Calculation of portable properties of some real gas mixtures at high temperatures

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Abstract. A method for calculating the power parameters of a potential of the Lennard-Jones type for a number of individual gases, which can be products released during the ignition and combustion of a gas-vapor discharge with a liquid electrode, is presented. The information obtained makes it possible to calculate the viscosity and diffusion coefficients of individual gases and gas mixtures, which will make it possible to solve a range of problems when modeling processes in the processing technology of various materials (substances) by vapor-gas discharge plasma with a liquid electrode.

1. Introduction
Mathematical modeling of processes combining elements of various types of effects on a substance (for example, electrical, plasma, chemical, electrochemical, plasma electrolytic, etc.) is associated with solving systems of equations in which it is necessary to use various simplifications. Introduction to the consideration of arbitrary functions often gives research a descriptive character, and the calculated expressions are reduced to empirical formulas [1]. Using empirical and semi-empirical equations, which contain constants depending on the characteristics of the technology (interelectrode distance, electrolyte composition, gas composition in which the discharge is on, portable gas characteristics, and many others), allows to obtain qualitative and comparative estimates, which gives an advantage in the speed of development models of an engineering experiment [2-5].

2. The relevance of research
Physico-chemical, chemical-technological processes are stochastic processes, since the change in the input and output data of experiments occurs randomly. The description of the processes is hindered by the laws of their course, the interaction and mutual influence of their parameters, and the lack of an unambiguous correspondence between output and input quantities. With a successful selection of constants depending on the experimental conditions, a satisfactory agreement between the calculated and experimental characteristics is possible. This direction involves the collection and processing of data on the technological parameters of the processing of substances.

3. Research Methods
In this paper, we propose a method that involves combining the effect on the workpiece of an electric discharge and electrochemical processes [1-6]. In Figure 1 shows the configuration of technological elements in the process of processing a substance (liquid or solid): 1. Electrochemical cell; 2. Electrolyte (liquid electrode); 3. Solid state metal electrode; 4. The metal plate.
The complexity of the phenomena occurring in the interelectrode gap in the pre-breakdown mode and during the breakdown is significant complicates the possibilities of mathematical modeling. These phenomena are the release of gaseous hydrogen or oxygen on the metal electrode with the formation of a gas and liquid layer, heat generation, transition of the gas-liquid state to the vapor-gas state, ionization, excitation of atoms and molecules from the vapor-gas phase.
Figure 1. Configuration of technological elements.

At the same time, when developing modern technologies for obtaining new materials, the paramount problem is to combine knowledge about a large number of processes and their mutual influences [3]. The process studied in the work is characterized by the effect on the result of uncontrolled input variables. This leads to a random change in the final result.

The calculation of the transport coefficients of gas mixtures was carried out on the basis of the Lennard-Jones model potential (8-6) in the framework of the classical kinetic theory of gases. The Lennard-Jones potential is used in modern research, for example, in [7]. In accordance with the kinetic theory, transport coefficients are expressed in terms of binary collision integrals (-integrals).

A potential of the Lennard-Jones type (8-6) is a central potential. Its dependence on the intermolecular distance $r$ is determined by the formula:

$$\phi(r) = \frac{256}{27} \varepsilon \left( \frac{\sigma}{r} \right)^8 - \left( \frac{\sigma}{r} \right)^{12},$$

where $\varepsilon$, $\sigma$ are the parameters of the potential (power parameters).

To calculate the reduced binary collision integrals, the numerical methods described in [8] were used. Then, to obtain the values of the parameters $\sigma$ and $\varepsilon/k$, where $k$ is the Boltzmann constant, the least squares method (LSM) was used [9]. In accordance with the least squares method, the required parameter values should minimize the sum of type:

$$\sum \left[ \omega^{(1,1)} + \omega^{(2,2)} - \sigma^2 \left( \Omega^{(1,1)} + \Omega^{(2,2)} \right) \right]^2,$$

where $\omega^{(1,1)}$ and $\omega^{(2,2)}$ are calculated from experiments on the scattering of a molecular beam [10–11], but $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are the reduced binary collision integrals calculated using potential (1); summation was carried out in the temperature range $20000$-$50000$ K. The value of the parameter $\varepsilon/k$, which determines the lowest value of the potential, was taken from the reference book [12]. It is determined from experimental data at low temperatures (up to $10000$ K) for the Lennard–Jones potential (12–6). From a number of experimental studies it follows that this value changes slightly with a change in potential. For example, in the case of the Buckingham potential for a gas molecules $\text{H}_2$, $\varepsilon/k = 37.3$, for a gas $\text{N}_2$, $\varepsilon/k = 101.2$, for CO $\varepsilon/k = 119.1$ [11].

4. Results

The value $\sigma$ was calculated using LSM. The obtained values of the power parameters for some real gases are presented in Table 1.

The values given in Table 1 were used to calculate the self-diffusion coefficients and viscosities of the individual gases listed in Table 1, as well as to calculate the diffusion and viscosity of their binary gas mixtures in the third order of decomposition in the Sonin polynomials of the Chapman–Enskog method [13].

The results of calculating the diffusion coefficient of the binary gas mixture $\text{N}_2$–$\text{O}_2$ are shown in Figure 2. Here, the number 1 denotes a curve calculated on the basis of potential (1) with the values of $\sigma$ and $\varepsilon/k$ taken from Table 1.
Table 1. Values of power parameters.

| Substance | $\sigma$, Å | $\varepsilon / k$, K |
|-----------|-------------|-----------------|
| H$_2$     | 2.786       | 34              |
| O         | 2.695       | 117             |
| N$_2$     | 3.586       | 96              |
| O$_2$     | 3.619       | 117             |
| NO        | 3.324       | 124             |
| CO        | 3.435       | 101             |

Figure 2 is a curve calculated in accordance with high-temperature data on the force parameters $\sigma$ and $\varepsilon / k$ of the Lennard-Jones potential with indices $n = 12$, $m = 6$, taken from the reference book [12]. Number 3 - data obtained from experiments on the scattering of a molecular beam. Number 4 is a curve, calculated using potential (1) for the values of the parameters $\sigma$ and $\varepsilon / k$, obtained by minimizing the sum (2) without fixing the value of the parameter $\varepsilon / k$. Number 5 – data, calculated using the Lennard – Jones potential with indices $n = 12$, $m = 6$ and force parameters [12], obtained from experimental data at low temperatures (up to 1000$^\circ$K).

Figure 2. Results of calculating the diffusion coefficient of a binary gas mixture N$_2$-O$_2$.

5. The discussion of the results
The impact on the processed substance of the indicated type of electric discharge is due to a combination of physicochemical processes occurring in the volume of the electrolyte and in the interelectrode gap. The development of technological processes using a gas-vapor discharge is associated with the need to understand these phenomena and the need for numerical simulation of physicochemical reactions in plasma electro-thermal installations with liquid electrodes. In particular, the problem arises of obtaining information on the interaction potential of gas particles at high temperatures, which allows one to evaluate the portable properties of gas mixtures. In this case, one has to deal with the selection and adaptation of numerical methods for calculating kinetic coefficients using the intermolecular interaction potential.
6. Findings
The results obtained for the power parameters of the potential of the Lennard-Jones type of a number of individual gases make it possible to calculate the transport coefficients of gas mixtures used in modeling processes in the processing technology of various materials (substances) by a vapor-gas discharge plasma with a liquid electrode.

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