

INFLUENCE OF FIRE ON THE OZONE LAYER OF ATMOSPHERE

V.V. Oshchapovsky¹, V.V. Kovalyshyn¹, S.L. Kuskovets¹, V.A. Marchenko²,
V.V. Shylo², A.I. Slipchenko¹

¹Lviv State Institute of Fire Safety
P.O.Box 10676, Lvov, 79000, UKRAINE
E-mail: asu@franko.lviv.ua and oshchapovsky@yahoo.com

²Lviv National University
1, Universitetska Str., Lvov, 79000, UKRAINE
E-mail: asu@franko.lviv.ua

Abstract.

Burning processes of atmospheric components during fire are studied insufficiently. However, their influence on the environment is important. These processes are accompanied by the oxygen consumption, discharge of burning-hot products into the atmosphere, thermal radiation, pyrolysis and thermooxidizing transformations of air components, water, used for fire extinguishing, and some extinguishing agents. Fire is a volley discharge of heat and radicals into the atmosphere. Evaluation and prognosis of corresponding high-temperature reactions are difficult. On the basis of G-potentials calculation of gaseous reactions thermodynamic analysis of systems N-O-H-C-S and N-O-H-C-S-F(Cl, Br) for 600-2000 K was conducted. Possibility of thermolysis, oxidation, thermooxidizing pyrolysis reactions, interaction of intermediates with atmosphere components, including vapor was evaluated. All reactions of thermal decomposition of atmospheric air main components are forbidden. During fire radicals OH can be formed already at 900 K. Radicals, nitrogen oxides, CO and CH₄ destroy ozone with the formation of molecular oxygen in the whole temperature diapason. Carbon dioxide destroys O₃ beginning from 900 K. Vapor (and its decomposition products) promotes the ozone destruction with formation of molecular oxygen and hydrogen or radicals, beginning from 900-1200 K. Results will be useful for estimation of the fire consequence, its influence on environment and health of people.

Introduction

High-temperature thermooxidizing processes into atmosphere are important components of those processes, which proceed during fires. However, despite of their great spread and range, these processes are studied insufficiently (1). The scale and influence of such phenomenon as fires, shows their quantity – approximately 6 millions a year. The knowledge of regularity of the given processes is important from the theoretical view-point and has considerable practical significance, since it can be useful for prevention and braking of burning, increase of the combustion products quantity and elimination of harmful impact of fires on the environment and organism of people.

Methods and Results

The aim of our investigation is the evaluation of possible development of high-temperature processes of thermal decomposition of the atmosphere components, the burning of them, i.e. oxidation by oxygen as well as the interaction of the products of these processes between themselves and with the decomposition components of vapour in the temperature diapason 800 – 2000 K.

Taking into account these processes, high temperatures of the reactions proceeding, the large quantity of uncontrolled factors etc. the thermodynamic analysis of reactions, which can proceed during the fires in atmosphere was applied.

The main components of atmosphere are nitrogen (78 %) and oxygen (21 %). The rest of the components are small quantities of such gases as: argon, carbon dioxide, methane, nitrogen and sulfur dioxide, ozone, vapour, formaldehyde, iodine, ammonia, CO, inert gases etc. Thus, the thermodynamic analysis of reactions in the system "N – O – H – C" was held.

It is known, that the possibility of proceeding of chemical reaction can be evaluated on the basis of the magnitude of Gibbs's energy ΔG . In the case when the magnitude of this energy is more than 0 (zero), the reaction is considered as thermodynamically forbidden and cannot go without assistance. The reaction can proceed independently in the given conditions, when $\Delta G < 0$. By evaluating the value of ΔG , one can find, what just reactions proceed at the fires and which of them are the low-probable in given conditions and thus can be ignored. It will permit to estimate the situation correctly and take corresponding measures.

To calculate the magnitudes of Gibbs's energy ΔG_T the equation of exact integration (2) was used:

$$\Delta G^\circ = \Delta H^\circ - T \int \frac{dT}{T^2} \int \Delta C_p dT + IT \quad (I)$$

in which ΔH_0 is reaction enthalpy; T is temperature; I is integration constant. Heat capacity of reaction ΔC_p is determined by the formula:

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2 + \Delta c' / T^2 \quad (II)$$

in which Δa , Δb , $\Delta c'$, Δc are the thermodynamic parameters of reaction, determined for each concrete substance. Knowing the magnitudes of Gibbs's energy ΔG_T for the corresponding groups of reactions, one can make a preliminary conclusion concerning the mechanism of either processes. For further evaluation of the quantity of new-created compound for the temperature T , on the basis ΔG_T , one can calculate the value of equilibrium constant K_{eq} of the reactions using formula:

$$\ln K_{eq} = -\Delta G_T / RT \quad (III)$$

By combining the equations (I) – (III) we obtain the final expression for the calculation of K_{eq} reactions:

$$\ln K_{eq} = -\frac{\Delta H_0^\circ}{RT} + \frac{1}{R} \int \frac{dT}{T^2} \int \Delta C_p dT + I \quad (IV)$$

The thermodynamic data was taken from the corresponding tables of physico-chemical magnitudes (2,3).

The certain main reactions, which were carried out, are indicated in the table 1. The sum total of the reactions studied contributes approximately three hundred, and this paper reports certain preliminary results. The considered reactions can be divided to

3 great groups: I) thermal decomposition of the atmosphere components; II) oxidation and thermooxidizing pyrolysis of the atmosphere components; III) thermal decomposition and thermooxidizing transformations of the products with the participation of vapour at high temperature.

Table 1. Certain reactions, which can proceed at the fires in the atmosphere.

<p>I. Thermal decomposition</p> <p>I.1. $N_2 \rightarrow 2 N$ I.2. $O_2 \rightarrow 2 O$ I.3. $3 O_2 \rightarrow 2 O_3$ I.4. $O_3 \rightarrow 3 O$ I.5. $CO_2 \rightarrow CO + 1/2 O_2$ I.6. $CO_2 \rightarrow CO + O$ I.7. $CO_2 \rightarrow CO + 1/3 O_3$ I.8. $CO_2 \rightarrow C_{ar} + O_2$ I.10. $CO_2 \rightarrow C_{ar} + 2/3 O_3$ I.11. $CO_2 \rightarrow C_{rp} + O_2$ I.13. $CO_2 \rightarrow C_{rp} + 2/3 O_3$ I.14. $CH_4 \rightarrow C_{rp} + 2 H_2$ I.15. $CH_4 \rightarrow C_{rp} + 4 H$ I.16. $CH_4 \rightarrow C_{ar} + 2 H_2$ I.18. $CH_4 \rightarrow 1/2 C_2H_4 + H_2$ I.19. $CH_4 \rightarrow 1/2 C_2H_4 + 2 H$ I.20. $CH_4 \rightarrow 1/2 C_2H_2 + 3/2 H_2$ I.34. $H_2 \rightarrow 2 H$ I.35. $NO_2 \rightarrow NO + 1/2 O_2$</p>	<p>I.36. $NO_2 \rightarrow NO + O$ I.46. $NO_2 \rightarrow 1/2 N_2 + 2/3 O_3$ I.56. $O_3 \rightarrow O_2 + O$</p> <p>III. Pyrolysis and transformations of products with the participation of H₂O</p> <p>III. 1. $H_2O = 2 H + O$ III. 2. $H_2O = H_2 + O$ III. 3. $H_2O = H_2 + 1/2 O_2$ III. 4. $H_2O = H_2 + 1/3 O_3$ III. 5. $H_2O = 2 H + 1/3 O_3$ III. 6. $H_2O = 2 H + 1/2 O_2$ III. 7. $H_2O = H + OH$ III. 13. $OH = H + 1/3 O_3$ III. 14. $OH = 1/2 H_2 + 1/3 O_3$ III. 15. $2 OH = H_2O + O$ III. 16. $2 OH = H_2O + 1/2 O_2$ III. 17. $2 OH = H_2O + 1/3 O_3$ III. 21. $N_2 + 4 H_2O = 2 NO_2 + 4 H_2$ III. 49. $N_2 + 7 OH = 2 NO_2 + O_3 + 3,5 H_2$ III. 50. $N_2 + 10 OH = 2 NO + O_3 + 5 H_2O$</p>
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The obtained results of thermodynamic calculations are showed on the figures 1-2. One can see from fig.1 that the main ingredients of atmospheric air – nitrogen and oxygen – are very stable and practically not decomposed in the investigated diapason of temperature: the curves $\lg K_{eq} = f(T)$ for the reactions of its decomposition go below the level 0 (zero), hence, the equilibrium of them is displaced to the initial substances. However, the atmospheric additives (nitrogen oxides, methane, ozone etc.), which are present in atmosphere in insignificant quantities, yield to the pyrolysis quite easy. It is especially characteristic for such atmospheric component as ozone. Methane and its derivatives can decompose in the given temperature diapason with the formation of soot C_{gr} (fig. 1). Hence, during the investigation of influence of burning products with the participation of atmospheric air components on an environment the main attention must be concentrated on the atmospheric additives and substances, which can be formed as result of the high-temperature oxidation of material that burns. One can see from fig. 1, that the thermal decomposition of molecules of water (vapour) is thermodynamically forbidden (low-probable) in all temperature diapason. However its derivative – the radical OH, which can be formed due to the other processes, – is capable of decomposition quite actively with the formation of oxygen as well as ozone. At the temperatures 600 – 1700 K the hydroxyl is decomposed quite easily according to the reaction (III.15):

$$2 OH \rightarrow O^* + H_2O,$$

forming vapour (steam) and atomic oxygen O^* , which, as it is known, is a very active oxidizer, initiator of radical-chain reactions.

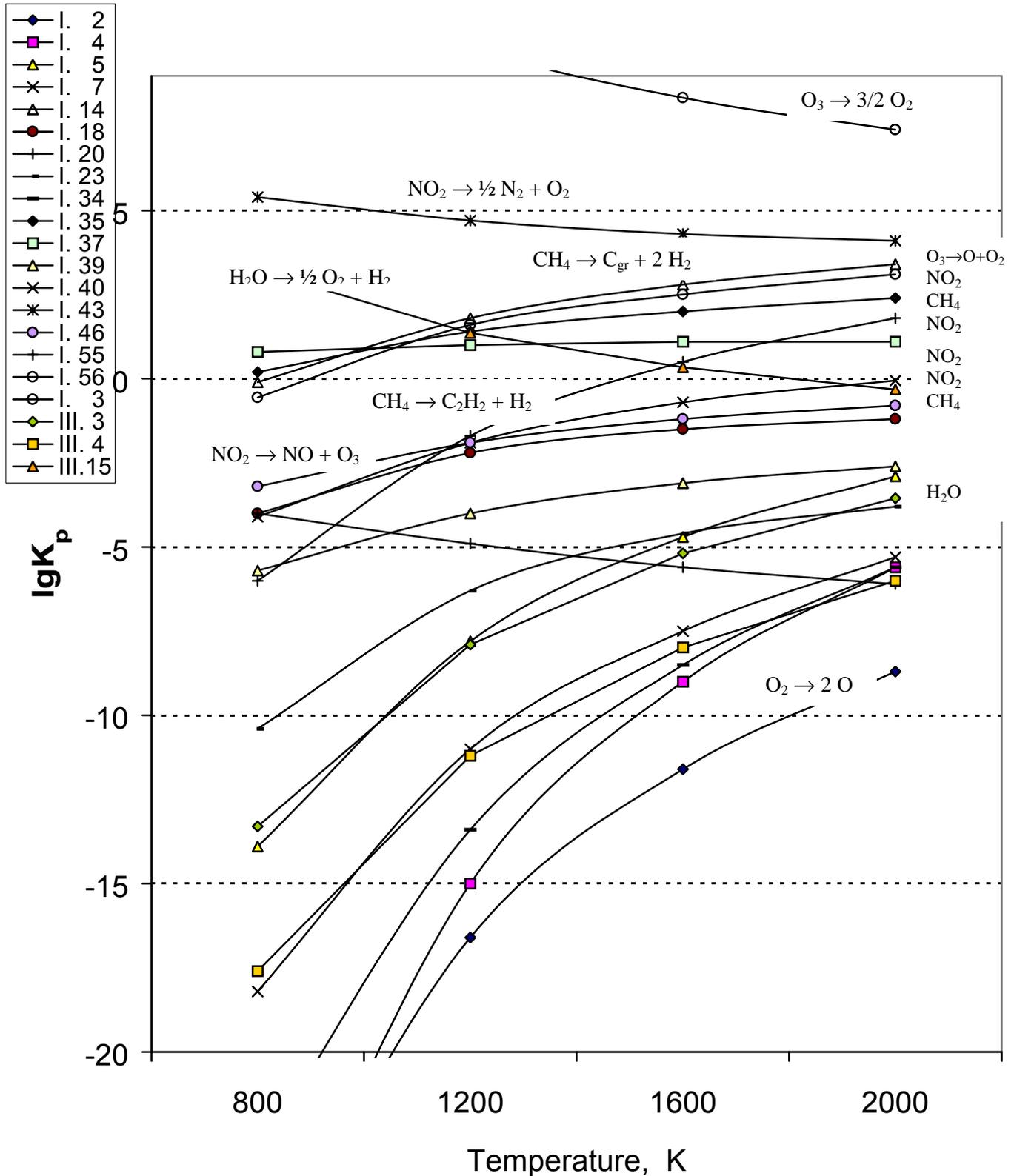


Fig. 1. Thermal decomposition of components atmosphere.

Under the influence of heat that enters into the stratosphere ozone is destroyed with the formation of oxygen (fig. 2). One can see from figure 2, that the burning products – CO₂ and CO – destroy ozone as well, beginning from temperature 600–900 °C.

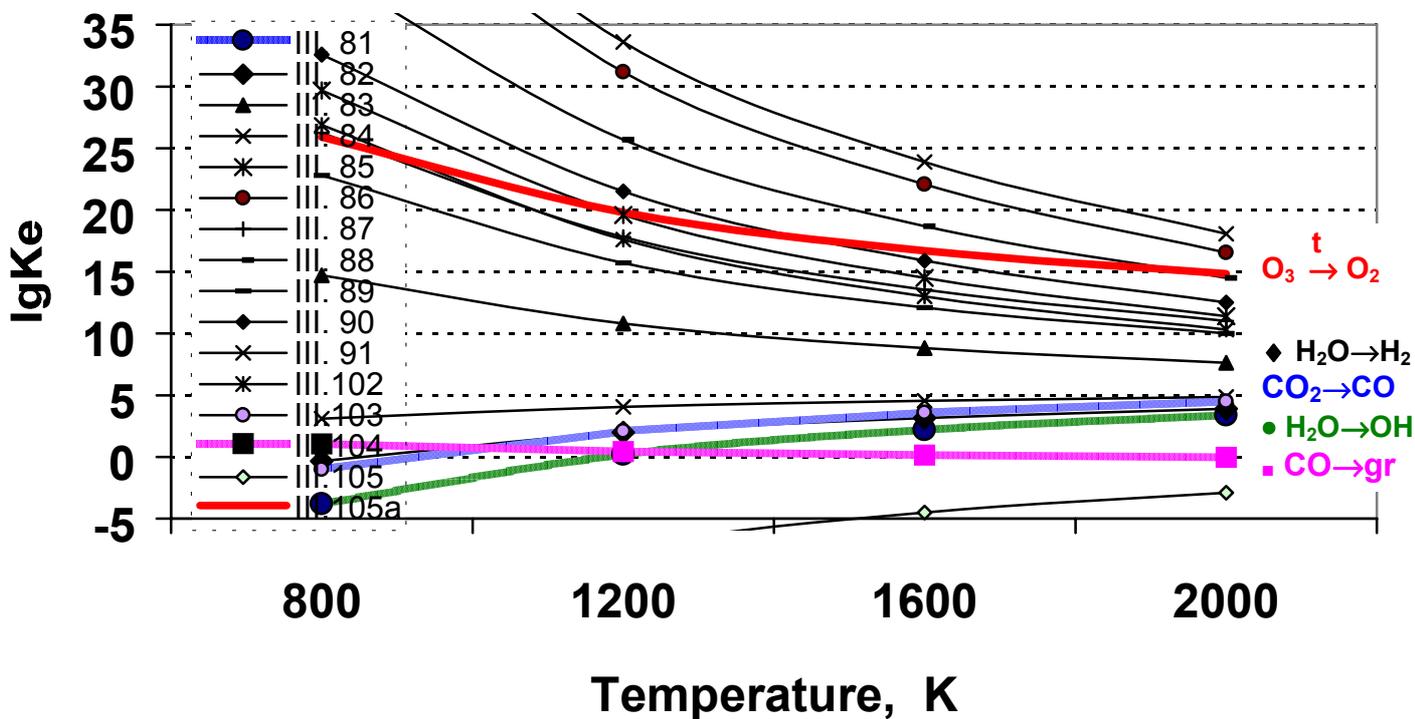


Fig. 2. Evaluation of the reactions of ozone decomposition.

The steam, formed as the consequence of evaporation of water, which is used for the extinguishing of fire, also destroys ozone. One should remember, that ~6 millions of fires takes place per year. Of course, the steam that was formed due to the burning itself, undoubtedly, makes a contribution into the negative consequences of fires to the atmospheric processes and causes the environmental damage.

Conclusions

The results of the conducted calculations indicate clearly very negative role of fires, and burning products on the ozone layer. Together with the powerful ascending flows they can easily reach the stratosphere and its interaction with O_3 will be favorable to the increase of the "ozone hole".

References

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