

Effective Intermolecular Interaction Potentials of Gaseous Fluorine, Chlorine, Bromine, and Iodine

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Abstract Results are presented for binary intermolecular interactions and thermophysical properties in the temperature range between 70 K and 1,000 K of gaseous fluorine (F_2), and between 200 K and 1,000 K of chlorine (Cl_2), bromine (Br_2), and iodine (I_2). Our studies are carried out with an $(n - 6)$ Lennard-Jones temperature-dependent potential (LJTDP). The underlying model takes into account the influence of vibrational excitations on the equilibrium distance $R_m(T)$ and potential well depth $\varepsilon(T)$. The potential parameters at $T = 0$ K have been obtained by minimization of the sum of squared deviations between experimentally determined and calculated second pVT - and acoustic virial coefficients, B and β , and viscosities η , normalized to their relative experimental error a_{exp} . The majority of the available experimental data are well reproduced within their experimental errors. Tables and fitting formulae for a fast and reliable prediction of the thermophysical properties and potential parameters are also presented.

Keywords Gases · Halogens · Lennard-Jones temperature-dependent potential · Thermophysical properties · Virial coefficients · Viscosity

Dedicated to the memory of Prof. Dr. Lydia Zarkova who passed away on 14 May 2009.

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1 Introduction

The halogens fluorine F_2 , chlorine Cl_2 , bromine Br_2 , and iodine I_2 are important chemicals with many applications in different aspects of technology and industry (for disinfecting of drinking water, production of steel and semiconductor devices, etc.). Despite their wide usage, because of their great chemical activity, there are not enough experimentally measured data of their thermophysical properties, like second pVT - and acoustic virial coefficients, B and β , viscosities η , and diffusion coefficients D . Whereas low-density F_2 and Cl_2 are comparatively well investigated, experiments for vapors of Br_2 and I_2 are few and scanty.

The first investigations of binary interactions between two halogen molecules date from 1954, when Hirschfelder et al. [1] published results for a (12-6) Lennard-Jones potential (LJP) for F_2 , Cl_2 , Br_2 , and I_2 . The potential parameters were based on experimental viscosity data [2–6]. In 1972, Hanley and Prydz [7] obtained ($m - 6 - 8$) potential parameters by fitting the B data, published by Prydz and Straty [8], and presented tables with calculated values for the thermal conductivity λ and viscosity η of gaseous and liquid F_2 in the temperature range between 70 K and 300 K for pressures up to 200 bar.

Two-center Lennard-Jones potentials were widely applied to calculate the second pVT -virial coefficient B of the lighter halogens. Whereas the calculations of Bohn et al. [9] for Cl_2 are not in good agreement with the experimental results of Morrison at low temperatures [10], more recent studies of Meng and Duan [11] compare favorably well with experiments. Rio and co-authors used the approximate nonconformal theory [12] to obtain the effective interaction potentials for a lot of gases, including F_2 and Cl_2 . Their results are in reasonably good agreement with experimental data [13]. In 1974, Tsionopoulos [14] presented an empirical correlation of B data for both polar and non-polar systems. His method is very valuable for estimating second virial coefficients for gases for which there are no experimentally measured data.

In 2002, Hurly [15] measured the second speed-of-sound virial coefficient β of Cl_2 . From these speed-of-sound measurements, he determined a hard-core square-well (HCSW) and a hard-core Lennard-Jones (HCLJ) potential. The latter potential was able to reproduce the measured speed of sound with an uncertainty of 0.2%. Although the temperature range of the measurements was rather narrow ($\Delta T = 260$ K to 440 K) the same potential was used to calculate B in the temperature range between 177 K and 1770 K.

Oh and Park [16] used a group contribution method on the basis of a Kihara potential in order to obtain thermophysical properties of F_2 and Cl_2 . This method, which was recently also applied to larger spherical molecules [17], seems to provide the only intermolecular interaction potential so far which is able to reproduce simultaneously transport and equilibrium properties of the halogens.

The goal of our study was first to investigate the applicability of the ($n - 6$) Lennard-Jones temperature-dependent potential (LJTDP) [18,19] to interactions between diatomic halogen molecules. Second, within our model, we obtain the temperature dependences of the potential parameters equilibrium distance $R_m(T)$ and potential well depth $\varepsilon(T)$, as well as of the thermophysical properties $B(T)$, $\eta(T)$, and $\rho D(T)$ ($\rho =$ density) at pressures $p \leq 0.1$ MPa in a wide temperature range between

200 K and 1,000 K. We also present simple fitting formulae which allow fast calculation of these properties which could compensate for the lack of experimental data. They are also helpful for an estimation of other potential-dependent properties of low-density halogen gases and their binary mixtures.

Our model of the $(n - 6)$ LJTDJ has been presented in detail elsewhere [19]. To be brief, the intermolecular interaction potential $U(R, T)$ is represented by

$$U(R, T) = \frac{\varepsilon(T)}{n - 6} \left[6 \left(\frac{R_m(T)}{R} \right)^n - n \left(\frac{R_m(T)}{R} \right)^6 \right] \quad (1)$$

R is the center-of-mass distance and n is the repulsive parameter, which is supposed to be independent of temperature. The temperature dependence of $R_m(T)$ and $\varepsilon(T)$ is due to vibrational excitation of the molecule with increasing temperature T . It is described by

$$R_m(T) = R_m(T = 0 \text{ K}) + \delta f(T) \quad (2)$$

$$\varepsilon(T) = \varepsilon(T = 0 \text{ K}) (R_m(T = 0 \text{ K})/R_m(T))^6, \quad (3)$$

where δ is a temperature-independent fit parameter, whereas the function $f(T)$ indicates the influence of the vibrational excitation of the molecule on its geometrical radius. $f(T)$ can be calculated via the vibrational partition function $Z(T)$ at any T if the vibrational frequencies of the molecule are known. In this work we use the harmonic oscillator approximation. In the case of very high vibrational frequencies (light molecules like F_2), the molecules stay in their ground state. Therefore, no effective enlargement of the molecule is observed, $R_m(T) \cong R_m(T = 0)$, which also results in $\delta \cong 0$. In this case, the $(n - 6)$ LJTDJ reduces to a temperature independent $(n - 6)$ LJP.

2 Procedure

The potential parameters at $T = 0 \text{ K}$ have been obtained by minimization of the sum of squared deviations F between M experimentally obtained and calculated data points of B , β , and η , normalized to their relative experimental errors a_{exp} . Standard procedures, as given by Hirschfelder et al. [1], are used for the calculation of B , β , and η . The reduced collision integrals are interpolated from tables given by Klein and Smith [20];

$$F = \sum X_i^2 = \sum_1^{M_B} \left[\frac{\ln \left(\frac{B_{\text{exp}}}{B_{\text{calc}}} \right)}{a_{\text{exp}_B}} \right]^2 + \sum_1^{M_\beta} \left[\frac{\ln \left(\frac{\beta_{\text{exp}}}{\beta_{\text{calc}}} \right)}{a_{\text{exp}_\beta}} \right]^2 + \sum_1^{M_\eta} \left[\frac{\ln \left(\frac{\eta_{\text{exp}}}{\eta_{\text{calc}}} \right)}{a_{\text{exp}_\eta}} \right]^2 \quad (4)$$

The available experimental data for the thermophysical properties B and η of F_2 , Cl_2 , Br_2 , and I_2 are collected in Table 1. In the case of the second speed-of-sound

Table 1 Sets of experimental input data used for the determination of the potential parameters of low-density gaseous halogens

Substance	References	Number of experimental data (M)	Temperature range ΔT (K)	Experimental error a_{exp} (%)
Fluorine	White et al. [21]	11 (B)	80–250	19–45 ($5 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $80 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Prydz and Straty [8]	45 (B)	80–300	1–23 ($0.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $40 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Kanda [2]	9 (η)	87–273	10
	Franck and Stober [22]	7 (η)	90–471	5
	Hanley and Prydz [7]	24 (η)	70–300	5
	Haynes [23]	8 (η)	155–300	5
Chlorine	Pier [24]	1 (B)	273	5 ($17 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Jaquered and Tourpaian [25]	2 (B)	273–298	5 ($17 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Eucken and Hoffman [26]	2 (B)	244–250	5 ($22 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Morrison [10]	4 (B)	298–650	3–7 ($4 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $11 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Hohm and Trümper [27]	9 (B)	296–1080	3–75 ($5 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Hurly [15]	14 (β)	260–440	0.5–0.9
	Rankine [28]	2 (η)	286–372	1.5
	Braune and Linke [3]	9 (η)	289–772	1.5
	Trautz and Ruf [4]	10 (η)	289–523	1.5
	Wobser and Müller [29]	6 (η)	293–523	1.5
Bromine	Tsonopoulos [14]	4 (B)	282–1041	7 ($3 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $62 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Rankine [5,28]	6 (η)	286–575	10
	Braune et al. [6]	22 (η)	292–867	5
Iodine	Tsonopoulos [14]	7 (B)	410–1137	7 ($9 \text{ cm}^3 \cdot \text{mol}^{-1}$ to $62 \text{ cm}^3 \cdot \text{mol}^{-1}$)
	Rankine [30]	3 (η)	397–520	10
	Braune and Linke [3]	7 (η)	379–796	5

virial coefficient β , only results for Cl_2 are given in the literature [15]. Although measured in the small temperature range between 260 K and 440 K, these measurements have a large impact on the resulting potential parameters due to their high accuracy (error about 0.5% to 0.9%).

In general, the experimental results for B at low temperatures seem to be the most inaccurate input data. In many cases, the experimental error of B is not less than 5% throughout the whole temperature range. These errors are directly taken from the original sources. In the case of the viscosity, the experimental errors are hardly calculated or even estimated by the various authors. Therefore, we assume that the relative experimental errors a_{exp} for η are in the range between 1.5% and 10%, depending on the method and on the reactivity and volatility of the substance.

Due to the obvious non-existence of experimental B data for Br_2 and I_2 , we used in our minimization procedure results from the correlation of Tsonopoulos [14] which are cited in the DIPPR801 database [31].

3 Results and Discussion

The obtained “best solutions” for the potential parameters of F_2 , Cl_2 , Br_2 , and I_2 at $T = 0\text{ K}$ are shown in Table 2. In the same table, the root-mean-square deviations $\text{RMS} = \sqrt{F/M}$ of the fit and the number of experimental input data $M = M_B + M_\beta + M_\eta$ are also given. Our results show that for interactions between two fluorine molecules the $(n - 6)$ LJTDTP turns into the usual $(n - 6)$ LJP ($\delta = 0$). In all cases, we observed that the $\text{RMS} \cong a_{\text{exp}}$ which proves the reasonability of our model to calculate thermophysical properties.

In order to provide a simple way of obtaining the potential parameters at any desired T , $R_m(T)$ was fitted to

$$R_m(T) = R_m(0) + A_1 \exp(-B_1/T) + A_2 \exp(-B_2/T). \quad (5)$$

The fit parameters A_1 , A_2 , B_1 , and B_2 are also included in Table 2. The sum of the two exponential terms reflect the increase in $R_m(T) - R_m(0) = \delta f(T)$, see Eq. 2. The potential well depth $\varepsilon(T)$ can be calculated by using Eqs. 3 and 5. Because of the limited number of experimental data for the thermophysical properties of Br_2 and I_2 , the intermolecular potentials can be considered as preliminary. In Table 3, we present recommended values of the second pVT virial coefficient B , the viscosity η , and the diffusion coefficient ρD calculated with the LJTDTP in the range between 200 K and 1,000 K. In the case of F_2 , the table is extended down to 70 K because experimental data are available for comparison. In Table 4, the parameters of fitting formulae are

Table 2 Potential parameters at $T = 0\text{ K}$, root-mean-square deviations and fit parameters of Eq. 5 for gaseous halogens

	F_2	Cl_2	Br_2	I_2
Mass (a.u.)	38.0	70.9	159.8	253.8
M	$104 (B + \eta)$	$59 (B + \beta + \eta)$	$32 (B + \eta)$	$17 (B + \eta)$
ε/k_B (K)	136.9 ± 3.0	497.04 ± 11.3	718.5 ± 15.8	1009.3 ± 22.0
R_m (10^{-10} m)	3.629 ± 0.018	4.262 ± 0.020	4.477 ± 0.022	4.915 ± 0.025
n	16.71 ± 1.34	25.93 ± 2.01	17.5 ± 1.36	19.82 ± 1.53
$\delta(10^{-10}$ m)	0.0	0.011 ± 0.010	0.086 ± 0.010	0.056 ± 0.010
RMS (a_{exp})	0.867	1.387	0.421	0.406
$A_1(10^{-10}$ m)	–	0.02544	0.24395	0.19485
B_1 (K)	–	844.0	528.5	389.6
$A_2(10^{-10}$ m)	–	0.03883	0.41957	0.34492
B_2 (K)	–	2391	1896	1679

Table 3 Dimensionless properties $B^* = B / (\text{cm}^3 \cdot \text{mol}^{-1})$, $\eta^* = \eta / (\mu\text{Pa} \cdot \text{s})$, and $\rho D^* = \rho D / (10^{-3} \text{g} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$ of F_2 , Cl_2 , Br_2 , and I_2

T (K)	F_2			Cl_2			Br_2			I_2		
	B^*	η^*	ρD^*	B^*	η^*	ρD^*	B^*	η^*	ρD^*	B^*	η^*	ρD^*
70	-296.0	6.073	8.006									
80	-228.8	6.880	9.100									
90	-183.6	7.709	10.19									
100	-151.2	8.528	11.28									
110	-126.9	9.350	12.36									
120	-108.0	10.18	13.41									
130	-93.0	10.99	14.46									
140	-80.7	11.80	15.51									
150	-70.5	12.59	16.53									
160	-61.9	13.37	17.52									
170	-54.5	14.14	18.49									
180	-48.2	14.91	19.45									
190	-42.7	15.65	20.40									
200	-37.8	16.38	21.33	-651.8	9.701	12.61	-2161	11.07	14.22	-8429	10.56	13.40
210	-33.5	17.09	22.25	-585.0	10.11	13.17	-1869	11.53	14.85	-6871	10.99	13.97
220	-29.6	17.80	23.15	-528.9	10.52	13.72	-1637	11.99	15.49	-5713	11.42	14.54
230	-26.1	18.49	24.03	-481.3	10.93	14.27	-1449	12.44	16.12	-4831	11.84	15.11
240	-23.0	19.17	24.90	-440.5	11.34	14.82	-1294	12.91	16.76	-4146	12.26	15.67
250	-20.2	19.83	25.74	-405.0	11.76	15.37	-1165	13.37	17.40	-3602	12.68	16.23
260	-17.6	20.49	26.57	-374.0	12.17	15.92	-1056	13.84	18.04	-3165	13.09	16.80
270	-15.3	21.14	27.39	-346.6	12.58	16.46	-963.5	14.31	18.68	-2808	13.51	17.36
280	-13.1	21.77	28.19	-322.4	12.99	17.01	-883.4	14.78	19.33	-2511	13.92	17.92

Table 3 continued

<i>T</i> (K)	F ₂		Cl ₂		Br ₂		I ₂	
	<i>B</i> [*]	<i>η</i> [*]	<i>B</i> [*]	<i>η</i> [*]	<i>B</i> [*]	<i>η</i> [*]	<i>B</i> [*]	<i>η</i> [*]
290	-11.1	22.39	-300.7	13.41	-813.9	15.24	-2263	14.33
300	-9.30	23.01	-281.2	13.82	-753.0	15.71	-2053	14.74
310	-7.61	23.61	-263.6	14.23	-699.3	16.19	-1874	15.16
320	-6.03	24.20	-247.7	14.64	-651.6	16.67	-1719	15.57
330	-4.57	24.79	-233.1	15.06	-609.0	17.16	-1584	15.98
340	-3.20	25.36	-219.8	15.47	-570.8	17.65	-1466	16.40
350	-1.93	25.93	-207.6	15.88	-536.3	18.13	-1362	16.81
360	-0.73	26.48	-196.4	16.29	-505.1	18.61	-1270	17.23
370	0.39	27.04	-186.0	16.70	-476.7	19.09	-1187	17.64
380	1.44	27.58	-176.4	17.11	-450.7	19.58	-1113	18.06
390	2.43	28.11	-167.4	17.51	-426.9	20.07	-1047	18.47
400	3.37	28.64	-159.1	17.92	-405.0	20.57	-986.9	18.89
420	5.08	29.68	-144.1	18.73	-366.1	21.58	-882.5	19.73
440	6.63	30.70	-130.8	19.54	-332.7	22.58	-795.1	20.58
460	8.01	31.69	-119.1	20.34	-303.5	23.58	-720.9	21.43
480	9.27	32.66	-108.7	21.13	-278.0	24.57	-657.3	22.29
500	10.4	33.61	-99.3	21.92	-255.5	25.57	-602.3	23.15
520	11.5	34.54	-90.8	22.70	-235.4	26.57	-554.1	24.00
540	12.4	35.45	-83.2	23.48	-217.4	27.58	-511.7	24.86
560	13.3	36.35	-76.2	24.25	-201.2	28.59	-474.1	25.73
580	14.1	37.23	-69.8	25.01	-186.6	29.60	-440.5	26.62
600	14.8	38.10	-63.9	25.76	-173.3	30.59	-410.4	27.50

Table 3 continued

<i>T</i> (K)	<i>F</i> ₂			<i>Cl</i> ₂			<i>Br</i> ₂			<i>I</i> ₂		
	<i>B</i> *	η^*	ρD^*	<i>B</i> *	η^*	ρD^*	<i>B</i> *	η^*	ρD^*	<i>B</i> *	η^*	ρD^*
620	15.5	38.95	50.46	-58.5	26.50	34.20	-161.1	31.57	41.43	-383.1	28.38	37.34
640	16.2	39.79	51.56	-53.6	27.24	35.11	-150.0	32.54	42.69	-358.5	29.25	38.49
660	16.7	40.61	52.65	-48.9	27.96	36.01	-139.7	33.50	43.93	-336.0	30.12	39.64
680	17.3	41.43	53.72	-44.7	28.68	36.90	-130.2	34.46	45.15	-315.4	30.98	40.78
700	17.8	42.23	54.78	-40.7	29.40	37.78	-121.5	35.41	46.36	-296.5	31.85	41.91
720	18.3	43.02	55.82	-36.9	30.11	38.66	-113.4	36.36	47.54	-279.1	32.72	43.02
740	18.8	43.81	56.85	-33.4	30.81	39.52	-105.8	37.31	48.72	-263.1	33.59	44.12
760	19.2	44.58	57.87	-30.2	31.50	40.38	-98.7	38.25	49.88	-248.2	34.47	45.21
780	19.6	45.34	58.88	-27.1	32.19	41.23	-92.1	39.18	51.03	-234.4	35.34	46.30
800	19.9	46.10	59.87	-24.2	32.86	42.07	-85.9	40.09	52.17	-221.5	36.21	47.39
820	20.3	46.84	60.86	-21.5	33.53	42.91	-80.1	40.99	53.31	-209.4	37.07	48.48
840	20.6	47.58	61.83	-18.9	34.19	43.73	-74.6	41.87	54.44	-198.2	37.92	49.56
860	20.9	48.30	62.79	-16.5	34.84	44.54	-69.5	42.75	55.56	-187.6	38.77	50.65
880	21.2	49.02	63.74	-14.2	35.49	45.35	-64.6	43.61	56.66	-177.7	39.60	51.72
900	21.5	49.74	64.68	-12.0	36.12	46.15	-60.0	44.47	57.75	-168.3	40.43	52.79
950	22.2	51.50	67.00	-7.0	37.69	48.10	-49.5	46.57	60.42	-147.2	42.49	55.41
1000	22.7	53.21	69.27	-2.5	39.22	50.01	-40.2	48.61	63.00	-128.7	44.53	57.96

Table 4 Fit parameters according to Eqs. 6 and 7 for the halogens

Property	Fit parameter	F ₂	Cl ₂	Br ₂	I ₂
<i>B</i>	<i>P</i> ₁	34.74 ± 0.12	81.58 ± 0.66	106.359 ± 0.061	154.69 ± 0.84
	10 ⁻⁴ <i>P</i> ₂	-1.1150 ± 0.0099	-8.256 ± 0.088	-12.4028 ± 0.0085	-23.40 ± 0.11
	10 ⁻⁶ <i>P</i> ₃	-0.553 ± 0.019	1.92 ± 0.35	-9.942 ± 0.029	-13.39 ± 0.40
	10 ⁻⁹ <i>P</i> ₄	0.01979 ± 0.00094	-2.936 ± 0.041	-1.855 ± 0.0086	-7.830 ± 0.073
	<i>P</i> ₅	0.0 (fixed)	0.0 (fixed)	66.532 ± 0.079	87.21 ± 0.16
	Δ <i>B</i> (cm ³ · mol ⁻¹)	0.33	0.42	0.029	0.51
<i>η</i>	<i>P</i> ₁	-0.760 ± 0.025	1.038 ± 0.036	2.585 ± 0.051	3.209 ± 0.051
	10 ² <i>P</i> ₂	10.201 ± 0.026	4.356 ± 0.021	3.824 ± 0.030	3.478 ± 0.030
	10 ⁵ <i>P</i> ₃	-9.383 ± 0.082	-0.185 ± 0.038	2.323 ± 0.054	1.400 ± 0.053
	10 ⁸ <i>P</i> ₄	6.37 ± 0.10	-0.357 ± 0.021	-1.553 ± 0.030	-0.744 ± 0.030
	10 ¹¹ <i>P</i> ₅	-1.786 ± 0.043	-	-	-
	Δ <i>η</i> (μPa·s)	0.025	0.019	0.027	0.027
<i>ρD</i>	<i>P</i> ₁	-0.600 ± 0.026	0.680 ± 0.033	1.471 ± 0.084	2.704 ± 0.032
	10 ² <i>P</i> ₂	13.045 ± 0.027	6.206 ± 0.019	6.121 ± 0.049	5.148 ± 0.019
	10 ⁵ <i>P</i> ₃	-12.081 ± 0.085	-1.334 ± 0.035	1.305 ± 0.088	1.249 ± 0.034
	10 ⁸ <i>P</i> ₄	8.51 ± 0.11	0.059 ± 0.019	-1.282 ± 0.049	-0.873 ± 0.018
	10 ¹¹ <i>P</i> ₅	-2.487 ± 0.045	-	-	-
	10 ⁵ Δ <i>ρD</i> (g · m ⁻¹ · s ⁻¹)	2.6	1.7	4.4	1.7

Δ*P* (*P* = *B*, *η*, or *ρD*) denotes the standard deviation of the fit

given, which can be used for a fast calculation of the thermophysical properties of the low-density gaseous halogens. The dimensionless quantities $P(T) = \eta/(\mu\text{Pa} \cdot \text{s})$ and $P(T) = \rho D/(10^{-3} \text{g} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$ are fitted to a polynomial in powers of the temperature *T* of the form,

$$P(T) = \sum_{i=1}^5 P_i(T/K)^{i-1} \quad (6)$$

whereas the dimensionless second *pVT*-virial coefficient $P(T) = B(T)/(\text{cm}^3 \cdot \text{mol}^{-1})$ is represented by

$$P(T) = \sum_{i=1}^4 P_i(T/K - P_5)^{1-i}. \quad (7)$$

The relative deviations between experimentally measured and calculated properties $P = B, \eta, \beta$ of F₂, Cl₂, Br₂, and I₂ are presented in Figs. 1, 2, 3, and 4. Generally the experimental data for the thermophysical properties of the halogens can be reproduced

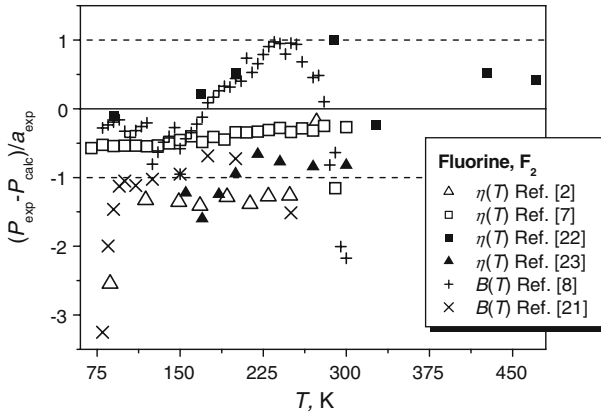


Fig. 1 Deviations $P_{\text{exp}} - P_{\text{calc}}$ between experimental and calculated properties $P = B$ or η for F_2 normalized to their individual experimental uncertainties a_{exp} . Calculations are carried out with an $(n - 6)$ LJP by using the potential parameters given in Table 2

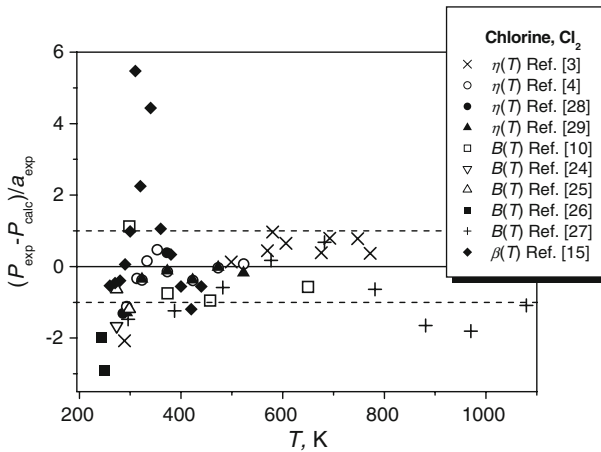


Fig. 2 Deviations $P_{\text{exp}} - P_{\text{calc}}$ between experimental and calculated properties $P = B, \beta$, or η for Cl_2 normalized to their individual experimental uncertainties a_{exp} . Calculations are carried out with an $(n - 6)$ LJTDJ by using the potential parameters given in Table 2

within their stated limits of accuracy. However, some exceptions can be observed. In the case of F_2 , Fig. 1, a systematic deviation of more than $\pm 1a_{\text{exp}}$ of the viscosity data of Kanda [2] is observed. This large inconsistency of these data was already mentioned by Hanley and Prydz [7]. As expected [11], White's measurements [21] of the second pVT -virial coefficient also deviate substantially from our findings and other measurements [8]. Hurly's measurements [15] on the second acoustic virial coefficient of Cl_2 , Fig. 2, show a considerable deviation of up to $6a_{\text{exp}}$. The reason for this may be the inadequacy of our model to reproduce β of Cl_2 or unrealistically small error bounds given by Hurly [15] for the second acoustic virial coefficient.

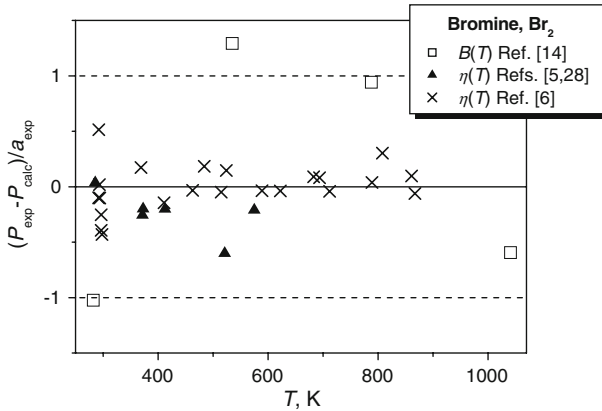


Fig. 3 Deviations $P_{\text{exp}} - P_{\text{calc}}$ between experimental and calculated properties $P = B$ or η for Br_2 normalized to their individual experimental uncertainties a_{exp} . Calculations are carried out with an $(n - 6)$ LJTDTP by using the potential parameters given in Table 2

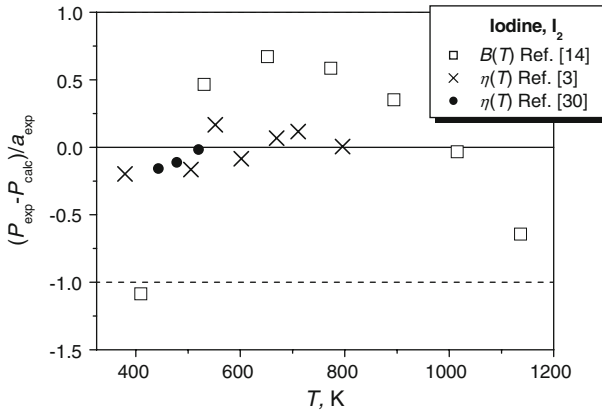


Fig. 4 Deviations $P_{\text{exp}} - P_{\text{calc}}$ between experimental and calculated properties $P = B$ or η for I_2 normalized to their individual experimental uncertainties a_{exp} . Calculations are carried out with an $(n - 6)$ LJTDTP by using the potential parameters given in Table 2

In Figs. 5, 6, and 7, we compare our results obtained with the LJTDTP with other correlations. The absolute deviation $\Delta B(T)$ of the second pVT -virial coefficient of F_2 and Cl_2 is shown in Fig. 5. Good agreement can be seen above 100 K for F_2 . In the case of Cl_2 , we notice small deviations between our results (zero line) and the data of Bohn et al. [9] and Oh and Park [16], which are obtained with different potential energy models. However, the correlations given by Dymond et al. [13] and the DIPPR database [31] deviate considerably. In the case of the viscosity, Fig. 6, we notice reasonably good agreement for F_2 . For Cl_2 again the data given by Oh and Park [16] are in fair agreement with our calculations, whereas the other data sources show a larger systematic deviation. All correlations of the viscosity for Br_2 and I_2 , Fig. 7, are well within $\pm 2\%$. We conclude that in this case the LJTDTP should be able to give

Fig. 5 Absolute deviations $\Delta B(T)$ of the second pVT -virial coefficient of F_2 and Cl_2 between the correlations given in Refs. [9, 13, 16, 31] and the results obtained with our LJTDTP (zero line)

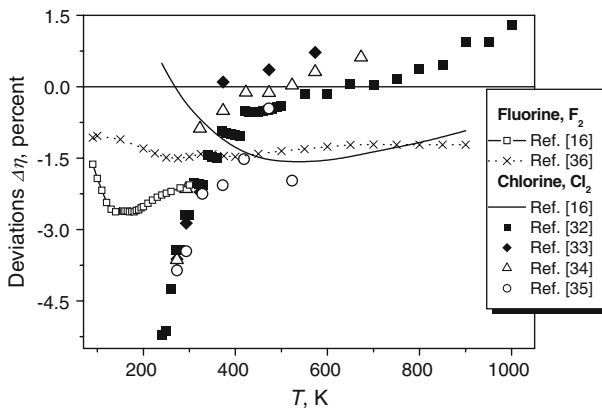
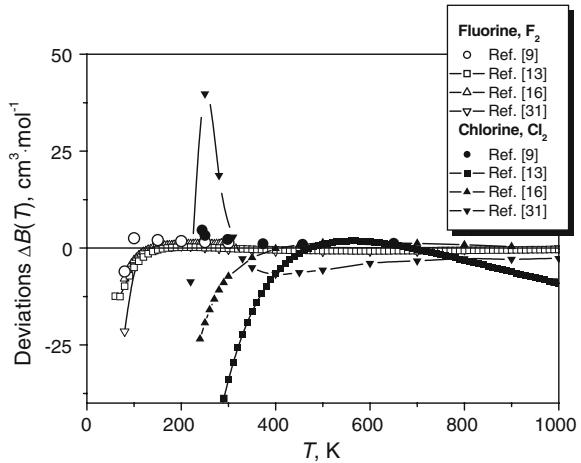


Fig. 6 Relative deviations $\Delta\eta(T)$ of the viscosity of F_2 and Cl_2 between the correlations given in Refs. [16, 32–36] and the results obtained with our LJTDTP (zero line)

the viscosity of Br_2 and I_2 with an uncertainty of about 5% in the temperature range between 250 K and 800 K.

4 Conclusions

We have shown that the spherically symmetric Lennard-Jones ($n - 6$) potential with temperature-dependent potential parameters $R_m(T)$ and $\varepsilon(T)$ is able to describe important equilibrium and transport properties of the low-density halogens F_2 , Cl_2 , Br_2 , and I_2 . Bearing in mind the deficiency and inconsistency of the experimental data for the second virial coefficients B and β and the viscosity η , and the lack of self-diffusion data D for all investigated gases, these potentials reproduce acceptably well the available thermophysical properties within their experimental error bars. Especially in the case of Br_2 and I_2 , however, these potentials are provisional since no

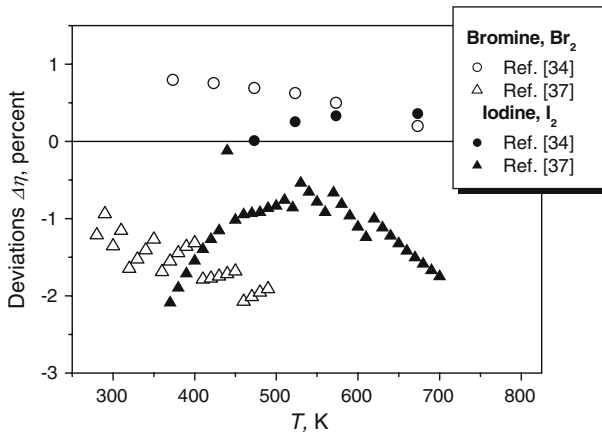


Fig. 7 Relative deviations $\Delta\eta(T)$ of the viscosity of Br_2 and I_2 between the correlations given in Refs. [34,37] and the results obtained with our LJTDP (zero line)

experimental thermophysical equilibrium data are available to check their accuracy. Where available, we also observe a reasonable agreement between our calculations and other theoretical predictions. Therefore, we use our values of the potential parameters to calculate the thermophysical properties B , η , and ρD over wider temperature ranges. We believe that with our consistent description, the equilibrium and transport properties of the halogens are obtained with reasonable accuracy even in temperature ranges where no measurements for comparison exist.

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References

1. J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, London, 1954)
2. E. Kanda, Bull. Chem. Soc. Japan **1**, 463 (1937)
3. H. Braune, R. Linke, Z. Phys. Chem. **A148**, 195 (1930)
4. M. Trautz, F. Ruf, Ann. Physik **20**, 127 (1934)
5. A.O. Rankine, Proc. Roy. Soc. **A89**, 575 (1913)
6. H. Braune, R. Basch, W. Wentzel, Z. Phys. Chem. **A137**, 176 (1928)
7. H. Hanley, R. Prydz, J. Phys. Chem. Ref. Data **1**, 1101 (1972)
8. R. Prydz, J. Straty, J. Res. Nat. Bur. Stand. **74A**, 747 (1970)
9. M. Bohn, R. Lustig, J. Fischer, Fluid Phase Equilib. **25**, 251 (1986)
10. P.A. Morrison, Ph.D. thesis, California Institute of Technology, Pasadena, 1972, cited [9]
11. L. Meng, Y.-Y. Duan, Mol. Phys. **104**, 2891 (2006)
12. F. del Rio, J.E. Ramos, I. McLure, Phys. Chem. Chem. Phys. **1**, 4937 (1999)
13. J.H. Dymond, K.N. Marsh, R.C. Wilhoit, K.C. Wong, *Landolt–Börnstein: Virial Coefficients of Pure Gases and Mixtures—Virial Coefficients of Pure Gases, New Series IV/21A* (Springer, Berlin, 2002)
14. C. Tsionopoulos, AIChE J. **20**, 263 (1974)
15. J.J. Hurly, Int. J. Thermophys. **23**, 455 (2002)
16. S.-K. Oh, K.-H. Park, Korean J. Chem. Eng. **22**, 268 (2005)

17. S.-K. Oh, *Fluid Phase Equilib.* **271**, 53 (2008)
18. B. Stefanov, *J. Phys. B: At. Mol. Opt. Phys.* **25**, 4519 (1992)
19. L. Zarkova, *Mol. Phys.* **88**, 489 (1996)
20. M. Klein, F.J. Smith, *J. Res. Nat. Bur. Stand.* **72A**, 359 (1968)
21. D. White, J.H. Hu, H.L. Johnston, *J. Chem. Phys.* **21**, 1149 (1953)
22. E.U. Franck, W. Stober, *Z. Naturforsch.* **A**, 8220 (1952)
23. W.M. Haynes, *Physica* **76**, 1 (1974)
24. M. Pier, *Z. Phys. Chem.* **62**, 385 (1908)
25. A. Jaquerod, M. Tourpaian, *J. Chim. Phys.* **11**, 17 (1919)
26. A. Eucken, G. Hoffmann, *Z. Phys. Chem.* **B5**, 442 (1929)
27. U. Hohm, U. Trümper, *J. Chem. Soc. Faraday Trans.* **91**, 1277 (1995)
28. A.O. Rankine, *Nature* **88**, 469 (1912)
29. R. Wobser, F. Müller, *Kolloid-Beihefte* **52**, 165 (1940/41)
30. A.O. Rankine, *Proc. Roy. Soc.* **A91**, 201 (1915)
31. BYU DIPPR801 database: <http://dippr.byu.edu>
32. NIST Thermophysical Properties Database for Semiconductor Process Gases, June 2006 Release: <http://properties.nist.gov/fluidsci/semiprop/gases/>
33. T. Laby, G. Kaye, *Tables of Physical and Chemical Constants*, 14th edn. (Longman Group Limited, London, 1973)
34. “Sprovochnik chimika”, Gosudarstvennoe nauchno-technicheskoe izdatelstvo chimicheskoi literaturi, Moskva, Leningrad, book I, p. 1002 (in Russian)
35. S. Bretsznader, *Prediction of Transport and Other Physical Properties of Fluids* (Elsevier, Amsterdam, 1971)
36. N.B. Vargaftik, *Handbook of the Physical Properties of Liquids and Gases*, 2nd edn. (Hemisphere, Washington, 1983)
37. Y.S. Touloukian, *Thermophysical Properties of Matter: The TCRC Data Series* (IFI/Plenum, New York, 1970)