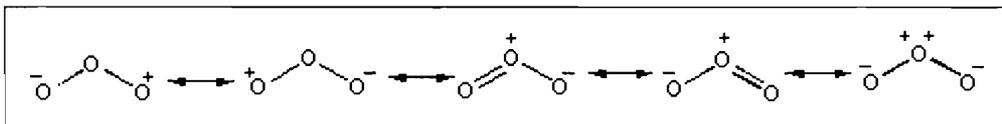


complexity in terrestrial regions, the reactions taking place in the atmosphere up to 50 km altitude are so important that the existence of life as we know it owes a great deal to these reactions. The driving force behind these reactions is solar radiation, particularly that in the UV range, which is capable of splitting the constituent molecules into free radicals, thereby setting off chain reactions even in highly rarefied parts of the atmosphere.

Many of the very important free radical species are present in less than 1 ppm (10^{-6}) by volume (1 ppmv), and some occur in less than 1 pptv (10^{-12}) concentration, e.g., hydroxyl radicals (HO^\bullet); yet they play a dominant role in atmospheric chemistry.

Ozone – A Defender and an Offender

Much attention has been focused on the reactions occurring in the stratosphere, because both formation and destruction of ozone, which protects living beings including humans from harmful solar UV radiation, are taking place in this region. Ozone is present at the ground level also in very small concentrations. Near the earth's surface, ozone is formed through the action of solar radiation on organic compounds as well as pollutants, and is a cause for photochemical smog during mid-day, when its concentration is maximal, particularly in urban areas where automobile and industrial pollution is high. Ozone is present in rural areas too, and its concentration remains almost the same, both during the day and night.



Scheme 1.

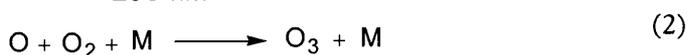
Ozone, a pale blue gas, is an allotrope of dioxygen (O_2), and contains three oxygen atoms in each molecule (O_3). It can be represented by various resonance structures as shown in *Scheme 1*.

Ozone is a highly reactive and powerful oxidant. It causes smog and is responsible for health problems if present beyond a limit in the atmosphere. Because of its destructive qualities, it is used in low concentration as germicide. However, up there in the stratosphere, in the form of a few kilometre thick gas blanket, ozone acts as our protector by filtering off the harmful solar UV radiation and preventing it from reaching the earth's surface.

Free Radicals Define Atmospheric Chemistry

Atmospheric ozone chemistry is complex and fascinating, involving a number of free radical reactions. Much of this has been clarified and understood due to sustained efforts of a number of researchers during the last 40-50 years (P Crutzen, a Dutchman, M Molina and F S Rowland, both Americans, received the 1995 Nobel Prize in Chemistry, for their work concerning the formation and destruction of ozone in the atmosphere). Much of the ozone drama is played out in the stratosphere and a brief low-key sideshow is conducted at the earth's surface, particularly in urban areas due to pollution. The story begins with the absorption of solar UV radiation by oxygen molecules, and proceeds as depicted in the following equations.

Formation of O_3 , the Ace Chemical in the Stratosphere

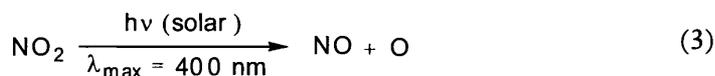


M is a third body required to take away the heat produced in the reaction. M could be N_2 , O_2 , or any other species available at the

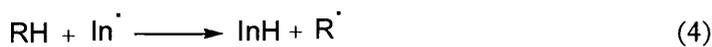
site of the reaction. This heat is responsible for re-warming the atmosphere in the stratospheric zone. At this height (10-30 km), the concentration of O_2 is sufficient to absorb most of UV radiation of $\lambda < 200$ nm. Above 30 km, O_2 is sparse and hence the reaction presented in equation (2) becomes insignificant.

Ozone Near the Ground (Lower Troposphere)

Closer to the earth's surface, a different route is available for the formation of atomic oxygen (equation 3), which then follows equation (2) for the formation of ozone. At this level, the 200 nm radiation is not available to dissociate the oxygen molecule as it has been filtered off at higher altitudes.



The sequence of reactions that contribute to this involves the volatile organic compounds (VOCs) like hydrocarbons, acetone, etc., oxides of nitrogen (NO_x , produced by natural phenomena, combustion processes, electrical discharge, etc.), and oxygen.



(RH = hydrocarbon, acetone, etc.)

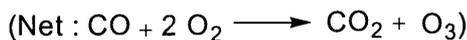
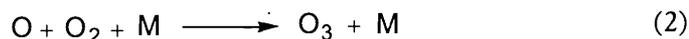
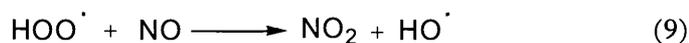
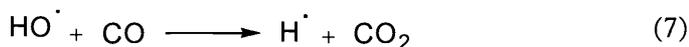
(In^\cdot = free radical initiator)



Aircraft Emissions Join the Upper Tropospheric Free Radical Fray

In the tropospheric region of commercial aircraft flights (approx. 15 km altitude), oxidation of CO produced by aircraft will lead to the formation of O_3 , as shown in the following equations.

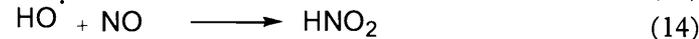
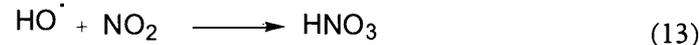
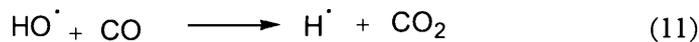




Both these phenomena (at the earth's surface and aircraft flight altitude) cause smog in the respective regions of the troposphere.

The Hydroxyl Radical – an Accomplished Assailant of Molecules

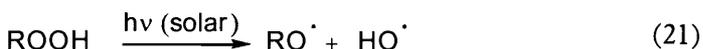
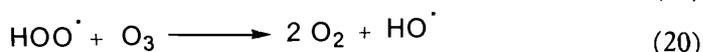
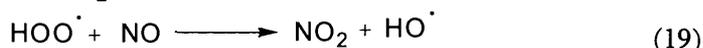
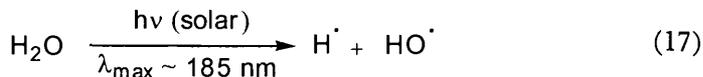
By virtue of its high reactivity, hydroxyl radical is a dominant primary radical species in atmospheric chemistry, although it occurs at only 1 ppt (10^{-12}) by volume. It plays a crucial role in initiating the reactions of gases emitted into the atmosphere by natural phenomena or human activities. Since it removes atmospheric chemicals efficiently, HO^\cdot is often called the atmosphere's 'detergent'. Some of the reactions are shown below.



The reaction in equation (4) is applicable to other hydrocarbons or any compound that has an abstractable hydrogen as in (10) and (16), including the compounds that have replaced the chlorofluorocarbons in recent times such as $\text{CF}_3\cdot\text{CH}_2\text{F}$, $\text{CHF}_2\cdot\text{CHF}\cdot\text{CHF}_2$, $\text{CF}_3\cdot\text{CF}_2\cdot\text{CH}_3$, etc., called hydrofluorocarbons, which do not contain chlorine in their molecules.

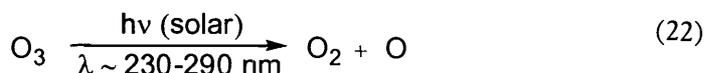


The generation of the HO[•] radicals in the atmosphere is a result of a variety of radical reactions occurring there, some of which are shown below.

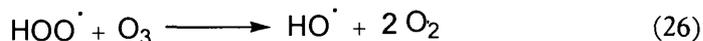
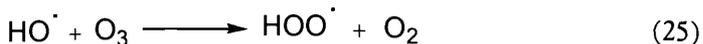
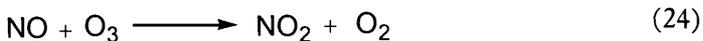


The Fate of O₃

An important aspect of ozone chemistry in the stratosphere occurs after it has absorbed solar radiation of wavelength 230-290 nm.



This removes virtually all the UV radiation in this wavelength range, and to some extent, down to wavelength ~350 nm, and ensures that this radiation is filtered out totally before reaching the troposphere. There are several other reactions that are also responsible for ozone destruction. They are, briefly,



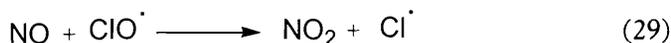
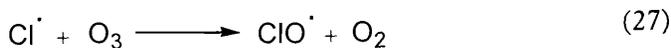
However, ozone gets restored and its balance is maintained by repetitive occurrence of reactions in equations (1) and (2). Thus, a life-friendly atmosphere has been preserved near the ground for millions of years.



Enter the Culprit Chlorine

As industrialisation advanced in the last century, ever increasing quantities of halogenated organic compounds have been produced for use as solvents, refrigerants, aerosols, fire extinguishers, pesticides, and many more. A lot of these compounds escape into the atmosphere. Many of them, particularly, chlorofluorocarbons (CFCs) are dissociated by stratospheric solar radiation to produce chlorine radicals (30-31), which are far more reactive than NO radicals, and bring about very rapid destruction of ozone (27-29). (Recall the preparation of nylon in Part 2² of this series, and note the importance of differential reactivities of Cl and NO radicals in two entirely different contexts),

² *Resonance*, Vol.10, No.3, pp.71-79, March 2005.



Since ClO[·] reacts with oxygen atoms needed to form O₃, and regenerates Cl[·] radicals, which will be back in action to destroy O₃ (27) repeatedly for many decades until they are slowly removed from the stratosphere, the above chlorine-initiated ozone decomposition reactions are highly detrimental to the ozone layer in its pristine protective role. Bromine radicals are also efficient in bringing down the ozone concentration by similar reaction sequences.

The threat of ozone depletion has necessitated the rejection of CFCs as refrigerants, aerosols, etc. The results of the research efforts in this direction are apparent in such gadgets as CFC-free refrigerators, air-conditioners and similar cooling systems, which use hydrofluorocarbons as substitutes for CFCs.

The Frozen Free Radicals and the Ozone Hole in Antarctic Stratosphere

The ozone hole is a term used for the reduced concentration of ozone in the stratosphere as compared to the normal average

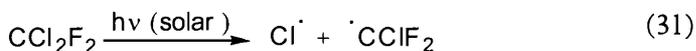
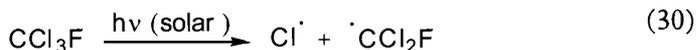


value during a particular season of the year. (Ozone concentration varies according to the time of the day, season of the year, the nature and amount of pollutants, and many other factors).

The thinning of ozone layer in stratosphere over Antarctica during spring was noticed for the first time in 1982, though attention was drawn to the ozone depleting power of chlorine radicals from CFCs as far back as 1973.

Extensive research has shown that the main culprit in the decomposition of O_3 is chlorine in the form of $ClO\cdot$.

CFCs, escaped into the atmosphere during use, stay for a long time in the troposphere. However, they are slowly transported into the stratosphere where they absorb solar UV radiation. The high-energy molecules dissociate and release the chlorine radicals (30-31).



The chlorine thus released will further react according to the equations (27-29).

At present the ozone depletion is mainly restricted to the Antarctic region. The reason attributed to this phenomenon is as follows. During the winter months, Antarctica receives no sunlight, causing the temperature to drop. The speed of westerly wind around the South Pole, moving in a vortex, increases, and reaches about 350 km/h. Because of the high speed, the air in the central region of the vortex experiences separation, in a way, from the surrounding air. The central air column of the vortex covering most of the Antarctic region, receives no light at all, and the temperature keeps dropping. The clouds start forming at an altitude of 25 km in the stratosphere. The ice crystals in the clouds would trap the oxides of nitrogen (NO , NO_2), $ClO\cdot$, $Cl\cdot$ and other radicals in their radical form. When the sun starts shining at the end of the winter, the trapped chlorine radicals, along with the others, are released, which break down ozone



according to (27-28). By the beginning of the Antarctic summer in October the vortex starts disintegrating. By then the ozone layer would have become thinner in most parts of Antarctic region, reaching even zero concentration at some altitudes. This depleted area is the so-called ozone hole. One can get some idea about this from *Figures 2a* and *2b*. Fortunately, the ozone concentration is maintained at normal level in the populated regions of the earth as well as the Arctic region, where the atmospheric cooling is not enough at present to trap the radicals.

Free Radical Oxidation and the Acid Rain

The chemical substances in the troposphere have shorter lifetime due to high air density and the consequent high rates of molecular collisions. They remain for a much shorter duration in this region as compared to substances in the stratosphere. This is because majority of them are washed off through precipitation events occurring only in the troposphere. Of the remaining, some are transported to the stratosphere and still others undergo

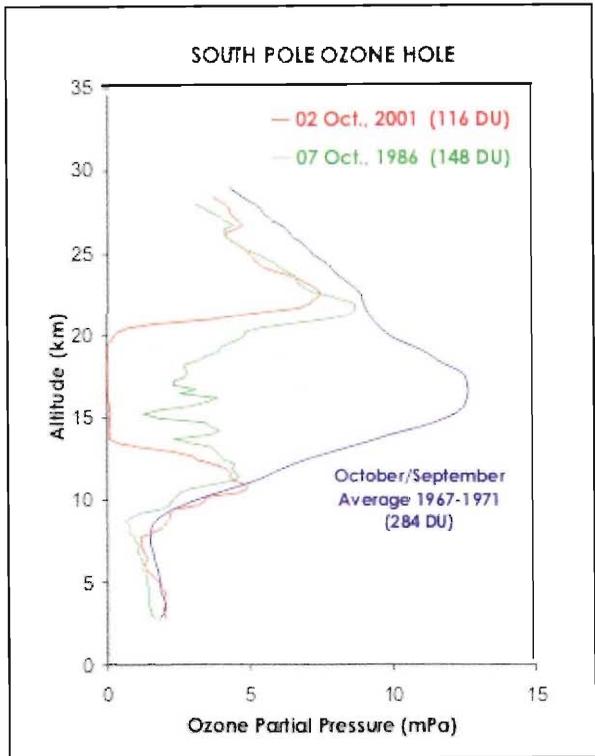


Figure 2a. Graph depicting the depletion of ozone over Antarctica from a concentration of 284 DU in 1971 (blue) to 116 DU in 2001 (red). (DU = Dobson unit, 0.01 mm of O₃ at STP).

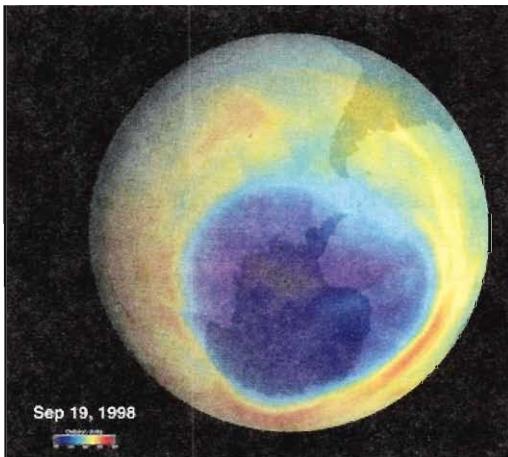
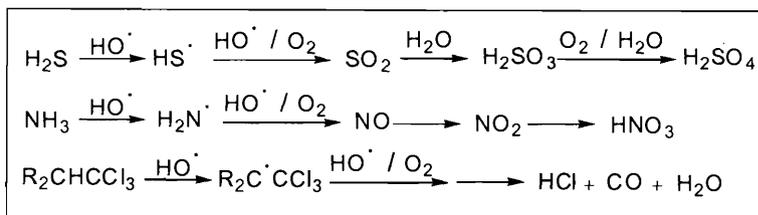


Figure 2b. Picture showing the depleted ozone layer over Antarctica (Deeper the blue, thinner is the ozone layer)



Scheme 2.



oxidation or other reactions. We have earlier referred to a few of the reactions occurring in this region. Among other reactions, several acid forming ones involve free radical oxidation processes. For example, H_2S is oxidised to SO_2 and further to H_2SO_4 , NH_3 to NO and then to HNO_3 , chlorohydro-carbons to HCl , CO , etc. These products are brought down to earth by precipitation events in the form of the so-called acid rain. The following reactions show these transformations, (Scheme 2).

In conclusion, the known chemistry of the atmospheric reactions is very vast, and newer information keeps pouring in through the research activities of a large number of scientists (chemists, physicists, astronomers, astrophysicists, meteorologists, mathematicians, engineers, etc.) and institutions, as it is very important for the survival of mankind. The information provided in this short article is like a tiny tip of a huge iceberg. Though the number of examples considered here are very few compared to their actual number, their variety and the diverse reactions they initiate and propel in the atmosphere, nonetheless, the purpose to illustrate the importance of free radicals in atmospheric chemistry and instil interest in the readers of *Resonance* about them is hopefully served.

Tailpiece

Recently, Barbara Albert, an Austrian director, has produced a feature film named 'Free Radicals'. (The film's title has nothing to do with chemistry). The film reviewers, Frederic and Mary Ann Brussart, say the following about it.

"*Free Radicals* would have us believe that these links go further than we can imagine and provide many sparks of light and meaning".

Suggested Reading

- [1] C Baird and M Cann, *Environmental Chemistry*, W H Freeman & Company, 2004.
- [2] P V Hobbs, *Introduction to Atmospheric Chemistry*, Cambridge University Press, 2000.
- [3] B J Finlayson-Pitts and J N Pitts, Jr, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 2000.
- [4] D Jacobs, *Introduction to Atmospheric Chemistry*, Princeton University Press, 1999.
- [5] JH Steinfeld and SN Pandis, *Atmospheric Chemistry and Physics*, Wiley-Interscience, 1998.
- [6] P S Sindhu, *Environmental Chemistry*, New Age Publishers, 2002.