

ANALYSIS OF METHODS FOR CALCULATING THE KINETICS OF CHEMICAL REACTIONS UNDER ADIABATIC COMPRESSION–EXPANSION

I. V. Bilera

A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, 29 Leninsky Pros., Moscow 119991, Russian Federation

Abstract: The methods of kinetic processing of experimental data obtained in free piston compressors (ballistic compressors) are analyzed. Among them are various techniques based on the joint solution of a system of equations consisting of the piston motion equation, Poisson's adiabatic equation, the law of conservation of energy, and the equation of state; techniques based on measuring the deviation from adiabaticity during compression of concentrated mixtures, an approximate technique developed at the A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences (TIPS RAS) as well as a method for determining kinetic constants during spontaneous ignition of a combustible gas proposed by Babkin and Senachin. It has been shown that at present, for adiabatic compression of gases by a free piston, there is no method for determining the rate of a chemical reaction based on experimental data in the full range of the conversion degrees of the test substance and, consequently, in a wide temperature range. The most promising way to create it is to improve the methodology of the TIPS RAS.

Keywords: adiabatic compression; ballistic compressor; free piston compressor; kinetics; method

DOI: 10.30826/CE22150201

EDN: ZRXVZY

Figure Captions

Figure 1 Pressure–time histories for experiments with different values of maximum pressure P_{\max}

Figure 2 Arrhenius plot for summary rate constants of *n*-butane decomposition: 1 — data [5] calculated by the method [24]; 2 — data [25]; and 3 — data [26]

Table Caption

Kinetic parameters of the reaction $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^*$

Acknowledgments

The work was performed within the framework of the state assignment of the A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences.

References

1. Ryabinin, Y. N. 1961. *Gases at high densities and temperatures*. New York, NY: Pergamon Press. 52 p.
2. Kolbanovskiy, Yu. A., V. S. Shchipachev, N. Ya. Chernyak, et al. 1982. *Impul'snoe szhatie gazov v khimii i tekhnologii* [Impulsive compression of gases in chemistry and technology]. Ed. Yu. A. Kolbanovskiy. Moscow: Nauka. 240 p.
3. Kolbanovskiy, Yu. A. 1989. Adiabatic compression in studies on the kinetics and mechanism of reactions involving fluorine-containing carbenes. *Russ. Chem. Rev.* 58(11):1024–1032.
4. Buravtsev, N. N., and Yu. A. Kolbanovsky. 1999. Intermediates of thermal transformations of perfluoro-organic compounds. New spectral data and reactions. *J. Fluorine Chem.* 96(1):35–42.
5. Bilera, I. V. 2014. Gomogennyy piroliz *n*-butana v usloviyakh adiabaticheskogo szhatiya [The homogeneous pyrolysis of *n*-butane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 7:35–41.
6. Bilera, I. V. 2020. Gomogennyy piroliz 2-metilpentana v usloviyakh adiabaticheskogo szhatiya [The homogeneous pyrolysis of 2-methylpentane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 13(1):33–41. doi: 10.30826/CE20130103.
7. Bilera, I. V. 2020. Sopiroliz dimetilovogo efira i etana v usloviyakh adiabaticheskogo szhatiya [Copyrolysis of

- dimethyl ether and ethane under pulsed adiabatic compression]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 13(4):20–28. doi: 10.30826/CE20130403.
8. Buravtsev, N. N., L. S. German, A. S. Grigor'ev, Yu. A. Kolbanovskii, A. A. Ovsyannikov, and A. Yu. Volkonskii. 1993. Trifluoromethylfluorocarbene formation and reactions under $C_2F_5SiF_3$ pulsed adiabatic compression pyrolysis. *Mendeleev Commun.* 3(4):133–134. doi: 10.1070/MC1993v003n04ABEH000254.
 9. Yampolskiy, Yu. P. 1990. *Elementarnye reaktsii i mekhanizm piroliza uglevodorodov* [Elementary reactions and mechanism of pyrolysis of hydrocarbons] Moscow: Khimiya. 216 p.
 10. Markevich, A. M., V. V. Azatyan, and N. A. Sokolova. 1962. Adiabaticeskoe szhatie kak metod izucheniya khimicheskikh protsessov v nestatsionarnykh usloviyakh [Adiabatic compression as a method for studying chemical processes under nonstationary conditions]. *Kinet. Catal.* 3(3):431–438.
 11. Volokhonovich, I. E., A. M. Markevich, I. F. Masterovoi, and V. V. Azatyan. 1962. Low-thermal processes. The thermocracking of methane. *Dokl. Akad. Nauk SSSR* 146(2):387–390.
 12. Kondratiev, V. N. 1965. Determination of the rate constant for thermal cracking of methane by means of adiabatic compression and expansion. *Symposium (International) on Combustion Proceedings* 10(1):319–322. doi: 10.1016/S0082-0784(65)80178-3.
 13. Vurzel', F. B., L. S. Polak, and V. S. Shchipachev. 1966. Razlozhenie tetrakhlorilana pri adiabaticeskem szhatii [Decomposition of tetrachlorosilane under adiabatic compression]. *Kinet. Catal.* 7(6):1068–1071.
 14. Kondrat'ev, V. N. 1966. Termicheskoe razlozhenie metana [Thermal decomposition of methane]. *Khimicheskaya kinetika i tseplnye reaktsii* [Chemical kinetics and chain reactions]. Moscow: Nauka. 165–172.
 15. Sargissian, V. K., and R. V. Paronian. 1972. Termicheskiy kreking atsetilena v usloviyakh adiabaticeskogo szatiya i rasshireniya [Thermal cracking of acetylene under adiabatic compression and expansion]. *Chem. J. Armenia* 25(7):551–559.
 16. Barannik, G. B., and V. S. Babkin. 1973. Decomposition of formaldehyde under adiabatic compression in the presence of oxygen. *Combust. Expl. Shock Waves* 9(3):363–366. doi: 10.1007/BF00745115.
 17. Sarkisyan, V. K. 1974. K raschetu kineticheskikh parametrov khimicheskikh gazovykh reaktsiy, izuchennykh metodom adiabaticeskogo szhatiya [On the calculation of kinetic parameters of chemical gas reactions studied by the adiabatic compression method]. *Kinet. Catal.* 15(3):560–564.
 18. Verem'ev, E. S., V. V. Kislykh, and A. E. Sidel'nikov. 1972. Issledovanie razlozheniya zakisi azota pri davleniyakh 1500–2000 atm [Investigation of the decomposition of nitrous oxide at pressures of 1500–2000 atm]. *Kinet. Catal.* 13(2):269–273.
 19. Olschewski, H. A., J. Troe, and H. Gg. Wagner. 1966. Niederdruckbereich und Hochdruckbereich des unimolekularen N_2O -Zerfalls. *Ber. Bunsen. Phys. Chem.* 70(4):450–459. doi: 10.1002/bbpc.19660700409.
 20. Rohrig, M., E. L. Petersen, D. F. Davidson, and R. K. Hanson. 1996. The pressure dependence of the thermal decomposition of N_2O . *Int. J. Chem. Kinet.* 28(8):599–608. doi: 10.1002/(SICI)1097-4601(1996)28:8%3C599::AID-KIN5%3E3.0.CO;2-Q.
 21. Merzhanov, A. G. 1973. Nonisothermal methods in chemical kinetics. *Combust. Expl. Shock Waves* 9(1):3–28. doi: 10.1007/BF00740357.
 22. Babkin, V. S., and P. K. Senachin. 2017. *Protsessy gorenija gaza v ogranicennykh ob'emakh* [Processes of gas combustion in limited volumes]. Barnaul: AltGTU. 143 p.
 23. Igonina, I. V., L. S. Polak, and V. S. Shchipachev. 1968. Raschet kinetiki prevrashcheniy metano-vodorodnoy smesi v usloviyakh adiabaticeskogo szhatiya i rasshireniya [Calculation of the kinetics of transformations of a methane–hydrogen mixture under conditions of adiabatic compression and expansion]. *Kinet. Catal.* 9(1):15–23.
 24. Glebov, D. V., M. E. Polyakova, and V. S. Shchipachev. 1978. Metody obrabotki rezul'tatov kineticheskikh eksperimentov na ustavnovkakh adiabaticeskogo szhatiya [Methods of processing the results of kinetic experiments on adiabatic compression units]. *Issledovanie khimicheskikh reaktsiy pri adiabaticeskem szhatii gazov* [Investigation of chemical reactions during adiabatic compression of gases]. Moscow: Nauka. 74–88.
 25. Shevel'kova, L. V., A. V. Ivanyuk, and N. S. Nametkin. 1980. Comparative study of pyrolysis of *n*-butane and isobutene. *Petroleum Chemistry U.S.S.R* 20(4):201–211. doi: 10.1016/0031-6458(80)90050-7.
 26. Wittig, S. L. K. 1969. Study of the thermal decomposition of *n*-butane. *Phys. Fluids* (1958–1988) 12(5):I-133–I-135.
 27. Kolbanovskiy, Yu. A., and M. E. Polyakova. 1981. Reshenie prosteyshoy obratnoy zadachi khimicheskoy kinetiki v naibolee obshchey postanovke metodom global'noy optimizatsii [The solution of the simplest inverse problem of chemical kinetics in the most general formulation by the method of global optimization]. *Kinet. Catal.* 22(4):882–887.

Received January 28, 2022

Contributor

Bilera Igor V. (b. 1968) — Candidate of Science in chemistry, leading research scientist, A. V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences, 29 Leninsky Prospekt, Moscow 119991, Russian Federation; bilera@ips.ac.ru