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POTENTIAL OF BINARY INTERACTIONS AND THERMOPHYSICAL PROPERTIES OF CHLORINE IN A GAS PHASE

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Two models: *(i)* (*n*-6) Lennard-Jones (LJ) potential and a *(ii)* Lennard Jones Temperature-Dependent Potential (LJTDP) were used for the determination of the intermolecular interaction potential parameters (PP) and simultaneous approximation of the measured experimental thermophysical properties (*pVT* and acoustic second virial coefficients B and β, and viscosity η) for gaseous chlorine (Cl_2). A comparison of the results shows slightly smaller deviations between measured and calculated data for LJTDP calculations compared to the (*n*-6) LJ potential. This unessential priority of the LJTDP is compensated by the simplicity of (*n*-6) LJ potential, which we recommend for calculations of different potential-dependent properties. We give tables with recommended data for of B, η, and self diffusion ρD, produced in the temperature range 200-900 K, which are convenient for inter- and extrapolations.

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1. Introduction

Chlorine is a gas with a huge importance in different branches of contemporary industry such as vinyl plastic chemistry, biochemistry, steel making, production of semiconductor devices, and as a source for disinfecting the drinking water. Despite of this there are not enough experimentally measured data for thermophysical properties.

The aim of our work is:

(i) to investigate interactions between two chlorine molecules using two models of intermolecular potentials (LJTDP and (*n*-6) LJ potential);

(ii) to predict the potential parameters and create tables with reference data for the temperature dependencies of the thermophisical properties: B(T), η(T), and ρD(T), calculated by means of a unique potential.

Previous researchers have compared their experimentally defined results of thermophysical properties of gaseous chlorine with the calculated ones obtained using simple spherically symmetric potentials. In 1986 a Two-Center LJ (2CLJ) potential was applied [1] to calculate B, but the results were not satisfying. In 2002 Hurly [2] fitted β extracted from speed of sound measurements to a Hard-Core Square-Well (HCSW) and a Hard-Core Lennard-Jones (HCLJ) potential. In these calculations he also had to determine B. With the second model the speed of sound was approximated with an accuracy of 0.2% and it was recommended as a more convenient. Although the temperature range of the measurements was rather narrow (ΔT = 260-440 K) Hurly used the same potential to calculate B at temperatures between 177 to 1770 K.

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2. Theoretical background

The calculations have been performed using two simple spherically symmetric potentials:

1. (n-6) Lennard Jones potential: $U(r)=\dfrac{\varepsilon}{n-6}\left[6\left(\dfrac{r_m}{r}\right)^n-n\left(\dfrac{r_m}{r}\right)^6\right]$
2. Lennard Jones temperature-dependent potential: $U(r,T)=\dfrac{\varepsilon(T)}{n-6}\left[6\left(\dfrac{r_m(T)}{r}\right)^n-n\left(\dfrac{r_m(T)}{r}\right)^6\right]$

where ε is a potential well depth, r_m is an equilibrium distance and n is a repulsive parameter.
In general, there is no difference between these two models except for the temperature dependence of the potential parameters ε and $\mathrm{r_m}$.

In the second model we consider the temperature dependence of the equilibrium distance $r_m(T)=r_m(0)+\delta(T)$ (δ is the effective enlargement of molecular size at given temperature) and of the potential well depth $\varepsilon(T)=\varepsilon(0)\left(\dfrac{r_m(0)}{r_m(T)}\right)^6$ as a result from the vibrational excitation of the molecule.

The motivation for this choice was that although Cl_2 is not spherically symmetric it is a rather simple small two atomic molecule with one vibrational frequency (ν=564.9 cm^{-1}). Therefore, the average over all orientations of pair interactions can be approximated spherically. The existence of the essential population of the vibrationally excited molecules supports the second considered model [3].

Our preliminary experience with planar BF_3 molecule encourages us to try the LJTDP [4] or (n-6) LJ potential models in this case.

3. Approximation of the existing experimental data by means of the LJTDP or (n-6) LJ potential

The parameters of the interaction potential between two chlorine molecules at T=0 K: $r_m(0)$, $\varepsilon(0)$, n and $\delta(0)$ are obtained by minimizing the sum F of squared deviations between M experimental (P_{exp}) and calculated (P_{calc}) values of the B, β and η, normalized to the accepted experimental error a_{exp}.

$$F=\sum_{i=1}^{M}R_i^2=\sum_{i=1}^{M}\left[\ln\left(\left|\frac{P_{calc,i}}{P_{\exp,i}}\right|\right)/a_{\exp,i}\right]^2$$

The details of the procedure are given elsewhere [5]

The transport and equilibrium properties of Cl_2 have been scarcely measured. Despite of its industrial importance only very few experimental input data are available. The set of existing experimental data is listed in Table 1. All 53 experimental values of B (5 works), β (1 work) and η (4 works) have been included in the simultaneous approximation in order to define the parameters of the used intermolecular potentials. Amongst them there are very precise measurements of the speed of sound in low-pressure [2]. The first experimental data for Cl_2 (B) have been determined from Pier in 1908 [6] and the last ones (β) from Hurly in 2002 [2]. Naturally, the last more sophisticated experiments and the new computational technique add more reliability to the results of modeling.

Table 1. Set of experimental data used for approximation.

Author	***M***	**Δ*T*/K**	***a*$_{exp}$/%**
Pier (1908) [6]	1*B*	273	5
Jaquerod and Tourpaian (1919) [7]	1*B*	298	5
Eacken and Hoffman (1929) [8]	3*B*	244-273	5
Morison (1972) [1]	4*B*	298-650	3-7
Hohm and Truemper (1995) [9]	9*B*	296-1080	2-75
Hurly (2002) [2]	13β	260-440	0.5-9
Rankine (1912) [10]	2η	286-372	2
Wobster and Muller (1940) [11]	6η	293-523	3
Trautz and Freytag (1934) [12]	5η	323-523	3
Braune and Linke (1930) [13]	9η	289-772	3
All *B* data	18*B*	244-1080	
All β data	13β	260-440	
All η data	22η	293-772	
All *B*, β, η data	53	244-1080	

4. Results and discussion

The potential parameters of the *"best"* solution of the ill-posed problem determine the most convenient potential of the selected type.

The *"best"* solution for the (*n*-6) LJ model was defined by 3 parameters: ε/k_B = 506.7±4.1 K, r_m=4.248±0.009×10^{-10}m, and *n* =27.89±0.53 with *RMS* = 1.484. Correspondingly, the values of the LJTDP parameters were found to be: ε/k_B= 499.4±5.5 K, r_m= 4.259±0.01×10^{-10} m, *n* = 26.34±0.80, and δ= 0.0088±0.0003×10^{-10} m with *RMS* = 1.473 [3].

A comparison of the results shows slightly smaller deviations between measured and calculated data for LJTDP calculations with compared with the (*n*-6) LJ potential. This unessential priority of the LJTDP is compensated by the simplicity of (*n*-6) LJ potential, which we recommend for calculations.

The deviations between measured and calculated by means of LJTDP *B*, β, η normalized to the experimental errors, a_{exp}, are shown on Fig. 1. It is transparent that the experimental points are situated symmetrically towards the calculated ones (zero line). Within one experimental error are about 75% (39 points) of all data. Unfortunately, the number of the experimental data (M=53) is not large enough to apply the Gauss distribution for further statistical analysis. The standard deviation (0.894) is nearly twice smaller than our *RMS*.

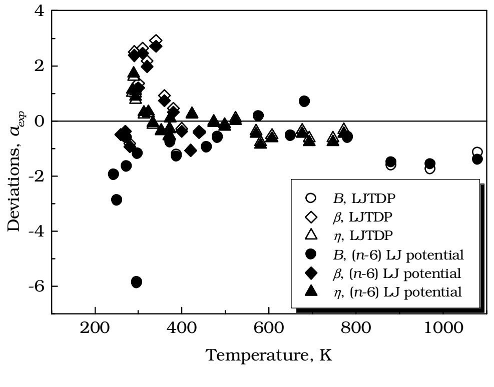

Fig. 1. Deviations between experimental and calculated with the both of potentials values of *B*, β, and η of Cl_2.

We recommend Table 2 of reference data for the thermophysical properties B, η and ρD.

Table 2. Thermophysical properties for gaseous chlorine obtained by means of the LJTDP and (n-6) LJ potential.

T, K	-B(LJ), cm^3/mol	-B(LJTDP), cm^3/mol	η(LJ), μPa.s	η(LJTDP), μPa.s	ρD(LJ).10^{-3}, g/m.s	ρD(LJTDP).10^{-3}, g/m.s
200	655.993	653.492	9.755	9.711	12.663	12.621
250	405.894	405.621	11.802	11.764	15.402	15.373
300	281.235	281.484	13.849	13.823	18.102	18.090
350	207.452	207.790	15.887	15.875	20.752	20.758
400	158.925	159.222	17.911	17.915	23.349	23.379
450	124.672	124.887	19.912	19.929	25.899	25.948
500	99.243	99.367	21.870	21.904	28.358	28.421
550	79.639	79.673	23.795	23.844	30.763	30.853
600	64.077	64.028	25.681	25.738	33.120	33.229
650	51.434	51.308	27.510	27.575	35.401	35.518
700	40.965	40.768	29.289	29.366	37.608	37.736
750	32.160	31.897	31.033	31.122	39.761	39.903
800	24.654	24.331	32.740	32.831	41.864	42.019
850	18.183	17.804	34.396	34.483	43.913	44.078
900	12.549	12.120	36.001	36.089	45.910	46.085

In Figs. 2 and 3 our calculations for B and η (full lines) are compared with the reference values recommended by the National Institute of Standards and Technology, USA (symbols). In both cases very good coincidence can be seen.

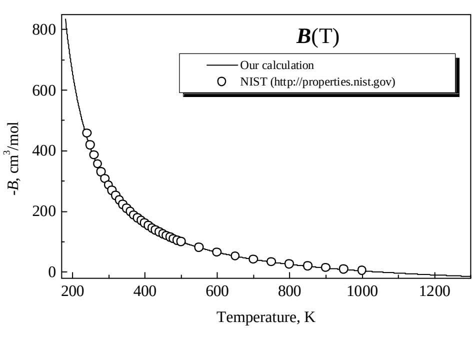

Fig. 2. Temperature dependence of B.

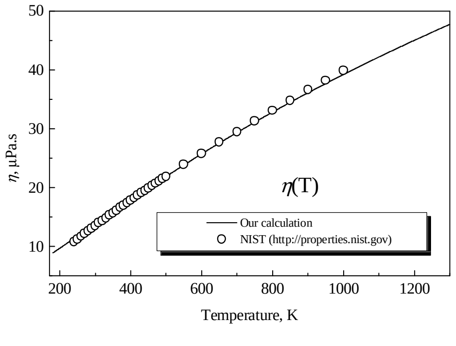

Fig. 3. Temperature dependence of η.

5. Conclusion

The calculations of the thermophysical properties of chlorine were successfully performed by two spherically-symmetric potentials. Our LJTDP gives slightly better *RMS* but we recommend using the (n-6) LJP for the sake of simplicity.

Algorithms for calculation the temperature dependencies $\eta(T)$, $\rho D(T)$ and B(T) are:

$$\eta(T) = 0.5805+0.04670828\times(T/\mathrm{K})-8.05020\times10^{-6}\times(T/\mathrm{K})^2,\ \mu\mathrm{Pa.s}$$

$$\rho D(T) = 1.10827+0.0600390\times(T/\mathrm{K})-1.106849\times10^{-5}\times(T/\mathrm{K})^2,\ 10^3\mathrm{g/m.s}$$

$$B(\mathrm{T}) = 78.630-82454.6/(\mathrm{T/K})+2784176/(\mathrm{T/K})^2-3.133953\times10^9/(\mathrm{T/K})^3,\ \mathrm{cm^3/mol}$$

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