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Second Virial Coefficients and Viscosity Property of Monatomic Alkali-Metal Gases

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Abstract

In this work, we have calculated the second virial coefficients B_2 of monatomic lithium, sodium, and potassium gases by using the most recent $^1\Sigma_g^+$ and $^3\Sigma_u^+$ Rydberg-Klein-Rees interatomic potentials. We have also determined the viscosity η and thermal conductivity λ coefficients of the alkali-metal vapors as a function of the temperature T. The results we have found of the collision integrals and of the coefficients η and λ agree quite well with some available experimental data. Besides, we have investigated the variation law with temperature T of the above thermophysical quantities. For temperatures ranging from 100 K to 3,000 K, the results can be reproduced by simple formulas $\eta(T) = AT^\alpha$ and $\lambda(T) = BT^\alpha$, where for T in Kelvin, η in micropoise, and λ in $10^{-3}\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$, for lithium Li: $A = 0.314$, $B = 0.1398$, and $\alpha = 0.863$; for sodium Na: $A = 0.624$, $B = 0.0846$, and $\alpha = 0.827$; for potassium K: $A = 0.400$, $B = 0.0320$, and $\alpha = 0.883$.

Keywords:

potential energy curve, transport cross section, collision integral, second virial coefficient, viscosity, thermal conductivity

1. Introduction

Most of previous computational works relative to the alkali thermophysical properties have been performed by using analytical or *ab initio* interatomic potentials. Besides, classical approaches have usually been adopted to describe the atom-atom collisions within dilute gases.

On the other hand, the growing interest in the Bose-Einstein condensation and in the ultracold atomic collisions has led to the need of precise interatomic potentials, which are presently widely available. This work aims at using such potentials to calculate the classical second virial coefficients of monatomic alkali-metal gases and to examine quantum-mechanically their viscosity properties with temperature.

The study is particularly concerned with dilute gases made up of lithium Li, sodium Na, or potassium K monatoms. We have used the singlet $X\ ^1\Sigma_\mathrm{g}^+$ and triplet $a\ ^3\Sigma_\mathrm{u}^+$ interatomic potentials as constructed by Côté *et al.* [1] for Li_2, Côté and Dalgarno [2] for Na_2, and Côté *et al.* [3] for K_2. These potentials $V_{s,t}(R)$ are constructed upon spectroscopic data and smoothly connected to the long-range R^{-n} form, with R being the internuclear separation and $n = 6, 8, 10$. They mainly allow the numerical resolution of the corresponding well-known radial wave equation and, therefore, the determination of the phase shifts $\delta_l^{(s,t)}(E)$ for both singlet (s) and triplet (t) molecular symmetries, with l being the angular momentum and E the relative energy.

2. Second virial coefficients

For one temperature T, these classical coefficients are defined by the formula [4]

$$B_2^{(s,t)}(T) = 2\pi N_\mathrm{A} \int_0^\infty R^2 \left[1 - e^{-V_{s,t}(R)/k_B T}\right] \mathrm{d}R, \quad (1)$$

where N_A is the Avogadro constant and k_B is the Boltzmann's constant.

The total second virial coefficients $B_2(T)$ are simply the weighted mean [5]

$$B_2(T) = \frac{1}{4} B_2^{(s)}(T) + \frac{3}{4} B_2^{(t)}(T). \quad (2)$$

Table 1 displays for some temperatures our results and compares them with published theoretical data [6-8]. The agreement is very good, mainly at higher values of T. In the range of lower temperature, the discrepancies between our results and those of Ref. [6] are important. That is because the authors of [6] have considered in their calculations the first and second quantum corrections.

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Table 1 The Li, Na, and K average second virial coefficients (in $\mathrm{m^3 \cdot mol^{-1}}$) as a function of temperature, compared with theoretical values from Nieto de Castro *et al.* [6], Holland *et al.* [7], and Holland and Biolsi [8].

	Li			Na			K	
T (K)	Present	[6]	[7]	Present	[6]	[8]	Present	[6]
1000	−0.90380	−0.81913		−0.04163	−0.03449	−0.03114	−0.00974	−0.00672
1500	−0.01975	−0.01861		−0.00306	−0.00271	−0.00262	−0.00154	−0.00117
2000	−0.00316	−0.00304		−0.00087	−0.00081	−0.00080	−0.00062	−0.00049
2250	−0.00175		−0.00185	−0.00058		−0.00054	−0.00046	
2500	−0.00110	−0.00107	−0.00104	−0.00041	−0.00039	−0.00039	−0.00035	−0.00028
2750	−0.00076		−0.00075	−0.00031		−0.00030	−0.00029	
3000	−0.00056	−0.00055	−0.00056	−0.00025	−0.00024	−0.00024	−0.00024	−0.00018

3. Viscosity and thermal conductivity

At intermediate temperatures, where the symmetry effects are negligible, the Chapman-Enskog approach to the solution of the Boltzmann equation leads to the expressions of the coefficients of viscosity and thermal conductivity [4]

$$\eta(T) = \frac{5}{4}\frac{\sqrt{2\mu\pi k_B T}}{\overline{\sigma}_V(T)} \qquad (3)$$

$$\lambda(T) = \frac{15}{4}\frac{k_B}{2\mu}\eta(T). \qquad (4)$$

In these relations, 2μ is the atom mass and, with $y = E/k_B T$,

$$\overline{\sigma}_V(T) = \int_0^\infty y^3 \sigma_V(k_B T y) e^{-y} \mathrm{d}y \qquad (5)$$

is the average cross section, also called collision integral. In this integral (5), the singlet and triplet viscosity cross sections $\sigma_V^{(s,t)}$ are given by [5]

$$\sigma_V^{(s,t)} = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}\frac{(l+1)(l+2)}{2l+3}\sin^2\left(\delta_{l+2}^{(s,t)} - \delta_l^{(s,t)}\right), \qquad (6)$$

$k = \sqrt{2\mu E}$ being the wave number. All quantities are in atomic units.

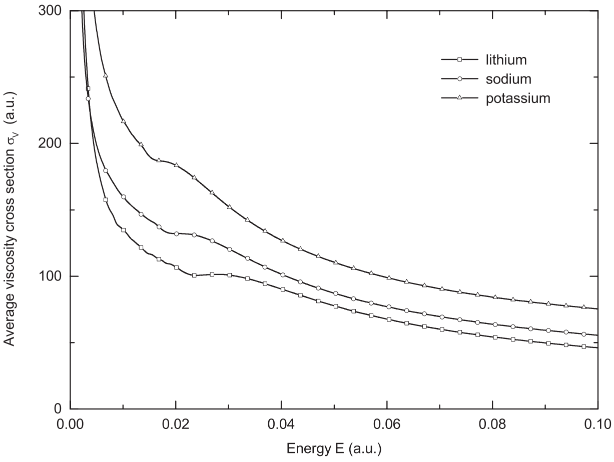

Fig. 1 Average viscosity cross section σ_V in terms of the energy E (a.u.).

Following the similar form as in Eq. (2), the total viscosity cross sections $\sigma_V(E)$ for the three ground alkali-metal systems are calculated. Their variations with E are shown in Fig. 1.

Equation (3) leads to the coefficient of viscosity $\eta(T)$. Figure 2 presents the variation of η with T and makes the comparison with the theoretical values esti-

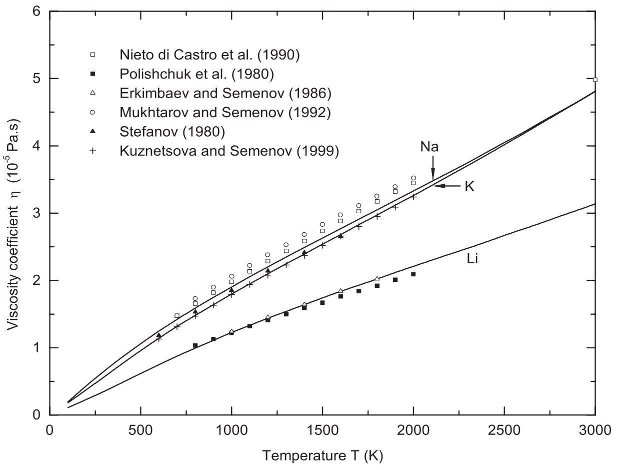

Fig. 2 Li, Na, and K viscosity coefficients η.

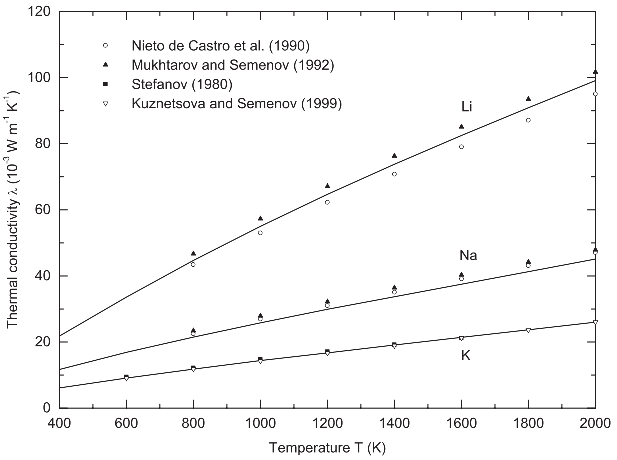

Fig. 3 Li, Na, and K thermal conductivity coefficients λ.

mated by several authors [6,9-12,14]. In comparing our results with those of Ref. [6], we find that the Li coefficients do not differ at any temperatures by more than 5.4 % and, contrary to the cases of Na and K, the lithium values of η in [6] are smaller than ours.

One may remark that the viscosity of gases increases in all cases with increasing temperature. This qualitative feature is particularly interesting, because the viscosity of liquids is observed to vary in exactly the opposite way.

Equation (4) gives the coefficient of thermal conductivity. Our numerical values of λ in $10^{-3}\ W{\cdot}\mathrm{m}^{-1}{\cdot}\mathrm{K}^{-1}$ are compared in Fig. 3 with those of Refs. [6] and [12] for Li and Na and with those of Refs. [11] and [14] for K.

There is in general a satisfactory accordance with the published results.

4. Temperature dependence

To find out the variation law of both thermophysical coefficients, we looked at the logarithmic derivative of the viscosity coefficient. From Eqs. (3) and (5), our analytical calculations lead to the expression

$$\frac{\mathrm{d}(\log_{10}\eta)}{\mathrm{d}(\log_{10}T)} = \frac{9}{2} - \frac{\int_0^\infty y^2\,\Phi_V(k_BTy)\mathrm{d}y}{\int_0^\infty y\,\Phi_V(k_BTy)\mathrm{d}y}, \qquad (7)$$

where $\Phi_V(k_BTy) = (k_BTy)^2\sigma_V(k_BTy)e^{-y}$. Figure 4 displays the behavior of this equation with T. It shows that at high temperatures it is approximately constant and has a value around 0.90.

The numerical values of $\eta(T)$ and $\lambda(T)$ can be reproduced, in the range of temperature $100 - 3{,}000$ K, by the simple formulas $\eta \sim AT^\alpha$ and $\lambda \sim BT^\alpha$. For η in $10^{-7}\,\mathrm{Pa}\cdot\mathrm{s}$, λ in $10^{-3}\,\mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}$, and T in K, we find $A = 0.314$, $B = 0.1398$, and $\alpha = 0.863$ for Li, $A = 0.624$, $B = 0.0846$, and $\alpha = 0.827$ for Na, and $A = 0.400$, $B = 0.0320$, and $\alpha = 0.883$ for K.

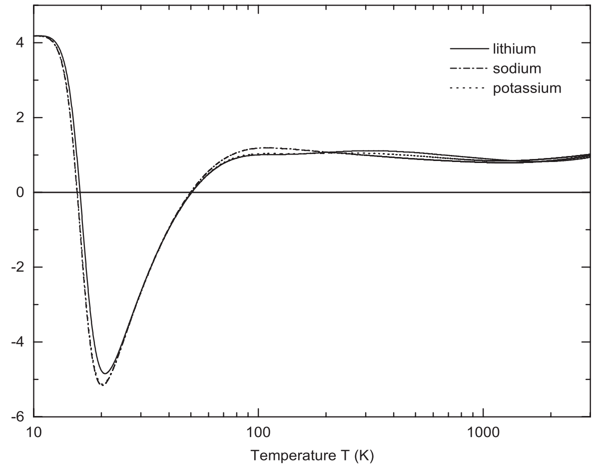

Fig. 4 Logarithmic derivative of $\eta(T)$ for the case of Li, Na, and K.

Acknowledgements

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