

HYSTERESIS IN CATALYTIC PROCESS FROM THE PERSPECTIVE OF NON-EQUILIBRIUM THERMODYNAMICS

Tsegelskiy V.G.

Keywords: catalysis, hysteresis, hysteresis loop, non-equilibrium thermodynamics.

Abstract. In this paper, the processes of concentrated hysteresis occurring as a result of methane oxidation on platinum nanoparticles are investigated from the perspective of non-equilibrium thermodynamics. It was revealed that the hysteresis is determined by a thermodynamic system transferring under certain conditions from a quasi-stationary state with lower entropy generation to another state with higher entropy generation and in reverse. It is demonstrated that the processes accompanying this hysteresis, similar to the processes of hysteresis in fluid dynamics, heat and mass transfer, aerodynamics, magnetism and other physically diverse systems investigated before, comply with the same validated laws of evolution of non-equilibrium macroscopic thermodynamic systems.

ГИСТЕРЕЗИС В КАТАЛИТИЧЕСКОМ ПРОЦЕССЕ С ПОЗИЦИИ НЕРАВНОВЕСНОЙ ТЕРМОДИНАМИКИ

Цегельский В.Г.

Ключевые слова: катализ, гистерезис, петля гистерезиса, неравновесная термодинамика.

Аннотация. В статье процессы, протекающие при концентрационном гистерезисе в реакции окисления метана на наноразмерных частицах платины, рассмотрены с позиции термодинамики необратимых процессов. Выявлено, что этот гистерезис обусловлен переходом при определенных условиях термодинамической системы из одного квазистационарного состояния с меньшим производством энтропии в другое состояние с большим производством энтропии и обратным переходом. Показано, что протекающие при рассматриваемом гистерезисе процессы, так же как и процессы в исследованных ранее гистерезисных явлениях в гидрогазодинамике, теплообмене, аэродинамике, магнетизме и других физически отличающихся системах, подчиняются одним и тем же экспериментально подтвержденным общим закономерностям эволюции неравновесных макроскопических термодинамических систем.

Hysteresis can be observed in various physical and chemical processes. It was theoretically and experimentally validated in [1, 2] that the hysteresis in fluid dynamics and heat-mass transfer is determined by the direct and reverse transitions between two quasi-stationary states of a non-equilibrium thermodynamic system, these states being characterized by a difference in the entropy generation. These transitions lead to changes both in state-related structures (for example, flow patterns and heat transfer character) as well as other parameters. During the transitions, the structure and parameters of a thermodynamic system fluctuate quite sharply, often intermittently. The same investigations formulated some general laws of changes in quasi-stationary states of non-equilibrium thermodynamic systems.

Hysteresis also occurs in catalytic processes. Let us study these processes from the perspective of non-equilibrium thermodynamics. The thermodynamic method is especially valuable here, since the same general laws can be applied to macroscopic thermodynamic systems characterized by diverse physical and chemical processes.

Before we conduct thermodynamic analysis, let us report the results of the experimental investigation of concentrated hysteresis in low-temperature oxidation of methane over disperse catalyst Pt/ γ -Al₂O₃ provided in [3].

The catalytic experiment was conducted at atmospheric pressure and constant temperature at zero-pressure and zero-concentration gradient across the catalyst layer. The schematic of the flow circulating facility used in the experiment is presented in Fig. 1, the design characteristics are specified in [4]. The initial reaction mixture fed into the reactor contained 1.1 vol% methane, which remained the same, while oxygen concentration varied from 0.6 to 2.5 vol%, the rest comprised N₂. For each given composition of the initial reaction mixture, the stationary value was achieved (the circulation rate of the reaction mixture through the catalyst ≈ 70), after that the final reaction mixture composition was analyzed. Chromatography was used to determine the content of H₂, CO, CH₄, O₂ and CO₂ in the final reaction mixture, the water vapor concentration was calculated using the mass balance.

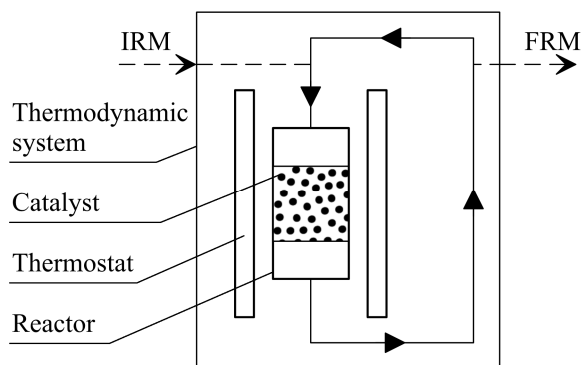


Fig. 1. Reaction facility schematic

Fig. 2 presents the methane conversion X curve for the successive increase and decrease in the oxygen concentration in the initial reaction mixture. The conversion is plotted for a reaction temperature $T = 703$ K, that was sustained by means of a thermostat. The degree of conversion was determined as a ratio of the converted reactant (CH₄) to the amount fed initially.

The graph in Fig. 2 is obviously characterized by hysteresis. As the O₂ concentration decreases from 2.5 vol% to ≈ 1.47 vol%, the CH₄ conversion remains stable equaling 28% (the lower branch of the hysteresis loop). As the O₂ concentration continues to decrease, the methane conversion increases abruptly, reaching $X = 0.67$ at a certain concentration ratio O₂:CH₄ (≈ 1.1) by the effect of the transition to the upper branch of the hysteresis loop. With the further increase in the oxygen concentration, the methane conversion increases smoothly to the maximum value $X = 0.99$, followed by a sharp drop and a transition to the lower branch of the hysteresis loop.

Here and in Fig. 3, concentration of CH₄ in IRM is 1.1 vol%, reaction temperature 703 K.

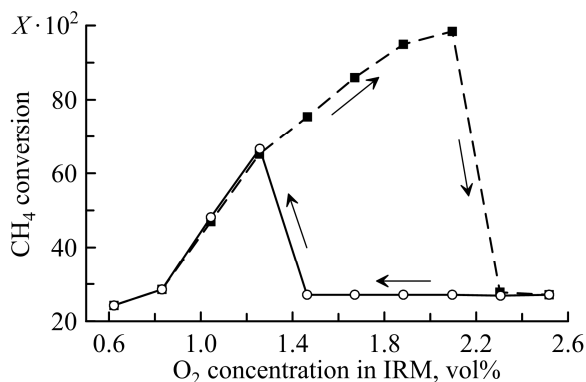


Fig. 2. Change in methane conversion during consecutive increase and decrease in oxygen concentration in initial reaction mixture (IRM)

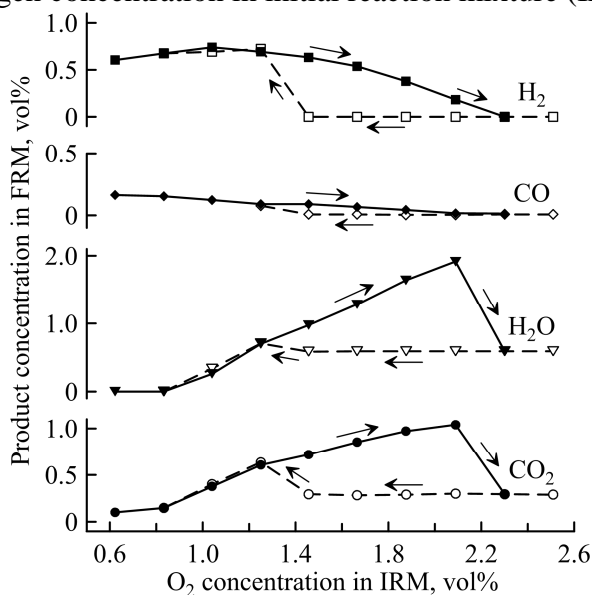
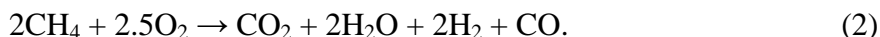


Fig. 3. Change in concentration of reaction products in final reaction mixture (FRM) for consecutive decrease (white symbols, dotted line) or increase (dark symbols and full line) in oxygen concentration in initial reaction mixture (IRM)

Analysis of the final reaction mixture composition (Fig. 3) revealed that the transitions are characterized by a cardinal change in the composition of the oxidation products, accompanied by the change in the catalyst activity. At the lower branch of the hysteresis loop, with the low catalytic activity, only the full oxidation products of CO_2 and H_2O are formed, in accordance with the reaction



At the upper branch of the hysteresis loop, with the catalyst activated, the final reaction mixture apart from the full oxidation products comprises the partial oxidation products in accordance with the reaction



Let us view the above processes from the perspective of the non-equilibrium thermodynamics with regard to its aspects specified in [1, 2].

Let us take a thermodynamic system comprising a reaction mixture, a catalyst and a thermostat (Fig. 1). The composition of the reaction mixture varies from the initial to the final state during the reaction time Δt . Let us find specific entropy generation in this system in Δt for its different states. The specific entropy generation IIS is the amount of entropy generated in a thermodynamic system in a unit of time as a result of processes inside the system relative to one mole of the initial reaction mixture.

Catalytic reactions (1) and (2) in the thermodynamic system under consideration occur at the atmospheric pressure and constant temperature T . The temperature is kept constant by means of a thermostat, which can be considered as a large-capacity thermal reservoir. The thermodynamic system under study is assumed to be isolated, as the test conditions presume that there no transfer energy by work with other systems and the feed mixture is heated to the reaction temperature T . This means that any spontaneous change in the system under study must be accompanied by an increase in the total entropy, i.e. the sum of entropies of the gas mixture, the gas reservoir (thermostat) and the catalyst must increase, even though individual entropies of each subsystem may decrease.

Since the reactions (1) and (2) occur at pressure equaling 1 atm, the reaction heat Q_R corresponds to the change in enthalpy ΔH : $Q_R = \Delta H$. The standard enthalpy change ΔH^0 per 1 mole of CH_4 for the reactions (1) and (2) can be determined using data from [5, 6]:

$$\Delta H_1^0 = -802.86 \text{ kJ/mole CH}_4; \Delta H_2^0 = -419.28 \text{ kJ/mole CH}_4.$$

Cumulative heat Q_M from the total reaction gas mixture, with methane conversion accounted for (Fig. 2) for every feed mixture composition and catalyst activity shall be written as

$$Q_M = M_M G_{\text{CH}_4} X \Delta H^0, \quad (3)$$

where M_M is the number of moles in the feed mixture; G_{CH_4} is mole fraction of methane in the feed mixture.

As per the conditions of the experiment, the volume fraction of methane in all feed mixture compositions remained constant, equaling 1.1 vol%. With the gases in the mixture assumed ideal, $G_{\text{CH}_4} = 0.011$.

Since the reaction mixture temperature was kept stable during the experiment, and the catalyst properties remain unchanged at the beginning and at the end of the reaction, all the heat generated, accurate within the difference in heat capacity between the initial reaction mixture and the final reaction mixture, must transfer from the reaction mixture to the heat reservoir (thermostat). Heat of the reaction mixture Q_M and of the heat reservoir Q_T will be equal in absolute magnitude and opposite in sign. Since the heat transfer occurs at constant temperature, the process can be considered equilibrated. The entropy change of the heat reservoir and consequently of the whole thermodynamic system can be determined using the formula

$$\Delta S = \frac{Q_T}{T} = -\frac{M_M G_{\text{CH}_4} X \Delta H^0}{T}. \quad (4)$$

It was taken into account that the catalyst remains chemically unchanged after the reaction finishes, the quantity and temperature of the catalyst remain stable, which means that the entropy of the catalyst is unchanged. The entropy of the reaction gas mixture is also practically unchanged due to its stable heat capacity and temperature.

Using (4) and taking into account that the total heat of the reaction mixture is generated at the time period Δt , let us present the specific entropy generation per mole of the feed mixture as

$$IIS = -\frac{M_M G_{CH_4} X \Delta H^0}{M_M T \Delta t} = -\frac{G_{CH_4} X \Delta H^0}{T \Delta t}. \quad (5)$$

When calculating the entropy generation IIS_1 in a thermodynamic system at the final stage of reaction (1), $\Delta H^0 = \Delta H_1^0$ and the X value corresponding to the lower branch of the hysteresis loop (Fig. 2) will be substituted into (5). To calculate the entropy generation IIS_2 in a thermodynamic system at the final stage of reaction (2), $\Delta H^0 = \Delta H_2^0$ and the X value from the upper branch of the hysteresis loop in Fig. 2 will be substituted into (5). For calculation purposes, it was assumed that $\Delta t = 100$ s. The value Δt determines the absolute magnitude of IIS , but does not affect the fluctuation pattern in IIS_1 and IIS_2 and the conclusions.

It should be noted that during the transition from the initial to the final reaction mixture in the time period Δt , the thermodynamic system is in the non-equilibrium state, as this time period is characterized by the change in the quantity of reactants, heat transferred to the thermostat, mixture composition and catalyst state. As soon as the reaction is completed, the thermodynamic system assumes a quasi-stationary state, since there are both direct and reverse chemical reactions occurring in this system in a chemical equilibrium. The specific entropy generations IIS_1 and IIS_2 belong to the two possible states realized in a thermodynamic system depending on the type of the reaction: (1) or (2) and the composition of the final mixture (thermodynamic system structure). Each of the two possible states of the thermodynamic system can be realized for the same concentration of O_2 in the initial reaction mixture depending on the way this state was achieved.

Fig. 4 presents IIS_1 and IIS_2 calculated as functions of O_2 concentration in the initial reaction mixture. It is evident from the graph that, as the concentration of oxygen decreases, it reaches such values when the given thermodynamic system transfers from a quasi-stationary state with a lower entropy generation IIS_1 to another quasi-stationary state with a higher entropy generation IIS_2 . As the concentration of O_2 continues to increase, it reaches such values that enable a reverse transition from the state with a higher entropy generation IIS_2 to a state with a lower entropy generation IIS_1 .

According to the axiom concerning the perfection of the natural processes formulated in [7] and experimentally confirmed for various physical processes in nature [1, 2, 8-10], *of the all possible stationary states of a thermodynamic system complying with the laws of nature, irreversible thermodynamics, boundary and other physical conditions, the state with the minimally possible entropy generation is the most likely.*

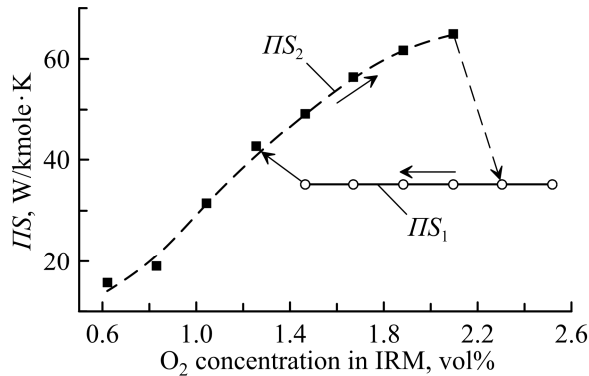


Fig. 4. IIS_1 and IIS_2 as function of O_2 concentration in IRM

In this case, the physical condition enabling the state with minimal entropy generation IIS_1 is the state that enables reaction (1) in the thermodynamic system under consideration. As the experiment results demonstrated (Fig. 2), this state becomes possible for the reaction temperature 703 K when the initial reaction mixture composition $O_2:CH_4 \geq 1.3$. When the ratio $O_2:CH_4$ is lower, the catalyst activity increases and the thermodynamic system progresses to the state with a higher entropy generation, which terminates at $O_2:CH_4 \approx 1.1$.

Previous works [1, 2] demonstrated that the range of the key parameter, which determines the lower entropy states, can be changed when certain conditions are created. For example, as the perturbations in the cylindrical pipe flow decrease, the transition from laminar (lower entropy) to turbulent (higher entropy) flow takes longer and may occur at such values of the Reynolds number which are orders of magnitude higher than its critical value at reverse transition. However, during the reverse transition from the higher to lower entropy state, the critical value of the Reynolds number remains approximately the same.

In the case under consideration, the change in the reaction temperature can result in change of the concentration ratio $O_2:CH_4$ in the initial reaction mixture, below which the reaction (1) can occur and at which the catalyst is activated. As the experiments demonstrated, the reverse transition from the higher to lower entropy state (Fig. 5) occurs at approximately the same concentration ratio $O_2:CH_4 \approx 1.9$ in a wider range of temperatures. The catalyst is deactivated and the reaction (2) converts to reaction (1).

In accordance with the general laws of changes in non-equilibrium thermodynamic states given in [1, 2], the transition of a system from a higher entropy (quasi-)stationary state to a lower entropy stationary state can occur only if in the process of its evolution, the difference in the entropy generation of these two states reaches a certain positive value. The transition of a thermodynamic system from a lower to a higher entropy state can be achieved only if in the process of its evolution, a physical condition is not fulfilled, preventing the existence of the initial state. Direct and inverse transitions between two stationary states of a non-equilibrium thermodynamic system are characterized by hysteresis. These transitions cause changes in the structures, according to these states (in the case

under consideration, compositions and concentrations of the reaction mixture), in the thermodynamic and other parameters.

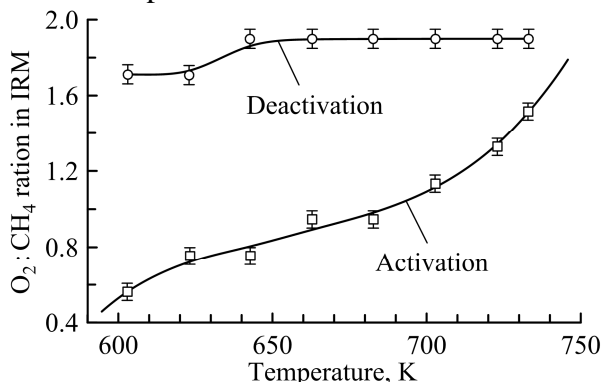


Fig. 5. Effect of methane oxidation temperature on composition of the initial reaction mixture, at which Pt-catalyst transition from low-active to high-active state (activation) terminates or reverse transition (deactivation) commences

All of the above is in full compliance with the curves in Fig. 4 and results of experiments in Fig. 2, 3.

Also, as was shown in [1, 2, 8-10], while a thermodynamic system is transferring from one stationary state to another, non-stationary (unstable) structures are formed. For a gas flowing in a pipe, the transition from the laminar regime to the stable turbulent regime passes through non-stationary flow structures in a certain narrow range of the Reynolds numbers accompanied by a continuous temporal and spatial fluctuation of the turbulent and laminar gas areas. For water boiling in a container, the transition from the nucleate (lower entropy) boiling regime to the film (higher entropy) boiling regime is accompanied by various combinations of film and nucleate boiling regimes formed in different areas of the heat-dissipating surface, randomly replacing one another. In the case of the Rayleigh-Benard convection, the transition from the stationary state with a honeycomb fluid motion pattern (Benard cells) into the stationary state with the roll current structure is achieved through some nonstationary flow structures. A detailed description of these nonstationary flow structures is given, for example, in [11].

It follows from all of the above that the nonstationary structures formed during transition can manifest themselves as chaotically fluctuating combinations of the initial and resulting stationary structures. However, nonstationary structures differing from the stationary structures can also be formed.

We do not believe that [3] can be used to determine the nature of the nonstationary structures formed in a narrow range of O₂:CH₄ concentration ratios, exhibiting both the increase and decrease of the catalyst activity for the thermodynamic system under study. An assumption can only be made with regard to the spatial and temporal chaotic fluctuations in the composition and concentration of the reaction mixture products. It is also quite possible that new products, such as ions of some substances, be formed adjacent to the catalytic areas.

It would be natural to assume that the above processes in the heterogeneous catalysis occur in the homogeneous catalysis. For example, it is noted in [12, 13] that during the Belousov-Zhabotinsky reaction in a continuously stirred tank reactor, apart from stable stationary states, complex nonstationary structures are formed fluctuating both in time and space.

In conclusion, we would like to note that the concentration hysteresis, similar to the hysteresis processes in fluid dynamics, heat and mass exchange, aerodynamics and magnetism and other processes complies with the same laws of the non-equilibrium macroscopic thermodynamic system evolution.

References

1. Tsegelskiy V.G. On application of non-equilibrium thermodynamics for solving of hydrodynamic problems and definition of human activity influence on Earth climate // Journal of Advanced Research in Technical Science. 2017. Issue 6. P.23-47.
2. Tsegelskiy V.G. Thermodynamic analysis of the impact of world energy and other aspects of human activity on the approach of the ice age on Earth // Journal of Advanced Research in Technical Science. 2018. Issue 9-1. P. 5-20.
3. Pakharukov I.YU., Bekk I.E., Matrosova M.M., Bukhtiyarov V.I., Parmon V.N. Concentration hysteresis in the oxidation of methane on nanoscale platinum particles // Reports of the Academy. 2011. V.439, No 2. P. 211-214.
4. Pakharukov I.YU., Bobrov N.N., Parmon V.N. Investigation of the kinetics of methane deep oxidation using an improved flow-circulation method // Catalysis in industry. 2008. No 6. P. 11-16.
5. Yeremin, E.N. The fundamentals of chemical thermodynamics. M.: Vysshaya shkola, 1974. 341 p.
6. Chemist's reference book, Vol. 1. M.-L.: Khimiya, 1966. 1071 p.
7. Tsegelskiy V.G. On the application of irreversible thermodynamics processes for the calculation of a supersonic ejector operating modes // News universities. Engineering, 2015. No 6. P. 26-45.
8. Tsegelskiy V.G. Hysteresis in magnetics from a position of non-equilibrium thermodynamics // Journal of Advanced Research in Technical Science. 2018. Issue 10-1. P. 28-38.
9. Tsegelskiy V.G. Jet devices. M.: MGTU im. N.E. Bauman, 2017. 576 p.
10. Tsegelskiy V.G., Krylovskiy A.E. Aerodynamic hysteresis from the perspective of non-equilibrium thermodynamics // Journal of Advanced Research in Technical Science. 2019. Issue 14-1. P. 45-57.
11. Getling A.V. Rayleigh-Benard convection. M.: Editorial URSS, 1999. 248 p.
12. Field R.J., Burger M. Oscillations and Traveling Waves in Chemical Systems. Wiley-Interscience, 1985. 681 p.
13. Kepper P., Boissonade J. Theoretical and experimental analysis of phase diagrams and related dynamical properties in the Belousov-Zhabotinskii system // J. Chem. Phys., Vol.75, №.1. July 1981. P. 189-195.

Список литературы

1. Цегельский В.Г. О применении неравновесной термодинамики в решении гидродинамических задач и в определении воздействия жизнедеятельности человека на климат Земли // *Journal of Advanced Research in Technical Science*. 2017. Issue 6. P. 23-47.
2. Tsegelskiy V.G. Thermodynamic analysis of the impact of world energy and other aspects of human activity on the approach of the ice age on Earth // *Journal of Advanced Research in Technical Science*. 2018. Issue 9-1. P. 5 20.
3. Пахаруков И.Ю., Бекк И.Э., Матросова М.М., Бухтияров В.И., Пармон В.Н. Концентрационный гистерезис в реакции окисления метана на наноразмерных частицах платины // *Доклады Академии наук*. 2011. Т.439, № 2. С.211-214.
4. Пахаруков И.Ю., Бобров Н.Н., Пармон В.Н. Исследование кинетики глубокого окисления метана с использованием усовершенствованного проточно-циркуляционного метода // *Катализ в промышленности*. 2008. №6. С. 11-16.
5. Ерёмин Е.Н. Основы химической термодинамики. М.: Высшая школа, 1974. 341 с.
6. Справочник химика, т.1. М.-Л.: Химия, 1966. 1071 с.
7. Цегельский В.Г. О применении термодинамики необратимых процессов в расчетах режимов работы сверхзвукового эжектора // *Изв. Вузов, Машиностроение*. 2015. № 6. С. 26-45.
8. Цегельский В.Г. Гистерезис в магнетизме с позиции неравновесной термодинамики // *Journal of Advanced Research in Technical Science*. 2018. Issue 10-1. P. 28-38.
9. Цегельский В.Г. Струйные аппараты. М.: МГТУ им. Н.Э. Баумана, 2017. 576 с.
10. Tsegelskiy V.G., Krylovskiy A.E. Aerodynamic hysteresis from the perspective of non-equilibrium thermodynamics // *Journal of Advanced Research in Technical Science*. 2019. Issue 14-1. P. 45-57.
11. Гетлинг А.В. Конвекция Рэлея-Бенара. М.: Эдиториал УРСС, 1999. 248 с.
12. Филд Р., Бургер М. Колебания и бегущие волны в химических системах. М.: Мир, 1988. 720 с.
13. Kepper P., Boissonade J. Theoretical and experimental analysis of phase diagrams and related dynamical properties in the Belousov-Zhabotinskii system // *J. Chem. Phys.*, Vol.75, №.1. July 1981. P 189-195.

Цегельский Валерий Григорьевич – доктор технических наук, главный научный сотрудник, Московский государственный технический университет им. Н.Э. Баумана, г. Москва, РФ, user46@post.ru

Tsegelskiy Valery Grigorievich – doctor of technical sciences, chief scientist of Bauman Moscow State Technical University, Moscow, Russian Federation, user46@post.ru

Received 06.06.2019