TRANSPORT PROPERTIES OF LITHIUM IN THE GAS PHASE

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The collision cross section of lithium atoms is determined by generalizing empirical data on the η and λ of Na, K, Rb, and Cs vapors and quantum calculations of the potential curves of Li_2. The η_1 and λ_1 of Li vapors are calculated.

The lack of published empirical data on the viscosity coefficient and thermal conductivity of gaseous lithium is explained by the considerable technical difficulties of working with lithium at high temperatures. Due to the low vapor pressures, investigations should be conducted at $T \geqslant 1200°K$, i.e., they should begin with temperatures at which experiments with other alkali metals are concluded. Studies of the viscosity and heat conductivity of Na, K, Rb, and Cs vapors have been conducted by many authors using various experimental methods. The results obtained in these studies are generally in agreement [1]. Table 1 shows collision cross sections found by averaging the bulk of the empirical data.

The error in the determination of σ_1^2 is 3-5% and depends on the metal and the temperature [1].

1. Determination of the Cross Section of Lithium Atoms from Empirical Data on the Transport Properties of the Vapors of Other Alkali Metals. The information available on transport properties permits several conclusions as to the features of change of cross sections σ_1^2 in vapors of alkali metals and makes it possible, on the basis of these conclusions, to determine the cross section of lithium atoms. Since hydrogen atoms interact in a manner similar to the atoms of alkali metals, we should include hydrogen in our search for laws describing cross-sectional behavior. There is no data on the cross sections of hydrogen atoms. Usually, the cross sections calculated by Vanderslice [2] are used. He determined the $^1\Sigma$ curve by combining the results calculated by Dalgarno [3] and spectroscopic data. For the $^3\Sigma$ curve, however, the data that was used [3] was inaccurate [4]. In our calculations, we used the more recent data of Kolos [5], which is very accurate and which agrees with the empirical data (within the limits of the experiment error). The approximation method of Hirschfelder and Eliason [6] was used to calculate the cross sections.

The potential curves [5] for $T = 700\text{-}1500°K$ are approximated by the exponents $U(r) = -198 \exp(-2.858r)$ and $U(r) = 111.7 \exp(-3.030r)$ (U in eV, r in Å). Table 1 shows curves calculated from these values and the tables of hydrogen-atom cross sections from [7, 8]. They exceed the values of the cross sections in [2] by ∿10%.

The covalent radius of the atom was chosen as the argument of the sought relation. According to [9], the value of R_{cov} for H, Li, Na, K, Rb, and Cs atoms is equal to 0.31, 1.34, 1.54, 1.96, 2.11, and 2.25 Å, respectively. It turns out that the calculated H cross

TABLE 1. Cross Sections of Atoms σ_1^2, Å²

T, K	H	Na	K	Rb	Cs
800	6,85	20,1	30,3	33,3	36,8
900	6,64	19,5	28,7	31,6	35,5
1000	6,46	19,0	27,2	30,2	34,4
1100	6,29	18,5	26,0	28,9	33,3
1200	6,14	18,0	24,9	27,8	32,3
1300	6,01	17,6	23,9	26,8	31,4
1400	5,89	17,2	23,1	25,9	30,6
1500	5,77	16,8	22,3	25,1	29,8

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TABLE 2. Coefficients of the Function $\sigma_1^2(R_{cov}) = a + bR_{cov}^2$ and Interpolational Lithium Cross Sections

T, °K	a	b	δa	δb	$\sigma_1^2 \pm \delta\sigma_1^2$, Å²
800	6,15	6,10	0,57	0,14	17,1±0,7
1000	5,95	5,53	0,34	0,08	15,9±0,4
1200	5,69	5,11	0,65	0,16	14,9±0,7
1500	5,37	4,61	0,97	0,24	13,7±1,0

sections and the averaged empirical cross sections of Na, K, Rb, and Cs atoms (Table 1) at the same temperature are described well by the linear function

$$\sigma_1^2(R_{cov}) = a + bR_{cov}^2 \tag{1}$$

Coefficients a and b of this function found by the least-squares method are shown in Table 2 for T = 800, 1000, 1200, and 1500°K. Equation (1) makes it possible to compute cross sections in lithium vapors. The quantity $\sigma_1^2 = 15.9$ Å² at T = 1000°K, with a standard deviation here of 0.4 Å² (see Table 2).

Performing the calculations using the σ_1^2 of hydrogen found by Vanderslice decreases the lithium cross section by about 2%, while the latter is increased by about 0.5% when the cross sections determined by the asymptotic method are used. The quadratic function $\sigma_1^2(R_{cov})$ gives the best average and the lowest error of the lithium σ_1^2. However, since the cross section changes only by several hundredths of a percent, Eq. (1) is sufficiently reliable.

2. Theoretical Methods of Determining the Lithium Cross Section. All known tables of the viscosity and thermal conductivity of lithium vapors [10-14] are based on theoretically calculated cross sections. Here, approximation methods were used to determine the potential curves of the atom interactions. The authors estimate the error of the cross sections to be 30%. The calculated cross sections are larger than those found from viscosity and heat conductivity experiments, the difference between these results increasing from cesium to sodium. For example, at T = 1000°K, the calculated Cs cross sections are 20% larger than the empirical values. The difference is 40% in the case of sodium. The theoretical Li cross sections exceed the cross sections determined from Eq. (1) by an even greater amount. Such large discrepancies are due mainly to the crudity of the methods used to determine the potential curve for the triplet state. There is spectroscopic data for the singlet state which makes it possible to determine the potential curve close to the equilibrium state, and it is necessary only to extrapolate into the region of low energies (large spacings). This has been done by various semiempirical methods [15, 16] and from the curve for hydrogen [17] using the method of reduced potential curves [18], which takes into account polarization of atomic shells. Thus, the difference in the cross sections obtained by different authors for the singlet state does not exceed 25%. As a result, the difference in the total cross sections is no more than 10%.

There is no empirical data for the triplet state. In [17], the results of which were used by Bonilla in compiling tables [10, 11], the potential curve was obtained by the same method using the same decay constant as for the curve of the singlet state, although the polarization of the shells is qualitatively different.

In the calculations in [15, 16], the curve was found as a first approximation by the Gaitler—London method. As is well known, this method produces results which agree only qualitatively with the empirical data.

In [14], the potential curves were determined by the asymptotic method. In calculating the cross sections, the authors ignored dispersion interactions. However, dispersion forces play a very large role in the case of atoms of alkali metals. This is shown by the large values of the Van der Waals coefficients, exceeding by three orders the values of the same coefficients for the hydrogen atom [19]. If the formulas and values of the constant in [14] are used, then the potential of the exchange forces for the atomic spacings calculated in the same work is only 20-40% greater than the potential of the dispersion forces. According to more accurate quantum-mechanical calculations [20], in the singlet state the exchange potential reaches only 0.9 the potential of the dispersion forces; in the triplet state,

TABLE 3. Cross Sections of Atoms and the Viscosity Coefficient and Thermal Conductivity of the Atomic Component of Lithium Vapors

T, °K	σ_1^2, Å^2	$\eta_1 \cdot 10^7$, Pa·sec	$\lambda_1 \cdot 10^4$, W/m·deg
1000	15,5	143	644
1100	15,2	153	690
1200	14,9	163	736
1300	14,6	173	780
1400	14,4	183	824
1500	14,1	193	867
1600	13,9	202	909
1700	13,7	211	951
1800	13,5	221	992
1900	13,3	230	1033
2000	13,2	239	1073

the former exceeds the latter only at spacings less than, and close to, the equilibrium spacing. Thus, dispersion forces cannot be ignored in calculations of the cross sections of lithium atoms or, in general, the atoms of alkali metals.

An error was made in the calculations in [14]: the atomic spacings for a viscous cross section in the triplet state were calculated using the formula for a diffuse cross section, so that the cross section in the triplet state turned out to be 30% smaller.

Attempts have been made to correct theoretical cross sections with allowance for experimental data. For example, the effective cross sections recommended in [12] and used in this book to compile viscosity and heat conductivity tables were obtained by combining theoretical and empirical data. However, the empirical data accumulated up to that time was not substantial, and the correction of the cross sections was only approximate.

3. Use of Quantum-Mechanical Potential Curves. The highly approximate character of the above-examined methods of calculating the cross sections of lithium atoms becomes all the more clear if the results of quantum-mechanical calculations of Li_2 potential curves are used. In recent years, these calculations have reached a degree of accuracy such that the binding energy of lithium atoms can be reliably computed not only for spacings close to equilibrium, but also for large spacings — when dispersion forces become decisive. Let us use the results of recent works: [20] for the states $^1\Sigma_g^+$ and $^3\Sigma_u^+$, and [21] for $^3\Sigma_u^+$. Both works employed the multiconfigurational method of a self-consistent field (MC SCF), with optimization of the valence configurations (OVC). For $T = 500\text{–}6500$°K, the data in [21] can be approximated by the exponent $U(r) = 1296.5 \exp(-r/0.3123)$. The data in [20] for the singlet state can be approximated by the exponent $U(r) = -50.55 \exp(-r/0.8527)$ (for $T = 600\text{–}7000$°K). Cross sections calculated from the curves using the tables of Monchik [7] and Brokaw [8] are shown in Table 3. The value of σ_1^2 changes within ±1.5% when the data in [21] is approximated in other temperature intervals. The error of the resulting cross sections is the sum of the error of the potential curves and the error of the method used to calculate the cross sections from the curves. Its maximum value may be determined ±1.5%. The cross sections of lithium atoms in the ground state calculated from the curves in [20] and determined from the spectroscopic data in [22] for temperatures at which cross sections could be calculated from the second curve differ by less than 0.6%, which is evidence of the great accuracy of the theoretical potential curve. As shown by the calculations in [23], the error of the Hirschfelder—Eliason approximation method does not reach 5% under our conditions ($T < 2000$°K). The viscosity coefficient and thermal conductivity of the atomic component of lithium vapors obtained on the basis of potential curves calculated by the quantum-mechanical method are shown in Table 3 and can be calculated from the equations

$$\eta_1(T) \cdot 10^7 = 143.9 + 0.0955\,(T - 1000) \text{ Pa·sec}, \tag{2}$$

$$\lambda_1(T) \cdot 10^4 = 647.5 + 0.4296\,(T - 1000) \text{ W/m·K} \tag{3}$$

The error in approximating the data with these equations is less than 0.6%.

The lithium cross sections σ_1^2 that were found agree well with the results of calculations by Eq. (1). The difference between these results lies within the limits of the standard deviation of interpolations according to Eq. (1). The error of σ_1^2 when determined from potential curves calculated by the quantum-mechanical method is roughly equal to the errors of the cross sections found from empirical data on the transport properties of alkali metal vapors. Thus, it is best to base determinations of the transport properties of the atomic component of lithium vapors on the results of current quantum-mechanical calculations of the binding energy of lithium atoms.

NOTATION

T, absolute temperature; P_{sat}, pressure on the saturation line; η, coefficient of absolute viscosity; λ, thermal conductivity; $\sigma_1^2 = \sigma_1^2\Omega^{(2,2)*}$, collision cross section; R_{cov}, covalent radius; U(r), potential binding energy of atoms at a distance r; δ, standard deviation of the value. The index 1 denotes the atomic component.

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INTERACTION POTENTIALS AND COLLISION INTEGRALS FOR HYDROGEN AND ALKALI METAL ATOMS

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Interaction potentials between hydrogen and alkali metal atoms have been calculated. Calculated values of collision integrals in the temperature range 700-1500°K are reported.

1. The calculation of transport coefficients for a mixture of hydrogen and alkali metals is of great interest for various practical purposes. Ordinarily these calculations are based on the well-developed Chapman—Enskog method which gives expressions for the transport coefficients in the form of determinants whose elements are collision integrals. Thus, the problem of calculating transport coefficients is reduced to the calculation of collision integrals in terms of interaction potentials.

The interaction potentials of particles separated by distances larger than their dimensions can be represented as the sum of an exchange part and a long-range part [1]. The long-range part has been thoroughly studied [1, 2], but calculations of the exchange part are quite difficult. The procedures presented in [3] for the interaction of identical alkali metal atoms, and in [4] when the ionization potentials of the atoms are very different cannot be applied in our case, since the ionization energy of a hydrogen atom is larger than the ionization energy of an alkali metal atom, and the difference between them is of the same order of magnitude as the quantities themselves.

2. We turn to the calculation of the exchange part of the interaction potential between hydrogen and alkali metal atoms.*

Let Ψ and Ψ^S be the wave functions of the valence s electron in an alkali metal atom M in the absence and presence of an excited hydrogen atom. The Schrödinger equation for these wave functions has the form

$$-\frac{1}{2}\Delta\Psi + V_M\Psi = E\Psi,$$

$$-\frac{1}{2}\Delta\Psi^s + V_M\Psi^s + V_H^s\Psi^s = E^s\Psi^s. \qquad (1)$$

Here V_M and $V_H{}^S$ are the interaction potentials of a valence electron of atom M with its own atomic core and with a hydrogen atom, respectively; the latter depends on the total combined spin of the two-electron system.

We multiply the first of Eqs. (1) by Ψ^S, the second by Ψ, subtract one from the other, and integrate the result over a volume excluding the hydrogen atom. In this region where the valence electron of atom M is largely concentrated $V_H{}^S = 0$, $\Psi \simeq \Psi^S$, and therefore we obtain for the exchange interaction

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*Another approach to this problem is presented in detail in [5].

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