

Thermophysical properties of CF₄/O₂ and SF₆/O₂ gas mixtures

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Abstract. Fitting formulae are presented for the calculation of the second interaction virial coefficients, mixture viscosities and binary diffusion coefficients for CF₄/O₂ and SF₆/O₂ gas mixtures in the temperature range between 200 K and 1000 K. The data recommended are obtained from the isotropic (n-6) Lennard-Jones intermolecular interaction potentials of the pure substances by using the Hohm-Zarkova-Damyanova mixing rules. In general, a good agreement is observed between our results and the experimental and theoretical data found in the literature.

1. Introduction

The determination of reliable thermophysical data for pure gasses and gas mixtures is an important but in many cases a cumbersome experimental and computational task. Such data related to the transport (viscosity, diffusion) and equilibrium (second virial coefficient) properties are needed in many practical applications. The fluorinated gases and gas mixtures, e.g. CF₄/O₂ and SF₆/O₂, are widely used for dry etching of silicon, some silicides, polymers etc. [1-3]. Also, there is evidence that the mixture SF₆/O₂ plays a significant role in studying the convective and diffusive intrapulmonary gas transport [4].

Despite the intensive use of the above mentioned mixtures in practical applications, there is still little knowledge about their thermophysical properties – second virial coefficients (interaction B_{12} and mixture B_{mix}), viscosities (interaction η_{12} and mixture η_{mix}), and diffusion coefficient D_{12} , especially in wide ranges of temperature and composition.

The published thermophysical data for both mixtures are very scarce and, in addition, they are given only in small temperature ranges. For example, we have found only three experimentally measured values for the interaction second virial coefficients, B_{12} , for both mixtures [5, 6] and the data are in the very narrow temperature range between 290 K and 320 K. There are no calculated values for B_{12} . Experimental data of the viscosity η_{mix} of both binary mixtures are measured with a high accuracy (uncertainty < 1%) only by Kestin et al. [7]. Using these measurements of the viscosity, the authors calculated the binary diffusion coefficients D_{12} for both mixtures. The uncertainty of their D_{12} values is

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about 2 %. Haghighi et al. [8, 9] published calculated η_{mix} and D_{12} values for equimolar CF_4/O_2 and SF_6/O_2 mixtures. They claim an uncertainty of their data of 1 % for viscosities and 5 % for diffusion coefficients. Experimental data for D_{12} are available only for the SF_6/O_2 mixture [10-12]. However, for both mixtures we have found calculated values of D_{12} [4, 7-10].

In this paper we show calculations of the thermophysical properties of CF_4/O_2 and SF_6/O_2 gas mixtures in the temperature range 200 -1000 K and present recommended fitting formulae for the calculation of the intermolecular potential parameters, and equilibrium and transport properties.

2. Theoretical background

The thermophysical properties of the gas mixtures depend on the intermolecular interaction potentials between the different kinds of mixture molecules. Each binary interaction between the molecules is described by our previously suggested [13] isotropic (n -6) Lennard-Jones temperature-dependent potential model (LJTDP), (1). In the case of pure gases, the indexes in (1) are the same, i.e. $1 = 2$.

$$U_{12}(R, T) = \frac{\varepsilon_{12}(T)}{n_{12} - 6} \left[6 \left(\frac{R_{m12}(T)}{R} \right)^{n_{12}} - n_{12} \left(\frac{R_{m12}(T)}{R} \right)^6 \right], \quad (1)$$

where: R_{m12} is the equilibrium distance, ε_{12} is the potential well depth and n_{12} is the repulsive parameter.

The intermolecular potential parameters for pure CF_4 and SF_6 were obtained earlier by Zarkova and Hohm [13], whereas those for O_2 were given by Damyanova *et al.* [14].

The temperature-dependent potential parameters for interactions between unlike molecules in the mixtures (R_{m12} and ε_{12}) are calculated by means of the mixing rule elaborated by Hohm-Zarkova-Damyanova (HZD) [15].

$$(R_{m12}(T))^{n_{12}-6} = \frac{\left\{ 0.5 \left[(\varepsilon_1(T))^\varphi (R_{m1}(T))^\psi + (\varepsilon_2(T))^\varphi (R_{m2}(T))^\psi \right] \right\}^{1/\varphi}}{(\varepsilon_1(T)\varepsilon_2(T))^{1/2} (R_{m1}(T)R_{m2}(T))^3}, \quad (2)$$

$$\varepsilon_{12}(T) = (\varepsilon_1(T)\varepsilon_2(T))^{1/2} \frac{(R_{m1}(T)R_{m2}(T))^3}{(R_{m12}(T))^6} \frac{2\alpha_1\alpha_2(C_6^{11}C_6^{22})^{1/2}}{C_6^{11}\alpha_2^2 + C_6^{22}\alpha_1^2}, \quad (3)$$

where $\varphi = \frac{1}{1+n_{12}}$ and $\psi = \frac{n_{12}}{1+n_{12}}$.

The repulsive parameter n_{12} is calculated as the arithmetic mean of the neat substances parameters.

Applying the mixing rule HZD for calculation of ε_{12} (eq.3), the dipole polarizability α and the dispersion-interaction energy constants C_6 of the pure substances have to be known.

All molecular parameters used for calculations in this work are given in table 1.

Table 1. Pure gas values for mass, dipole polarizabilities, dispersion-interaction energy constants and zero temperature potential parameters used in this work; k_B is the Boltzmann constant.

Substance	Molar mass/ (g/mol)	$(\varepsilon_{11}(0)/k_B)/$ K	$10^{10} R_{m11}(0)/$ m	n	$\alpha/$ a.u. ^a	$C_6/$ a.u. ^a
CF_4	88.005	328.40 [13]	4.329 [13]	52.71 [13]	19.10 [16]	254.0 [18]
SF_6	146.1	417.80 [13]	5.041 [13]	34.76 [13]	30.04 [16]	585.8 [19]
O_2	32.0	185.53 [14]	3.460 [14]	23.20 [14]	10.585 [16]	61.57 [17]

^a Conversion factors are for α : 1 a.u.=1.64878 $\cdot 10^{-41}$ C²m²J⁻¹ and C_6 : 1 a.u. = 9.57345 $\cdot 10^{-80}$ Jm⁶.

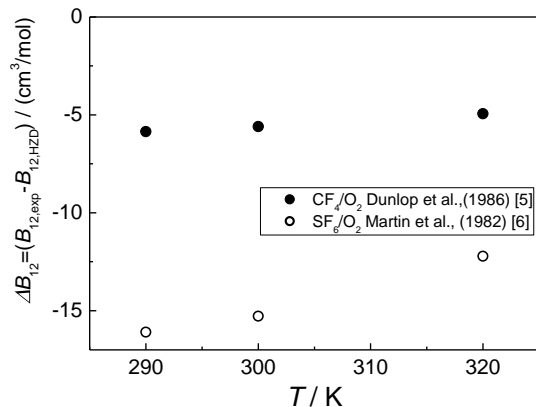


Figure 1. Absolute deviations between measured $B_{12,\text{exp}}$ [5, 6] and calculated $B_{12,\text{HZD}}$ interaction second virial coefficients of this work for CF_4/O_2 and SF_6/O_2 gas mixtures.

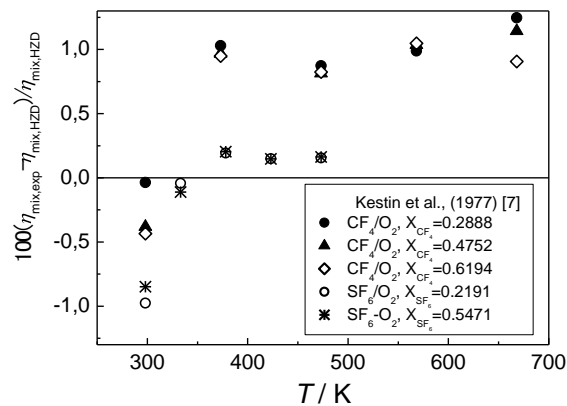


Figure 2. Relative deviations between our data $\eta_{\text{mix,HZD}}$ and measured viscosities $\eta_{\text{mix,exp}}$ [7] for different mole fractions of the binary mixtures CF_4/O_2 and SF_6/O_2 .

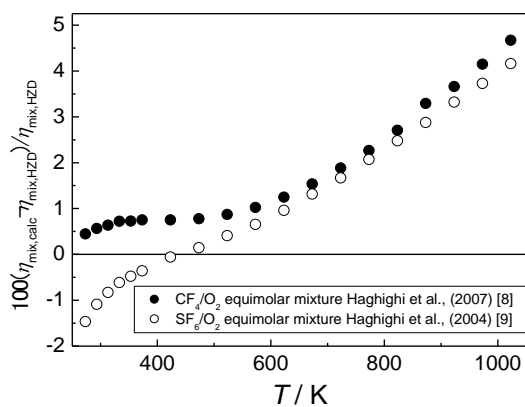


Figure 3. Relative deviations between our data $\eta_{\text{mix,HZD}}$ and calculated viscosities $\eta_{\text{mix,calc}}$ [8,9] for equimolar binary mixtures of CF_4/O_2 and SF_6/O_2 .

3. Results and discussion

Based on the LJTD model – equation 1, and the HZD mixing rule – equations 2 and 3, all thermophysical properties for CF_4/O_2 and SF_6/O_2 gas mixtures are calculated. In figures 1-5, the calculated data of this work are compared to those existing in the literature.

In figure 1, the absolute deviations between our results for B_{12} and the data from the literature are plotted. A slightly better agreement is observed for the CF_4/O_2 mixture. The relative deviations for both mixtures are in the range of 20 %.

In figures 2 and 3, the relative deviations are presented between the data of this work and the experimentally determined and calculated data from the literature.

The comparison between the binary diffusion coefficients obtained in this work and the data from the literature is shown in figures 4 and 5.

For a fast evaluation and compact representation, our recommended values of $R_{m12}(T)$, $\varepsilon_{12}(T)$, $B_{12}(T)$, $\eta_{12}(T)$ and $D_{12}(T)$ in the temperature range between 200 K and 1000 K are presented in the form of fitting formulae. The equilibrium distance $R_{m,12}(T)$ is fitted to the dimensionless expression

$$R_{m12}(T)/(10^{-10}\text{m}) = R_{m12}(0) + A_1 \exp\left(-\frac{A_2}{(T/K)}\right) + A_3 \exp\left(-\frac{A_4}{(T/K)}\right).$$

The well depth $\varepsilon_{12}(T)$ can be calculated by

$$\varepsilon_{12}(T) = \varepsilon_{12}(0) \left(\frac{R_{m12}(0)}{R_{m12}(T)} \right)^6.$$

The zero temperature constants for the CF_4/O_2 gas mixture are given as

$$R_{m12}(0)/(10^{-10}\text{m}) = 3.90226 \quad \text{and}$$

$$(\varepsilon_{12}(0)/k_B)/\text{K} = 233.272.$$

For the SF_6/O_2 gas mixture they are

$$R_{m12}(0)/(10^{-10}\text{m}) = 4.28103 \quad \text{and}$$

$$(\varepsilon_{12}(0)/k_B)/\text{K} = 239.149.$$

In the case of the thermophysical properties of the mixtures the following formulae are used:

$$B_{12}(T)/(\text{cm}^3/\text{mol}) = \sum_{k=1}^5 A_k \left(\frac{T}{\text{K}} \right)^{1-k},$$

$$\eta_{12}(T)/(\mu\text{Pa} \cdot \text{s}) = \sum_{k=1}^5 A_k \left(\frac{T}{\text{K}} \right)^{k-1} \quad \text{and}$$

$$D_{12}(T)/(10^{-6}\text{m}^2/\text{s}) = \sum_{k=1}^5 A_k \left(\frac{T}{\text{K}} \right)^{k-1}.$$

The fitting constants are given in table 2. Here ΔP is the standard error of the fit.

Table 2. Fitting constants

	Property	A_1	A_2	A_3	A_4	A_5	ΔP
CF ₄ /O ₂	$R_{m12}(T)$	0.065063	745.759	0.206229	2003.72	-	$1.3 \cdot 10^{-5}$
	$B_{12}(T)$	62.528	$-2.4517 \cdot 10^4$	$-2.06341 \cdot 10^5$	$-2.24496 \cdot 10^8$	$7.33932 \cdot 10^9$	0.0024
	$\eta_{12}(T)$	-0.35780	$7.41461 \cdot 10^{-2}$	$-5.40712 \cdot 10^{-5}$	$2.72262 \cdot 10^{-8}$	$-5.71621 \cdot 10^{-12}$	0.0048
	$D_{12}(T)$	-1.04543	$1.14184 \cdot 10^{-2}$	$1.22530 \cdot 10^{-4}$	$-5.45932 \cdot 10^{-8}$	$1.31318 \cdot 10^{-11}$	0.00599
SF ₆ /O ₂	$R_{m12}(T)$	$2.197297 \cdot 10^{-4}$	-428.364	0.245725	850.655	-	$4.5 \cdot 10^{-4}$
	$B_{12}(T)$	76.811	$-2.6582 \cdot 10^4$	$-5.13901 \cdot 10^6$	$7.00884 \cdot 10^8$	$-6.94799 \cdot 10^{10}$	0.047
	$\eta_{12}(T)$	-0.69580	$6.62836 \cdot 10^{-2}$	$-4.56954 \cdot 10^{-5}$	$2.02217 \cdot 10^{-8}$	$-3.21890 \cdot 10^{-12}$	0.0064
	$D_{12}(T)$	-0.72638	$7.00914 \cdot 10^{-3}$	$1.04792 \cdot 10^{-4}$	$-5.08581 \cdot 10^{-8}$	$1.37097 \cdot 10^{-11}$	0.0050

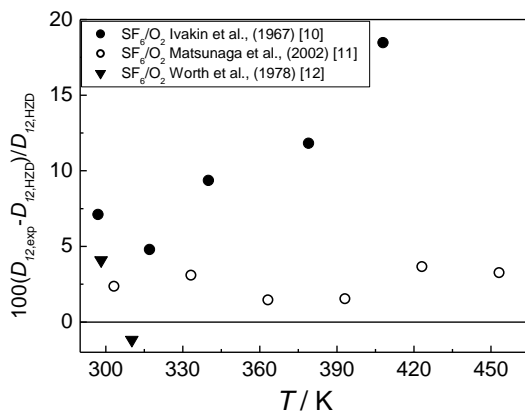


Figure 4. Relative deviations between experimentally determined $D_{12,exp}$ [10-12] and calculated $D_{12,HZD}$ binary diffusion coefficients of this work for SF₆/O₂ gas mixture.

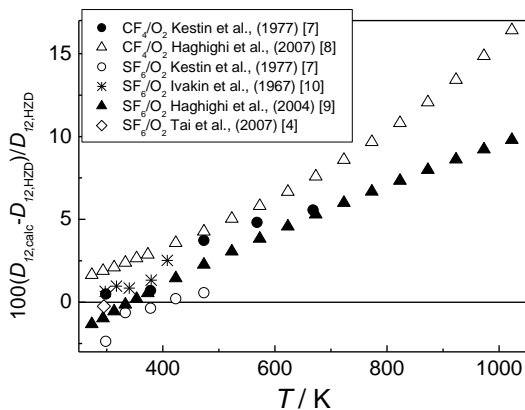


Figure 5. Relative deviations between calculated $D_{12,calc}$ [4,7-9] and binary diffusion coefficients of this work, $D_{12,HZD}$, for CF₄/O₂ and SF₆/O₂ gas mixtures.

4. Conclusions

Our proposed fitting formulae can be used for a fast calculation of the potential parameters, interaction second virial coefficient B_{12} , viscosity η_{12} and diffusion coefficient D_{12} for the binary mixtures CF₄/O₂ and SF₆/O₂ in the temperature range between 200 K and 1000 K. A comparison with the available experimental data suggests an accuracy of 20 % for B_{12} values better than 1 % for η_{mix} and 13 % for D_{12} , (see figures 1, 2, and 4). In figures 3 and 5, a nearly linearly increasing mismatch between our results presented in this paper and other theoretical data of the literature is observed. In the temperature range between 300 K and 1000 K, the deviations do not exceed 5 % in the case of the viscosities. We conclude that in this case the different underlying theories lead to comparable results. However, in the case of the binary diffusion coefficients, the relative deviations grow up to 15 % and the calculated results are significantly different. Only experiments carried out at higher temperatures would be capable of deciding between the different theories.

References

- [1] Grigoryev Yu N and Gorobchuk A G 2007 *Russ. Microelectr.* **36** 321-332
- [2] Chow T P and Fanelli G M 1985 *J. Electrochem. Soc.* **132** 1969-1973
- [3] Meichsner J, Schmidt M, Schneider R and Wagner H 2012 *Nonthermal Plasma Chem. and Phys.* (CRC Press, Boca Raton)
- [4] Tai R C, Chang H and Farhi L 1980 *Resp. Physiology* **40** 253-267
- [5] Dunlop P J, Bignell C M and Robjohnes H L 1986 *Ber. Bunsenges. Phys. Chem.* **90** 351-353
- [6] Martin M L, Trengove R D, Harris K R and Dunlop P J 1982 *Ber. Bunsenges. Phys. Chem.* **86** 626-627
- [7] Kestin J, Khalifa H E, Ro S T and Wakeham W A 1977 *Physica* **88A** 242-260
- [8] Haghghi B, Djavanmardi A H and Papari M M 2007 *Int. J. Comp. Methods* **4** 59-80
- [9] Haghghi B, Djavanmardi A H, Papari M M and Najafi M 2004 *J. Theor. Comp. Chemistry* **3** 69-90
- [10] Ivakin B A, Suetin P E and Plesovski W P 1967 *J. Techn. Phys.* **37** 1913-1914
- [11] Matsunaga N, Hori M and Nagashima A 2002 *Nippon Kikai Gakkai Ronbunshu, B-hen* **68** 550-555
- [12] Worth H, Nüsse W and Piiper J 1978 *Resp. Physiology* **32** 15-26
- [13] Zarkova L and Hohm U 2002 *J. Phys. Chem. Ref. Data* **31** 183-216
- [14] Damyanova M, Hohm U, Balabanova E and Zarkova L 2010 *J. Phys.: Conf. Ser.* **223** 012012
- [15] Hohm U, Zarkova L and Damyanova M 2006 *Int. J. Thermophys.* **27** 1725-1745
- [16] Hohm U 2013 *J. Mol. Struct.* **1054-1055** 282-292
- [17] Kumar A, Meath J W, Bündgen P and Thakkar A J 1996 *J. Chem. Phys.* **105** 4927-4937
- [18] Bulanin M O and Kislyakov I M 2002 *Opt. Spectr.* **93** 27-32
- [19] Kumar A, Fairley G R G and Meath W J 1985 *J. Chem. Phys.* **83** 70-77