

Influence of Nonequilibrium Processes of Radiation Cooling of Combustion Products on the Content of Nitrogen Oxides in Atmospheric Emissions

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A method was developed for the experimental and theoretical determination of nonequilibrium radiation cooling of a flame based on experimental data on its temperature and chemical composition of fuel. We obtained information about the influence of nonequilibrium radiation processes on radiation cooling of an optically thin flame. The influence of nonequilibrium processes on the formation of nitrogen oxides (NO_x) is analyzed. It is shown that nonequilibrium radiation decreases the concentration of NO_x, while the mechanisms of nonequilibrium radiation cooling can be used for controlling and optimizing the furnace process. Application of additives, which activate nonequilibrium radiation of flames, would make it possible to decrease emissions of NO into the atmosphere with combustion products.

Previous spectral radiometric measurements of flames [1–4] revealed the presence of nonequilibrium radiation in ultraviolet and optical spectral regions related to the effect of chemoluminescence during fuel combustion. The main ingredients determining nonequilibrium radiation are OH, CH, NO₂, NO, and SO₂. It is possible that the fragments formed during dissociation of complex hydrocarbon compounds in an excited state also influence the process.

Nonequilibrium radiation is formed by the core of the flame distributed over the entire volume of the medium. Thus, the radiation is transformed and involved in the heating of fuel particles and heating surfaces. Radiation cooling of molecules takes place during the time of their relaxation (~10⁻⁴ s), which is comparable with the time of chemical reaction. The cooling decreases adiabatic temperature of combustion products at the peaks of chemical reactions. Radiation

beyond the chemical reaction zone is an equilibrium process.

Nonequilibrium radiation is generated predominantly by electronic radiation bands of excited molecules of combustion products in the ultraviolet and optical spectral regions. Temperature T of the combustion zone in experiments [1–4] was measured using optical devices with an error not exceeding 2%. The known chemical composition of the gas fuel allows us to calculate adiabatic temperature T_a in the chemical reaction zone and determine the value of $\Delta T = T_a - T$, which characterizes radiation cooling in the active combustion zone. Radiation cooling can be either in equilibrium or nonequilibrium. Equilibrium radiation cooling ΔT_p can be calculated from absolute spectra of flame radiation or from measured temperature and chemical composition of combustion products and the jet flow velocity, which makes possible to determine radiation cooling ΔT_n caused by nonequilibrium radiation. It is convenient to characterize nonequilibrium radiation cooling

$\Delta T_n = \Delta T - \Delta T_p$ by the value of $\xi = \frac{\Delta T_n}{T_a}$. According to our data, this value varies from 0.02 to 0.13 and directly correlates with temperature ΔT_a .

Our method for determining nonequilibrium radiation cooling of a flame based on experimental data of its temperature and optical characteristics of combustion products made it possible for the first time to determine the influence of nonequilibrium processes on radiation cooling of an optically thin flame when the role of nonequilibrium processes in radiation cooling was maximal. The analysis of physical processes in flames under the influence of nonequilibrium radiation allows us to conclude that nonequilibrium radiation decreases the temperature of the flame and concentration of the harmful component NO_x released to the atmosphere. Owing to the decrease in the equilibrium temperature of combustion products in the chemical reaction zones, the theoretical predictions of NO concentrations in combustion products appear overestimated. The degree of

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overestimation has a positive correlation with the adiabatic temperature of the flame. Let us consider the method of calculation of ΔT_p and the results of the determination of ΔT_n based on measurements of the actual temperature T of the flame. The actual radiating volume, whose radiation is recorded by the spectrometer, has a conical fanlike shape. The projection of the input slot of the spectrometer is located at the top of this cone. For a uniform radiating medium, the rate of radiation cooling is determined by the following formula:

$$\frac{\partial T}{\partial t} = \frac{\oint (F^\uparrow(S) - F^\downarrow(S)) dS}{\bar{C}_p(T) \rho(T) V}, \quad (1)$$

where integration is performed over closed surface S comprising the entire radiating volume V . The value of $F^\downarrow(S)$ determines the integral flux of equilibrium radiation entering the radiating volume V at point S ; $F^\uparrow(S)$ is an integral flux of equilibrium radiation emitted from the radiation volume V at point S . The specific thermal capacity of the medium at constant pressure is given by the following formula:

$$\bar{C}_p(T) = \frac{\sum_i C_{pi}(T) P_i(T)}{\sum_i P_i(T)}, \quad (2)$$

where P_i is the partial pressure of component i . The summation in Eq. (2) is performed over all gas components included in the composition of combustion products; $\rho(T)$ is the density of the gas medium whose dimension is determined by the dimension of $\bar{C}_p(T)$,

$$F^\uparrow(S) = \int_0^{\pi/2} \int_0^{2\pi} \int_0^\infty J_\lambda^\uparrow(S, \theta, \varphi) \sin \theta \cos \theta \, d\theta \, d\varphi \, d\lambda, \quad (3)$$

$$F^\downarrow(S) = \int_0^{\pi/2} \int_0^{2\pi} \int_0^\infty J_\lambda^\downarrow(S, \theta, \varphi) \sin \theta \cos \theta \, d\theta \, d\varphi \, d\lambda. \quad (4)$$

In Eqs. (3) and (4), the zenith angle θ is calculated from the normal to closed surface at observation point S . The method of calculating J_λ^\uparrow in a nonscattering gas medium is described in [5–8]. The boundary conditions for solving the equation of transport were specified according to the constructive solution of measurement complexes [1, 2]. The functions of spectral transmission were calculated using a two-parameter method of equivalent mass along continuous pathways from the radiating volume to the observation point according to the recommendations in [7, 8].

Table

| T_a , K | $\xi = \frac{\Delta T_n}{T_a}$ | Flame type |
|-----------|--------------------------------|-----------------------|
| 1860 | 0.021 | propane–butane–air |
| 2100 | 0.032 | " |
| 2350 | 0.048 | " |
| 2500 | 0.06 | " |
| 2360 | 0.055 | propane–butane–oxygen |
| 2600 | 0.069 | " |
| 2800 | 0.085 | " |
| 3120 | 0.13 | acetylene–oxygen |
| 2360 | 0.051 | hydrogen–oxygen |
| 2500 | 0.056 | " |
| 2700 | 0.068 | hydrogen–oxygen |
| 3060 | 0.095 | " |
| 3220 | 0.105 | " |

Parameter $\xi = \frac{\Delta T_n}{T_a}$, where $\Delta T_n = \Delta T_a - \Delta T_p$, $\Delta T_p =$

$\frac{\partial T}{\partial t} \Delta t$, Δt is the residence time of combustion products in the radiating volume and is determined by the velocity of the gas flow motion.

Table 1 presents the results of the experimental and theoretical determination of $\xi = \frac{\Delta T_n}{T_a}$ for hydrogen–oxygen, hydrogen–air, propane–butane–oxygen, propane–butane–air, and acetylene–oxygen flames. If adiabatic temperature ΔT_a increases, the value of $\xi = \frac{\Delta T_n}{T_a}$ increases. At $T_a = 1800$ – 3200 K, this value varies from 2 to 13%.

The results of experimental determination of source function B_λ and nonequilibrium coefficients $\eta_\lambda = \frac{B_\lambda(T)}{B_\lambda^{abb}(T)}$ [1–4], where $B_\lambda^{abb}(T)$ is the spectral brightness of an absolutely black body (Planck function), showed that nonequilibrium radiation is predominantly formed in electronic radiation spectra of molecules located in ultraviolet and optical spectral regions. The nonequilibrium effect of radiation in rotation-vibration bands of the infrared spectral region is notable only at adiabatic temperatures $T_a > 2500$ K.

Significant cooling of the chemical reaction ξ zones during a $\sim 10^{-4}$ -s period, which is comparable with the time of the chemical reactions, is a peculiarity of nonequilibrium processes. Owing to this, the equilibrium temperature of the flame decreases significantly, which

leads to much lower concentrations of nitrogen monoxide NO. Indeed, according to [9, 10],

$$[\text{NO}]_{\max} = 4.6 \sqrt{C_{\text{N}_2} C_{\text{O}_2}} \exp\left(\frac{-21500}{RT_{\max}}\right), \quad (5)$$

and if fuel is burned in the air, the concentrations are

$$C_{\text{O}_2} = \frac{21(\alpha - 1)V_0}{1 + \alpha V_0}, \quad (6)$$

$$C_{\text{N}_2} = \frac{79\alpha V_0}{1 + \alpha V_0}.$$

Here, T_{\max} is the maximal absolute temperature at the peak volumes of chemical reactions, R is the gas constant, V_0 is the theoretical amount of air needed for burning the fuel, and α is the coefficient of excess air. The real concentration of NO in the combustion products is one order of magnitude lower than the value obtained from Eqs. (5), (6). From our point of view, this is caused by nonequilibrium radiation cooling of the peaks of chemical reactions. The real concentration of NO can depend on the degree of turbulization of burning and the spectrum of turbulent motions.

While considering the dependence of nonequilibrium radiation absorption by the combustion products, we shall pay attention to the intensification of absorption with increasing power of the furnace chamber. Hence, if the power of the furnace chamber increases, nonequilibrium radiation is more intensely transformed into the thermal energy of fuel particles and the thermal energy of combustion products. Nonequilibrium radiation cooling decreases and the concentration of NO_x increases with increasing power of the furnace. This is actually evident from the results of statistically reliable observations [9].

Determinations of the chemical composition of wood combustion products revealed increased concentrations of NO_2 . The ratio of concentrations $\frac{C(\text{NO}_2)}{C(\text{NO})}$ changes from ~ 0.1 in the case of burning of black oil and gases to $\sim 1/3$ in the case of wood. This indicates that an increase in the concentration of NO_2 decreased the flame temperature and, consequently, the concentration of NO. The concentration of NO in smoke gases would increase with increasing fineness of liquid fuel

dispersion and crushing of solid fuel. From the point of view of ecological impact of the atmospheric emissions on flora and fauna, chamber combustion of coarsely crushed and dispersed fuel is expedient. In order to minimize the human impact on the environment, it is reasonable to burn fuel at lower pressures, since nonequilibrium radiation cooling inversely correlates with pressure in the furnace (extinction of chemoluminescence directly correlates with pressure).

The presence of sulfur compounds in fuel produces nonequilibrium radiation of SO_2 in the spectral region $\lambda < 0.4 \mu\text{m}$ [7, 8], which decreases the flame temperature and consequently the concentration of NO_x .

In the future perspective, the mechanisms of nonequilibrium radiation cooling can be used for regulation and optimization of the furnace process, while application of additives that reactivate the nonequilibrium radiation of flames would allow us to reduce the emissions of NO into the atmosphere with combustion products.

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