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CHEMICAL CYCLES OF THE STRATOSPHERE OZONE DISINTEGRATION

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Abstract. *The rapid industrialisation in the part of this century caused the discharging of pollutants like Cl, CO, NO_x, CH_4 into the atmosphere. Their accumulation in the upper parts of the Earth atmosphere causes the disintegration of the chemical reactions according in the stratosphere is given in this work.*

Key words: *ozone, chlorine, carbon (II)-oxide, azote-oxides, methane.*

1. INTRODUCTION

It is estimated that our galaxy, the Milky Way, was formed 4,5 to 5 billion years ago. The Sun is a gaseous sphere, its diameter is $2R_S = 1{,}319 \times 10^6$ km. It consists of a core, radiation zone, convective zone and photosphere. The Sun atmosphere consists of homosphere and corona. In the Sun core the energy is made by thermonuclear reactions of the fusion of hydrogen into helium in the form of gamma-rays, neutrinos and energy particles. gamma-rays lose the energy in manyfold non-elastic collisions which is transfered to the Sun's surface through radiation layer. From the Sun surface the energy comes to the Earth in the form of electromagnetic waves. The intensity of electromagnetic waves is reduced because of the absorption on molecules, atoms and ions in the Earth atmosphere (Fig.1.).

From the Sun to the Earth surface come electromagnetic radiation of the wavevlengths from 0,015 to 1000 μm. About 3% of the radiation is from the ultraviolet (UV) area, about 42% is from visible (VIS) area and about 55% is from infrared (IC) area of the spectrun of electromagnetic radiation. To the Earth come 97% of the Sun radiation in the range of 0,3 – 2,5 μm and 3% in the range over 2,5 μm [1].

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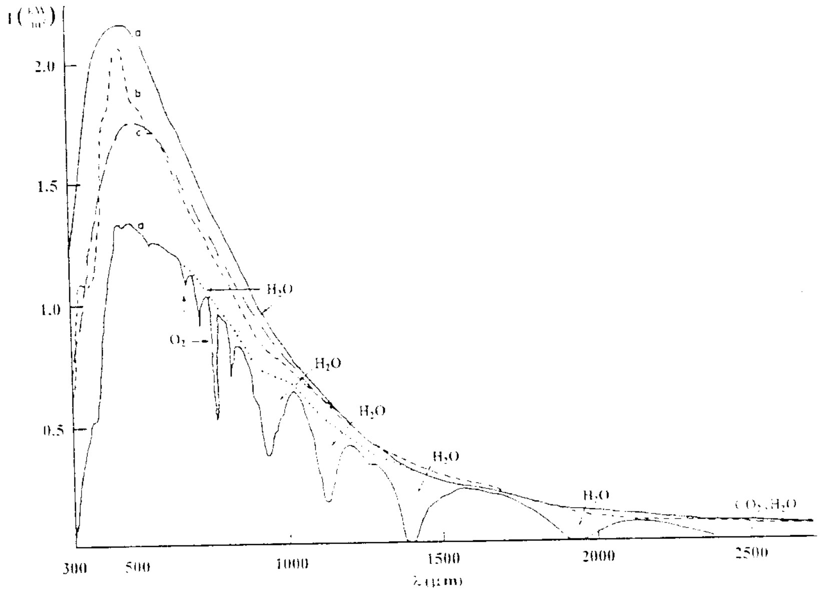

Fig.1. Spectral distribution of the intensity of a) the radiation of a blackbody on 5727 °C, b) the extraterrestrial sun radiation, c) the radiation of a black body on 5357°C, d) the sun radiation on the Earth.

2. THE EARTH ATMOSPHERE AND ITS CHEMICAL COMPOSITION

The Earth gaseous sphere consists of three main layers:

– homosphere which goes up to 100 km over the Earth surface and which consists of three main parts: troposphere (0 – 12 km), stratosphere (12 – 50 km), and mezosphere (50 – 100 km),
– heterosphere goes up to the height of 100 – 700 km from the Earth surface and
– egzosphere that goes up to the height of 700 – 3000 km from the Earth surface (Fig.2.).

The composition of the Earth atmosphere changes depending on its height. In the lower parts of the Earth atmosphere there is the presence of the molecules of bigger mass which are under the influence of more powerful force of the Earth gravity. In the layer up to 200 km there is the dominant presence of the nitrogen molecules with the mass of 28 g/mol and the oxigen molecules with the mass of 32 g/mol. In this layer of the atmosphere the nitrogen molecules are represented with 78,088 volume % and the oxigen moleculs are represented with 20,949 volume %. In the heights more than 200 km occurs the breaking of the great number of oxigen molecules into atoms under the influence of the ultraviolet radiation. Monoatomic oxigen with the mass of 16 g/mol that is lighter than molecular oxigen goes to the higher layers of the atmosphere up to 1100 km. Above 1100 km there is the presence of helium (He) with the molecule mass of 4 g/mol. Helium spreads up to 3500 km, and above this height there is the presence of the lighter hydrogen molecules (H) with the molecule mass of 2 g/mol. The concetration of hydrogen decreases with the further growth of height. In the height of 35 000 km hydrogen from the Earth atmosphere amalgamates with interplanetar hydrogen (Fig.3.) [2].

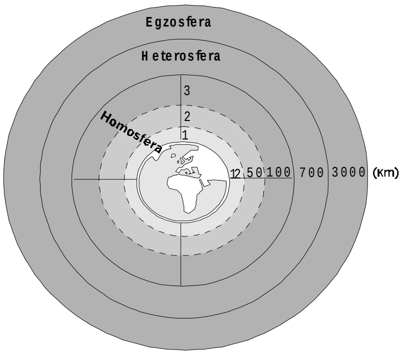

Fig. 2. The strukture of the Earth atmosphere: Homosphere (1-troposphere, 2-stratosphere, 3-mezosphere), Heterophere, Egzophere

INTRAPLANETARY HYDROGEN

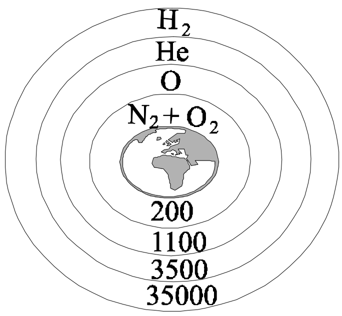

Fig. 3. The most frequent supstances that comes into the composition of the Earth atmosphere depending on its height

3. THE FORMATION AND IMPORTANCE OF THE STRATOSPHERE OZONE

The oxigen that forms ozone by photochemical reactions on the heights from 15 to 37 km comes into the composition of the Earth atmosphere.

Oxigen cycle of forming and decomposing of ozone

Forming and decomposing of ozone by oxigen cycle occurs in the highest and lowest layers of stratosphere in three phases:

In the first phase molecular oxigen by the influence of UV radiation with wave lenght less than 242 nm,

$$O_2 \xrightarrow{< 242\ nm} O + O$$

In the second phase the generated oxigen joins together with already presence of any molecules that can recieve the energy released from the chemical reaction and not to be changed.

$$O_2 + O + M \rightarrow O_3 + M$$

In the third phase ozone shows the tendency to release one atom of oxigen and change into more stable molecular oxigen. The disintegration of ozone in the stratosphere begins by the absorption of UV radiation of 280 − 300 nm wave-lenght and the results is the forming of molecular and atomic oxigene.

$$O_3 \xrightarrow{from\ \ 280\ \ to\ 300\ nm} O_2 + O$$

It can be concluded that the third phase of oxigen cycle of photochemical reactions in the stratosphere represents the disintegration of ozone and regeneration of molecular oxigene that is disintegrated into atomic oxigene by the influence of UV radiation and makes it possible new forming of ozone (Fig.4.). The oxigence cycle contributes to the relative by constant concetration of ozone in the stratosphere which is under the unchanged natural conditions about 0,2 ppm. But it is perceived that the concetration of stratosphere ozone is cousantly reducing from the beginning of industrialisation. The ozone holes represents the conequence of reducing of the concentration of ozone in the stratosphere.

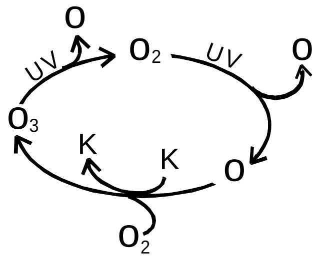

Fig. 4. The schematic presentation of oxigene cycle in the stratosphere

The systematic study of the causes that bring to the reducing of the concentration of ozone in the stratosphere begins in the seventies of this century. The researches showed that the reducing of the chlorofluorocarbonhydrogens, nitrogenoxides, carbon (II) − oxides and methane into the atmosphere. The discharging of these pollutants causes the reduction of ozone concentration from 0,4 − 0,6% in a year. from the more than 15% related to the natural concentration of ozone in the stratosphere. On the basis of theoretical calculations it has been estimated that by 2010 the reduction of concentration of ozone will be 30% if it continues with discharging already mentioned pollutants with the same speed [3,4].

The stratosphere ozone totally absorbs the UV radiation of the wave-lengths from 200 to 280 nm and in a large percentage the radiation of the wave-lengths from 280 − 320 nm. The reduction of the concentration of the stratosphere ozone causes the excessive penetration of the ultraviolet radiation on the Earth. The ultraviolet radiation of the wave-lengths from 200 − 280 nm is mortal for people and live organisms on the Earth and the radiation of the wave-lengths from 280 − 320 nm is mortal for many forms of life on the Earth. The stratosphere ozone does not absorb the ultraviolet radiation of the wave-lengths over 320 nm. The disability of ozone molecules to absorb this radiation is of no greater importance because it has not great influence on the living world on the Earth.

4. SUBSTANCES THAT REDUCE THE CONCENTRATION OF THE STRATOSPHERE OZONE

Reduction of the concentration of the stratosphere ozone may be also caused by the penetration of the halogen carbonhydrogens into the stratosphere. At the end of the sixties of this century it was noticed the presence of chlorofluorocarbonhydrogens in the stratosphere. Chlorofluorocarbonhydrogens (freons and halons) are used, because they are inert, in the production of refrigerators, sprays, insulations (polyuretan), microelectronic elements etc. In 1974 the scientists of the California University concluded that the chlorohluorocarbonhydrogens are long lasting in the atmosphere depending on the degree of the halogenity of the molecules. Completely halogenised freons stay in the atmosphere for about 100 years. This time is long enough for freon from troposphere to spread into to stratosphere. Partially halogenised freons have shorter life time (about 20 years) and their disintegration begins in the troposphere and only a small part stays in the stratosphere [3,4].

4.1. The disintegration of ozone by halogen elements

In the stratosphere chlorofluorocarbonhydrogens disintegrate under the influence of the short wave UV radiation to an atom of chlorine and an organic part. For example dichlorodifluoromethane disintegrates to chlorodifluoromethanol and an atom of chlorine under the following reaction:

$$CCl_2\,F_2 \xrightarrow{UV} CClF_2 + Cl$$

Chlorinecycle of ozone disintegration

In the stratosphere ozone is disintegrated evenly according to the height. An atom of chlorine in the chlorine cycle ties a molecul of ozone and makes chloromonoxide (ClO) which reacts with a free atom of oxigene and in this way an atom of chlorine and new molecules of oxigene are formed again. In this way a new atom of chlorine is regenerated and begins a new cycle of O_3 disintegration.

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

If chloromonoxide does not react with oxigene it can chemicaly tie a molecule of ozone with releasing O_2 and ClO_2. The created ClO_2 chemicaly reacts with atomic oxigene and a molecule of ClO is regenerated.

$$ClO + O_3 \rightarrow ClO_2 + O_2$$
$$ClO_2 + O \rightarrow ClO + O_2$$

The schematic presentation of the chlorine cycle of the stratosphere ozone disintegration is given in Fig.5.

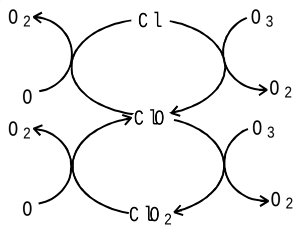

Fig. 5. The schematic presentation of the chlorine cycle of the stratosphere ozone disintegration

It is considered that by the reactions of the chlorine cycle one atom of Cl can disintegrate 10 000 to 100 000 molecules of O_3. The chlorine cycle occurs in the stratosphere until the atom of chlorine transforms into some other compound. For example if chloromonoxide reacts with azote (IV) – oxide the stable chloronotrat will be formed.

$$ClO + NO_2 \rightarrow ClNO_3$$

In the last thirty years of this century the discharge of gases that disintegrate the layer of ozone increased for about 4% a year. If the discharge of freon does not stop in the first half of the 21st century it may come to the "chlorine catastrophy", that is to say it may come to the appearence of a great concentration of chlorine atoms and reduction of the concentration of ozone molecules in the stratosphere (Fig. 5.) [4].

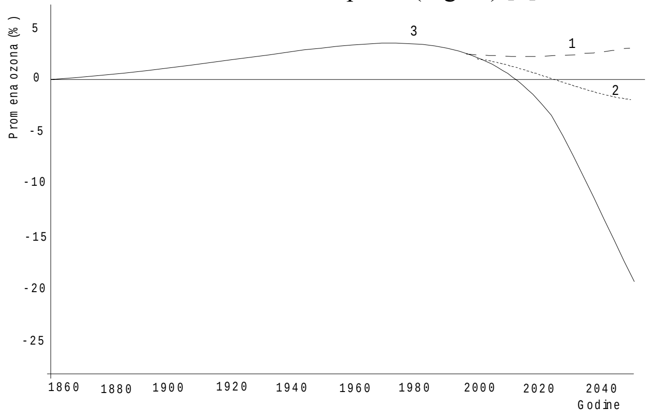

Fig. 6. Estimated percentage of the stratosphere ozone damage depending on the production of freon, 1 – under unchanged discharge of freon, 2 – under the increase of discharge of freon for 2% a year, 3 – under the increase of freon for 4% a year

It can be seen in Fig. 6. that estimated loss of ozone in the stratosphere until 2050, under the unchanged discharge increases for 30%, if the discharge of freon increases for 2% a year the atmosphere losses 50% of stratosphere ozone and if the discharge of freon increases for 4% a year the concetration of stratosphere ozone is reduced for 70%.

4.2. The disintegration of ozone by OH – radical, carbon (II) – oxide, water steam, methane and azote (II) – oxide

In the disintegration of stratosphere ozone, except halogen elements like chlorine, hydroxide radical (OH), carbon (II) – oxide, methane and azote (II) – oxide also take part.

Hydrogen cycle

The part of the hydrogen radical in the depletion of the layer of ozone can be show by the help of hydrogen cycle.

In the first phase of hydrogen cycle monoatomic oxigen chemicaly reacts with a molecule of water steam and then a hydroxide radical appears:

$$O + H_2O \rightarrow 2^{\bullet}\,OH$$

In the second phase a hydroxide radical disintegrates ozone:

$$^{\bullet}OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O_3 \rightarrow {}^{\bullet}OH + 2O_2$$

The exact experimental data are not available about the concentration of •OH and HO_2 in the stratosphere. On the basis of chemical reactions already mentioned and measuring of the concentration of ozone in the stratosphere it has been concluded that hydroxide radical may have a great influence on the total quantity of ozone in the atmosphere. Because of its ability to regenerate hydroxide radical disintegrates a great number of ozone molecules in the stratosphere. The schematic presentation of the stratosphere ozone disintegration cycle by •OH radical is given in Fig.7.

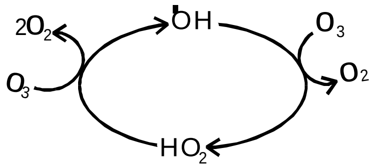

Fig. 7. The schematic presentation of the stratosphere ozone disintegration by •OH – radical

The disintegration of ozone carbon (II) – oxide

The hydroxide radical can be formed by chemical reaction of carbon (II) – oxide and ozone:

$$CO + O_3 \rightarrow OH + O_2$$

The part of carbon (II) – oxide in ozone disintegration may be seen through two phases. The first phase is characterised by direct reaction of carbon (II) – oxide and ozone and the second phase is csaracterised by the action of already built •OH – radical which continues the further disintegration of ozone through hydrogen cycle.

In the stratosphere carbon (II) – oxide may be formed by integration of methane and oxigen:

$$CH_4 + 3O \rightarrow CO + 2H_2O$$

The disintegration of ozone by water steam

In the previous reaction water steam was formed which continues to disintegrate ozone according the following reaction:

$$H_2O + O_3 \rightarrow O_2 + H_2O_2$$

The disintegration of stratospere ozone causes the penetration of short – wave UV rays into the troposphere and rising the temperature in it. Since the troposphere and stratosphere are in dynamic physicochemical balance the rising of temperature in the troposphere for a few degrees causes the increase of water steam concentration. The water steam in stratosphere has influence on changing of the meteorogical and climatic factors on the Earth.

The flying of supersonic planes in the lower parts of the atmosphere causes the increase of the concentration of water steam and azote (II) – oxide. By burning of high octane gasoline, which is used as fuel for these planes, water steam and carbon (IV) – oxide are formed with releasing of temperature

4.3. Ozone disintegration by ozone – oxides

The azote (II) – oxide which comes to the troposphere from anthropogenic sources reacts with ozone in the stratosphere and then azote (IV) – oxide is formed:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Azote cycle of ozone disintegration

Azote cycle of ozone disintegration in the stratosphere begins with the reaction of azote (IV) – oxide and monoatomic oxigen. Monoatomic oxigen in the stratosphere is formed by the disintegration of ozone by the influence of UV radiation. In the reaction of azote (IV) – oxide and molecular oxigen two molecules of azote (II) – oxides are formed one of which reacts with NO_3 and makes it possible the regeneration of a molecule of NO_2 and forming another molecule of NO_2 which ties the stratosphere ozone. The chemical reaction of NO_3 and releasing molecular oxigene and in this way the azote cycle is closed.

$$O_2 \xrightarrow{UV} O + O$$
$$NO_2 + O \rightarrow 2NO$$
$$NO + NO_3 \rightarrow NO_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

The schematic presentation of the cycle of the stratosphere ozone disintegration is given in Fig. 8.

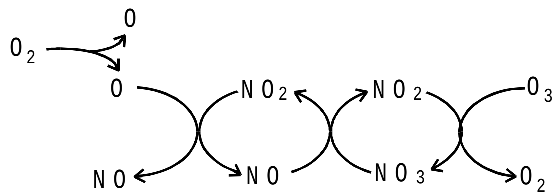

Fig. 8. The schematic presentation of the cycle of the stratosphere ozone disintegration

The disintegration of ozone by azote cycle occurs in the medial layer of stratosphere.

5. CONCLUSION

On the basis of already mentioned it can be concluded:

1. The sun radiation comes to the Earth like electromagnetik waves of wave-lenghs from 0,015 to 1000 μm.
2. The stratosphere is a vital covering of the Earth that protects it from excessive sun radiation of UV – radiation.
3. The atmosphere ozone that absorbs UV – radiation has the greatest concetration in the height of 15 – 37 km.
4. The stratosphere ozone is formed through oxigene cycle occurs in three phases and makesit possible a relatively constant ozone concentration which is about 0,2 ppm.
5. The disintegration of the stratosphere ozone is caused by the substances that are dis-

charged into the troposphere and penetrate into the stratosphere. They are: chlorofluorocarbonhydrogens, azote – oxides, carbon (II) – oxides, hydroxide radicals and methane.

6. The cycle by which the disintegration of the stratosphere ozone occure are done through molecules, atoms or a chemical element that tie the stratosphere ozone, transform it chemicaly and then regenerate it. In these cycles which occurs in several phases a great number of ozone molecules are disintegrated.
7. By the chlorine cycle ozone disintegrates evenly according to the height. By the azote cycle ozone disintegrates in the medial layer of the stratosphere. The oxigen cycle of forming and disintegration of ozone occurs in the highest and in the lowest layers of the stratosphere.
8. Ozone disintegration is twice quicker then its synthesis.
9. The disintegration of the stratosphere ozone causes the penetration of UV rays into the troposphere and rising its temperature.
10. Because of the reducing of ozone concentration in the stratosphere a great quantum of ultraviolet radiation than normal comes to the Earth which has negative consequences for living forms on it.
11. The considerable progress in the regeneration of distroyed molecules of the stratosphere ozone can be done by ceasing the discharging of halogen carbonhydrogens and by reducing the discharging of azote oxides into the atmosphere.

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HEMIJSKI CIKLUSI RAZGRADNJE STRATOSFERSKOG OZONA

Danilo Popović, Amelija Đorđević, Jasmina Radosavljević

Ubrzana industrijalizacija u drugoj polovini ovoga veka dovela je do emitovanja zagađujućih supstanci u atmosferu kao što su Cl, CO, NO_x, CH_4. Njihovo nagomilavanje u gornjim slojevima zemljine atmosfere dovodi do razgradnje stratosferskog ozona. U radu je dat pregled hemijskih reakcija po kojima se formira i razgrađuje ozon u stratosferi.

Ključne reči: *ozon, hlor, ugljenik (II) – oksid, azotni oksidi, metan*