Low-parametric equation for calculating the viscosity coefficient of sulfur hexafluoride

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Abstract. A low-parametric equation for calculating the SF₆ viscosity coefficient in liquid, gaseous, and fluid states was derived using previously obtained unambiguous dependence of the “excess” viscosity of liquids and dense gases on the density of internal energy. The equation describes the viscosity of sulfur hexafluoride at the temperatures from 230 K to 650 K and pressures of up to 50 MPa in the limits of experimental error.

1. Introduction
Information about the thermophysical properties of SF₆ in different areas of state is important for many technological processes because due to high heat capacity, low thermal conductivity and low viscosity, SF₆ is used as a refrigerant; due to high breakdown voltage, it is used as a dielectric gas, as well as a working fluid in gas chemical lasers, processes of isotope separation, etc.

Viscosity is one of the most important physical-chemical and technical characteristics of a substance in the liquid and gaseous states and one of the most hard-to-achieve parameters for a precise experiment, especially in the ranges of low and high temperatures and pressures. However, there are no theoretically grounded, fundamental-derived simple equations for calculating and describing the experimental data and extrapolating to a little-studied and hard-to-reach measurement area, except for the molecular theory of viscosity of dilute and medium-density gases.

Now, the empirical dependences of viscosity as a function of temperature and density are widely used to describe experimental data on viscosity in a fairly wide range of state parameters. Various versions of equations for calculation of viscosity allow the description of experimental data in a wide range of state parameters. However, they contain a large number of coefficients, which increases significantly when trying to describe the viscosity of gas and liquid simultaneously.

The authors of [1] proposed a correlation for the viscosity of sulfur hexafluoride, based on the generalized approach of the friction theory. This model has five parameters for correlation of rarefied gas and 21 parameters for the excess viscosity. In addition, SF₆ viscosity was also considered in [2] using the Enskog-2σ model (based on the kinetic theory). The analysis is limited only to the supercritical region. The Enskog-2σ model reproduces the viscosity of SF₆ with a maximum deviation of 2.4%.

Application of three physical models for representing the dynamic viscosity of sulfur hexafluoride in a very wide range of thermodynamic conditions (from 225.18 to 473.15 K and from 0.0264 to 51.21 MPa) is also described in detail in [3]. These approaches are a free-volume viscosity model [4], thermodynamic scaling model [5], and corresponding correlation based on the Lennard-Jones fluid representation (LJ) [6]. It is important to emphasize that these three models use some adjustable
parameters (only one for the LJ model, three for the free-volume viscosity model and six for the thermodynamic scaling model), which makes them semi-empirical. The absolute mean deviation is 3.8% for the Lennard-Jones model (one parameter), 1.7% for the free-volume model (three parameters) and 1.5% for the thermodynamic scaling model (six parameters). Nevertheless, it can be considered that the characteristics of the free-volume model and thermodynamic scaling model are satisfactory in comparison with those based on the reference model of the friction theory. In addition, these two approaches, and in particular the free-volume model, can be probably extrapolated beyond the adjustment range.

2. Equations for calculating viscosity in a wide range of parameters

It was found out in [7] that excess viscosity $\Delta \eta$ in a wide range of state parameters is a single-valued function of internal energy density, and it is described by equation

$$\Delta \eta = A x \exp \left( \alpha \frac{x_0}{(x_0 - x)} \right)$$

(1)

Excess viscosity, where the “field” momentum transfer mechanism prevails, is determined as the difference between the viscosity of a substance in a given state and viscosity of hard sphere system by Enskog formula

$$\Delta \eta = \eta(T, P) - \eta_m,$$  \hspace{1cm} (2)

here $P$, $V$ and $T$ are pressure, specific volume and temperature of the system; $\eta(T, P)$ is viscosity of the system in a given state, $\mu$Pa s; $\eta_m(T, \rho) = \eta_0(T) \Psi(\beta \rho)$ is viscosity of the hard sphere system, according to Enskog; $\eta_0(T)$ is viscosity of dilute-gas, $\mu$Pa s;

$$\Psi(y) = \frac{1}{g} (1 + 0.8y + 0.761y^2 + 0.1103y^3 + 0.0386y^4 + 0.0127y^5),$$

(3)

$$g = 1 + 0.625y + 0.287y^2 + 0.1103y^3 + 0.0386y^4 + 0.0127y^5,$$

where $y = \beta \rho, \rho = 1/V$ is the substance density; $x = \Delta U/V$ is density of interaction energy; $\Delta U = U_{ig}(T) - U(P, T)$ is interaction energy; $U_{ig}(T)$ is internal energy of ideal gas; $U(P, T)$ is internal energy of system in a given state; $x_0 = \frac{H_0^0}{V_0}$, $V_0 = \lim_{T \to 0, P \to 0} (T(V(T, P)))$ is hypothetical volume supercooled to absolute zero of liquid, $H_0^0 = U_{ig}(0) - U(0, 0)$ is evaporation enthalpy at absolute zero temperature and zero pressure; and $A$, $\alpha$, $b$ are individual adjustable constants of a substance.

According to equation (1), excess viscosity $\Delta \eta$ is univocal density of interaction energy $x = \Delta U/V$ (figure 1).

The description of experimental data, close to optimal, is achieved at $b = V_0$. The values of $V_0$ and $H_0^0$ are usually given in the tables of thermodynamic properties of substances. In this case, the equations for viscosity (1) and (2) contain only two empirical constants $A$ and $\alpha$ as well as the well-known Arrhenius equation. In the case when there are no data on $V_0$ and $H_0^0$, the number of empirical coefficients in equations (1) and (2), which must be found from the data on viscosity, increases to four: $A$, $\alpha$, $V_0$ and $x_0$.

The previous detailed analysis of experimental and tabular data on the viscosity of argon and xenon [12] made it possible to determine that the largest systematic deviations of calculated viscosity values from the original tabular data are in the transition region from the rarefied to mildly dense gas.
In this regard, the equation for viscosity calculation in the transition region was supplemented by some crossover function, which should provide a transition from one (collision) mechanism of momentum transfer in a shear flow to another (field). Thus, the equation for calculating the viscosity in a wide range of state parameters will be written as

\[ \eta(T,P) = \alpha x \exp \left[ \frac{\alpha x}{x_0 - x} \right] + B \left( \frac{T}{T_c} \right)^{1/2} \left( \frac{x}{x_0} \right)^{2} \exp \left( -\frac{\beta x}{x_0} \right) + \eta_m. \] (4)

The density and internal energy of sulfur hexafluoride, which are included in the equation for calculating the viscosity coefficient, were calculated using the single low-parametric equation of state developed by us to calculate the thermodynamic characteristics of substances. This equation contains 13 adjustable coefficients [13].

To calculate the coefficient of viscosity of a system of hard spheres according to Enskog \( \eta_{en} \), we used the equation for dilute gas viscosity \( \eta_0 \) [1]:

\[ \eta_0 = d_0 + d_1 T_1^{1/4} + d_2 T_1^{1/2} + d_3 T_1^{3/4} + d_4 T_1, \] (5)

Where \( T_1 = T/T_c \) is the reduced temperature, \( T_c \) - the critical temperature, the parameters \( (d_i) \) are given in the table 1.

3. Comparison of calculated values of viscosity with experimental and tabular data

To calculate the coefficients included in the equations on SF_6 viscosity, the data were used in the following range of parameters: temperatures of up to 650 K, pressures of up to 50 MPa, density from 0 to the density at a triple point. The averaged experimental data [8–11], [14-15] were used as the initial data for calculation of coefficients \( A, B, \alpha, \beta \). Coefficient \( V_0 \) was found by the Filippov-Timmermans rule \( V_0/V_C = Z_C \). The calculations used the values of \( H_0^0 \) given in [16]. The results of calculation of SF_6 viscosity are shown in Table 1 and in figures 2-3. Table 1 gives the physical parameters of SF_6 (parameters of characteristic points) and values of coefficients \( A, B, \alpha, \beta, H_0^0, V_0, x_0 \) and \( d_\eta \), required for calculating the viscosity by equations (1)–(5), and the ranges of description parameters.
Table 1. Physical parameters of sulfur hexafluoride; coefficients $A$, $\alpha$, $B$, $\beta$, $H_0$, and $V_0$, $d_i$ in equations (1), (4), and (5) for calculation of viscosity; ranges of description parameters: temperature $\Delta T$, pressure $\Delta P$.

| Parameters | Sulfur hexafluoride |
|------------|---------------------|
| $T_C$, K   | 318.709             |
| $P_C$, MPa | 3.755               |
| $\rho_C$, kg m$^{-3}$ | 742.255          |
| $T_R$, K   | 223.575             |
| $\rho_R$, kg m$^{-3}$ | 1845.16          |
| $A$, $10^{-12}$ s | 0.0458           |
| $\alpha$   | 2.615               |
| $B$        | 20.10               |
| $\beta$    | 10.66               |
| $x_0 = H_0^0/V_0$, MPa | 577.06       |
| $H_0^0$, J g$^{-1}$ | 216.0          |
| $b = V_0$, cm$^3$ g$^{-1}$ | 0.3743         |
| $\Delta T$, K | 223.575…650 |
| $\Delta P$, MPa | 0.1…50            |
| $d_0$, mPa s | 0.118561           |
| $d_1$      | $-0.378103$        |
| $d_2$      | 0.416428           |
| $d_3$      | $-0.165295$        |
| $d_4$      | 0.0245381          |

The values of viscosity coefficient calculated by formula (4) are presented in figure 2 as a function of temperature and pressure on the isobars in comparison with experimental data of [8–11], [14–15]. Deviation of SF$_6$ experimental data of [8–11], [14–15] from viscosities calculated by (4) are shown in figure 3.

Figure 2. Comparison of SF$_6$ viscosities on isobars (lines), calculated by formula (4) with experimental data of [8-9], [11], [15]. Deviation of SF$_6$ experimental data of [8–11], [14–15] from viscosities calculated by (4) are shown in figure 3.

According to the analysis, the discrepancies between viscosity values calculated by (4) and taken from the tables (averaged experimental) of [8–11], [14–15] do not exceed 3-5%, which is not higher than the discrepancies between the experimental data on viscosity of other authors. As it can be seen from figure 3, a noticeable increase in the discrepancies between the viscosity values calculated by (4)
and taken from [8–11], [14–15] (up to 10%) occurs both in the region of critical temperatures and pressures, and at low temperatures (near the melting point of SF₆) and high pressures.

However, in this area the experimental and tabular data obtained by other authors also differ significantly. In addition, it should be taken into account that the error in calculating the viscosity coefficient, performed by equation (4), includes all the errors in calculation of equations and relations in (4). In particular, this error includes both the errors caused by the approximate character of a single equation of liquid and gas state, used for density and internal energy calculations, and the approximate character of equations (1), (2), (4).

![Figure 3. Deviation of experimental data on viscosity of [8–11], [14, 15] from the values calculated by formula (4) for full pressure range.](image)

### Conclusion

A low-parametric single equation has been obtained for calculating the viscosity coefficient of SF₆ in liquid and gaseous states; this equation describes the viscosity of sulfur hexafluoride in the temperature range of up to 650 K and pressures of up to 50 MPa. This equation contains four individual empirical coefficients that must be found from experimental or tabular data on viscosity. It is shown that the values of viscosity calculated by equation (4) are consistent with experimental and tabular data within the experimental errors.

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