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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  $\Psi$  and  $\Psi^s$  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

$$\begin{aligned} -\frac{1}{2}\Delta\Psi + V_M\Psi &= E\Psi, \\ -\frac{1}{2}\Delta\Psi^s + V_M\Psi^s + V_H^s\Psi^s &= E^s\Psi^s. \end{aligned} \quad (1)$$

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  $\Psi^s$ , the second by  $\Psi$ , 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  $V_H^s = 0$ ,  $\Psi \approx \Psi^s$ , and therefore we obtain for the exchange interaction

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

TABLE 1. Parameters of Interaction Potentials of Hydrogen and Alkali Metal Atoms, Atomic Units

M	Li	Na	K	Rb	Cs
J <sup>(0)</sup>	-11,96	-11,45	-4,50	-3,60	-2,78
J <sup>(1)</sup>	1,94	1,89	0,90	0,75	0,61
C <sub>6</sub>	66,5	73,3	105,7	114,6	132,9
C <sub>8</sub>	3127	3742	7076	8186	10690

$$U_{\text{ex}} = E^s - E = \frac{1}{2} \oint_S [\Psi^s \nabla \Psi - \Psi \nabla \Psi^s] ds, \quad (2)$$

where S is the inside of a surface of radius  $r_0 \ll R$  bounding the volume enclosing the hydrogen atom.

We write the wave function  $\Psi^s$  in the form

$$\Psi^s = \Psi \chi^s, \quad (3)$$

where  $\chi^s$  is a correction factor to take account of the distortion of the wave function as a result of the interaction with the hydrogen atom.

Since  $r_0 \ll R$ , we can use the asymptotic form for  $\Psi$  [1, 5]:

$$\Psi = \frac{A}{\sqrt{4\pi}} R^{1/\beta-1} \exp(-\beta R) \exp(-\beta(n, r)), \quad n = \frac{\mathbf{R}}{R}, \quad (4)$$

in evaluating (2), where  $\beta^2/2$  is the ionization potential of the alkali metal atom, and the factor A determining the asymptotic behavior is given in [1].

Using Eq. (4) to evaluate (2), we find

$$U_{\text{ex}}^s = \frac{A^2}{4\pi} B^s R^{2/\beta-2} \exp(-2\beta R), \quad (5)$$

$$B^s = \frac{1}{2} \oint_S ds \left( \frac{\partial}{\partial r} \chi^s \right) \exp(-2\beta r_0 \cos \theta).$$

Substituting (3) into (1), we find the equation for  $\chi^s$ :

$$\beta n \nabla \chi^s + V_{\text{H}}^s \chi^s = 0. \quad (6)$$

As a result of choosing the surface S with a radius  $r_0 \gg 1/\alpha$  ( $\alpha^2/2$  is the ionization potential of a hydrogen atom), the second derivatives could be neglected in deriving (6). As a boundary condition for Eq. (6) it is necessary to assume  $\chi^s \rightarrow 1$  near atom M.

Equation (6) is of first order, and its solution contains one arbitrary constant. Since Eq. (6) is homogeneous, this constant determines only the normalization of the solution for  $\chi^s$ . We note that in evaluating the surface integral in (5) it is important to know the nature of the variation of  $\chi^s$  near the surface S, which means also that the character of the variation of the potential is important only in this narrow region. Since an accurate calculation of  $V_{\text{H}}^s$  generally requires solving a complicated two-electron problem, taking account of the minor requirements imposed on the region in which the potential  $V_{\text{H}}^s$  must be known, it is convenient to model it by a simple relation such as  $V_{\text{H}}^s = -\alpha^s/2r^k$ . In this case we solve Eq. (6) to within a normalization factor which is evaluated from the condition for joining the solution found with the solution near atom M, which is equal to unity by virtue of the boundary conditions.

For concrete calculations we chose  $k=4$ , for which the solution of Eq. (6) has the form

$$\chi^s = \exp \left\{ \frac{\alpha}{2\beta r^3} f(\theta) \right\},$$

$$f(\theta) = \frac{\cos \theta \sin \theta - \theta}{2 \sin^3 \theta}, \quad 0 \leq \theta \leq \frac{\pi}{2},$$

TABLE 2. Collision Integrals for Hydrogen and Alkali Metal Atoms

M	T, °K	$\sigma^2\Omega_a^{(1,1)*}$	$\sigma^2\Omega_s^{(1,1)*}$	$\sigma^2\Omega^{(1,1)*}$	$\sigma^2\Omega_a^{(2,2)*}$	$\sigma^2\Omega_s^{(2,2)*}$	$\sigma^2\Omega^{(2,2)*}$
Li	700	9,5	27,1	13,9	12,8	25,2	15,9
	400	8,8	25,7	13,0	11,9	23,8	14,9
	1100	8,2	24,6	12,3	11,2	22,7	14,1
	1300	7,7	23,6	11,7	10,7	21,8	13,5
	1500	7,3	22,6	11,2	10,2	21,1	12,9
Na	700	9,7	27,6	14,2	13,0	25,6	16,2
	900	8,9	26,1	13,2	12,1	24,3	15,2
	1100	8,3	25,1	12,5	11,4	23,2	14,4
	1300	7,8	24,0	11,9	10,9	22,2	13,7
	1500	7,4	23,2	11,4	10,4	21,5	13,2
K	700	11,8	33,3	17,2	16,0	30,9	19,8
	400	10,8	31,6	16,0	14,9	29,2	18,5
	1100	10,0	30,1	15,0	14,1	27,8	17,5
	1300	9,4	29,0	14,3	13,4	26,7	16,7
	1500	8,9	28,0	13,7	12,8	25,7	16,0
Rb	700	12,1	34,2	17,7	16,7	32,5	20,7
	900	11,2	32,5	16,5	15,5	30,1	19,2
	1100	10,3	31,1	15,5	14,6	28,7	18,1
	1300	9,7	29,8	14,7	13,8	27,5	17,5
	1500	9,1	28,8	14,0	13,2	26,5	16,5
Cs	700	13,6	38,1	19,7	18,6	35,3	22,8
	900	12,5	35,9	18,4	17,3	33,3	21,3
	1100	11,6	34,3	17,3	16,3	31,7	20,2
	1300	10,8	32,9	16,3	15,5	30,3	19,2
	1500	10,2	31,7	15,6	14,7	29,2	18,3

$$f(\theta) = \frac{\pi - \theta + \cos \theta \sin \theta}{2 \sin^2 \theta}, \quad \frac{\pi}{2} \leq \theta \leq \pi, \quad (7)$$

where  $\theta$  is the angle between  $\mathbf{n}$  and the radius vector  $\mathbf{r}$  from the hydrogen atom.

We note that (5) depends explicitly on the choice of  $r_0$ ; this is related to the approximate character of the solution of the problem. To ensure that the choice of  $r_0$  has the smallest effect on the solution for  $B^S$ , it is reasonable to choose it from the condition  $\partial B^S / \partial r_0 = 0$ . Since the dependence in the exponential in (5) is determined mainly by the factor  $2\beta r_0 \cos \theta$ , we find  $r_0 = 3/2\beta$ , which satisfies the condition  $r_0 \gg 1/\alpha$ . A comparison with the results in [6] for Li gives  $\alpha^{(0)} = 21.9$  and  $\alpha^{(1)} = -7.2$ . These values were used in Eqs. (7) and (5) to calculate  $J^{(s)} = (A^2/2\pi)B^S$  for all the alkali metal atoms. A numerical analysis shows that the results vary slowly with  $k$  and  $r_0$ . Finally the expression for the H-M potential has the form

$$U^s(R) = \frac{J^{(s)}}{2} R^{2/\beta-2} \exp(-2\beta R) - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \dots \quad (8)$$

The parameters of the potential (8) are listed in Table 1. The values for  $C_6$  and  $C_8$  were taken from [2]. The series determining the long-range interaction is asymptotic, and therefore each subsequent term must be retained if it is not larger than the preceding [1].

3. We report the results of calculating the collision integrals by using the potentials described by Eq. (8) and Table 1. Denoting by subscripts  $\alpha$  and  $s$  the collision integrals when the total spin of the atoms is equal to 1 and 0, respectively, we have

$$\begin{aligned} \sigma^2\Omega^{(1,1)*} &= \frac{3}{4} \sigma^2\Omega_a^{(1,1)*} + \frac{1}{4} \sigma^2\Omega_s^{(1,1)*}, \\ \sigma^2\Omega^{(2,2)*} &= \frac{3}{4} \sigma^2\Omega_a^{(2,2)*} + \frac{1}{4} \sigma^2\Omega_s^{(2,2)*}. \end{aligned} \quad (9)$$

In evaluating the collision integrals for triplet scattering we take account of the fact that the triplet potential falls off sharply and is repulsive for energies of the order of thermal and higher. Therefore, we can use the hard-sphere model proposed in [7, 8], according to which

$$\begin{aligned}\sigma^2\Omega_a^{(1,1)*} &= R_{1-1}^2, U^{(3)}(R_{1-1}) = 2.25 T, \\ \sigma^2\Omega_a^{(2,2)*} &= R_{2-2}^2, U^{(3)}(R_{2-2}) = 0.83 T.\end{aligned}\quad (10)$$

Here T is the temperature and  $U^{(3)}$  is the triplet potential calculated in Sec. 2. The difference in the numerical coefficients of T on the right-hand sides of Eqs. (10) determining  $R_{1-1}$  and  $R_{2-2}$  is related to the correct account of the dependence of the scattering angle on the impact parameter [7, 8].

In the singlet state the interaction corresponds to attraction, and therefore it is expedient to use the "capture" model. According to this model of scattering a long-lived complex is formed which subsequently decays isotropically in all directions. The cross section  $\sigma_0(E)$  for the formation of the complex at a relative kinetic energy E is given by the relation [9]

$$\sigma_0(E) = \pi R_0^2 [1 + |U^{(1)}(R_0)/E|], \quad U^{(1)}(R_0)/E = 1 - (R_0 U^{(1)'}(R_0))/2E. \quad (11)$$

The collision integrals are expressed in terms of  $\sigma_0(E)$  [7]:

$$\sigma^2\Omega_s^{(1,1)*} = \frac{1}{\pi} \sigma_0(2.52 T), \quad \sigma^2\Omega_s^{(2,2)*} = \frac{1}{\pi} \sigma_0(3.51 T). \quad (12)$$

The values of the collision integrals calculated by Eqs. (9)-(12) are listed in Table 2.

4. The Li-H collision integrals have been calculated earlier. The values in [10, 11] are larger than our results by 50-60%, which corresponds to the authors' estimate of their computational error [10]. The difference is accounted for by the overestimate by almost a factor of two of the values of the interaction energy of Li and H atoms in the triplet state, and is related to the very crude method of obtaining the triplet curve.

Unfortunately, the lack of experimental data makes it difficult to estimate the accuracy of our calculation directly, but an indirect estimate can be made. A comparison of the values of collision integrals calculated by the asymptotic method for atomic vapors of alkali metals [7] with calculations [10] for Li-Li shows that the values in [10] are larger than those in [7], as in our case, by 50-60%, and a comparison of the results in [7] with the experimental paper [12] shows a difference of ~15-20%. Since the collision integrals in [7] were evaluated by the same method as ours, we estimate the accuracy of our results is ~15-20%.

#### NOTATION

$\Psi$ , wave function of valence electron of alkali metal atom;  $\psi^s$ , wave function of this same electron taking account of the interaction with a hydrogen atom; E,  $E^s$ , energy levels of valence electron;  $V_M$ ,  $V_H^s$ , interaction potentials of electron with core of alkali metal atom and with a hydrogen atom;  $U_{ex}$ , exchange interaction potential;  $\chi^s$ , correction to wave function;  $\alpha^2/2$ ,  $\beta^2/2$ , ionization potentials of hydrogen and alkali metal atoms;  $J^{(s)}$ , parameter determining exchange interaction;  $C_6$ ,  $C_8$ , long-range interaction parameters;  $\sigma^2\Omega_a(i,j)^*$ ,  $\sigma^2\Omega_s(i,j)^*$ , collision integrals for triplet (a) and singlet (s) scattering;  $R_{1-1}$ ,  $R_{2-2}$ , collision parameters;  $\sigma_0(E)$ , cross section for formation of complex;  $U^{(s)}(R)$ , interaction potential of atoms; R, distance between atoms.

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SPECIFIC HEATS OF THALLIUM SULFIDE, SELENIDE,  
AND TELLURIDE AT LOW TEMPERATURES

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Specific heats of TlX (X = S, Se, and Te) semiconductor crystals were studied at low temperatures. The Debye temperatures and the thermodynamic parameters of these compounds were determined.

The physical properties of type AIII<sub>1</sub>B<sub>2</sub>VI (A = Ga, In, Tl; B = S, Se, Te) semiconductor compounds have been studied intensively in the last few years. These crystals are strongly anisotropic, and various semiconductor devices based on them have been produced — lasers, memory elements, switching mechanisms, etc. The operating conditions of these devices are determined largely by the thermal characteristics of the crystal employed. On the other hand, the study of thermal properties, in particular the specific heat, is of great interest for the development of crystal physics.

The specific heats of certain representative semiconductors of the AIII<sub>1</sub>B<sub>2</sub>VI type were studied at low temperatures in [1, 2].

Samples of TlX (X = S, Se, Te) were obtained by vacuum ( $1.33 \cdot 10^{-2}$  N/m<sup>2</sup>) melting of the elementary components in a stoichiometric ratio with subsequent annealing of the compounds formed to homogenize them. An x-ray analysis showed single-phase samples were present; the tetragonal lattice constants at room temperature were:  $a = 7.75$ ,  $c = 6.80$ ;  $a = 8.03$ ,  $c = 7.00$ ;  $a = 12.96$ ,  $c = 6.18$  Å, respectively, for TlS, TlSe, and TlTe, and are in good agreement with values in [3, 4].

It should be noted that the thallium monochalcogenides we studied have a tetragonal lattice structure. However, a study [5] of the TlTe structure showed that the spatial distribution of atoms in a unit cell of TlTe is significantly different from that in TlS and TlSe.

The specific heats of TlX (X = S, Se, Te) crystals were measured with the arrangement described in [6]. Adiabatic conditions were maintained by automatic precision temperature controls of the PRT-2M type. The temperature of the calorimeter was measured with TSG-2, and TSPN-2B germanium and platinum resistance thermometers. The error of the measurements below 4°K was estimated as 5% or less, and above 5°K as 1.5-0.2%.

The experimental values of the specific heats of TlX (X = S, Se, Te) compounds are shown in Fig. 1 together with earlier data [7, 8] and data from [9]. The smoothed-out values of  $C_p(T)$  are listed in Table 1.

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