Determination of potential energy function and transport properties of sulphur hexafluoride

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The potential energy function of sulphur hexafluoride has been determined via the inversion of reduced viscosity collision integrals at zero pressure and fitted to obtain an analytical potential form. A comparison of the potential with the previously determined potential has been included. The interaction potential energy from the inversion procedure reproduces, within experimental error, viscosity, self-diffusion coefficient, thermal conductivity and isotopic thermal diffusion factor of sulphur hexafluoride over a wide temperature range. These properties have also been fitted to very accurate equations.

The forces between molecules are of interest to scientists in a wide range of disciplines as these interactions control the progress of molecular collisions and determine the bulk properties of matter 1. Intermolecular pair potential can be obtained from both experimental observations and theoretical calculations. Two procedures have been used for extracting the intermolecular potential energy function from the experimental data, fitting and inversion methods. In fitting procedure, a model potential is adopted with a certain number of adjustable parameters which are varied until a good fit is obtained to a given set of experimental data. It is now accepted that this procedure usually yields little more than a crude estimate of the intermolecular potential energy function 1. The aim of an inversion method is to obtain the potential by considering the experimental data as a functional instead of fitting the data to a constrained potential form having a few parameters 1,2. Direct inversion techniques for the potential energy function, derived from gaseous transport coefficients, for example viscosity, have been developed that do not require any explicit assumption about the functional form of the potential 3-6. There is a close correspondence between a viscosity-temperature datum and a point on the intermolecular energy-separation curve 1. Previous studies have represented the interaction between two SF₆ molecules by a spherically symmetric part arising from the attractive dispersion forces in the short-range while the repulsive contribution has no physical form 7.

The temperature dependence of the zero-density viscosity coefficient is to be recommended for the generation of the intermolecular potential surface of sulphur hexafluoride 8. The primary goal of this work is to determine the SF₆ potential energy function by inversion of the reduced viscosity collision integrals at zero pressure and present the tables of necessary collision integrals at zero pressure which are needed to compute the transport coefficients of SF₆ at different temperatures for any pressure.

Tables with reliable thermophysical data of heavy globular gases such as CF₄, SiF₄, and SF₆ in a wide temperature range are requested in contemporary industry. They are used in different microelectronic and chemical technologies (chemical vapour deposition, thin-film epitaxy, etc). The experimental determination of the thermophysical properties of these toxic and aggressive gases is complicated and expensive, particularly, at high temperatures 9. The alternative is to calculate their thermophysical properties by means of reliable intermolecular interaction potentials. Thus, the second objective of the present work is to compute the transport properties of SF₆ at different temperatures and pressures using the resulting potential. We have computed the viscosity, thermal conductivity, isotopic thermal diffusion factor, and self-diffusion...
coefficients of SF6 at atmospheric pressure for different temperatures and compared to experiment. The viscosity of sulphur hexafluoride has been calculated at zero pressure. The viscosity of SF6 at two constant low densities as a function of temperature has been also computed and compared with experiment.

Theory

Transport properties

Molecular transport processes deal with the transfer or movement of a given property by molecular movement through a system which can be a fluid (gas or liquid) or a solid.

The transport properties of a dilute gas can be expressed in terms of a set of collision integrals $\Omega^{(l,s)}(T)$, characterized by the value of $l$ and $s$ over the intermolecular potential for each of the possible binary encounters in the system. For example, the viscosity and self-diffusion coefficient of a pure gas depend on the collision integrals $\Omega^{(2,2)}(T)$ and $\Omega^{(1,1)}(T)$, respectively.

\[
\eta = \frac{5}{16} \left( \frac{mkT}{\pi} \right)^{1/2} \frac{f_n}{\sigma^2 \Omega^{(2,2)}(T^*)} \quad \text{... (1)}
\]

\[
D = \frac{3}{16} \left( \frac{kT}{\pi m} \right)^{1/2} \frac{f_D}{n \sigma^2 \Omega^{(1,1)}(T^*)} \quad \text{... (2)}
\]

where $m$ is the mass of the molecule, $n$ number density, $k$ is Boltzmann constant, $f_n$ and $f_D$ represent the higher-order corrections to the first kinetic theory approximation of viscosity and diffusion coefficients, respectively, and $T^*$ is reduced temperature, namely $T^* = kT/e$ ($e$ is well depth of potential).

The parameters of $\Omega^{(4,10)}$ and $\Omega^{(2,2)*}$ are the reduced collision integrals which are defined in general as:

\[
\Omega^{(l,s)*}(T^*) = \frac{\Omega^{(l,s)}(T)}{\pi \sigma^2} \quad \text{... (3)}
\]

where $\pi \sigma^2$ is the collision integral for the rigid sphere of diameter $\sigma$, and $\Omega^{(l,s)}$ is the collision integral.

The collision integrals are determined by the dynamics of binary collisions between molecules and hence depend upon the intermolecular potential. All the information about the intermolecular potential from transport coefficients is therefore contained in the collision integrals.

The temperature-dependent collision integral $\Omega^{(2,2)}(T)$ is explicitly related to potential energy function, $V(r)$ through the classical mechanical expressions:

\[
\Omega^{(2,2)}(T) = \frac{1}{6(kT)^{1/2}} \int_0^{\infty} Q^{(2)}(E) e^{-E/T} E^3 dE \quad \text{... (4)}
\]

\[
Q^{(2)}(E) = 3\pi \int_0^{\infty} b(1 - \cos^2 \chi) db
\]

and

\[
\chi(b,E) = \pi - 2b \int_r^{\infty} \left( 1 - \frac{b^2}{r^2} - \frac{V(r)}{E} \right)^{-1/2} \frac{dr}{r^2}
\]

where $E$ is the relative kinetic energy of a pair of colliding molecules, $Q^{(2)}(E)$ is a transport cross section, $b$ is the impact parameter, $\chi$ is the scattering angle, and $r_0$ is the classical distance of closest approach in a collision.

The initial density correction to gaseous transport properties

The physical properties of moderately dense gases may be expanded in powers of the density, $\rho$ by the expressions of the form:

\[
X(P,T) = X_o(T) \left[ 1 + B_1(T) \rho + \ldots \right]
\]

\[
\eta = \eta_o (1 + B_{\eta}(T) \rho + \ldots)
\]

where $X_o(T)$ is the zero-density physical property. For example, the viscosity is expanded as:

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\]

where $B_{\eta}$ is second viscosity virial coefficient. The parameter $\eta_o$ represents the viscosity coefficient at zero pressure.

Najafi and co-workers have calculated the second viscosity virial coefficient of some gases based on the Rainwater-Friend theory using the most accurate potentials available for these gases. According to this correlation, the viscosity of moderate dense gas (up to 2 mol dm$^{-3}$) at specified temperature can be calculated via the equation:

\[
\eta = \eta_o (1 + N_\lambda \sigma^2 B_{\eta} \rho)
\]

where $N_\lambda$ is Avogadro’s number and $B_{\eta}$ is the reduced second viscosity virial coefficient. The
parameter, \( B_\eta^* \) is the universal function of \((T^*)^3\) in the form of a sixth order polynomial:

\[
B_\eta^* = \sum_{i=1}^{6} b_i (T^*)^i 
\]

where \( b_i \) is the coefficient of the universal correlation function. The values of \( b_i \) for the gases are given in ref. 11.

According to the theory of Rainwater-Friend\(^{12,13}\), the second transport virial coefficients, \( B_\mu \) (\( \mu \) can be viscosity \( \eta \), thermal conductivity, etc.), consists of three contributions:

\[
B_\mu = B_\mu^{(2)} + B_\mu^{(3)} + B_\mu^{(M-D)} 
\]

where \( B_\mu^{(2)} \) is the contribution of two free monomers, \( B_\mu^{(3)} \) represents the effect of three monomer contributions, and \( B_\mu^{(M-D)} \) is the contribution from monomer-dimer collisions.

The direct determination of intermolecular forces: Inversion method

The remarkable feature of the inversion procedure based on viscosity is that it identifies a point on the experimental \( \Omega^{(2,2)*} \) versus temperature curve with a single point on the \( V(r) \) function. There exists a number of mathematical approximations of the various integrals linking the collision integral at a particular temperature to the potential\(^{1}\).

It is customary to use the extended principles of corresponding states\(^{6,14-18}\) to obtain the experimental values of collision integrals. It has been proved that these principles are capable of correlating equilibrium and transport properties of the noble gases, some polyatomic gases, and multicomponent mixtures over a very wide temperature range with an accuracy comparable to the best measurements\(^{14-16}\).

In the inversion method based on transport property, it has been assumed that the influence of the initial density dependence of transport properties is small and negligible in comparison with the uncertainties associated with the experimental method\(^{17,18}\). The law of corresponding states\(^{14-16}\) is based on experimental values at relatively low densities (atmospheric pressure) since values at zero density are not accessible to direct measurements. In principle, such an assumption cannot be accepted because the initial density dependence must surely affect the low-density values.

The reduced viscosity collision integral at zero pressure, \( \Omega_0^{(2,2)*} \), can be obtained by inserting Eq. (1) into Eq. (8):

\[
\frac{1}{\Omega_0^{(2,2)*}} = \frac{1}{\Omega_0^{(2,2)*}}[1+N_s \sigma^3 B_\eta^* \rho] 
\]

where \( \Omega_0^{(2,2)*} \) is taken from corresponding states correlation\(^{14}\). The values of \( \Omega_0^{(2,2)*} \) can be used to determine the interaction potential by an inversion procedure as described before\(^{4,16,17,18}\).

**Results and Discussion**

The intermolecular potential energy function of SF\(_6\) has been calculated using the inversion of reduced viscosity collision integrals obtained at zero pressure and compared with Aziz's potential\(^7\) and presented in Fig. 1. As Fig. 1 shows, Aziz potential is evidently unrealistic since the repulsive contribution has no physical form. Hence, it can be claimed that our potential obtained using the inversion of reduced viscosity collision integrals at zero pressure is superior representation of SF\(_6\)-SF\(_6\) interaction potential than that provided by Aziz et al.\(^7\) We have also fitted our potential to get an analytical potential form:

\[
V'(x) = \begin{cases} 
A' + \alpha (1-\exp(-\beta x^2)) & x \leq 1 \\
-(\frac{a}{x^2} + \frac{b}{x^4} + \frac{c}{x^5} + \frac{d}{x^6}) & x \geq 1 
\end{cases} 
\]

where \( x = r/\sigma \), and \( V' = V/\epsilon \) that \( \sigma \) is where potential has zero value and \( \epsilon \) is the well depth of the potential. The value of parameters of the potential have been given in Table 1.

<table>
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<th>Table 1 — Parameters for SF(_6)-SF(_6) potential</th>
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<td>Parameter</td>
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Fig. 1 — Reduced pair potentials of SF<sub>6</sub> obtained by inversion of the reduced viscosity collision integrals at zero pressure (●) compared with Aziz potential (—).<br><br>Fig. 2 — Viscosity of SF<sub>6</sub> against temperature at atmospheric pressure for experimental values (●) and our calculated values (solid line).<br><br>Fig. 3 — Plot of the percent deviation %Dev = (\eta_{exp} - \eta_{calc}) \times 100 of the experimental viscosity values with our calculated values against temperature for SF<sub>6</sub> at constant density 7.25 × 10<sup>-5</sup> mol L<sup>-1</sup>.<br><br>Fig. 4 — Same as Fig. 3 at constant density 28.18 × 10<sup>3</sup> mol L<sup>-1</sup>.<br><br>Fig. 5 — Plot of the percent deviation %Dev = (\eta_{calc} - \eta_{exp}) \times 100 of the experimental thermal conductivity coefficients with our calculated values against temperature for SF<sub>6</sub> at atmospheric pressure.<br><br>Fig. 6 — Self-diffusion coefficients of SF<sub>6</sub> against temperature at atmospheric pressure for experimental values (●) and our calculated values (solid line).<br><br>Figure 2 shows the viscosity of SF<sub>6</sub> at atmospheric pressure at different temperatures. It is obvious that there exists a very good accordance between the experimental values and our calculated values in the temperature range from 273 K to 3273 K at atmospheric pressure. The curve follows Eq. (14):<br><br>\[
\eta(\mu \text{Pa s}) = -5.7756 + 0.611101 T^{0.62975}
\] ...(14)
Figures 3 and 4 show percent deviation of the experimental viscosity of SF$_6$ with our calculated values against temperature at constant density $7.25 \times 10^{-3}$ and $28.18 \times 10^{-3}$ mol L$^{-1}$, respectively.

The viscosity of SF$_6$ at zero pressure has been calculated from 20.77 to 6500 K and it obeys Eq. (15)

$$\eta_p(\mu \text{Pas}) = -3.03586 + 0.431252T^{0.667395}$$  \quad (15)"

Figure 5 shows percent deviation of the experimental thermal conductivity coefficients of SF$_6$ with our calculated values against temperature at atmospheric pressure. The experimental and our calculated values of thermal conductivity of SF$_6$ from 223 K to 850 K obey the equation:

$$\chi (\text{mW m}^{-1} \text{K}^{-1}) = -16.8612 + 0.691626T^{0.69826}$$  \quad (16)"
To examine the validity of the potential, we have calculated the different transport properties of \( \text{SF}_6 \) at zero pressure and compared with the experiment. The results of these calculations have justified that the iterative method works well. The results of these calculations and also our previous works on different compounds such as argon\(^{17} \), krypton\(^{17} \), xenon\(^{17} \), helium\(^{20} \), methane\(^{18} \) and carbon tetrafluoride\(^{6} \) justify the ability of inversion method to obtain the potential energy function of different compounds and calculate different transport properties of these compounds using the resulting potentials. For the first time, we have calculated the reduced collision integrals of \( \text{SF}_6 \) at zero pressure which are needed for calculation of the transport properties of this compound at any temperature and pressure.

**References**