

# The study of thermodynamic properties and transport properties of multicomponent systems with chemical reactions

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**Abstract.** In case of system with chemical reaction the most important properties are heat conductivity and heat capacity. In this work we have considered the equation for estimate the component of these properties caused by chemical reaction and ionization processes. We have evaluated the contribution of this part in heat conductivity and heat capacity too. At the high temperatures contribution in heat conductivity from ionization begins to play an important role. We have created a model, which describe partial and full ionization of gases and gas mixtures. In addition, in this work we present the comparison of our result with experimental data and data from numerical simulation. We was used the data about transport properties of middle composition of Russian coals and the data of thermophysical properties of natural gas for comparison.

## 1 Introduction

When we solve a number of scientific and technical problem, the high temperature processes with chemical reaction play a significant role. Experimental methods for investigating these phenomena are usually expensive and therefore becomes very important numerical experiment to analyze the processes and draw conclusions about the behavior of the systems based on the model assumptions. Due to the fact that the transport properties are present in all the equations describing fluid flow and heat transfer processes, their detection is an important task. Separately possible to allocate the problem of determining the transport properties of carbon dioxide and its mixtures, which are one of the main products of combustion of solid fuels and interesting from an environmental point of view [1]. Contribution in the reaction component of the heat capacity and thermal conductivity is the most significant. Besides that, very interesting studying the properties of gaseous mixtures at high temperatures, where the substantial contribution of ionization.

The obtained results can be used in design and development of systems related to heat transfer, gas dynamics, solid and liquid fuels, such as boilers, engines.

## 2 Method

Calculation of the chemical composition and thermodynamic functions performed under the following assumptions:

- 1) The phase boundary is flat;
- 2) The forces of surface tension at the interface between phases is negligible;
- 3) The gas phase is a mixture of ideal gases;
- 4) Condensed phases is either pure substances or ideal solutions of various substances;
- 5) When mixed condensed substances we assumed then volume and energy are additive.

The system consisting from  $n$  components is considered. A current index of component number from  $n$  we designate  $i$  ( $i = 1, 2, 3 \dots n$ ), current indexes of phase number from  $r$  we designate  $\gamma, \beta$  ( $\gamma, \beta = 1, 2, 3 \dots n$ ). From a set of all components  $n$  we can allocate  $k$  linearly independent components. A current index of linearly independent components from  $k$  we designate  $j$  ( $j = 1, 2, 3 \dots k$ ). Any of  $i$  components can be expressed through linearly independent components  $j$  by means of set of stoichiometric factors  $\Phi_{ij}$ . It is possible to form a rectangular matrix  $\|\Phi_{ij}\|$  of these stoichiometric factors.

If we designate a chemical symbol as  $A_i^\gamma$ , that

$$A_i^\gamma = \sum_{\beta} \sum_{j(\beta)} \Phi_{i(\gamma)j(\beta)} A_{j(\beta)}, \text{ where } A_{j(\beta)}$$

basic components of  $j(\beta)$ , somehow distributed on  $r$  phases. For a finding the solid fuels combustion products

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structure the system of chemical thermodynamic equations for numbers of moles  $N_i^\gamma$  all a component is uses. This system looking like:

$$\begin{cases} N_i^\gamma = K_i^\gamma p^{j(1)} \prod_{\beta=1}^r (N_{j(\beta)}^{\delta_{j\beta}})^{\delta_{j\beta} - \sum_{j(\beta)} \Phi_{ij(\beta)}} \prod_{j(\beta)} N_{j(\beta)}^{\Phi_{ij(\beta)}} & (1) \\ \sum_{\gamma=1}^r \sum_i \Phi_{ij} N_i^\gamma - C_j^{o\gamma} = 0 & (2) \\ N^\gamma = \sum_i N_i^\gamma & (3) \end{cases}$$

$$K_i^\gamma = \exp\left(-[\chi_i^\gamma(T) - \sum_{j(\beta)} \Phi_{ij(\beta)} \chi_{j(\beta)}(T)] / RT\right)$$

$$\chi_i^\gamma(T) = H_i^\gamma(T) - TS_i^\gamma(T).$$

For calculations using the program TETRAN must specify the source of the atomic structure, the list of condensed and gaseous substances, which may be formed during the combustion, and thermodynamic potentials of all substances and the enthalpy of formation at standard conditions of the elements in standard states. Thermodynamic potentials and the enthalpy of formation are taken from the database for the corresponding elements. TETRAN program provides the ability to calculate multiphase systems. Types of the condensed phases are set preliminary, and their number is defined by Gibbs phase rule  $w = 2 + k - r$ , where  $w$  – number of free intensive variables,  $k$  – number of independent components in the system,  $r$  – number of phases. Algorithm of the linear iterative equations system decision is universal for change of quantity or structure of the condensed phases. Calculation is conducted, beginning from high temperatures where the concentrations of system atoms are set as initial approximation. Calculation is conducted simultaneously for two pairs independent parameters:  $V, T$  and  $p, T$ . In case of occurrence of problems with process convergence on one of pairs of variables the program automatically continues to consider and give out correct results only on variables  $V, T$  or  $p, T$ . After several steps on temperature «the bad point» manages and further calculation again on two pairs of variables is made.

The program is provided by base of the thermodynamic given individual substances formed as a result of various reactions more than for 3000 substances, they are presented in the form of coefficients of approximation of Gibbs energy in the corresponding temperature range for the following polynomial:

$$G = \varphi_0 + \varphi_1 \ln x + \varphi_2 x^{-2} + \varphi_3 x^{-1} + \varphi_4 x + \varphi_5 x^2 + \varphi_6 x^3$$

$$x = T * 10^{-4}$$

The choice of the Gibbs function as the main due to the fact that it easily can be obtained any other thermodynamic functions for the substance, such as

enthalpy  $H = \Delta H_{298.15}^0 + x^2 * 10^4 \cdot G'$ , entropy

$S = G + G'$ , heat capacity  $C_p = 2xG' + x^2 G''$ . In

addition, the database includes a range of temperatures at which this approximation is applicable, the molar mass of the substance, its enthalpy of formation, chemical formula, and elemental composition.

In addition to determining the composition of the combustion products of fuels the program also includes a calculation of the thermodynamic properties of individual phases and the entire system. Some of the calculated properties include internal energy, entropy, enthalpy, Gibbs energy, isochoric and isobaric heat capacity, coefficient of thermal expansion of the gas, the coefficient of isothermal compressibility, thermal efficiency of the gas pressure, the speed of sound in the gas phase (at constant mass of gas phase).

At heat conductivity calculation the big role have internal degrees of freedom and inelastic collisions of particles, including the collisions leading to chemical transformations. If inelastic collisions are frequent and probability of chemical reactions is great enough, so all components of gas are in local balance, with the big accuracy it is possible to use following expressions for forward heat conductivity of heavy components  $\lambda_H$ , internal heat conductivity  $\lambda_{int}$  and reaction heat conductivity  $\lambda_R$ :

$$\lambda = \lambda_H + \lambda_e + \lambda_{int} + \lambda_R \quad (4)$$

$$\lambda_H = 0.7392T^{0.5} \begin{vmatrix} L_{ij} & x_i + y_i \\ x_i & 0 \end{vmatrix} \times |L_{ij}|^{-1} \quad (5)$$

$$\lambda_{int} = 0.05914T^{0.5} \sum_i C_{int,i} x_i \beta_{ii}^{-1} + 0.7392T^{0.5} \begin{vmatrix} L_{ij} & x_i \\ x_i + y_i & 0 \end{vmatrix} \times |L_{ij}|^{-1} \quad (6)$$

$L_{ij}$  – function of  $\Delta_{ij}$ ,  $Z_{ij}$ ,  $C_{int,i}$ ,  $C_{rot,i}$ ,  $T^*$ ,

$Q(1,1)$ ,  $Q(2,2)$ ,  $B_{ij}^*$ .  $\Delta_{ij}$  – ratio of the diffusion

coefficient of the rotational degrees of freedom to the diffusion coefficient of mass [2],

$$Z_{ij} = Z_{ij}^\infty \left[ 1 + \frac{\pi^{3/2}}{2} \left( \frac{1}{T^*} \right)^{0.5} + \left( 2 + \frac{\pi^2}{4} \right) \left( \frac{1}{T^*} \right) + \pi^{3/2} \left( \frac{1}{T^*} \right)^{3/2} \right]$$

– the number of collisions of particles of type  $i$  with particles grade  $j$ , leading to the establishment of rotational equilibrium in the particles of species  $j$  [3],

$Z_{ij}^\infty = Z_{ij}$  when  $T \rightarrow \infty$ .

$C_{int,i} = C_{p,i} \cdot 0.5034 - 2.5$  – internal heat capacity of

particle  $i$  in terms of the Boltzmann constant,  $C_{p,i}$  –

heat capacity at constant pressure in terms of the Boltzmann constant,  $C_{rot,i}$  – heat capacity of the

rotational degrees of freedom in terms of the universal

gas constant.  $T^* = T/E_{ij}$  – reduced temperature;

$$B_{ij}^* = \frac{5\Omega_{ij}^{(1,2)} - 45\Omega_{ij}^{(1,3)}}{\Omega_{ij}^{(1,1)}}.$$

To determine the reaction component of thermal conductivity, we used two different methods. The first was based on the work [4, 5], the second by using the expression

$$\lambda_R = \left(n^2/\rho\right) \sum_{k=1}^{\mu} \sum_{i=1}^{\nu} \Delta H_i D_{ik} M_k \frac{\partial x_k}{\partial T} \quad (7)$$

We use the data on the dependence of the system composition from the temperature  $\partial x_k/\partial T$ , obtained by solving the above equations.

When considering electronic transfer coefficients we should separate region of partial ionization from the region of complete ionization. For the region of complete ionization, in the approximation of continuous interaction, changing the distribution function is described by the kinetic equation of the Fokker-Planck equation. Based on the solution of this equation in [6] by numerical integration, the following expression for the electric conductivity  $\sigma_{SH}$ , electronic thermal diffusion

$\varphi_{SH}$  and electronic thermal conductivity  $\lambda_{SH}$ :

$$\sigma_{SH} = 1.523 \cdot 10^{-2} (1 + 0.53 \lg Z_e) T^{1.5} (Z_e \ln \Lambda)^{-1} \quad (8)$$

$$\varphi_{SH} = 0.925 \cdot 10^{-6} (1 + 1.74 \lg Z_e) T^{1.5} (Z_e \ln \Lambda)^{-1} \quad (9)$$

$$\lambda_{SH} = 2.407 \cdot 10^{-10} (1 + 2.36 \lg Z_e) T^{2.5} (Z_e \ln \Lambda)^{-1} \quad (10)$$

$Z_e = \sum_i \frac{x_i Z_{e,i}^2}{x_e}$  – average charge of ions,

$$\Lambda = 1.45 \cdot 10^{-7} T^2 \left( p x_e Z_e^2 (1 + Z_e) \right)^{-0.5} \quad \text{Coulomb}$$

logarithm,  $p, \text{amm}$  – pressure in gas.

Expressions for  $\sigma_{SH}$ ,  $\varphi_{SH}$ ,  $\lambda_{SH}$  was obtained in assumption that  $\ln \Lambda \gg 1$ . If  $\Lambda \gg 1$  necessary corrections to these formulas. Such correction factors calculated on the basis of unified theory of Kihara and Aono, see the book [7] and can be approximated by the curves:

$$F_\sigma = 1 + 0.425/(\ln \Lambda - 1.5) \quad (11)$$

$$F_\varphi = 1 - 0.035/(\ln \Lambda - 2.37) \quad (12)$$

$$F_\lambda = 1 + 0.31/(\ln \Lambda - 1.5) \quad (13)$$

In the region of partial ionization significant electron-atom collision processes with a finite radius of interaction and, therefore, is not described by the equation of the Fokker-Planck equation. Therefore, in many practical cases to calculate the electronic transport coefficients of partially ionized gas used approximate formulas, called the rules of the mixture. The most accurate values for the electron transport coefficients give a mixture of rules proposed by Frost [7]. In these formulas the Lorentz

expressions for  $\sigma, \varphi, \lambda'$ , which have been modified in such a way that in the limit of a fully ionized gas, they move to the exact Spitzer-Herm expressions:

$$\sigma = \int_0^\infty \theta^{5/2} e^{-\theta} \left( \sum_n 2.61 \cdot 10^{-9} \frac{x_n T^{0.5} \theta^{1.5} Q_{en}(E) + 3.32}{x_l \sigma_{SH}} \right)^{-1} d\theta \quad (14)$$

$$\varphi = \int_0^\infty \theta^{5/2} (\theta - 2.5) e^{-\theta} \left( \sum_n 0.302 \cdot 10^{-5} \frac{x_n T^{0.5} \theta^{1.5} Q_{en}(E) + 3.32}{x_l \varphi_{SH}} \right)^{-1} d\theta \quad (15)$$

$$\lambda'_e = \int_0^\infty \theta^{5/2} (\theta - 2.5)^2 e^{-\theta} \left( \sum_n 0.35 \frac{x_n T^{-0.5} \theta^{1.5} Q_{en}(E) + 14.95}{x_l \lambda_{SH}} \right)^{-1} d\theta \quad (16)$$

$$\lambda_e = \lambda'_e - \frac{T \varphi^2}{\sigma} \quad (17)$$

Collision cross sections of charged particles with each other were considered in a number of papers, in particular in [8] to describe the interaction between charged particles was used by the screened Coulomb potential. Calculations performed in the framework of classical mechanics, showed that, in general, cross-sections for the attractive potential of the cross sections for different repulsive potential. Based on the tables in [8], the values  $Q^{(l,s)}$  can be represented as:

$$Q^{(l,s)} = 2.8 \cdot 10^{10} \left( Z_{e,i} Z_{e,j} / T \right)^2 A^{(l,s)} \quad (18)$$

$$T^* = Z_e \Lambda / \left( 3 Z_{e,i} Z_{e,j} \right), \quad x = \lg T$$

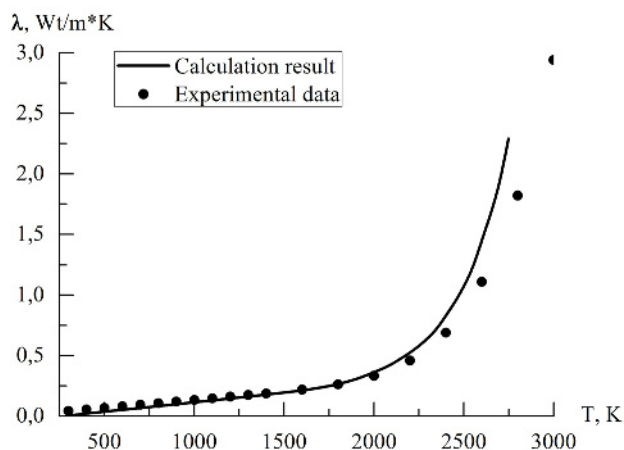
$$A^{(1,1)}(x) = \begin{cases} 1.15x - 0.12 + 0.57 \exp(-x) & \text{attraction} \\ 1.15x - 0.12 + 0.37 \exp(-0.25x) & \text{repulsion} \end{cases}$$

$$A^{(2,2)}(x) = \begin{cases} 1.15x + 0.12 + 0.33 \exp(-x) & \text{attraction} \\ 1.15x + 0.12 + 0.21 \exp(-0.25x) & \text{repulsion} \end{cases}$$

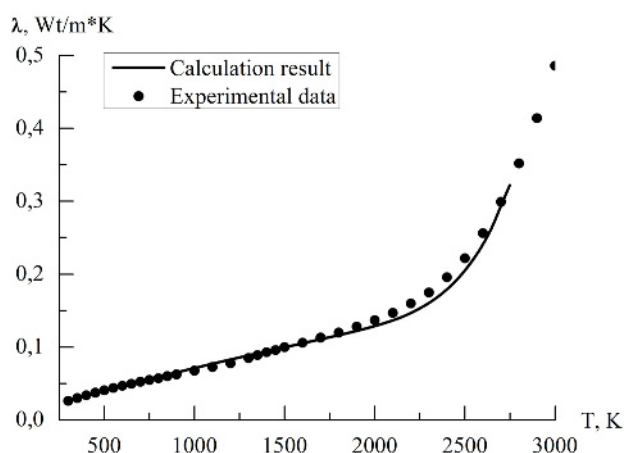
$$B^*(x) = \begin{cases} 1 + 0.467/(x + 1.44) & \text{attraction} \\ 1 + 0.51/(x + 1.2) & \text{repulsion} \end{cases}$$

### 3 Results

Figure 1 and figure 2 show the data for the water vapor and air. In these graphs, one can observe the typical increase in conductivity due to chemical reactions, in particular the direct decomposition of water molecules and the subsequent dissociation of oxygen and hydrogen. It should be noted good agreement of the experimental data with the calculated results. In addition to data on air and water vapor, we have a comparison results for nitrogen and carbon dioxide.

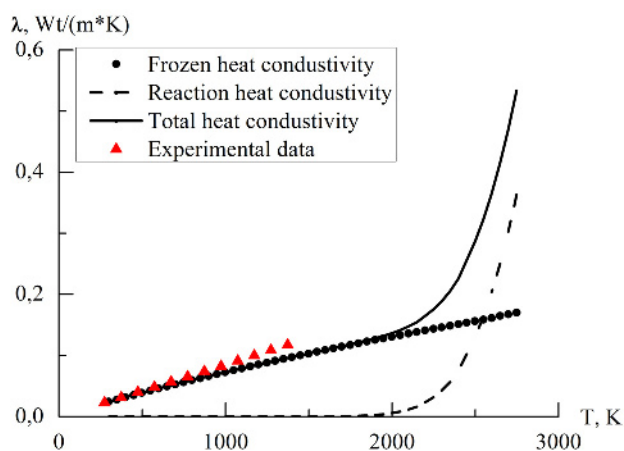


**Fig. 1.** Comparison of calculation result for water steam with experimental data



**Fig. 2.** Comparison of calculation result for air with experimental data

Figure 3 shows the results of the calculation of thermal conductivity for coal TROK I of coal basin Kuzneckiy. We also show the reaction heat conductivity and frozen heat conductivity to demonstrate the possible contribution of the part due to chemical reactions.



**Fig. 3.** Different contributions in heat conductivity and their comparison with experimental data

## 4 Conclusions

This paper describes the methodology and algorithm to calculate the composition and thermophysical properties of complex gas systems. We take into account when calculating the existence of chemical reactions in gaseous system and its possible ionization.

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