ABOUT THE TERM “LAW OF EXPONENT IN POSITIVE EXPONENT” WHICH IS INTRODUCED IN SCIENTIFIC LITERATURE TO EXPLAIN THE FEATURES OF THE CHAIN BRANCHING CHEMICAL REACTIONS IN GAS MIXTURES

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Abstract: The term “law of exponent in positive exponent” was introduced and used many times by V. V. Azatyan in his publications to explain the features of the chain branching reactions in gas mixtures. The mathematical basis of the law is the formula for the rate of oxygen consumption which was obtained by partial integration of the simplified scheme of kinetic equations written using the method of quasi-stationary concentrations for hydrogen + oxygen mixtures. The expressive form of the formula, which under certain assumptions can be written as an exponent within an exponent, was considered in the works of V. V. Azatyan as a manifestation of a particularly strong temperature dependence of the rate of chain gas reactions. However, this paper shows that the formula itself allows one to analyze only the isothermal case when the time integral included in it can be taken explicitly. To consider the temperature dependence of the conversion rate, additional information is needed in the form of the derivative of temperature over time. As such information, this paper uses the calculation results on the autoignition of a stoichiometric hydrogen + air mixture in a constant-volume adiabatic reactor. The calculations were carried out using the detailed kinetic mechanism NUIGMech 1.1 (2020) in the CHEMKIN software package. It is shown that the results of kinetic calculations of the temperature dependence of the oxygen consumption rate during autoignition do not correspond to the estimates made using the formula proposed by V. V. Azatyan. An explanation of the reasons for this discrepancy is given. In general, the calculations do not confirm the existence of the “law of exponent in positive exponent.” In scientific and educational literature, this term should be used with caution.

Keywords: exponential dependence on temperature; Arrhenius law; chemical reactions in gas mixtures; chain branching reactions

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Figure Captions

Figure 1 Time change of temperature (*1*) and mole fractions of H (*2*) and O_2 (*3*). Autoignition of the stoichiometric hydrogen–air mixture at $T_0 = 1000$ K and $P_0 = 1$ atm

Figure 2 Dependence of logarithm of the modulus of oxygen consumption rate on the inverse temperature: 1–4 — four characteristic domains; dashed line — example of an exponential dependence with an activation energy of 16 kcal/mol in the temperature range 1200–1500 K. Autoignition of hydrogen–air mixture at $T_0 = 1000$ K and $P_0 = 1$ atm

Figure 3 Dependence of logarithm of the modulus of oxygen consumption rate W on the inverse temperature: line — numerical calculation; *1* and *2* — estimates using Eq. (2) at $B = 5 \cdot 10^3$ (*1*) and $5 \cdot 10^5$ (*2*). Autoignition of hydrogen–air mixture at $T_0 = 1000$ K and $P_0 = 1$ atm

Figure 4 Dependence of the logarithm of time derivative of temperature on the inverse temperature. Calculation is made for autoignition of hydrogen–air mixture at $T_0 = 1000$ K and $P_0 = 1$ atm

Figure 5 Dependence of the logarithm of oxygen consumption rate modulus on time. Calculation is made for autoignition of a hydrogen–air mixture at $T_0 = 1000$ (*a*) and 850 K (*b*) and $P_0 = 1$ atm: dashed lines shows the sections of linear dependence

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