

An approximate method for calculating composition of the non-equilibrium explosion products of hydrocarbons and oxygen

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Abstract. We develop a method for calculating the changes in composition of the explosion products in the case where the complete chemical equilibrium is absent but the bimolecular reactions are in quasi-equilibrium with the exception bimolecular reactions with one of the components of the mixture. We investigate the possibility of using the method of "quasi-equilibrium" for mixtures of hydrocarbons and oxygen. The method is based on the assumption of the existence of the partial chemical equilibrium in the explosion products. Without significant loss of accuracy to the solution of stiff differential equations detailed kinetic mechanism can be replaced by one or two differential equation and a system of algebraic equations. This method is always consistent with the detailed mechanism and can be used separately or in conjunction with the solution of a stiff system for chemically non-equilibrium mixtures replacing it when bimolecular reactions are near to equilibrium.

1. Introduction

The chemical kinetics models are important for analysis and design in many chemistry and industrial processes. The chemical reactions that occur in the explosion products change their composition and, consequently, thermodynamic parameters. During cooling, expansion and mixing with air the internal energy, temperature and density are changed. The changed thermodynamic parameters correspond to a different chemical equilibrium composition of the mixture. The time evolution of the composition is calculated using a stiff system of chemical kinetics equations. This is the most general approach. At a large number of individual species in the explosion products and a large number of chemical reactions involved, calculation of the mixture composition requires a long computation time. Typically, the time it takes for calculating the mixture composition is much longer than that spent on solving the gasdynamics equations.

The applicability of the chemical equilibrium mixture model to the products of explosion of fuel–oxygen and fuel–air mixtures was discussed in detail in [1–6]. The applicability of the chemical equilibrium model to hydrogen–oxygen mixtures in the case of heat supply at constant density was assessed in [1]. In [2, 5], a sufficient condition for the applicability of the chemical equilibrium mixture model to gasdynamic calculations was obtained. The authors of [6] compared the results of gasdynamic calculations performed using the system of equations of chemical kinetics for calculating the composition of the explosion products with the results of gasdynamic calculations within the framework of the chemical equilibrium mixture model and the constant composition mixture model.



It was demonstrated [1, 2, 4, 5] that the process of establishment of chemical equilibrium in the products of explosion of gas mixtures proceeds in several stages. First, partial chemical equilibrium is established, without changes in the total number of molecules in the system. That is, even in cases where there is no chemical equilibrium, it suffices to know the molar mass of the mixture and two required thermodynamic parameters (for example, specific internal and density) to determine the composition of the mixture.

The existence of quasi-equilibrium in exchange reactions was discussed in [6]. This same assumption underlies an approximate model for calculating the molar mass of gas mixtures at high temperatures [7]. The author of [7, 8] proposed an approximate kinetic equation for calculating the molar mass of the mixture and then the thermodynamic parameters.

In [9–11] we made an effort to speed up directly chemical integrator for some special case. In [9–11] we developed a method for calculating the changing composition of the explosion products in the case where there is no complete chemical equilibrium, but the bimolecular reactions are in equilibrium. A detailed kinetic mechanism is used, but without the need to solve the stiff system of equations. The core of our approach is to replace the complete system of chemical kinetics equations by an equivalent system composed of a differential and a few algebraic equations. The proposed method is based on a physically reasonable assumption that equilibrium in the bimolecular reactions is established much faster than the complete chemical equilibrium, being applicable when this assumption holds. According to [9–11] the method includes only one differential equation for calculating the change in the number of molecules per unit mass of the mixture due to the reactions of recombination and dissociation. This equation is used instead of dozens of equations of chemical kinetics. In the present work, we propose to supplement this equation with an algebraic equations for calculating the equilibrium composition at given values of the density, internal energy, molar mass and the linear combinations of logarithms of the concentration. The equations are derived based on the characteristic function (entropy or Helmholtz free energy) extremum method.

The applicability of the model was demonstrated by solving the test problems in [9–11]. It was shown that the proposed model can be used to calculate the characteristics of the explosive transformation process after the induction period in hydrogen-oxygen mixtures.

The aim of the work described here was to develop a method for calculating the changes in composition of the explosion products in the case where the complete chemical equilibrium is absent but the bimolecular reactions are in quasi-equilibrium with the exception bimolecular reactions with one of the components of the mixture. In addition we have investigated the possibility of using the method of "quasi-equilibrium" for mixtures of hydrocarbons and oxygen.

2. Equation for calculating the partial chemical equilibrium composition of the mixture

According to [9] we obtain equations to calculate the mixture composition assuming that the entropy of the mixture reaches its maximum value at a given temperature, density, number of molecules per unit volume and the linear combinations of logarithms of the concentration. The entropy of a mixture of ideal gases with known dependence of the heat capacity on the temperature is given by

$$S = \sum_{i=1}^k \left\{ S_i - RT \ln \left[RT M_i / (v P_0) \right] \right\} M_i$$

The total amount of each element j , internal specific energy and the number of molecules in the system are known

$$\sum_{i=1}^k \alpha_{ij} M_i - \beta_j = 0, \quad (j=1, \dots, m),$$

$$U_0 - \sum_{i=1}^k U_i M_i = 0,$$

$$\sum_{i=1}^k M_i - M_0 = 0, \quad (1)$$

where k is number of individual compounds in the mixture; M_i is the number of moles of the i -th substance per 1 kg of mixture, R is the universal gas constant, T is the temperature of the mixture, v is the specific internal volume of the mixture, S_i is the standard entropy, U_i is the internal energy of one mole of mixture component i at a given temperature T and $P_0 = 10^5$ Pa, $M_0 = c / \rho$ and c is the total number of moles of all mixture components per unit volume, m is the number of different chemical elements in the mixture, β_j is the number of kilogram-atoms of the j -th element in 1 kg of mixture, α_{ij} is the number of atoms of the j -th element in a molecule of the i -th substance.

If $A+B \leftrightarrow C+D$ is the nonequilibrium bimolecular reaction we can use additional condition on the concentrations

$$\ln(M_A) + \ln(M_B) - \ln(M_C) - \ln(M_D) - \ln(W_K) = 0, \quad (2)$$

where W_K is the additional independent variable and is calculated by solving differential equation. K is the index of the reaction.

If all reactions with the specie A are nonequilibrium the differential equation for the concentrations of A is used. The additional condition on concentrations is

$$M_A = W_A. \quad (3)$$

Following the Lagrange procedure, we write the function

$$L = \sum_{i=1}^k \{S_i - R \ln[R T M_i / (v P_0)]\} M_i + \sum_{j=1}^m (\sum_{i=1}^k \alpha_{ij} M_i - \beta_j) \lambda_j + (U_0 - \sum_{i=1}^k U_i M_i) \lambda_u + \sum_{i=1}^k (M_i - M_0) \lambda_\mu + G \lambda_R,$$

where λ_j , λ_μ , λ_u and λ_R are the Lagrange multipliers, which, along with M_i , are the independent variables of the Lagrangian. If the additional condition (2) is used

$$G = \ln(M_A) + \ln(M_B) - \ln(M_C) - \ln(M_D) - \ln(W_K),$$

and G is found from

$$G = M_A - W_A$$

for additional condition (3).

At equilibrium, the derivatives of the Lagrangian with respect to the independent variables must be equal to zero. This condition allows us to obtain $k + m + 3$ algebraic equations (1-3) for $k + m + 3$ unknowns

$$S_i - R \ln[R T M_i / (v P_0)] + \sum_{j=1}^m \alpha_{ij} \lambda_j - H_i / T + \lambda_\mu + (\partial G / \partial M_i) \lambda_R = 0, (i=1, \dots, k) \quad (4)$$

$$\sum_{i=1}^k \alpha_{ij} M_i - \beta_j = 0, (j=1, \dots, m) \quad (5)$$

$$U_0 - \sum_{i=1}^k U_i M_i = 0, \quad (6)$$

$$\sum_{i=1}^k M_i - M_0 = 0, \quad (7)$$

$$G(M_1, \dots, M_k, W) = 0 \quad (8)$$

This system of algebraic equations has no analytical solution, so it is solved approximately by the Newton method.

When the chemical kinetics equations are applied to calculating the composition of the mixture, the following a system of equations is used

$$\frac{\partial c_i}{\partial t} = \omega_i, \quad i=1, \dots, k. \quad (9)$$

$$\sum_{i=1}^N \nu_{ij}' \chi_i \rightleftharpoons \sum_{i=1}^N \nu_{ij}'' \chi_i, \quad j=1, \dots, J,$$

$$\omega_i = \sum_{j=1}^J k_j (\nu_{ij}'' - \nu_{ij}'),$$

$$\frac{\partial c}{\partial t} = \sum_{i=1}^k \omega_i, \quad (10)$$

$$\frac{\partial \ln(W_k)}{\partial t} = \frac{\omega_A}{c_A} + \frac{\omega_B}{c_B} - \frac{\omega_C}{c_C} - \frac{\omega_D}{c_D}, \quad (11)$$

$$\frac{\partial c_A}{\partial t} = \omega_A \quad (12)$$

where ω_i is the rate of production of species i per unit volume; c_i are the molar concentrations of the mixture components; c is the rate of production of the total number of moles of all species per unit volume, k_j is the rate of reaction j calculated according to the law of mass action, χ_i is the chemical formula of species i participating in the reaction j ; ν_{ij}'' and ν_{ij}' are the stoichiometric coefficients of the product or reactant i in reaction j , J is the number of reactions in the kinetic scheme. W_k is the parameter of nonequilibrium of selected reaction, $W_A = c_A/\rho$.

3. Results of calculations

The proposed approximate method for solving stiff systems of kinetic equations was applied to a test problem. Consider the chemical equilibrium explosion products of stoichiometric acetylene–oxygen. The composition of the mixture given in Table 1 correspond to the so called instantaneous explosion of the initial mixture. The composition is calculated for an initial mixture at 0.1 MPa and 298 K.

Table 1. Equilibrium products composition (mole fraction) at $T=3985$ K and $\rho=1.24$ kg/m³.

O ₂	H ₂	OH	H ₂ O	CO	H	O	CO ₂	HO ₂
0.120	0.0364	0.109	0.0963	0.343	0.0712	0.120	0.102	0.000216

We reduce the temperature of the mixture to 2800 K at constant volume and constant composition. The mixture relaxes to the new state of chemical equilibrium at constant density and constant specific internal energy. It is assumed that there are no expansion and heat loss. The calculations were performed by numerical solving the system of differential equations of chemical kinetics, corresponding to the selected detailed mechanism (blue lines in figures 1 – figures 4).

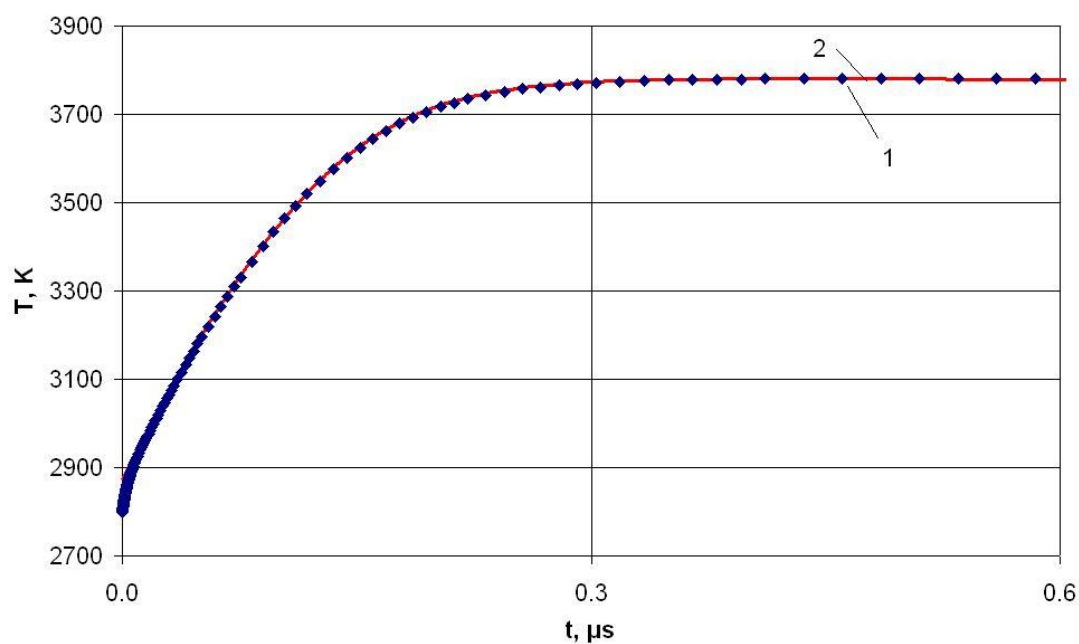


Figure 1. Temperature vs time: 1—exact method including 10 differential equations, 2—proposed method with one differential equation (6) for c .

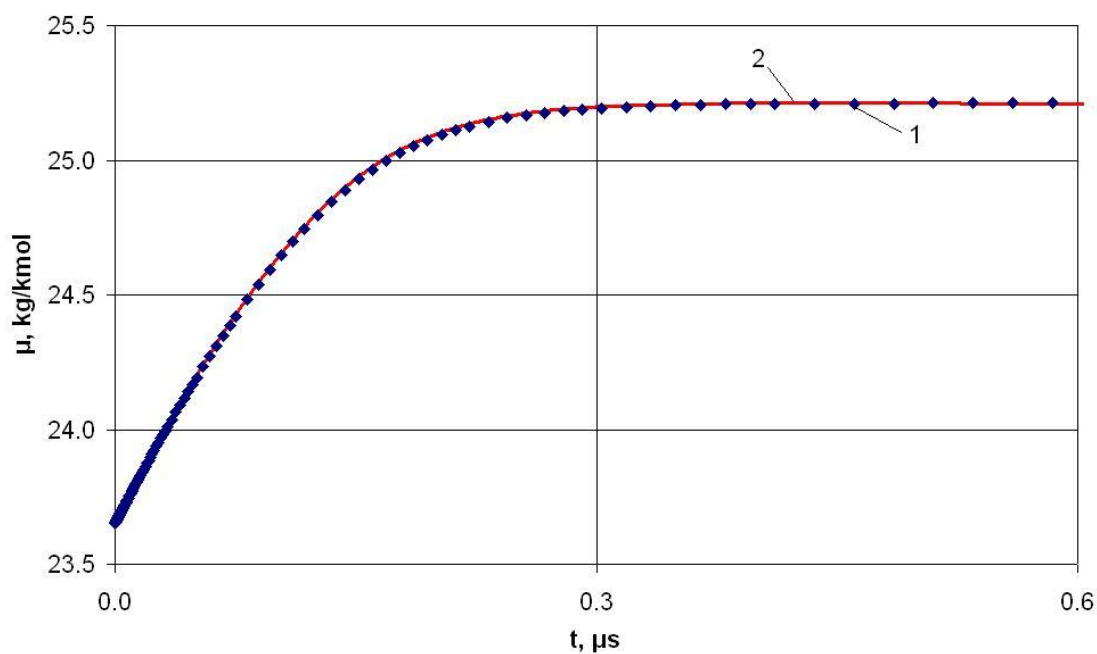


Figure 2. Molar mass of the explosion products vs time: 1—exact method including 10 differential equations, 2—proposed method with one differential equation (6) for c .

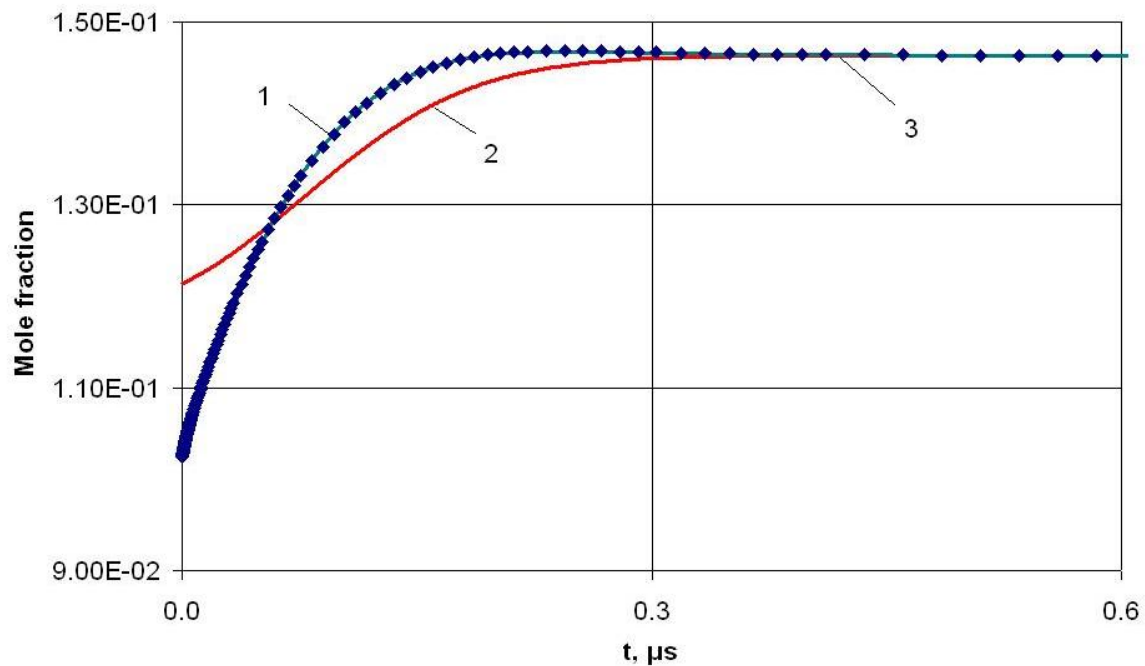


Figure 3. Molar mass CO_2 vs time: 1—exact method including 10 differential equations, 2—proposed method with one (6) differential equation for c , 3 -proposed method with two differential equations (6) for c and (8) W_{CO_2} .

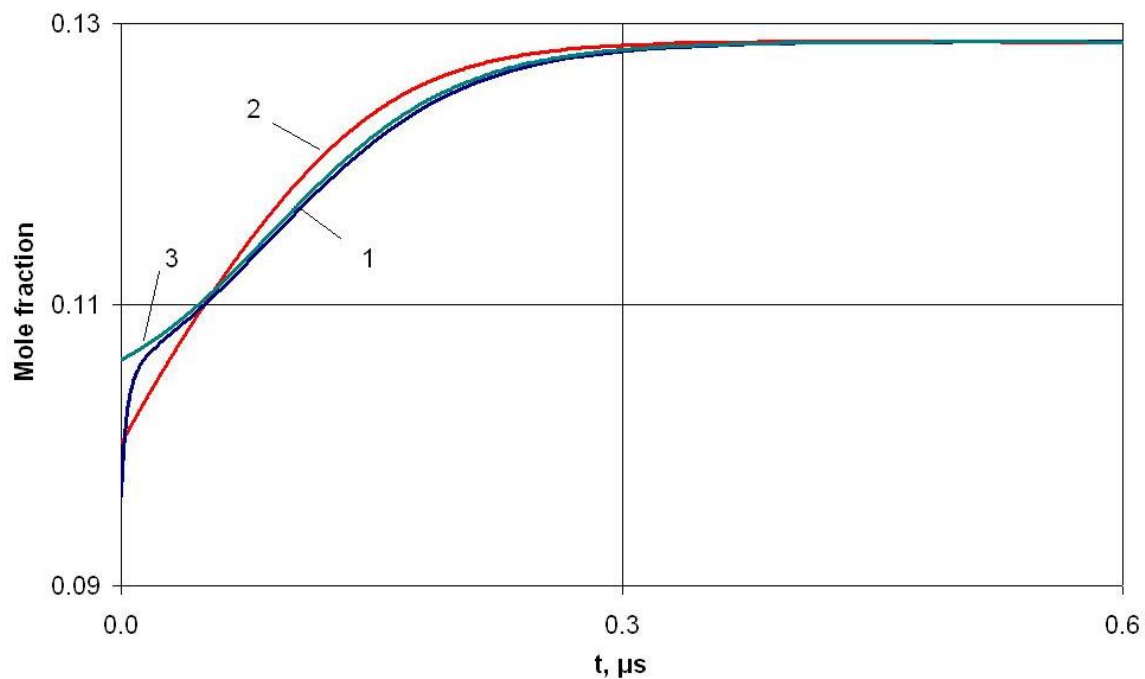


Figure 4. Molar mass of H_2O products vs time: 1—exact method including 10 differential equations, 2—proposed method with one (6) differential equation for c , 3 -proposed method with two differential equations (6) for c and (8) W_{CO_2} .

It was necessary to solve a stiff system of ten differential equations (the system (8) of 9 equations for the concentrations and one equation for the temperature). The calculation was performed until the state of the mixture was close to the equilibrium. The species that are taken into account in the

explosion products are CO, CO₂, H, H₂O, HO₂, H₂, O, OH and O₂. We use the detailed kinetic mechanism including 18 reactions: $O+CO+M=CO_2+M$, $O+H+M=OH+M$, $O+O+M=O_2+M$, $H+OH+M=H_2O+M$, $H+H+M=H_2+M$, $H+O_2+M=HO_2+M$, $O_2+CO=O+CO_2$, $H+O_2=O+OH$, $O+H_2=H+OH$, $OH+CO=H+CO_2$, $O+H_2O=OH+OH$, $H+H_2O=OH+H_2$, $OH+HO_2=O_2+H_2O$, $OH+OH=H+HO_2$, $O_2+H_2=H+HO_2$, $O+H_2O=H+HO_2$, $OH+O_2=O+HO_2$, $HO_2+CO=OH+CO_2$. The data on the rate constants are borrowed from [12]. The rate constants of the reverse reactions were calculated from those for direct reactions using the equilibrium constants

In addition, we conducted calculations by the proposed methods. A single differential equation (10) for total concentration c and a system (4) – (7) of 14 algebraic equations are solved to calculate the time evolution of the mixture (red lines in figures 1 – figures 4). The results for temperature-time history and molar mass-time histories are in excellent agreement with data obtained by the detailed kinetic calculations. Temperature and molar mass is used to calculate pressure of the explosion products.

Figure 3 and Figure 4 show that the approximate method with one differential equation (10) for total concentration c does not provide very good accuracy in calculating the mole fraction of CO₂ and H₂O. The concentration of CO₂ has not reached complete equilibrium in the bimolecular reactions $O_2+CO=O+CO_2$, $OH+CO=H+CO_2$, $HO_2+CO=OH+CO_2$. A partial equilibrium is established for bimolecular reactions between H, H₂, O, O₂, OH, H₂O. We have recomputed the test problem using the approximate method with two differential equations for total concentration c (10) and for concentration of CO₂ (12). The system (4) – (8), of 15 algebraic equations are solved to calculate the quasi-equilibrium composition and temperature. The calculation of CO₂ and H₂O mole fractions - time histories based on the approximate method with two differential equation improves the agreement with exact solution (curves 3 in figure 3 and in figure 4).

4. Conclusions

We developed the approximate method to calculate composition and thermodynamic parameters of explosion products based on the assumption of the existence of a partial chemical equilibrium. Without significant loss in accuracy, the respective stiff system of detailed kinetics differential equations can be replaced by one or two differential equations and a system of algebraic equations. This method is always consistent with the detailed kinetic mechanism and can be used separately or in conjunction with the stiff system, replacing it when almost all of the bimolecular reactions reach the quasi-equilibrium state. The constituent equations of the model were derived and the respective computer code written. The applicability of the model was demonstrated by solving a test problem. It was shown that the proposed model can be used to calculate the characteristics of the explosion products of hydrocarbons and oxygen.

Acknowledgments

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References

- [1] Nikolaev Y A and Fomin P A 1982 *Fiz. Goreniya Vzryva* **18** 66-72
- [2] Borisov A A, Gubin S A and Shargatov V A 1991 *Prog. Astronaut. Aeronaut.* **134** 138–53
- [3] Wintenberger E, Cooper M, Pintgen F and Shepherd J E 2004 *J. Propuls. Power* **20** 957-59
- [4] Bryakina U F, Gubin S A, Tereza A M and Shargatov V A 2010 *Russ. J. Phys. Chem. B* **4** 969–76
- [5] Bryakina U F, Gubina T V and Shargatov V A 2011 *Russ. J. Phys. Chem. B* **5** 482–90
- [6] Bryakina U F, Gubin S A, Shargatov V A and Lyubimov A V 2012 *Russ. J. Phys. Chem. B* **6** 261–70
- [7] Nikolaev Y A 2001 *Combust. Explos.* **37** 4–12
- [8] Nikolaev Y A 1978 *Combust. Explos.* **14** 468–71
- [9] Gubin S A and Shargatov V A 2013 *Russ. J. Phys. Chem. B* **7** 154–60
- [10] Shargatov V A, Gubin S A and Okunev D Y 2015 *J. Phys.: Conf. Ser.* **653** 012054 1-8
- [11] Shargatov V A, Gubin S A and Okunev D Y 2015 *Phys. Proc.* **72** 342–6
- [12] Dautov N G and Starik A M 1997 *Kinet. Catal.* **38** 185–208