

Methodology for Determining Parameters of Ozone-Safe Fire Extinguishing Substances

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Abstract. In this work, the objects of research are individual chemical substances and multicomponent mixtures (gaseous and liquid) used in extinguishing fires.

The design of automatic gas fire extinguishing installations is associated with the solution of many scientific and technical issues and is based on the calculation and forecasting of such important data as the thermophysical properties of individual substances and mixtures consisting of them. Phase equilibria parameters data are of particular interest. Also, such data are necessary for scientific and practical research in the creation of the latest, more progressive fire extinguishing agents. It is often difficult or simply impossible to obtain experimentally thermophysical characteristics and parameters of phase equilibria for a wide range of states. Moreover, experimental information is expensive and time-consuming.

The work is dedicated to the development of theoretical methods for determining the parameters of phase equilibria of both individual chemicals used to extinguish fires and multicomponent fire-extinguishing mixtures. The use of the proposed techniques makes it possible to obtain numerical values of the required characteristics of fire extinguishing agents by calculation with the required accuracy using a minimum of initial data.

The method of mathematical modeling makes it possible to obtain a mathematical model of phase equilibria based on thermodynamic perturbation theory in order to determine the basic functions of the state in the absence of empirical parameters.

The proposed method for calculating the parameters of phase diagrams for multi component fire-extinguishing mixtures was used to determine the thermodynamic parameters of the ozone-safe fire-extinguishing composition

Introduction

Over the past decades, the ozone layer above the Earth's surface has changed significantly, which indicates the danger that threatens the life of future generations. According to the World Health Organization, 92% of the world's population lives in places where air quality levels exceed recommended limits [1, 2]. The presence of harmful and dangerous gases, as well as suspended particles and aerosols in the atmosphere, poses a serious threat to biological diversity and human health. Constant increase in their concentration leads to a decrease in the level of environmental safety [3, 4]. A state of health and life expectancy of the population depends on the level of environmental safety in general and the quality of atmospheric air in particular [5, 6]. Thus, the Vienna Convention [7] for the Protection of the Ozone Layer (1985) and the Montreal Protocol [8] on Substances that Deplete the Ozone Layer (1987), as well as the amendments to the Montreal Protocol adopted in London, Copenhagen, Beijing and Montreal, that globally, emissions of some ozone-depleting substances can significantly deplete or otherwise alter the ozone layer, with potentially adverse effects on human health and the environment; and as well as detrimental effects on the climate [9, 10]. Large-scale fires cause acid precipitation and subsequent pollution of aquifers [11, 12]. The consequences of fires increasingly often force one to consider the improvement of fire-fighting technologies [13, 14].

In this regard, it is urgent to find ways to solve the problem of preserving, and, if possible, restoring, the vital ozone layer. The authors [15] present the results of determination of conditions for the production of modified pyrotechnic compositions that allow initiating atmospheric precipitation, neutralizing their acidity and scavenging toxic substances from the atmosphere. In particular, one of the proposed methods for solving this problem is to replace ozone-depleting fire-extinguishing substances (114B2, 13B1 and compositions of the "3.5" type) with ozone-safe ones, which are used in the production of new and modernization of existing automatic fire extinguishing installations at critical facilities. For example, it is proposed to use the following extinguishing agents and their mixtures: carbon dioxide; nitrogen; argon; helium, mixtures of inert gases; (compositions such as "Argonite" (IG-550, [50% N₂ + 50% Ar]); "Inergen" (IG-541, [52% N₂ + 40% Ar + 8% CO₂]). The authors [16] analyze the ecological properties of fire extinguishing substances used in fire extinguishing of classes A and B. Gel-forming systems containing inorganic substances as components for extinguishing fires of petroleum products are proposed.

For such replacement of ozone-hazardous freons with ozone-safe fire extinguishing agents, various changes and improvements in the design of already existing fire extinguishing systems will be required.

An important stage in the design of automatic gas fire extinguishing installations is the calculation of the geometry, volumes, hydrodynamic characteristics, structural strength of working cavities, communications, valves, spraying devices and other elements of fire extinguishing installations [17]. For the effective performance of such calculations, information on the thermophysical properties is necessary, especially on the density of working fluids, gases, or two-phase multicomponent mixtures.

Carrying out scientifically and practically important research in the creation of the latest fire extinguishing compositions can be based on predicting the necessary characteristics of fire extinguishing compositions obtained by calculation. In this work, the problem of calculating the density of fire-extinguishing compositions is solved and a comparison of the calculation results and experimental data given in the literature is carried out.

The main aspects of the methodology described in articles [18, 19] make it possible to determine the thermodynamic properties of one-component substances and mixtures consisting of these substances for a range of temperatures and pressures that are technically important. The densities for gaseous, liquid and vapor-liquid equilibrium states are determined using a unified technique. This technique is based on an original statistical-mechanical scheme – a modified thermodynamic perturbation theory.

Modeling (lattice gas model, dilatation, intermolecular interaction)

This work outlines the foundations for the formation of a mathematical model that describes the vapor-liquid equilibrium in multicomponent mixtures, which are fire extinguishing compositions used in fire extinguishing systems (argonite, inergen), as well as new fire extinguishing compositions being developed. The mixtures are considered as a set of particles of various sizes interacting with each other.

The determination of the quantities included in the mathematical model and the modeling of phase equilibria in fire extinguishing compositions (at a given temperature, pressure and composition) is based on the calculation of the thermodynamic potential – the Helmholtz free energy.

Two-parameter potentials are usually used to describe intermolecular interactions. In this work, we use fairly simple and realistic Lennard-Jones potential

$$u_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} [(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6], \quad (1)$$

where $\sigma_{\alpha\beta}$, $\varepsilon_{\alpha\beta}$ are the parameters of the interaction potential of dissimilar molecules α and β in the mixture.

One of the most effective methods in solving statistical-mechanical problems is the method of thermodynamic perturbation theory. This method presents the characteristics of the systems under study in the form of series in terms of parameters characterizing the differences between the real potential $u_{\alpha\beta}(r)$ and the potential $u_{\alpha\beta}^{(0)}(r)$ of the zero-order system.

In this work a modified scheme of the perturbation theory is used, and the hard-sphere model is taken as the zero-order approximation [18].

The specific (per particle) free energy of the n -component mixture in the second order of the modified perturbation theory scheme has the following form

$$\beta f_m = \beta f_m^{(0)} + \sum_{\alpha,\beta=1}^n x_\alpha x_\beta (\rho_{\alpha\beta}^* I_{\alpha\beta}^{(1)} / T_{\alpha\beta}^* + \rho_{\alpha\beta}^* I_{\alpha\beta}^{(2)} / T_{\alpha\beta}^{*2}), \quad (2)$$

where $\beta = 1/(kT)$; $f_m^{(0)}$ – free energy of the n -component mixture of the hard-spheres; $T_{\alpha\beta}^* = kT/\varepsilon_{\alpha\beta}$; $\rho_{\alpha\beta}^* = \rho\sigma_{\alpha\beta}^3$; ρ is the density of the number of particles in the mixture; x_α, x_β – concentrations (mole fractions) of components α and β ; $I_{\alpha\beta}^{(1)}, I_{\alpha\beta}^{(2)}$ – group integrals of the first and second orders of the modified perturbation theory scheme [7] for mixtures.

For pair potentials, depending on the parameters $\varepsilon_{\alpha\beta}, \sigma_{\alpha\beta}$ of interparticle interaction for pure components and dissimilar interactions ($\alpha \neq \beta$), there are combination rules (1) connecting them to each other.

$$\begin{cases} \varepsilon_{\alpha\beta} = \zeta_{\alpha\beta} \sqrt{\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta}}; \\ \sigma_{\alpha\beta} = 0,5(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}), \end{cases} \quad (3)$$

where $\zeta_{\alpha\beta}$ are energy parameters describing deviations from the well-known Bertello's rule ($\zeta_{\alpha\beta} = 1$) and are determined using experimental data.

There are mixtures where the components are some substances with no experimental information as for their binary combination properties. Such mixtures are out of the description. Thus, it significantly narrows the class of mixtures under study.

In the combination rule for the energy parameters (3), for the first time, two alternative forms of the analytical expression for the coefficient $\zeta_{\alpha\beta}$, including the ionization (I) and molecular polarizability (α) potentials, were obtained theoretically.

Below are the expressions for $\zeta_{\alpha\beta}$:

$$\zeta'_{\alpha\beta} = (\delta_{\alpha\beta}^+ / 2)^{-6} 2 \sqrt{\omega_\alpha \omega_\beta} / (\omega_\alpha + \omega_\beta), \quad (4)$$

where $\omega_\beta = \varepsilon_{\beta\beta} \sigma_{\beta\beta}^6 / \alpha_\beta^2$,

and $\delta_{\alpha\beta}^+ = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta}) / \sqrt{\sigma_{\alpha\alpha} \sigma_{\beta\beta}}$

$$\zeta'_{\alpha\beta} = (\delta_{\alpha\beta}^+ / 2)^{-6} 2 \sqrt{I_\alpha I_\beta} / (I_\alpha + I_\beta). \quad (5)$$

Calculation of the parameters $\zeta_{\alpha\beta}$ according to expressions (4) and (5) gives almost the same values. Possible insignificant discrepancies between them can be explained by inaccuracies in the experimental determination of the parameters I, α of the components [20, 21].

The values of these parameters determine the degree of imperfection of real mixtures. For a mixture of argon and nitrogen, the calculated value is $\zeta(\text{Ar}, \text{N}_2) = 0,989$.

When studying an equilibrium process in a mixture, the main issue is to determine the phase state of the mixture: liquid, gas, or a two-phase vapor-liquid system.

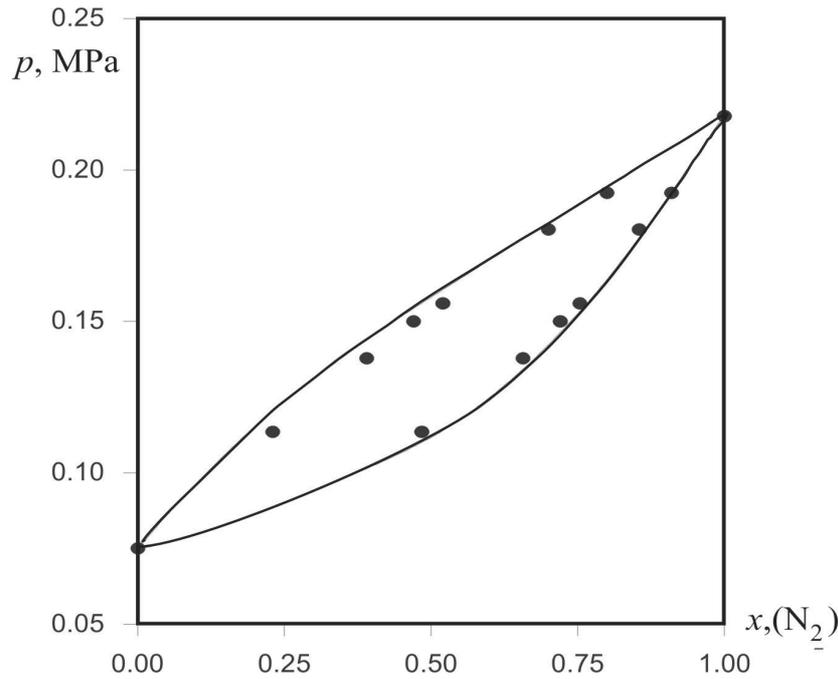


Fig. 1. Diagram of liquid – vapor phase equilibrium of a nitrogen – argon mixture ("Argonite") at a temperature of $T = 84.5$ K; • – experiment [7]

The graph shows that the mixture is in a homogeneous gaseous state at a temperature $T = 84.5$ K and a pressure $P < 0.07498$ MPa, and at a pressure $P > 0.2178$ MPa – in a homogeneous liquid state. Comparison of the calculated values of the compositions of the liquid and vapor phases with the experimental data available in the literature [22] makes it possible to estimate the errors in describing the compositions of the L - and V -phases of about 4–5 mol. %.

The results of calculating the densities for the above-mentioned fire-extinguishing compositions, obtained using the developed technique, and the experimental data from [20] are given in table. 1. The density values were determined at a pressure of 0.1013 MPa and a temperature of 293 K.

Table 1. Comparison of experimental [23] and calculated values of the density of gaseous fire-extinguishing compositions

| Fireextinguishing compositions | Density (kg/m^3) | |
|--------------------------------|-----------------------------|-----------------|
| | Calculation | Experiment [23] |
| CO ₂ | 1,8032 | 1,84 |
| N ₂ | 1,1477 | 1,17 |
| Ar | 1,662 | 1,6371 |
| "Argonite" IG-550 | 1,3950 | 1,41 |
| "Inergen" IG-541 | 1,3984 | 1,42 |

Table 2, 3 compares the values of Ar and CO₂ densities available in the literature [24] and calculated by the method [18, 19] at different values of temperatures and pressures.

Table 2. Comparison of experimental [9] and calculated values of the density of Ar, (kg/m^3)

| T , [K] | P , [MPa] | 0,1 | 0,2 | 0,4 | 0,6 | 0,8 | 1,0 |
|-----------|-------------|--------|-------|-------|--------|--------|--------|
| 250 | Experiment | 1,924 | 3,854 | 7,728 | 11,623 | 15,538 | 19,473 |
| | Calculation | 1,918 | 3,829 | 7,629 | 11,402 | 15,143 | 18,858 |
| 300 | Experiment | 1,602 | 3,207 | 6,423 | 9,643 | 12,873 | 16,11 |
| | Calculation | 1,599 | 3,193 | 6,366 | 9,518 | 12,651 | 15,765 |
| 350 | Experiment | 1,373 | 2,746 | 5,495 | 8,251 | 11,001 | 13,757 |
| | Calculation | 1,371 | 2,738 | 5,461 | 8,17 | 10,863 | 13,54 |
| 400 | Experiment | 1,201 | 2,402 | 4,805 | 7,209 | 9,606 | 12,014 |
| | Calculation | 1,1997 | 2,397 | 4,782 | 7,156 | 9,518 | 11,87 |

Table 3. Comparison of experimental [24] and calculated values of the density of, CO₂, (kg/m³)

| <i>T</i> , [K] | <i>P</i> , [MPa] | 0,1 | 0,2 | 0,4 | 0,6 | 0,8 | 1,0 |
|----------------|------------------|-------|-------|-------|--------|--------|--------|
| 250 | Experiment | 1,9 | 3,828 | 7,75 | 11,78 | 15,94 | 20,19 |
| | Calculation | 1,887 | 3,766 | 7,503 | 11,21 | 14,89 | 18,337 |
| 300 | Experiment | 1,77 | 3,564 | 7,199 | 10,91 | 14,7 | 18,58 |
| | Calculation | 1,76 | 3,516 | 7,006 | 10,471 | 13,911 | 17,325 |
| 350 | Experiment | 1,66 | 3,334 | 6,72 | 10,16 | 13,67 | 17,2 |
| | Calculation | 1,65 | 3,297 | 6,572 | 9,824 | 13,054 | 16,26 |
| 400 | Experiment | 1,516 | 3,04 | 6,119 | 9,23 | 12,39 | 15,58 |
| | Calculation | 1,51 | 3,015 | 6,012 | 8,99 | 11,95 | 14,89 |
| 400 | Experiment | 1,323 | 2,65 | 5,33 | 8,026 | 10,74 | 13,48 |
| | Calculation | 1,32 | 2,639 | 5,265 | 7,875 | 10,472 | 13,5 |
| 400 | Experiment | 1,059 | 2,12 | 4,246 | 6,377 | 8,518 | 10,662 |
| | Calculation | 1,057 | 2,113 | 4,216 | 6,311 | 8,396 | 10,47 |

The main quantity for technical calculations in the design of automatic gas fire extinguishing installations is the mass (and, accordingly, the density) of the gas extinguishing agent, which is necessary to extinguish a fire. Let us consider the methodology given in [23] for calculating the parameters of automatic gas fire extinguishing installations. The density of the extinguishing agent is calculated using the formula, which is based on the vapor density of the extinguishing compositions at a temperature of 293 K and atmospheric pressure of 0.1013 MPa. Further, the resulting value is refined using correction factors that take into account the specified temperature and the height of the object relative to sea level. This technique allows you to obtain the required characteristics without using various correction factors.

Conclusions

Good agreement between the results obtained by the method proposed in [18, 19] and the experimental data [23, 24] of the density values of fire extinguishing compositions indicates the reliability of the results obtained and the sufficient adequacy of the mathematical model of vapor-liquid equilibria. This makes it possible to calculate phase diagrams for fire extinguishing compositions of complex fractional compositions (such as "Argonit", "Inergen"). It also becomes available to predict the behavior of developed new modern fire-extinguishing compositions in wide ranges of temperatures and pressures.

The developed mathematical model of phase equilibria ensures its applicability for a wide range of fire extinguishing compositions of complex fractional compositions in any practically significant ranges of states.

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