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MATHEMATICAL MODEL FOR SOOT FORMATION DURING NATURAL-GAS BURNING. 2. SOOT FORMATION PARAMETER AND POLYATOMIC CARBON COMPLEXES

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The first part of our work [1] was concerned with the elements of the mathematical model for methane dehydrogenation and its radicals. Relations were obtained for determining critical temperatures of the above process. The second part is aimed at finding a soot formation parameter and considers the mechanism of forming polyatomic hydrocarbon complexes that determine the concentration and the sizes of soot particles in a natural gas flame.

As shown in [1], the critical dehydrogenation temperatures, T_i^*, of methane molecules and its radicals regulate the number of free hydrogen atoms H that enter a gas volume. The final stage of this process is completed with the destruction of the radical $\dot{C}\ddot{H}$. As a result of an energetic break-up of the C−H bond in this radical, free carbon atoms, which are the nucleation centers for soot particles, enter the gas volume.

The development of the above process is determined by the probabilities $W_{(3-1)}$, $W_{(2-1)}$, and $W_{(1-1)}$ of the break-up of the C−H bonds in methane molecules and in its radicals. Naturally, the concentrations of the so-formed free hydrogen atoms are proportional to those of the initial compounds N_{CH_4}, $N_{\dot{C}H_3}$, $N_{C\ddot{H}_2}$ and $N_{\dot{C}\ddot{H}}$.

Considering [1], it may be written that

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$$N_{H(4-1)} = N_{CH_4} W^{+}_{(4-1)} = \frac{N_{CH_4}}{\tau_0} \exp\left[-\frac{E_{(4-1)}}{kT}\right], \tag{1}$$

$$N_{H(3-1)} = N_{\dot{C}H_3} W^{+}_{(3-1)} = \frac{N_{\dot{C}H_3}}{\tau_0} \exp\left[-\frac{E_{(3-1)}}{kT}\right], \tag{2}$$

$$N_{H(2-1)} = \frac{N_{\ddot{C}H_2}}{\tau_0} \exp\left[-\frac{E_{(2-1)}}{kT}\right], \tag{3}$$

$$N_{H(1-1)} = \frac{N_{\dddot{C}H}}{\tau_0} \exp\left[-\frac{E_{(1-1)}}{kT}\right], \tag{4}$$

where τ_0 is the period of hydrogen atom eigenfrequencies in the hydrocarbon radical [1].

The total volume concentration of the free hydrogen atoms that enter the gas volume in this fashion will be

$$N_H = \frac{1}{\tau_0} \sum_{n=1}^{4} CH_n \exp\left[-\frac{E_{n-1}}{kT}\right]. \tag{5}$$

In this case, the ratio N_H/N_{CH_4} will determine the fraction of the methane molecules subjected to complete dehydrogenation (see the notation in [1]).

A calculation of the quantity N_H requires a preliminary determination of the equilibrium concentrations of $\dot{C}H_3$, $\ddot{C}H_2$ and $\dddot{C}H$. radicals in the gas volume. For this purpose, the corresponding kinetic equations may be used:

$$\begin{aligned}
\frac{d}{d\tau}(N_{\dot{C}H_3}) &= W^{+}_{\dot{C}H_3} - W^{-}_{\dot{C}H_3} = \frac{1}{\tau^{+}_{(4-1)}} N_{CH_4} - \frac{1}{\tau^{-}_{(3-1)}} N_{\dot{C}H_3}, \\
\frac{d}{d\tau}(N_{\ddot{C}H_2}) &= W^{+}_{\ddot{C}H_2} - W^{-}_{\ddot{C}H_2} = \frac{1}{\tau^{+}_{(3-1)}} N_{\dot{C}H_3} - \frac{1}{\tau^{-}_{(2-1)}} N_{\ddot{C}H_2}, \\
\frac{d}{d\tau}(N_{\dddot{C}H}) &= W^{+}_{\dddot{C}H} - W^{-}_{\dddot{C}H} = \frac{1}{\tau^{+}_{(2-1)}} N_{\ddot{C}H_2} - \frac{1}{\tau^{-}_{(1-1)}} N_{\dddot{C}H}.
\end{aligned} \tag{6}$$

The kinetic equation

$$\frac{d}{d\tau}(N_C) = W_C^{+} - W_C^{-} = \frac{1}{\tau^{+}_{(1-1)}} N_{\dddot{C}H} - \frac{1}{\tau^{-}_{(0-1)}} N_C \tag{7}$$

yields, in this case, the equilibrium concentration of free carbon atoms in the gas volume. Here the quantity $\tau_{(0-1)}^{-} = \tau_0^{-}$ is the mean-free time of the free carbon atom.

If we assume that the appearance probability of each subsequent radical in the gas volume does not depend on those of their preceding radicals, from kinetic Eqs. (6) it is easy to determine the equilibrium concentrations of all intermediate radicals and, finally, of free carbon atoms:

for radicals $\dot{C}H_3$ with $W_{\dot{C}H_3}^{+} = W_{\dot{C}H_3}^{-}$

$$N_{\dot{C}H_3} = N_{CH_4} \frac{\tau^{-}_{(3-1)}}{\tau^{+}_{(4-1)}}; \tag{8}$$

for radicals $\dddot{C}H_2$ with $W_{\ddot{C}H_2}^{+} = W_{\ddot{C}H_2}^{-}$

$$N_{\ddot{C}H_2} = N_{\dot{C}H_3} \frac{\tau^{-}_{(2-1)}}{\tau^{+}_{(3-1)}} = N_{CH_4} \frac{\tau^{-}_{(3-1)}\tau^{-}_{(2-1)}}{\tau^{+}_{(4-1)}\tau^{+}_{(3-1)}}; \tag{9}$$

for radicals $\dddot{\mathrm{C}}\mathrm{H}$ with $W_{\dddot{\mathrm{C}}\mathrm{H}}{}^{+} = W_{\dddot{\mathrm{C}}\mathrm{H}}{}^{-}$

$$N_{\dddot{\mathrm{C}}\mathrm{H}} = N_{\ddot{\mathrm{C}}\mathrm{H}_2} \frac{\tau^{-}_{(1-1)}}{\tau^{+}_{(2-1)}} = N_{\mathrm{CH}_4} \frac{\tau^{-}_{(3-1)}\,\tau^{-}_{(2-1)}\,\tau^{-}_{(1-1)}}{\tau^{+}_{(4-1)}\,\tau^{+}_{(3-1)}\,\tau^{+}_{(2-1)}}; \tag{10}$$

and, lastly, for free carbon with $W_{\mathrm{C}}{}^{+} = W_{\mathrm{C}}{}^{-}$

$$N_{\mathrm{C}} = N_{\dddot{\mathrm{C}}\mathrm{H}} \frac{\tau^{-}_{(0-1)}}{\tau^{+}_{(1-1)}} = N_{\mathrm{CH}_4} \frac{\tau^{-}_{(3-1)}\,\tau^{-}_{(2-1)}\,\tau^{-}_{(1-1)}\,\tau^{-}_{(0-1)}}{\tau^{+}_{(4-1)}\,\tau^{+}_{(3-1)}\,\tau^{+}_{(2-1)}\,\tau^{+}_{(1-1)}}. \tag{11}$$

Formula (11) relates the volume equilibrium concentration, N_C, of free carbon atoms to the methane molecule concentration, N_{CH_4}, as well as to the corresponding mean dissociation times and to the mean-free times of free hydrocarbon radicals.

Here, the numerator is the product of the mean-free times of the hydrocarbon radicals and of the carbon atoms

$$\tau^{-}_{(3-1)} = \tau^{-}_{\dot{\mathrm{C}}\mathrm{H}_3};\quad \tau^{-}_{(2-1)} = \tau^{-}_{\ddot{\mathrm{C}}\mathrm{H}_2};\quad \tau^{-}_{(1-1)} = \tau^{-}_{\dddot{\mathrm{C}}\mathrm{H}};\quad \tau^{-}_{(0-1)} = \tau^{-}_{\mathrm{C}},$$

and the denominator is the product of the mean dissociation times of a hydrogen atom from a CH_4 molecule and from intermediate hydrocarbon radicals

$$\tau^{+}_{(4-1)} = \tau^{+}_{\mathrm{CH}_4};\quad \tau^{+}_{(3-1)} = \tau^{+}_{\dot{\mathrm{C}}\mathrm{H}_3};\quad \tau^{+}_{(2-1)} = \tau^{+}_{\ddot{\mathrm{C}}\mathrm{H}_2};\quad \tau^{+}_{(1-1)} = \tau^{+}_{\dddot{\mathrm{C}}\mathrm{H}}.$$

With allowance for the aforesaid, we rewrite (11) in the form

$$N_{\mathrm{C}} = A \frac{\tau^{-}_{\mathrm{C}}}{\tau^{+}_{\mathrm{CH}_4}} N_{\mathrm{CH}_4}, \tag{12}$$

where

$$A = \frac{\tau^{-}_{\dot{\mathrm{C}}\mathrm{H}_3}\,\tau^{-}_{\ddot{\mathrm{C}}\mathrm{H}_2}\,\tau^{-}_{\dddot{\mathrm{C}}\mathrm{H}}}{\tau^{+}_{\dot{\mathrm{C}}\mathrm{H}_3}\,\tau^{+}_{\ddot{\mathrm{C}}\mathrm{H}_2}\,\tau^{+}_{\dddot{\mathrm{C}}\mathrm{H}}}. \tag{13}$$

As already mentioned, the quantities $1/\tau^{-}_{\dot{\mathrm{C}}\mathrm{H}_3}$, $1/\tau^{-}_{\ddot{\mathrm{C}}\mathrm{H}_2}$, and $1/\tau^{-}_{\dddot{\mathrm{C}}\mathrm{H}}$ are the destruction probabilities of the corresponding hydrocarbon radicals after hydrogen atoms attach to them. Their product

$$\frac{1}{\tau^{-}_{*}} = \frac{1}{\tau^{-}_{\dot{\mathrm{C}}\mathrm{H}_3}}\,\frac{1}{\tau^{-}_{\ddot{\mathrm{C}}\mathrm{H}_2}}\,\frac{1}{\tau^{-}_{\dddot{\mathrm{C}}\mathrm{H}}} \tag{14}$$

characterizes, in this case, the generation probability of hydrocarbon radicals, i.e., it predetermines the soot formation process.

The parameter

$$A = \frac{1/\tau^{+}_{*}}{1/\tau^{-}_{*}} = \left(\frac{\tau^{-}}{\tau^{+}}\right)_{\dot{\mathrm{C}}\mathrm{H}_3}\left(\frac{\tau^{-}}{\tau^{+}}\right)_{\ddot{\mathrm{C}}\mathrm{H}_2}\left(\frac{\tau^{-}}{\tau^{+}}\right)_{\dddot{\mathrm{C}}\mathrm{H}} \tag{15}$$

is, thus, the soot formation parameter and characterizes a relationship between the probabilities of developing and ceasing the soot formation process in its initial stages. The greater the quantity A, the more probable and strong will be the soot formation, i.e., the possibility of burning methane in a bright flame. Note that the aforesaid concerns the equilibrium conditions for the thermal decomposition of methane and its radicals.

In practice, of most interest are the nonequilibrium processes when the generation and destruction rates of free monatomic carbon are not equal. Just such a process is typical of the conditions for burning hydrocarbon fuels in commercial plants. Under these conditions, the quantities $\tau^{\pm}_{\mathrm{CH}_4}$, $\tau^{\pm}_{\dot{\mathrm{C}}\mathrm{H}_3}$, $\tau^{\pm}_{\ddot{\mathrm{C}}\mathrm{H}_2}$, $\tau^{\pm}_{\dddot{\mathrm{C}}\mathrm{H}}$ and $\tau^{\pm}_{\mathrm{C}}$ may be considered to be the corresponding relaxation times.

The relaxation time, τ_{C^-}, of free monatomic carbon characterizes the time during which carbon atoms in equilibrium pass to another equilibrium but bound state. Thus, this relaxation time specifies a lifetime of free carbon atoms.

If the relaxation time, τ_{C^-}, of monatomic carbon is large compared to that of the intermediate hydrocarbon radicals, then soot formation may be assumed to be in quasi-equilibrium. This means that all intermediate nonequilibrium hydrocarbon radicals rapidly pass to the equilibrium state, and the nonequilibrium state must be taken into account only in the destruction stage of the radical $\dot{C}H$, i.e., in forming free monatomic carbon.

Conversely, if the relaxation time, τ_{C^-}, is small compared to that of the hydrocarbon radicals, then all intermediate stages of the dehydrogenation process are nonequilibrium, and the corresponding relaxation times are necessary for their description. This implies that when integrating the above kinetic equations we must take into account that $W^+ \neq W^-$.

Based on Eqs. (6), we may write for the radical $\dot{C}H_3$:

$$\frac{d}{d\tau}(N_{\dot{C}H_3}) = W^+_{\dot{C}H_3} - \frac{N_{\dot{C}H_3}}{\tau^-_{\dot{C}H_3}} \tag{16}$$

or

$$\frac{d\left(W^+_{\dot{C}H_3} - \dfrac{N_{\dot{C}H_3}}{\tau^-_{\dot{C}H_3}}\right)}{\left(W^+_{\dot{C}H_3} - \dfrac{N_{\dot{C}H_3}}{\tau^-_{\dot{C}H_3}}\right)} = -\frac{1}{\tau^-_{\dot{C}H_3}}\,d\tau.$$

Upon integration, we have for the initial condition $N_{\dot{C}H_3}\,|_{\tau=0} = 0$

$$N_{\dot{C}H_3} = W^+_{\dot{C}H_3}\tau^-_{\dot{C}H_3}\left[1 - \exp\left(-\frac{\tau}{\tau^-_{\dot{C}H_3}}\right)\right]. \tag{17}$$

Equation (17) determines the time dependence of the volume concentration of the hydrocarbon radical $\dot{C}H_3$. As was to be expected, with the relaxation time, CH_3. being small, the volume concentration of radicals $\dot{C}H_3$ tends to its equilibrium value $N^0_{\dot{C}H_3}$:

$$N_{\dot{C}H_3} = W^+_{\dot{C}H_3}\tau^-_{\dot{C}H_3} = N^0_{\dot{C}H_3}.$$

In determining the concentration of the radicals $\dot{C}H_3$, their formation rate, $W^+_{\dot{C}H_3}$, was taken to be constant since the number of the mentioned hydrocarbon radicals ($\dot{C}H_3$) formed per unit time was proportional to the time-independent assigned concentration, N_{CH_4}, of the methane molecules in the gas volume.

It is more difficult to determine the volume concentration, $N_{\dot{C}H_2}$, of the radicals $\dot{C}H_2$, as their formation rate $\dot{C}H_2$, in turn, depends on the time-dependent concentration, $N_{\dot{C}H_3}$, of the radicals $\dot{C}H_3$. Writing, according to (16), the equation

$$\frac{d}{d\tau}(N_{\dot{C}H_2}) = W^+_{\dot{C}H_2} - \frac{N_{\dot{C}H_2}}{\tau^-_{\dot{C}H_2}} \tag{18}$$

and bearing in mind that under the considered conditions

$$W^+_{\dot{C}H_2} = \frac{N_{\dot{C}H_3}}{\tau^+_{\dot{C}H_3}}\left[1 - \exp\left(-\frac{\tau}{\tau^-_{\dot{C}H_2}}\right)\right], \tag{19}$$

we obtain an equation to determine the concentration of the radical $\dot{C}H_2$:

$$\frac{d}{d\tau}(N_{\dot{C}H_2}) = \frac{N^0_{\dot{C}H_3}}{\tau^+_{\dot{C}H_3}}\left[1 - \exp\left(-\frac{\tau}{\tau^-_{\dot{C}H_3}}\right)\right] - \frac{N_{\dot{C}H_2}}{\tau^-_{\dot{C}H_2}}, \tag{20}$$

where $N^0_{\dot{C}H_3}$ is the equilibrium concentration of the radicals $\dot{C}H_3$ in the gas volume.

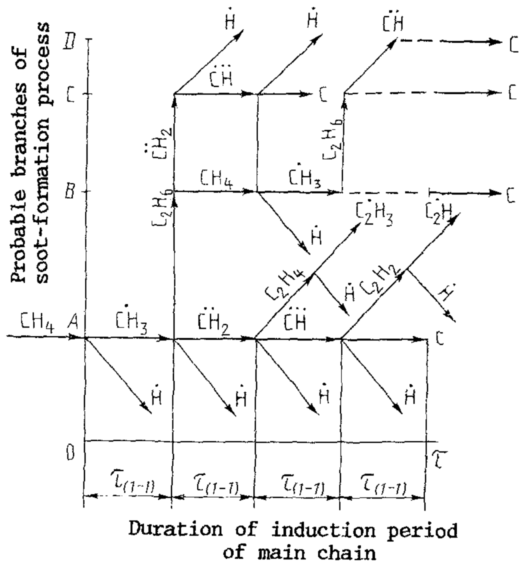

Fig. 1. Scheme of probable trends in developing the soot formation mechanism. τ, sec.

As was to be expected, at small relaxation times $\tau^{-}_{\dot{C}H_3} << \tau$, the quantity $W^{+}_{\ddot{C}H_2}$, tends to its equilibrium value:

$$W^{+}_{\ddot{C}H_2}\Big|_{\left(\frac{\tau}{\tau^{-}_{CH_3}}\right)\to\infty} = W^{0}_{\ddot{C}H_2} = \frac{N^{0}_{\ddot{C}H_2}}{\tau^{-}_{\dot{C}H_3}}.$$

By integrating Eq. (20), it is not difficult to determine the volume concentration of the radicals $\ddot{C}H_2$ in the gas volume:

$$N_{\ddot{C}H_2} = N^{0}_{\dot{C}H_3}\frac{\tau^{-}_{\dot{C}H_3}}{\tau^{+}_{\dot{C}H_3}}\left[1-\exp\left(-\frac{\tau^{+}_{(1-1)}}{\tau^{-}_{\dot{C}H_3}}\right)\right]\left[1-\exp\left(-\frac{\tau}{\tau^{-}_{\ddot{C}H_2}}\right)\right]. \tag{21}$$

Similarly, the volume concentration of the hydrocarbon radicals $\ddot{C}H$ may be found to be

$$N_{\ddot{C}H} = N^{0}_{\dot{C}H_3}\frac{\tau^{-}_{\ddot{C}H_2}\tau^{-}_{\ddot{C}H}}{\tau^{+}_{\dot{C}H_3}\tau^{+}_{\ddot{C}H_2}}\left[1-\exp\left(-\frac{\tau^{+}_{(1-1)}}{\tau^{-}_{\dot{C}H_3}}\right)\right]\times\left[1-\exp\left(-\frac{\tau^{+}_{1-1)}}{\tau^{-}_{\ddot{C}H_2}}\right)\right]\left[1-\exp\left(-\frac{\tau}{\tau^{-}_{\ddot{C}H}}\right)\right]. \tag{22}$$

As already noted, the quantity $N^{0}_{\dot{C}H_3}$ that enters into Eqs. (20)-(22) is the equilibrium concentration of the hydrocarbon radicals $\dot{C}H_3$ in the gas volume and is related to the initial concentration of the methane molecules CH_4 by:

$$N^{0}_{\dot{C}H_3} = N_{CH_4}\frac{\tau^{-}_{\dot{C}H_3}}{\tau^{+}_{\dot{C}H_4}}. \tag{23}$$

Bearing in mind Eq. (22), allowing for Eq. (23), and denoting

$$z = \left[1-\exp\left(-\frac{\tau^{+}_{(1-1)}}{\tau^{-}_{\dot{C}H_3}}\right)\right]\times\left[1-\exp\left(-\frac{\tau^{+}_{(1-1)}}{\tau^{-}_{\dot{C}H_3}}\right)\right]\left[1-\exp\left(-\frac{\tau}{\tau^{-}_{\ddot{C}H}}\right)\right],$$

we arrive at

$$N_{\ddot{C}H} = \frac{\tau^{+}_{\ddot{C}H}}{\tau^{+}_{\dot{C}H_4}} A z N_{CH_4}. \tag{24}$$

Equation (24) determines the volume concentration, $N_{\ddot{C}\dot{H}}$, of the radicals $\ddot{C}\dot{H}$, directly from which the free carbon atoms enter the gas volume due to the energetic dissociation of the C−H bond. Thus, this equality is the reference point in calculations of the concentration N_C of the free carbon atoms in the gas volume. Also, the rate of forming free hydrocarbon atoms is determined by:

$$W_{C}^{+} = Az\,\frac{N_{CH_4}}{\tau^{+}_{CH_4}}. \tag{25}$$

According to the adopted reaction scheme which is based on the main kinetic concepts [4] of the mechanism of methane thermal transformation (see Fig. 1), during a time period $\tau_{(1\text{-}1)}{}^{+}$ one free carbon atom that forms on the corresponding chain is added to the system. This means that the above time period $\tau_{(1\text{-}1)}{}^{+}$ must be preceded by a chain of processes for the formation of one radical $\ddot{C}\dot{H}$ from the radical $\dot{C}\dot{H}_2$, one radical $\dot{C}\dot{H}_2$ from the radical $C\dot{H}_3$, and, finally, one radical $C\dot{H}_3$ from a CH_4 molecule, thereby providing for a continuous dehydrogenation, with pyrolysis end product in the form of free monatomic carbon, assuming that a gas temperature T exceeds the critical dehydrogenation temperatures T_i^*.

The forming monatomic carbon represents nucleation centers on which, due to their polymerization, the polyatomic carbon complexes appear, i.e., soot particles, whose sizes and masses are determined by the number of carbon atoms they contain. These form when free carbon atoms or hydrocarbon complexes C_m collide with CH_4 molecules, radicals $C\dot{H}_3$, $\dot{C}\dot{H}_2$, and $\ddot{C}\dot{H}$, as well as with other carbon atoms and polycarbon complexes. Simultaneous with the above collisions, the polycarbon complexes may also grow when the complexes containing different numbers of carbon atoms collide. Free carbon atoms and carbon complexes C_m interact with CH_4 molecules and hydrocarbon radicals according to the reaction

$$C_m + CH_4 \rightarrow C_{m+1} + nH, \quad n = 1,\ 2,\ 3,\ 4, \tag{26}$$

thereby resulting in the formation of the carbon complexes C_{m+1} consisting of (m+1) carbon atoms in the presence of collisions. The interaction of the free carbon atoms among themselves as well as with polycarbon complexes and the interaction of the complexes between themselves proceed according to the reaction

$$C_m + C_p \rightarrow C_{m+p} \tag{27}$$

and result, at each collision, in the formation of higher carbon complexes composed of (m+p) carbon atoms.

The interactions (26) and (27) are dominant in monatomic carbon polymerization.

A mass, M_m, of an arbitrary carbon complex C_m composed of m carbon atoms varies due to two oppositely directed processes: during collisions of the complex C_m with the hydrocarbon units CH_n that occur according to Eq. (26) and during collisions between different hydrocarbon complexes C_p that occur according to Eq. (27). One of them is connected with increasing the mass of the complex due to the carbon atoms attached to it during collisions of the complex with the units CH_n and other carbon complexes; the other is connected with decreasing the complex C_m mass due to the fact that a part of carbon atoms with energies exceeding carbon bond energies in the complex C_m can leave this complex as a result of thermal motion.

Hence, varying the mass, M_m, of the carbon complex is a continuous dynamic process which is determined by the system temperature and is described by the equation

$$\frac{dM_m}{d\tau} = U_m^{+} - U_m^{-}. \tag{28}$$

Here $U_m{}^{+}$ is the rate of increase of the mass of the carbon complex C_m due to carbon atom attachment to it, and $U_m{}^{-}$ is the rate of decrease of the mass of the complex due to carbon atom detachment. According to the kinetic theory of gases, the quantity $U_m{}^{+}$ depends on the volume concentration N_{CH_n} of the associations CH_n, on the volume concentration N_{Cp} of the complexes C_p, as well as on the effective collision cross-sections σ_{CH_n}, σ_{C_p} and the mean relative velocities $\bar{V}_{CH_n}$ and $\bar{V}_{C_p}$:

$$U_m^{+} = \sum_{n=1}^{4} N_{CH_n}\sigma_{CH_n}\bar{V}_{CH_n} + \sum_{p} N_{C_p}\sigma_{C_p}\bar{V}_{C_p}, \tag{29}$$

where

$$\sigma_{CH_n} = \pi (r_{C_m} + r_{CH_n})^2; \tag{30}$$

$$\sigma_{C_p} = \pi (r_{C_m} + r_{C_p})^2. \tag{31}$$

By the relative velocities $\bar{V}_{CH_n}$ and $\bar{V}_{C_p}$ are understood the thermal velocities of the associations CH_n and complexes C_p with respect to the complex C_m. The quantities $\bar{V}_{CH_n}$ and $\bar{V}_{C_p}$ are equal to:

$$\bar{V}_{CH_n} = \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{\mu_{CH_n}} \right)^{1/2}, \tag{32}$$

$$\bar{V}_{C_{(p)}} = \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{\mu_{C_p}} \right)^{1/2}. \tag{33}$$

Here,

$$\mu_{CH_n} = \frac{M_m M_{CH_n}}{M_m + M_{CH_n}}, \tag{34}$$

$$\mu_{C_{(p)}} = \frac{M_m M_p}{M_m + M_p}, \tag{35}$$

where M_{CH_n} and M_p are the masses of the hydrocarbon associations CH_n and the carbon complexes C_p, respectively.

Taking into account that $M_m >> M_{CH_4}$, and $r_{C_m} >> r_{CH_4}$, the expression for the rate of increase of the mass of the carbon complex C_m vs. temperature T may be written as:

$$U_m^- = 4\pi r_{C_m}^2 \sqrt{\frac{kT}{2\pi M_{CH_4}}} N_{CH_n}. \tag{36}$$

On the other hand, the quantity U_m^- depends on temperature and, according to the kinetic theory of fluids, is a measure of the carbon atom evaporation rate, $\bar{\pi} r^2_{C_m}$, from the surface of the carbon complex C_m:

$$U_m^- = N_m \sqrt{\frac{kT}{2\pi M_C}}\, 4\pi r_m^2 \exp\left(-\frac{E_m}{kT} \right), \tag{37}$$

where N_m is the volume concentration of carbon atoms in the complex C_m; and E_m is the carbon atom binding energy on the surface of the complex C_m.

By simplifying, Eq. (37) reduces to:

$$U_m^- = \frac{\rho_C}{m_C} \sqrt{\frac{kT}{2\pi m_C}} \exp\left(-\frac{E_m}{kT} \right) 4\pi r_{C_m}^2, \tag{38}$$

It may be noted that the evaporation rate U_m^- is a function of the ratio of the binding energy of the carbon atoms in the hydrocarbon complex E_m and the quantity kT. For $kT \ll E_m$, the quantity U_m^- is small and atom evaporation may be neglected.

As T grows the evaporation rate increases significantly.

Allowing for the aforesaid, it may be written that

$$\frac{dM_m}{d\tau} = 4\pi r_{C_m}^2 \sqrt{\frac{kT}{2\pi M_{CH_4}}} N_{CH_4} \left[1 - \frac{\rho_C}{m_C} \exp\left(-\frac{E_m}{kT} \right) \right]. \tag{39}$$

Equation (39) determines the time variation of the mass of one carbon complex C_m. Multiplying this expression by the number of carbon complexes C_m per unit volume makes it easy to determine the time variation of the weight concentration of carbon complexes C_m.

The process of forming the carbon complexes C_m starts with the formation of a free monatomic carbon which is then transformed into polyatomic carbon complexes C_m.

Assuming that the formation of monatomic carbon occurs by a successive detachment of separate hydrogen atoms, an induction time, τ_{ind}, for soot formation may be determined as a sum of the detachment times of each hydrogen atom:

$$\tau_{\mathrm{ind}} = \tau_0 \sum_{n=1}^{4} \exp\left[\frac{E_n}{kT}\right]. \tag{40}$$

Here, τ_0 is the period of natural oscillations of hydrogen atoms in the hydrocarbon associations.

Without coagulation, the total number of the soot particles formed will be equal to the number of nucleation centers formed during the induction period. Therefore, a determination of the concentration of nucleation centers yields the magnitude of the number concentration of soot particles in a gas flame.

As follows from the probability reaction chart of soot formation (see Fig. 1), in a gas volume there take place several dehydrogenation chains (branches B, C, and D) which are induced by the intermediate hydrocarbon radicals. In this case, the beginnings of the secondary chains B, C, and D are shifted in time with respect to the dehydrogenation onset in the main chain. Moreover, the induction periods of the secondary chains may have different durations which are dependent on the conditions for the formation of the secondary branch, thus yielding the conditions at which polydispersed soot particles may be formed. During the induction period of separate branch processes, nucleation centers are formed continuously and start to grow directly after each nucleus is formed. From this it follows that for each nucleation center the growth starts at different times even during the induction period of the main chain A. So, by the end of this stage of the main chain A, different nucleation centers will have different sizes depending on their residence time during the induction period. Hence, by the end of the induction period a full spectrum of sizes of the hydrocarbon complexes are formed which are responsible for a further size distribution of soot particles. After end of the induction period, nucleation centers are no longer formed, and by the end of this period different-size carbon complexes enlarge.

Thus, a polydispersion spectrum develops during the induction stage, and the magnitude of the soot particle concentration is mainly determined by the mass transfer process which starts at the end of the induction period. The longer the induction period τ_{ind}, the higher is the degree of the polydispersion of the forming hydrocarbon complexes. Upon reducing the induction period, the degree of polydispersion decreases.

The induction time calculated by Eq. (40) for the equilibrium conditions is $8.46 \cdot 10^{-6}$ sec, which in order of magnitude coincides with the observed one [2]. Apparently, proceeding from the generally accepted representations of the high chemical activity of radicals, the chain breaks as methylene radicals recombine with the formation of a C_2H_4 molecule, followed by its thermal decomposition [3, 4].

The dehydrogenation process may be controlled by developing suitable temperature fields in a turbulent flow when affecting the turbulent exchange intensity. As a local temperature field develops for a certain time interval, its duration is, in essence, the residence time of a hydrocarbon molecule in the thermal decomposition zone and, thus, the induction time is closely connected with the turbulent exchange in the gas flame.

The above mathematical model for soot formation and for the mechanism of forming hydrocarbon complexes opens wide possibilities for predicting the radiation properties of a natural gas flame and for controling the heat exchange characteristics of a gas flame by affecting the aerodynamic microstructure.

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