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# KINETICS OF THE QUENCHING OF $N_2-O_2-NO$ MIXTURES

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A simple method is proposed to estimate nitrogen oxide yield after quenching of the equilibrium mixture, the cooling rate being hyperbolical or exponential.

Kinetic studies of the decomposition of the nitrogen oxide formed during high-temperature combustion of the gas mixture is of high interest both from the practical and the theoretical view [1—5]. However, quantitative approaches to the quenching process of the initial equilibrium mixture are cumbersome owing to time-consuming mathematical computations [1, 6]. In the present paper an attempt is made to demonstrate a simple and universal method for the estimation of the product yield after quenching.

It is known that the decomposition kinetics of NO, according to [1, 6], can be described in the general form by the differential equation

$$\mathrm{d}[\mathrm{NO}]/\mathrm{d}t = k_1[\mathrm{N}_2][\mathrm{O}_2] - 2k_2[\mathrm{NO}]^2 \tag{1}$$

or, taking into account the equilibrium constant $K_p$ for the reversible reaction $N_2 + O_2 \rightleftharpoons 2\,NO$, Eq. (1) can be written in the following form:

$$\mathrm{d}[\mathrm{NO}]/\mathrm{d}t = 2k_2(K_p[\mathrm{N}_2][\mathrm{O}_2] - [\mathrm{NO}]^2) \tag{2}$$

where $k_2 = A\exp(-E/RT)$ and $K_p = B\exp(-\Delta H/RT)$. If the thermodynamical equilibrium concentration $[\mathrm{NO}^{\circ}_{p}]$ at some high starting temperature $T_0$ has been determined and rapid cooling of the system to ambient temperature follows, this initial equilibrium concentration $[\mathrm{NO}]^{\circ}_{p}$ will decrease to some [NO] value. A solution for this kinetic task at the conditions that $[\mathrm{N}_2]$ and $[\mathrm{O}_2] \gg [\mathrm{NO}]^0_p$, and cooling of the equilibrium mixture proceeds hyperbolically, i.e. $1/T = 1/T_0 + at$, has been given by Zeldovich, Sadovnikov and Frank-Kamenetsky [1] by reducing the kinetic equation (2) to the Rickett-type differential equation

$$\mathrm{d}y/\mathrm{d}x = x^3(y^2 - x^2) \tag{3}$$

which was subsequently solved by numerical integration.

In the followings let us consider a simple method for solving the problem in question, yielding results sufficiently accurate for practical purposes. Let us mentally assume that the initial mixture $N_2 + O_2$ is heated from ambient temperature to the temperature $T_0$ at the identical hyperbolical rate of quenching: $1/T = 1/T_{\mathrm{amb}} - at$. Then the amount of nitrogen oxide formed, leaving apart its partial decomposition, can be expressed by the equation

$$\int_0^{[\mathrm{NO}]_x} \mathrm{d}[\mathrm{NO}] = \int_0^t 2k_2K_\mathrm{p}[\mathrm{N}_2][\mathrm{O}_2]\mathrm{d}t \tag{4a}$$

or, after integration,

$$[\mathrm{NO}]_\mathrm{x} = \frac{2ABR\,[\mathrm{N}_2][\mathrm{O}_2]}{a(E + \Delta H)} \exp\left(-\frac{E + \Delta H}{RT_0}\right) \tag{4b}$$

Hence the total amount of nitrogen oxide in the dynamic system may *conditionally* be assumed to be equal to $[\mathrm{NO}]_\mathrm{x} + [\mathrm{NO}]_\mathrm{p}^\bullet$. Simultaneously, the initial equilibrium concentration $[\mathrm{NO}]_\mathrm{p}^\circ$ will be reduced owing to partial decomposition of nitrogen oxide following the equation

$$\int_{[\mathrm{NO}]^\circ_\mathrm{p}}^{[\mathrm{NO}]_\mathrm{y}} \frac{\mathrm{d}[\mathrm{NO}]}{[\mathrm{NO}]^2} = -\int_0^t 2k_2\mathrm{d}t \tag{5a}$$

or, after integration,

$$\frac{1}{[\mathrm{NO}]_\mathrm{y}} = \frac{1}{[\mathrm{NO}]_\mathrm{p}^\circ} + \frac{2AR}{aE} \exp\left(-E/RT_0\right). \tag{5b}$$

Finally, the percentage yield of nitrogen oxide, after quenching at the chosen hyperbolical rate, can be estimated by using the following formula:

$$\eta, \% = \frac{\gamma \cdot [\mathrm{NO}]_\mathrm{x} + [\mathrm{NO}]_\mathrm{y}}{[\mathrm{NO}]_\mathrm{x} + [\mathrm{NO}]_\mathrm{p}^\circ} \cdot 100 \simeq \frac{[\mathrm{NO}]_\mathrm{x} + [\mathrm{NO}]_\mathrm{y}}{[\mathrm{NO}]_\mathrm{x} + [\mathrm{NO}]_\mathrm{p}^\circ} \cdot 100 \tag{6}$$

where at very high quenching rate $\gamma \to 1$, and then the factual yield of nitrogen oxide is given by

$$[\mathrm{NO}] = \frac{\eta}{100}[\mathrm{NO}]_\mathrm{p}^\circ.$$

To illustrate the above-expounded concept, let us carry out a calculation using starting data from [6]: $T_0 = 2500$ K, $T_0 \gg T_{\mathrm{amb}}$, $a = 10^{-3}$, $[\mathrm{NO}]_p^\circ = 2.6 \cdot 10^{-4}$ mol/l, $[\mathrm{N}_2] = 8.6 \cdot 10^{-3}$ mol/l, $[\mathrm{O}_2] = 2.15 \cdot 10^{-3}$ mol/l, $K_\mathrm{p} = 21.3 \exp\left(-\frac{43000}{RT}\right)$ and $k_2 = 5.4 \cdot 10^{12} \exp\left(-\frac{86\,000}{RT}\right)$. After the required computations the result obtained is $[\mathrm{NO}]_\mathrm{x} = 3.5 \cdot 10^{-4}$ mol/l, $[\mathrm{NO}]_\mathrm{y} = 0.9 \cdot 10^{-4}$ mol/l, $\eta = 72\%$; according to data from Emanuel and Knorre [6] the yield is 71%.

Let us estimate nitrogen oxide yield by the above concept using the assumption that quenching proceeds exponentially: $T = T_0 \exp(-bt)$ from $T_0 = 2500$ K to ambient temperature (e.g. 291 K) during the same period of time necessary for hyperbolic quenching $1/T = 1/T_0 + at$ ($\sim$3 s). The corresponding value of the parameter $b$ will then be 0.716. According to [7] Eqs (4a) and (5a) in the integrated form for exponential quenching are

$$[\mathrm{NO}]_x = \frac{2ABRT_0[\mathrm{N_2}][\mathrm{O_2}]}{b(E + \varDelta H + RT_0)} \exp\left(-\frac{E + \varDelta H}{RT_0}\right) \tag{7}$$

$$\frac{1}{[\mathrm{NO}]_y} = \frac{1}{[\mathrm{NO}]_p^o} + \frac{2ART_0}{b(E + RT_0)} \exp\left(-\frac{E}{RT_0}\right). \tag{8}$$

After the required computations: $[\mathrm{NO}]_x = 1.18 \cdot 10^{-3}$ mol/l, $[\mathrm{NO}]_y = 0.36 \cdot 10^{-4}$ mol/l and $\eta = 84\%$. It may therefore be concluded that exponential quenching rates – *at otherwise equal conditions* – may be more effective than hyperbolic quenching rates.

## References

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