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# ANALYSIS OF THE KINETICS OF THE AFTER-BURNING PROCESS UPON INJECTING AN OXIDIZER INTO A HIGH TEMPERATURE FLOW

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# ANALYSIS OF THE KINETICS OF THE AFTERBURNING PROCESS UPON INJECTING AN OXIDIZER INTO A HIGH TEMPERATURE FLOW

Z. G. Shaykhutdinov

When $N_2O_4$ is injected into a high temperature gas flow containing the products of the incomplete combustion of CO and $H_2$, effective afterburning of these products can be expected. This article deals with the calculation tables used for a rough analysis of the kinetic laws governing these processes.

The injection of $N_2O_4$ can be accompanied by the following elementary processes which take place in a high temperature flow:

a) acceleration and vaporization of liquid $N_2O_4$

b) decomposition of vaporized $NO_2$ according to the reaction

$$N_2O_4 \rightarrow 2NO_2, \qquad (1)$$

c) decomposition of $NO_2$ according to the reaction

$$2NO_2 \rightarrow 2NO + O_2, \qquad (2)$$

d) decomposition of NO according to the reaction

$$2NO \rightarrow N_2 + O_2, \qquad (3)$$

e) afterburning of the products of the incomplete combustion of CO and $H_2$ according to the reaction

$$2CO + O_2 \rightarrow 2CO_2 \qquad (4)$$

and

$$2H_2 + O_2 \rightarrow 2H_2O. \qquad (5)$$

In principle, a number of other chemical reactions can also occur (reversible for all the above and for the decomposition of $O_2$ and $H_2$ molecules into atoms, etc.) but when dealing with moderate static temperatures in high speed flows they can be disregarded in a rough analysis.

An analysis of the acceleration of a diffused liquid and its vaporization is beyond the scope of this article. There is a widespread opinion that these processes occur instantaneously, i.e., the topic of concern henceforth will be the homogeneous gas mixture composed of the combustion products of a basic propellant and the products of $N_2O_4$ vaporization.

The following relationships [1-3] are used in dealing with the individual rates at which chemical reactions (1-5) occur:

$$-\frac{dC_{N_2O_4}}{d\tau} = K_{N_2O_4}(T)\,C_{N_2O_4}, \qquad (1a)$$

$$-\frac{dC_{NO_2}}{d\tau} = K_{NO_2}(T)\,C^2_{NO_2}, \qquad (2a)$$

$$-\frac{dC_{NO}}{d\tau} = K_{NO}(T)\,C^2_{NO}, \qquad (3a)$$

$$-\frac{dC_{CO}}{d\tau} = K_{CO}(T)\frac{C_{CO}}{C_\varepsilon}\cdot\left(\frac{C_{O_2}}{C_\varepsilon}\right)^{0,25}\left(\frac{C_{H_2O}}{C_\varepsilon}\right)^{0,5}, \qquad (4a)$$

$$-\frac{dC_{H_2}}{d\tau} = K_{H_2}(T)C^{3/2}_{H_2}C_{O_2}, \qquad (5a)$$

where

$$K_{N_2O_4}(T) = 10^{16}\exp\left(-\frac{1300}{RT}\right),$$

$$K_{NO}(T) = 1,3\cdot 10^{12}e^{\frac{-63000}{RT}},$$

$$K_{NO_2}(T) = 10^{9,6}\exp\left(-\frac{26900}{RT}\right),$$

$$K_{CO}(T) = 1,04\cdot 10^{12}\exp\left(-\frac{32000}{RT}\right),$$

$$K_{H_2}(T) = 1,14\cdot 10^{10}\exp\left(-\frac{6860}{RT}\right),$$

Here C are the absolute values of the reacting components in moles per liter; $C\varepsilon$ is the total concentration of all components of the mixture in the same units (i.e., moles per liter); R and T are the universal gas constant and temperature of the mixture respectively; $\tau$ is the reaction time; Ki(T) is the reaction rate constant.

The table gives the results of calculations for the reaction rates in the actually expected range of change in concentration of the reacting components and temperatures of the mixture.

The table shows that reaction (1) takes place so rapidly in comparison with reaction (2) that its velocity can be taken as infinite and that the $NO_2$ yield can be determined on the basis of the $N_2O_4$ evaporation rate directly. It is worth mentioning that the calculation analysis discloses that this reaction actually takes place concurrently with evaporization in the immediate vicinity of the drop surface in the "reduced" film.

Table

| $T°K$, $C_i$ $\frac{\text{moles}}{\text{liters}}$ | $\frac{dC_{N_2O_4}}{d\tau}$ | $\frac{dC_{NO_2}}{d\tau}$ | $\frac{dC_{NO}}{d\tau}$ | $\frac{dC_{CO}}{d\tau}$ | $\frac{dC_{H_2}}{d\tau}$ |
|---|---|---|---|---|---|
| 1500°; $10^{-3}$ | $0,65 \cdot 10^{13}$ | $0,48 \cdot 10^{9}$ | $0,4 \cdot 10^{-3}$ | $\approx 10^{9}$ | $1,14 \cdot 10^{9}/^{8}$ |
| 1500°; $10^{-2}$ | $0,65 \cdot 10^{14}$ | $0,48 \cdot 10^{8}$ | $0,4 \cdot 10^{-1}$ | $\approx 10^{5}$ | $1,14 \cdot 10^{9}/^{3}$ |
| 2000°; $10^{-3}$ | $0,72 \cdot 10^{13}$ | $0,44 \cdot 10^{4}$ | $1,3 \cdot 10^{-3}$ | $\approx 10^{4}$ | $0,2 \cdot 10^{9}/^{8}$ |
| 2000°; $10^{-2}$ | $0,72 \cdot 10^{14}$ | $0,44 \cdot 10^{9}$ | $1,3 \cdot 10^{-1}$ | $\approx 10^{9}$ | $0,2 \cdot 10^{9}/^{2}$ |
| 2300°; $10^{-2}$ | $0,72 \cdot 10^{10}$ | $1,1 \cdot 10^{9}$ | $1,5 \cdot 10^{9}$ | $\approx 10^{9}$ | $0,2 \cdot 10^{9}/^{0}$ |

Reaction rate (2) is more or less commensurate with reaction rate (3) while afterburning reactions (4) and (5) again occur at an "infinite" speed in comparison with (3) and even with (2).

Therefore, when calculating the overall reaction rate, we can, it seems, consider only the kinetics of reactions (2) and (3) since reactions (1), (4) and (5) transpire instantaneously.

In such cases, the afterburn of CO and $H_2$ products is limited by the release of $O_2$ resulting from $NO_2$ and NO decomposition while the oxygen already released is immediately completely consumed in the oxidation of CO and $H_2$ according to the equilibrium conditions:

$$\frac{(C_{CO_2})_i \cdot (C_{H_2})_i}{(C_{H_2O})_i \cdot (C_{CO})_i} = K_p(T), \qquad (6)$$

where Kp(T) is the equilibrium constant for the components of $CO_2$, CO, $H_2O$ and $H_2$, dependent on temperature only.

Here (Ci) are the total concentrations of the reacting i-th components. The correct relationships for them are:

$$(C_{CO_2})_i = C^0_{CO_2} + \Delta CO_2$$
$$(C_{H_2O})_i = C^0_{H_2O} + \Delta H_2O$$
$$(C_{CO})_i = C^0_{CO} + \Delta CO$$
$$(C_{H_2})_i = C^0_{H_2} + \Delta H_2,$$

where $\Delta Ci$ is the change in Ci concentration during afterburning; $C^0i$ is the original concentration.

Oxygen release occurs by means of two complete reactions:

a) $$N_2O_4 \rightarrow 2NO_2 \rightarrow 2NO + O_2 \qquad (7)$$

b) $$N_2O_4 \rightarrow 2NO_2 \xrightarrow{\nearrow O_2'} 2NO \xrightarrow{\nearrow N_2} O_2'' \qquad (8)$$

The $O_2$ formation rate by the first reaction will be

$$\frac{dC'_{O_2}}{d\tau} = -\frac{1}{2}\frac{dC_{NO_2}}{d\tau} = \frac{1}{2}K_{NO_2}C^2_{NO_2}, \qquad (9)$$

by the second reaction,

$$\frac{dC''_{O_2}}{d\tau} = -\frac{1}{2}\frac{dC_{NO}}{d\tau} = \frac{1}{2}\times(K_{NO}C^2_{NO} - K_{NO_2}C^2_{NO_2}) \qquad (10)$$

The overall oxygen "production" rate in the afterburning reaction for $N_2O_4$ will be

$$\frac{dC_{O_2}}{d\tau} = +\left(\frac{dC'_{O_2}}{d\tau} + \frac{dC''_{O_2}}{d\tau}\right) = \frac{1}{2}K_{NO}C^2_{NO}. \qquad (11)$$

The $C_{NO}$-time relationship which enters into equation (11) is discovered by solving regular differential equations (9) and (10).

To integrate the equations let us exclude the time factor immediately since it is an independent variable; having divided (10) into (9) we realize:

$$\frac{dC_{NO}}{dC_{NO_2}} = \frac{K_{NO}C^2_{NO} - K_{NO_2}C^2_{NO_2}}{K_{NO_2}\cdot C^2_{NO_2}} = -1 + \frac{K_{NO}}{K_{NO_2}}\cdot\left(\frac{C_{NO}}{C_{NO_2}}\right)^2 \qquad (12)$$

Having performed the substitution

$$C_{NO} = C_{NO_2} \cdot y, \tag{13}$$

we obtain

$$\frac{dy}{d\ln C_{NO_2}} = \frac{K_{NO}}{K_{NO_2}} \cdot y^2 - y - 1 \tag{14}$$

The result is an equation with separable variables of the type

$$\frac{dy}{ay^2 + by + C} = d\ln C_{NO_2}, \tag{15}$$

where

$$a = K_{NO}/K_{NO_2}, \ b = -1, \ c = -1. \tag{16}$$

An analysis of the kinetic relationships for reactions (2) and (3) shows that $KNO_2$ always exceeds KNO by at least two-thirds. Therefore,

$$\Delta = \sqrt{b^2 - 4ac} > 0, \tag{17}$$

Under these conditions integrating (15) will produce

$$\frac{1}{\Delta} \ln \frac{2ay + b - \Delta}{2ay + b + \Delta} = \ln \frac{CNO_2}{\theta} \tag{18}$$

or

$$\frac{2ay + b - \Delta}{2ay + b + \Delta} = \left(\frac{CNO_2}{\theta}\right)^{\Delta}. \tag{19}$$

The expression for $\theta$ in (19), on condition that $y^0 = 0$ when $C_{NO_2} = C^0_{NO_2}$, is

$$\theta^{\Delta} = (C^0_{NO_2})^{\Delta \frac{b+\Delta}{b-\Delta}}. \qquad (20)$$

Inserting (20) into (19) and having performed the appropriate transformations, we obtain the equation for y

$$y = \frac{-(b-\Delta)\left[1 - \left(\frac{C_{NO_2}}{C^0_{NO_2}}\right)^{\Delta}\right]}{2\frac{K_{NO}}{K_{NO_2}}\left[1 - \left(\frac{C_{NO_2}}{C^0_{NO_2}}\right)^{\Delta\frac{b-\Delta}{b+\Delta}}\right]} \qquad (21)$$

Considering the above remarks on the relationship between $K_{NO}$ and $K_{NO_2}$, we can insert into this equation

$$\Delta = \sqrt{1 + 4\frac{K_{NO}}{K_{NO_2}}} \approx 1$$

in all places where there is no deduction of similar-valued magnitudes. In addition, the units in the denominator enclosed by the square brackets can be disregarded when comparing this value with the calculated value. Then, instead of (21) we can write

$$y = \frac{b+\Delta}{2}\,\frac{K_{NO_2}}{K_{NO}}(C^0_{NO_2} - C_{NO_2}) \qquad (22)$$

The relationship $C_{NO_2} = f(\tau)$ is determined by integrating (9) for $C_{NO_2} = C^0_{NO_2}$, when $\tau = 0$:

$$C_{NO_2} = \frac{C^0_{NO_2}}{1 + K_{NO_2}C_{NO_2}\tau} \qquad (23)$$

Inserting (23) and (22) into (13), we finally obtain the expression for the variation of NO concentration with respect to time,

$$C_{NO} = \frac{b+\Delta}{2}\,\frac{K_{NO_2}}{K_{NO}}\left(C^0_{NO_2} - \frac{C^0_{NO_2}}{1+K_{NO_2}C^0_{NO_2}\tau}\right) \qquad (24)$$

while for oxygen "production" rate we have

$$\frac{dC_{O_2}}{d\tau} = \frac{(b+\Delta)^2}{8}\,\frac{K^2_{NO_2}}{K_{NO}}\left(C^0_{NO_2} - \frac{C^0_{NO_2}}{1-K_{NO_2}C^0_{NO_2}\tau}\right)^2 \qquad (25)$$

The resultant differential equation has separable variables. Integrating it within the limits $\tau = 0$ to $\tau$ gives the oxygen production rate in time $\tau$:

$$\Delta C_{O_2} = \frac{(b+\Delta)^2}{8}\,\frac{K_{NO_2}}{K_{NO}}\left[C^0_{NO_2}\tau - \frac{1}{K_{NO_2}C_0{}_{NO_2}}\ln\left(1+K_{NO_2}C^0_{NO_2}\tau\right) - \frac{1}{K_{NO_2}C^0_{NO_2}\left(1+K_{NO}C^0_{NO_2}\tau\right)}\right]$$

thus allowing us to calculate the intensity of the afterburning processes for CO and $H_2$ at the expense of the incoming oxygen (realizing that these rates are greater than the rate of $O_2$ "production"):

$$\Delta C_{CO} = -2x\Delta C_{O_2}. \qquad (27)$$

$$\Delta C_{H_2} = -2(1-x)\Delta C_{O_2}, \qquad (28)$$

$$\Delta C_{CO_2} = 2x\Delta C_{O_2}, \qquad (29)$$

$$\Delta C_{H_2O} = 2(1 - x)\Delta C_{O_2}. \qquad (30)$$

The result of inserting these relationships into equilibrium equation (6) and appropriate transformation is

$$\frac{(C^0_{CO_2} - 2x\Delta C_{O_2})\,(C^0_{H_2} - 2\Delta C_{O_2} + 2x\Delta C_{O_2})}{(C^0_{CO} - 2\Delta C_{O_2})\,(C^0_{H_2O} + 2\Delta C_{O_2} - 2x\Delta C_{O_2})} = Kp\,(T). \qquad (31)$$

At this point, provided $C^0_{CO_2} \cdot C^0_{H_2} = Kp(T)\, C^0_{CO} C^0_{H_2O}$, we obtain the quadratic equation for x which when solved gives the relationship of quantity x as a function of the state of the reactive system in the form

$$x = -\frac{1}{2}\left(b + \sqrt{b^2 - 4ac}\right);$$

where

$$\begin{gathered} b = [C^0_{CO_2} + C^0_{CO}Kp\,(T) + C^0_{H_2} + C^0_{H_2O}Kp(T) - 2\Delta_{CO_2} + \\ 2\Delta C_{O_2}Kp\,(T)]; \\ a = 2\Delta C_{O_2}[1 - Kp\,(T)]; \quad C = [-C^0_{CO_2} - C^0_{CO}Kp\,(T)]. \end{gathered} \qquad (32)$$

Equation (26) was derived under the condition T = const and can be used reliably for an evaluation of afterburn intensity in the final time interval of the isothermal process only. However, considering the actual smooth change in temperature which occurs during afterburning along the channel length, equations (26),(27-30) and (32) can also be used for a rough estimate of afterburning intensity in the non-isothermal case. If a more accurate calculation is desired, the entire afterburn time interval can be divided into several parts for which a slight temperature change is expected. Meanwhile, the afterburn length divided by the rate can be used as the argument in equation (26).

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