Model for calculating the reaction rates of nitrogen oxide formation in a diesel cylinder

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Abstract. For the purpose of considering the activated complex, the uncertainty relation from quantum mechanics is used. It is assumed that at the peak of the parabola, the complex corresponds to a volume with finite dimensions. In classical theories, such assumptions exist, and since the barrier has a flat shape, the accepted assumptions do not change the overall picture of the main chemical reactions of combustion. It follows that you can use a statistical average from a set of complexes, which will allow you to get the same result. Statically, the reaction rates are considered with the assumption that the initial substances and activated complexes are found in the equilibrium state. The presented model makes it possible to calculate the values of the pre-exponential multiplier of chemical reactions and, consequently, the absolute rate of formation of nitrogen oxides (NOx) in the diesel cylinder.

Let's draw schematically the potential energy of the system of elements N, OH, NO, and H of the reaction \( N + OH \rightarrow NO + H \) depending on the characteristic of the mutual spatial configuration of the atoms (figure 1).

![Potential energy diagram](image)

**Figure 1.** Potential energy of the system of chemical elements of the reaction \( N + OH \rightarrow NO + H \): \( E \) - potential energy, \( J \); \( x \) - decomposition coordinate, micron.

According to the theory of chemical kinetics, when a reaction occurs at the top of a potential barrier responsible for the convergence of reacting substances, and in its vicinity, an activated complex is formed. Suppose that all the complexes that are formed are consumed in the direction of the reaction products, then the reaction number of acts will be equal to the number of consumption of complexes divided by the time of their existence [1-5]. So, conditionally denoting the values of the reaction...
components with the symbols $A (N)$, $B (OH)$, and $M (NO·H)$, we get that the number of acts of a direct reaction in $1 \text{ cm}^3$ in $1 \text{ s}$ will be equal $k_i r_A r_B = P r_M / \tau$, then the rate constant will take the form of a direct reaction

$$k_i = P \frac{1}{\tau} \left( \frac{r_M}{r_A r_B} \right), \quad (1)$$

where $P$ - is the value of the change in the actual reaction rate from the ideal one (steric factor).

Table 1 shows the dependence of the steric factor on the type of reacting substances.

| Type of reactants                        | $P$                      |
|-----------------------------------------|--------------------------|
| Atom + atom                             | $\frac{Z_V}{Z_R}$        |
| Diatomic molecule + atom                | $(\frac{Z_V}{Z_R})^2$    |
| Polyatomic molecule + atom              | $(\frac{Z_V}{Z_R})^3$    |
| Diatomic molecule + diatomic molecule   | $(\frac{Z_V}{Z_R})^4$    |
| Diatomic molecule + polyatomic molecule | $(\frac{Z_V}{Z_R})^5$    |

Decompose the statistical sum into a product:

$$Z = Z_T Z_R Z_V. \quad (2)$$

On a segment $\delta$ comparable to the "volume" occupied by complexes along the mutual spatial configuration of atoms, the statistical sum of a particle with a mass $m$ that produces a one-dimensional translational motion will be equal to:

$$Z_T = \left(2 \pi m k T / h^2 \right)^{1/2} \delta, \quad (3)$$

where $h$ - Planck's constant, $h=6.65 \cdot 10^{-34}$ J·s; $\kappa$ - Boltzmann constant, $\kappa=1.38 \cdot 10^{-23}$ J/K; $m$ - particle mass, kg.

Expression for the rotational sum of a particle

$$Z_R = \frac{8 \pi^2 I k T}{h^2} \frac{1}{\sigma^2}, \quad (4)$$

where $I$ - the moment of inertia of the particle, kg·m$^2$; $\sigma$ - the symmetry factor.

The symmetry factor corresponds to the number of permutations of identical atoms in a molecule, increased by one and corresponding to its rotation as a whole ($\sigma=1$ - for a diatomic molecule that consists of different atoms; $\sigma=2$ - of identical ones).

Given the statistical sum of the harmonic oscillator for the frequency the quantum expression is defined

$$Z_V = \left(1 - e^{-E_j / k T} \right)^{-1}. \quad (5)$$

The expression of the moment of inertia of the complex is written as follows

$$I = d_{AB}^2 \frac{m_A m_B}{m_A + m_B}, \quad (6)$$
where $d_{AB}$ – the average diameter of the reagent $A$ and $B$, $d_{AB} = (d_A + d_B)/2$, m.

The activated complexes are located at the top of the energy barrier located between the points of the initial and final States (figure 1). The duration of the reaction depends on the speed at which the activated complex passes the top of the barrier. Let's assume that the type of activated state corresponds to the properties of a standard molecule. That is, activated complexes are resistant to movement in all directions, except one, when moving in which their division occurs. The presence of a relatively flat vertex at the energy barrier makes it possible to consider the degree of freedom corresponding to the expansion coordinate as a one-dimensional translational motion. Therefore, the activated complexes retain the degree of freedom $3n$, where $n$ is the number of atoms contained in the activated complex [6-11].

In order to consider a single activated complex, we use the uncertainty relation from quantum mechanics, assuming that at the peak of the parabola, the complex corresponds to a volume with finite dimensions. In classical theories, such assumptions exist, and since the barrier has a flat shape, the accepted assumptions do not change the overall picture of the main chemical reactions of combustion. Therefore, it is possible to use a statistical average from a set of complexes, which will allow you to get the same result. Considering statically the reaction rates, we assume that the initial substances and activated complexes are in an equilibrium state, and the chemical reactions will be accompanied by the preservation of the equilibrium concentrations of the complexes and their decomposition at a certain speed. Let's assume that at the peak of the parabola, the activated complex corresponds to a certain length segment (figure 1), the actual size of which is insignificant [12-19].

Let's assume that the mean square velocity of the particle $\bar{v}$ acts in the $x$ direction, then the collisions of the molecules under consideration with the wall will be equal to the average change in the amount of motion $2m\bar{v}$. A molecule located at a distance of $x$ from the wall should reach it in a unit of time. If we denote the number of molecules $N$ contained in volume $V$, then in a unit of time, each cm$^2$ of the wall will be hit by a number $N\bar{v}/V$ of molecules [20-25]. Therefore, it is possible to determine the value of the rate of change in the amount of movement related to the square centimeter of the surface of the molecules on the wall

$$\Theta = 2mN\bar{v}^2/V.$$ (7)

Since the kinetic (translational) energy along the $x$-axis for one degree of freedom is $0.5m\bar{v}^2$, the objective possibility of a molecule having a velocity corresponding to the range from $\bar{v}$ to $\bar{v} + d\bar{v}$ in this direction is equal to:

$$\Theta(\bar{v}) = \int_{\bar{v}}^{\bar{v} + d\bar{v}} \frac{m\bar{v}^2}{2\kappa T} d\bar{v}.$$ (8)

To determine the average speed of the complexes moving in the direction of a direct reaction, assume that there is a separation of reaction rates in the activated state, then the speed can be expressed by the equation:

$$\bar{v} = \frac{\int_{0}^{\infty} e^{-2\kappa T \bar{v}}} {\int_{-\infty}^{\infty} e^{-2\kappa T \bar{v}}}$$ (9)

The integration is done in the range from $\infty$ to $-\infty$, which allows to take into account the actual speed of complexes in forward and reverse directions, and the integration in the numerator is performed in the range of $0$ to $\infty$ that allows you to calculate the average speed in the direction of flow [26-29]. Thus, it is possible to obtain the value of the average speed of passage of the activated complex in the forward direction by the coordinate of the parabola peak expansion:
\[
\tilde{v} = \left(\frac{\kappa T}{2\pi m}\right)^{1/2},
\]

where \(m\) – weight of the complex in this direction, kg.

The average barrier passage time \(\tau\), which is the lifetime of the activated complex, is determined from equation (10) as follows:

\[
\tau = \frac{\delta}{\tilde{v}} = \delta \left(\frac{2\pi m}{\kappa T}\right)^{1/2},
\]

where \(\delta\) - the length of the top of the barrier, m; \(\tilde{v}\) - average speed, m/s.

The activated complexes, or rather the part of them that passes through the segment \(\delta\) of the decomposition coordinate per unit of time, is equal to \(1/\tau\). Denoting that in the interval \(\delta\) of the decomposition coordinate is \(r_M\) the number of activated complexes per unit volume, then the ratio \(r_M/\tau\) will be equal to the number of complexes following through the segment in unit volume per unit time [30-34]. Transmission coefficient \(\phi = 1\) provided that all activated complexes following the value \(\delta\) are consumed and the ratio \(r_M/\tau\) corresponds to the reaction rate

\[
\nu = \frac{r_M}{\tau} = r_M \left(\frac{\kappa T}{2\pi m}\right)^{1/2} \frac{1}{\delta}.
\]

Thus, using the transmission coefficient, it is possible to show the percentage of substances that passed to the final state from the initial state and did not return back to the initial state (figure 1).

Reacting with each other elements \(A, B\) form an activated complex, the specific reaction rate \(k\) of which is expressed in units of concentration, and the number of molecules that have decayed in a unit of volume per unit of time, i.e. the actual speed will be equal to \(kr_A\), where \(r_A, \ r_B\) are concentrations determined by the numbers of molecules in a unit of volume [35-39]. Therefore, the expression (1) taking into account the equation (11) can be written as follows

\[
k_i = \frac{P - r_M}{r_A r_B} \left(\frac{\kappa T}{2\pi m}\right)^{1/2} \frac{1}{\delta}.
\]

Since we assumed that the activated complexes and initial substances are in an equilibrium state, then the equilibrium constant for this model will be written

\[
K = \frac{\alpha_M}{\alpha_A \alpha_B},
\]

where \(\alpha\) - activity of the substance.

Considering this process to be ideal, we replace the activity of the substance with a concentration:

\[
K_r = \frac{r_M}{r_A r_B}.
\]

Taking into account the law of active masses, the quantitative ratio of elements that take part in the chemical reaction \(A + B \rightarrow M\) in the equilibrium state is equal to the ratio of the statistical sums of particles. By selecting type \(\exp(-E_0/\kappa T)\) components from the statistical sums that correspond to almost zero particle energy, replacing the Boltzmann constant \(\kappa\) with the gas constant \(R\) (since \(E_0\) refers to one mole), the equilibrium constant is rewritten as follows

\[
K = \frac{Z_M}{Z_A Z_B} e^{-\frac{E_0}{RT}},
\]
where $E_0$ – activation energy at 0 K, obtained by the initial substances for the transition to the activated state with the subsequent reaction, i.e. the difference between the energies of the initial substances and the zero level per mole of the activated complex.

Taking the expression $e^{-E_0/RT}$ as the sign of the sum of states, when determining the value of Z in the formula (16) for the beginning of the energy reference, you can take the values of the zero energy levels of the corresponding components [40-43]. The accepted condition will not complicate the calculations and is consistent with the methods for determining the sum of states.

Given the expressions (15) and (16), we write an equation to determine the value of the direct reaction rate constant (1)

$$k_i = P \frac{Z_M}{Z_A Z_B} \left( \frac{\kappa T}{2\pi m} \right)^{1/2} \frac{1}{\delta} e^{-E_0/RT}.$$  
(17)

The length of the barrier vertex will be equal to

$$\delta = h/\left(2\pi m\kappa T\right)^{1/2}.$$  
(18)

The expression (16) is written as follows

$$k_i = P \frac{\kappa T}{h} \frac{Z_M}{Z_A Z_B} e^{-E_0/RT}.$$  
(19)

The expression $\kappa T/h$ will be the same for all reactions and starting substances, therefore, it will have a frequency dimension and can represent a universal constant at each temperature, i.e. this expression $\kappa T/h$ characterizes the frequency of the activated complex passing the vertex of the parabola for a given temperature [44-47].

Since not all activated complexes reach the top of the parabola and move along the decomposition coordinate, it is necessary to introduce the transmission coefficient $\varphi$ to account for the activated complexes that actually disintegrated and gave reaction products. Therefore, the equation (19) is written as follows

$$k_i = P \varphi \frac{\kappa T}{h} \frac{Z_M}{Z_A Z_B} e^{-E_0/RT}.$$  
(20)

With the help of the presented expression it is possible to calculate the constants of the rates of chemical reactions of nitrogen oxides formation in the diesel cylinder.

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