

OZONE DECAY IN CHEMICAL REACTOR WITH THE DEVELOPED INNER SURFACE

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The ozone decay was investigated in a chemical reactor with a developed inner surface on which it dissociates or absorbs. Ozone concentration behaves differently with time depending on where mainly decays ozone - in the volume or on the reactor surfaces. If ozone mainly decays on the reactor surface, the ozone concentration decreases with time as $\exp(-\delta t)$, where δ is determined by the decay process at the inner surface of the reactor and its total area. If ozone decay occurs primarily in the volume, the ozone concentration decreases with time as $1/(1 + \sigma t)$, where σ is determined by the common process of ozone decay in the volume.

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INTRODUCTION

Ozone is an environmentally friendly oxidant [1]. It can be used in a wide range of plasma-chemical technologies in various fields of human activity, such as medicine and veterinary medicine [2], agriculture [3], food production and storage, waste recycling [4-6] and other. This paper is devoted to the usage of ozone in food storage.

The development of ozone technologies includes solution of the three major problems: the problem of energy efficient ozone production, the problem of ozone delivery, with minimal loss, to the interaction point, and the problem of the chemical interaction of ozone with the substance to be treated. The first problem was solved with the help of barrier-free ozonizer [7] based on the streamer discharge [8-11]. The paper is devoted to the solution of the second problem.

The ozone decay in the refrigerated container for the transportation of perishable products is investigated. The loaded container can be considered as a chemical reactor with a developed inner surface on which the ozone dissociates or absorbs. Ozone is synthesized in the barrier-free streamer discharge ozonizer with the high-speed air-flow. Only a given part of the circulating cooling air flow is passed through the ozonizer. After switching ozonizer off, the ozone concentration in reactor decreases with time as a result of the ozone decay in the volume and on the inner surfaces of reactor. It was found that ozone concentration behaves differently with time depending on where mainly decays ozone - in the volume or on the reactor surfaces. If ozone mainly decays on the reactor surface, the ozone concentration decreases with time proportional to $\exp(-\delta t)$, where δ is determined by the decay process at the inner surface of the reactor and its total area. If ozone decay occurs primarily in the volume, the ozone concentration decreases with time as $1/(1 + \sigma t)$, where σ is determined by the common process of ozone decay in the volume. The analytical expressions for ozone concentration in the reactor have been obtained as function of time and parameters, such as the initial ozone concentration, the reaction rate constants, temperature, humidity, the reactor volume and its inner

surface. It is shown that the analytical results are in good agreement with the experimental data.

THEORY, EXPERIMENT AND DISCUSSION

Most of the known data on the ozone decomposition can be explained in terms of the simple atomic mechanism [1]:



In the equations (1) $\xi = \{N_2, O_2, H_2O, O_3, CO_2, He, Ar, N_2O\}$. $k_f^\xi(T)$ is the rate constant of the forward reaction. It depends on the temperature T like the rest of the reaction rate constants. $k_r^\xi(T)$ is the reverse reaction rate constant, $k_f^O(T)$ is a forward reaction rate constant. The forward reaction in first equation of (1) shows unimolecular ozone decay. This reaction is not elementary. It consists of a multi-stage process which includes activation and decay of the excited molecule through the activated complex. The reverse reaction is also not elementary. It flows in two bimolecular stages: formation of excited ozone with subsequent relaxation. The second reaction in (1) is exothermic. The excess energy is distributed over the vibrational degrees of freedom of the oxygen molecule. As a rule, vibrationally excited oxygen relaxes to the ground state.

The system of kinetic equations describing the ozone decay mechanism (1), if $\xi = \{N_2, O_2, H_2O, O_3\}$, generally is the following:

$$\frac{dC_{O_3}}{dt} = -C_{O_3} \sum_{\xi} k_f^\xi C_\xi + C_{O_2} C_O \sum_{\xi} k_r^\xi C_\xi - k_f^O C_{O_3} C_O, \quad (2)$$

$$\frac{dC_{O_2}}{dt} = C_{O_3} \sum_{\xi} k_f^\xi C_\xi - C_{O_2} C_O \sum_{\xi} k_r^\xi C_\xi + 2k_f^O C_{O_3} C_O, \quad (3)$$

$$\frac{dC_O}{dt} = C_{O_3} \sum_{\xi} k_f^\xi C_\xi - C_{O_2} C_O \sum_{\xi} k_r^\xi C_\xi - k_f^O C_{O_3} C_O, \quad (4)$$

where $C_\xi(t)$ is a concentration of ξ . For $\xi = \{N_2, H_2O\}$, the density of particles $C_\xi(t)$ may depend on time only through the initial conditions. Therefore, $C_{N_2} = \text{const}$, $C_{H_2O} = \text{const}$. The following equation can be obtained using the method of steady-state concentrations for O:

$$C_{O_3}(t) = \frac{C_{O_3}(t) \sum_{\xi} k_f^{\xi} C_{\xi}(t)}{C_{O_3}(t) \sum_{\xi} k_r^{\xi} C_{\xi}(t) + k_f^o C_{O_3}(t)}. \quad (5)$$

It is convenient to introduce the following notations:

$$F(t, T) = \sum_{\xi} k_f^{\xi}(T) C_{\xi}(t), \quad G(t, T) = \sum_{\xi} k_r^{\xi}(T) C_{\xi}(t). \quad (6)$$

The equations (2), (3) may be presented in a simple form:

$$\frac{dC_{O_3}}{dt} = -2 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2, \quad (7)$$

$$\frac{dC_{O_2}}{dt} = 3 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2. \quad (8)$$

The numerical estimations of F and G , using the rate constants of the corresponding reactions from [1], for the ozone-air mixture at the atmospheric pressure and the temperature $T \sim 300$ K, for the mass ozone concentration $MC_{O_3} < 20$ g/m³ and water concentration $MC_{H_2O} < 25$ g/m³, show that the main input to F will be achieved due to ozone decay at the collision with nitrogen. Ozone collision with oxygen and water gives the input to F by several times lower. Ozone collision with ozone gives the input by two orders lower than the ozone decay on nitrogen. This allows highly accurate calculation of F in accordance with the initial densities of nitrogen, water and oxygen – $F \approx k_f^{N_2}(T) \cdot C_{N_2} + k_f^{H_2O}(T) \cdot C_{H_2O} + k_f^{O_2}(T) \cdot C_{O_2}$. A similar analysis can be carried out for G . As a result, G with high accuracy, as well as F , does not depend on time and is defined by the initial bulk densities of nitrogen, water and oxygen – $G \approx k_r^{N_2}(T) \cdot C_{N_2} + k_r^{H_2O}(T) \cdot C_{H_2O} + k_r^{O_2}(T) \cdot C_{O_2}$.

The equations (7) and (8) show that in general case the ozone decay is described by the variable order kinetics, from the 1-st to the 2-nd order depending on the parameters of the problem. If $k_f^o C_{O_3} \gg GC_{O_2}$, ozone decay is described by the first order kinetics: $dC_{O_3}/dt = -2k_f^o F C_{O_3} / k_f^o$. In the opposite case, if $k_f^o C_{O_3} \ll GC_{O_2}$, ozone decay is described by the second order kinetics: $dC_{O_3}/dt = -2k_f^o F C_{O_3}^2 / GC_{O_2}$.

By comparing $k_f^o(T) \cdot C_{O_3}$ and $G \cdot C_{O_2}$, for the parameters of ozone-air mixture presented above, it can be found that $G \cdot C_{O_2}$ is higher than $k_f^o(T) \cdot C_{O_3}$ by more than two orders, i.e. $k_f^o(T) \cdot C_{O_3}$ can be neglected in the equations (7), (8):

$$\frac{dC_{O_3}}{dt} = -2 \frac{k_f^o F}{GC_{O_2}} C_{O_3}^2, \quad \frac{dC_{O_2}}{dt} = 3 \frac{k_f^o F}{GC_{O_2}} C_{O_3}^2, \quad (9)$$

i.e. ozone decay is defined by the second order kinetics. By defining $k = k_f^o F / GC_{O_2}$, the equations (9) can be easily integrated:

$$C_{O_3} = \frac{C_{O_3}^*}{1 + 2k C_{O_3}^* t}, \quad C_{O_2} = C_{O_2}^* + \frac{3k(C_{O_3}^*)^2 t}{1 + 2k C_{O_3}^* t}, \quad (10)$$

where $C_{O_3}(t=0) = C_{O_3}^*$, $C_{O_2}(t=0) = C_{O_2}^*$ are the initial conditions. At $t \rightarrow \infty$ $C_{O_3}(t) \rightarrow 0$, $C_{O_2}(t) \rightarrow C_{O_2}^* +$

$1.5C_{O_3}^*$. If the set of experimental points for $C_{O_3}(t_k)$ is built in the coordinates $\{t_k, 1/C_{O_3}(t_k)\}$, a straight line with the tangent ratio equal to $2k$ can be obtained:

$$1/C_{O_3}(t) = 1/C_{O_3}^* + 2kt. \quad (11)$$

It can be shown that the system of equations (9) corresponds to the following ozone decay scheme:

$2O_3 \xrightarrow{k} 3O_2$, where the effective «reaction rate constant» k is obviously dependant on the initial densities of nitrogen, water and oxygen as well as on the reaction rate constants which are included in the scheme (1).

The ozone decay on the surface can be included in the equations (7), (8). To do this, the continuity equations should be integrated over the volume:

$$\frac{\partial C_{O_3}}{\partial t} + \text{div}(\vec{\Gamma}_{O_3}) = -2 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2, \quad (12)$$

$$\frac{\partial C_{O_2}}{\partial t} + \text{div}(\vec{\Gamma}_{O_2}) = 3 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2, \quad (13)$$

where $\vec{\Gamma}_{O_3}$, $\vec{\Gamma}_{O_2}$ are the ozone and oxygen fluxes. As a result, the following equations can be obtained:

$$\frac{dN_{O_3}}{dt} + \iint_S \vec{\Gamma}_{O_3} d\vec{S} = -2 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2 V, \quad (14)$$

$$\frac{dN_{O_2}}{dt} + \iint_S \vec{\Gamma}_{O_2} d\vec{S} = 3 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2 V. \quad (15)$$

Here, V is a vessel volume where ozone decay takes place, S is a surface limiting the volume V , N_{O_3} , N_{O_2} are the number of particles in volume V . The fluxes of particles to the surface S can be estimated in the following way:

$$\vec{\Gamma}_{O_3} = (\vec{v}_{T_{O_3}} + \langle \vec{v}_{O_3} \rangle) C_{O_3}, \quad \vec{\Gamma}_{O_2} = (\vec{v}_{T_{O_2}} + \langle \vec{v}_{O_2} \rangle) C_{O_2}, \quad (16)$$

where $\vec{v}_{T_{O_3}}$, $\vec{v}_{T_{O_2}}$ are the thermal particle velocities, $\langle \vec{v}_{O_3} \rangle$, $\langle \vec{v}_{O_2} \rangle$ are the convective velocities. After the integration over the container surface the following expression can be obtained for a number of particles reaching the container surface:

$$\Delta N_{T_{O_3}} = \alpha v_{O_3} C_{O_3} S, \quad \Delta N_{T_{O_2}} = \alpha v_{O_2} C_{O_2} S, \quad (17)$$

where v_{O_3} , v_{O_2} are particle velocities, α is a coefficient considering the problem geometry. By introducing the probability of the particle decay on the surface γ_{O_3} , γ_{O_2} , the equations (14), (15) can be presented in the following way:

$$\frac{dC_{O_3}}{dt} = -2 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2 - \alpha \gamma_{O_3} v_{O_3} \frac{S}{V} C_{O_3}, \quad (18)$$

$$\frac{dC_{O_2}}{dt} = 3 \frac{k_f^o F}{GC_{O_2} + k_f^o C_{O_3}} C_{O_3}^2 - \alpha \gamma_{O_2} v_{O_2} \frac{S}{V} C_{O_2}. \quad (19)$$

Further, only the equation (18) will be considered. In accordance with the calculations for the ozone-air mixture at the atmospheric pressure and the initial mass concentrations of ozone $MC_{O_3} \leq 20$ g/m³, $K = k_f^o F / (GC_{O_2} + k_f^o C_{O_3})$ does not depend on time and is defined by the initial concentration of reagents. This

allows integration of the equation (18) using substitution $u(t) = \exp(2K \int C_{O_3}(t) dt)$:

$$\frac{d^2 u}{dt^2} + \beta \frac{S}{V} \frac{du}{dt} = 0, \quad (20)$$

where $\beta = \alpha \nu_{O_3} \gamma_{O_3}$. The solution of (20) can be presented in the following way: $u(t) = C_1 + C_2 \exp(-\beta S t / V)$. After simple transformations for $C_{O_3}(t)$, the following expression may be obtained:

$$C_{O_3}(t) = -\frac{1}{2K} \frac{C_2 \beta \frac{S}{V} \exp(-\beta \frac{S}{V} t)}{C_1 + C_2 \exp(-\beta \frac{S}{V} t)}. \quad (21)$$

Taking into consideration that at the initial time $C_{O_3}(t=0) = C_{O_3}^*$, after substitution in (21), the following expression can be obtained:

$$C_1 = -C_2 (bC_{O_3}^* + a) / (bC_{O_3}^*), \quad (22)$$

where $b = 2K$, $a = \beta S / V$. This allows rewriting the solution (21) in the following way:

$$C_{O_3}(t) = \frac{aC_{O_3}^* \exp(-at)}{a + bC_{O_3}^* [1 - \exp(-at)]}. \quad (23)$$

The solution (23), where ozone decay in volume and on the surface is taken into consideration, differs from the solution (10), where ozone decay is considered to be only in volume. In (23), the multiplier $\exp(-at)$ appeared. The multiplier is defined only by the decay on the walls. If it is dominant, ozone decay is determined by the decay on the walls, but not by the decay in the volume. The limiting cases should be analyzed. The expression (23) can be rewritten as:

$$\frac{C_{O_3}(t)}{C_{O_3}^*} = \frac{\exp(-at)}{1 + \frac{bC_{O_3}^*}{a} [1 - \exp(-at)]}. \quad (24)$$

Let us assume that $bC_{O_3}^* / a \ll 1$. This means either small initial ozone concentrations or large surface areas in relation to the volume, or both at the same time: $C_{O_3}^* \ll 1, \beta S / V \gg 1$. As the denominator of (24) has the product $[1 - \exp(-at)] bC_{O_3}^* / a$ in which $bC_{O_3}^* / a \ll 1$, and $[1 - \exp(-at)] \leq 1$, $1 / (1 + [1 - \exp(-at)] bC_{O_3}^* / a)$ may be expanded as $1 / (1 + x) \approx 1 - x$. The following expression may be obtained:

$$\frac{C_{O_3}(t)}{C_{O_3}^*} \approx \exp(-at). \quad (25)$$

It is shown that ozone decay is defined only by the decay on the surface.

Let us assume that $bC_{O_3}^* / a \gg 1$. This means either large initial ozone concentrations or small surface areas in relation to the volume, or both at the same time. Under large initial ozone concentrations, the expression (24) cannot be applied, as it considers that K does not depend on time and is defined by the initial concentrations of reagents. In this case, the equations (18), (19) should be solved numerically. Therefore, let

us analyze the case $a \ll 1$, taking into consideration that K does not depend on time. In (24), $\exp(-at)$ may be expanded:

$$\frac{C_{O_3}(t)}{C_{O_3}^*} \approx \frac{1}{1 + bC_{O_3}^* t} - \frac{at}{1 + bC_{O_3}^* t}. \quad (26)$$

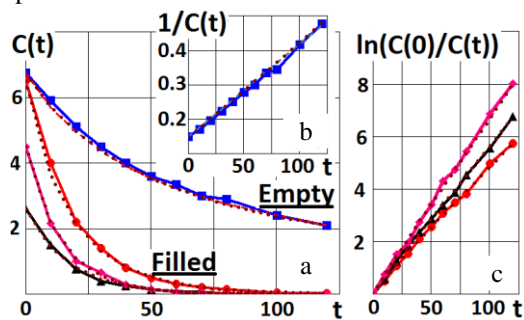
The first term in the right part (26) is the solution (10) for the ozone decay in the vessel volume, and the second term defines a small influence of the wall.

If the set of experimental points for $C_{O_3}(t_k)$ is built in the coordinates $\{t_k, \ln(C_{O_3}^* / C_{O_3}(t_k))\}$, the curve $\ln(C_{O_3}^* / C_{O_3}(t_k)) = at_k + \ln[1 + bC_{O_3}^* (1 - \exp(-at_k)) / a]$ will be obtained. At $t_k = 0$, it starts from $\ln(C_{O_3}^* / C_{O_3}(0)) = 0$, and at $t_k \rightarrow \infty$ it is almost straight:

$$\ln(C_{O_3}^* / C_{O_3}(t_k)) = at_k + \ln[1 + \frac{bC_{O_3}^*}{a}]. \quad (27)$$

Thus, there are two limiting modes of ozone decay in the vessel. The first mode considers small initial ozone concentrations, or large surface areas in relation to the volume, or both at the same time. This mode can be called the **surface dominated ozone decay mode**. In this case, ozone concentration decreased in accordance with the exponential law $C_{O_3}(t) \approx C_{O_3}^* \exp(-\delta t)$, where the exponent is determined by the surface – $\delta = \beta S / V$. The second mode can be called the **volume dominated ozone decay mode**. This mode is realized when the surface areas are small in relation to the volume, and ozone concentrations are not too large. In this case $C_{O_3}(t) \approx C_{O_3}^* / (1 + \sigma t)$, and the ozone decay is determined by the decay in the vessel volume.

Figure shows ozone decay in the empty and differently filled container for perishable products transportation.



Ozone decay in the empty and differently filled container. Concentration vs time, as well as its approximation using (10), (23). The empty container corresponds to the volume dominated ozone decay mode, and the filled container corresponds to the surface dominated ozone decay mode

The ozone concentrations vs time at given temperature and humidity are presented in Figure a. The initial ozone concentrations are little bit different. The approximations of experimental data by (10) and (23) for empty container are also shown in Figure a. The equation (23) was used for approximation of experimental data in the filled container (see Figure a). It is clear that equations (10) and (23) are good approximations for ozone decay in empty and filled

containers. Figure *b* shows ozone concentration vs time for empty container in the coordinates $\{t_k, 1/C_{O_3}(t_k)\}$, and its approximation by (10) and (23) with sufficiently small a . This is the volume dominated ozone decay mode. Figure *c* show ozone concentration vs time for differently filled container in the coordinates $\{t_k, \ln(C_{O_3}^*/C_{O_3}(t_k))\}$, and its approximation by (24). This is the surface dominated ozone decay mode. Due to increase of the container filling, the decay of ozone on its inner surface increases. This leads to an increase of the parameter a in (24), (25), (27), as can be seen from the Figure, *c*.

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РАСПАД ОЗОНА В ХИМИЧЕСКОМ РЕАКТОРЕ С РАЗВИТОЙ ВНУТРЕННЕЙ ПОВЕРХНОСТЬЮ

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Исследована кинетика распада озона в реакторе с развитой внутренней поверхностью, на которой может происходить его распад. В зависимости от того, какой из процессов распада является основным – распад в объёме, или распад на поверхности – концентрация озона ведёт себя по-разному со временем. Если распад озона происходит, в основном, на поверхности, то его концентрация уменьшается со временем пропорционально $\exp(-\delta t)$, где δ определяется процессом распада на внутренней поверхности реактора и её полной площадью. Если же распад озона происходит, в основном, в объёме, то его концентрация уменьшается со временем пропорционально $1/(1 + \sigma t)$, где σ определяется обычным процессом распада озона в объёме.

РОЗПАД ОЗОНУ В ХІМІЧНОМУ РЕАКТОРІ З РОЗВИНЕНОЮ ВНУТРІШНЬОЮ ПОВЕРХНЕЮ

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Досліджено кінетику розпаду озону в реакторі з розвиненою внутрішньою поверхнею, на якій може відбуватися його розпад. Залежно від того, який із процесів розпаду є основним – розпад в об'ємі або розпад на поверхні – концентрація озону поводить себе по-різному з часом. Якщо розпад озону відбувається, в основному, на поверхні, то його концентрація зменшується з часом пропорційно $\exp(-\delta t)$, де δ визначається процесом розпаду на внутрішній поверхні реактора та її повною площею. Якщо ж розпад озону відбувається, в основному, в об'ємі, то його концентрація зменшується з часом пропорційно $1/(1 + \sigma t)$, де σ визначається звичайним процесом розпаду озону в об'ємі.