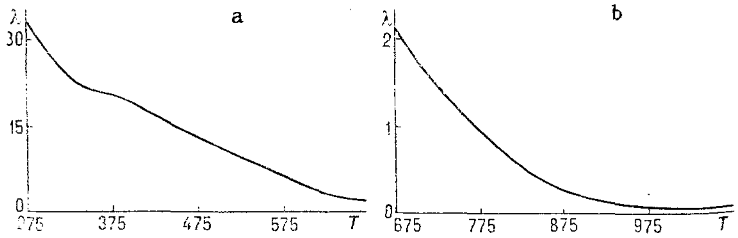

Fig. 3. Dependence of λ on T for the material studied in the two temperature ranges, K: a) 275-675; b) 675-875.

It is, moreover, lower than that of pure aluminum oxide. This is explained by the presence in the test material, apart from aluminum oxide, of other specially chosen components which also give it the necessary durability and guarantee high production effectiveness in the manufacture of various heat-reflecting components and coatings.

NOTATION

$\lambda(T)$, temperature dependence of thermal conductivity; Θ, quantity introduced by Kirchhoff substitution; $T_{\min}$, $T_{\max}$, bounds of the temperature range; E, difference value; s, number of intervals; R_C, thermal contact resistance; C, undefined constant; x, spatial coordinate; L, length; q, heat flux density.

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CALCULATION OF THE DIFFUSION COEFFICIENTS OF ALKALI AND ALKALI-EARTH METAL VAPOR IN HELIUM BY EXCHANGE PERTURBATION ANALYSIS

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UDC 535.15

The potential energy of metal–helium interaction is calculated by the quantum-mechanical exchange perturbation theory. The results are used to calculate the diffusion coefficient of alkali and alkali-earth metal vapor in helium. The values of the saturated-vapor pressure of barium at 1170-1420 K are refined from a comparison with experimental diffusion data.

Calculation of the diffusion coefficient of monoatomic vapor of metals in helium from the formula of the first-approximation Enskog–Chapman theory [1]

$$PD_{12}=\frac{3}{16\pi}\,\frac{\sqrt{2\pi\,(kT)^3/m_{12}}}{\sigma_{12}^2\Omega_{12}^{(1,1)*}}\qquad(1)$$

requires that the potential energy $\varphi(R)$ of the interatomic interaction be known. The reduced collision integral $\Omega_{12}^{(1,1)*}$ and the cross section $Q_{12}^{(1,1)}\equiv\sigma_{12}^2\Omega^{(1,1)*}$ depend on this energy.

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The main contribution to the cross section $Q_{12}^{(1,1)}$ comes from the potential-energy range roughly from fractions of the calculation temperature T to 4T. The potential $\varphi(R)$ can be calculated by quantum-mechanical methods in the Born—Oppenheimer approximation of arrested atomic nuclei [2].

Complete nonempirical quantum-mechanical calculations by the Hartree—Fock self-consistent field method with the molecular electron orbitals represented by linear combinations of the respective atomic orbitals are extremely complicated in regard to computation, especially when the configuration interaction (CI) is incorporated. This must be done to determine the potential energy correctly at large interatomic distances and to refine its values at small and intermediate distances. The number of such calculations is limited. For the cases of interest to us, i.e., interaction with helium atoms, nonempirical calculations incorporating CI have been done for lithium [3] and magnesium atoms [4, 5] and without CI for lithium, sodium [6] and beryllium [7]. Semi-empirical quantum-mechanical calculations have also been carried out for the interaction with helium atoms of atoms of all alkali metals and magnesium (e.g., [8,9]). All such calculations are variational and require much computer time.

At the same time a number of simpler versions of the nonempirical exchange perturbation theory (EPT) [2, 10] have been developed, making it possible to calculate the potential interaction energy at intermediate as well as long distances. This theory takes the overlapping of electron shells of atoms into account and the interaction of the shells is treated as a perturbation. thus far EPT has been used only to calculate interactions in the simplest systems (e.g., He—He, H^+—H, H—H) [10, 11]. The more complex Cs—He and Rb—He systems were calculated in [12], but for large distances (R > 7 a.u.).

Exchange perturbation theory can be used in calculations of the potential $\varphi(R)$ of the interaction of alkali and alkali-earth metals with helium atoms in order to determine the cross section $Q_{12}^{(1,1)}$ and in subsequent calculations of the diffusion coefficients from Eq. (1). As in the calculations in [5, 8], in this case only the interaction of the valence electrons of a metal atom (one electron in the case of alkali metals and two in the case of alkali-earth metals) with two electrons of a helium atom can be taken into account explicitely. Valence electrons and a positively charged core are thus distinguished in the metal atom. The (Coulomb and exchange) interaction of the valence electrons and the core electrons as well as the all-electron wave function orthogonality are taken into account by introducing pseudopotentials U(r) and valence electron pseudofunctions, e.g., of the type in [13]. The valence electron pseudofunctions are constructed so that at distances greater than the core radius they coincide with the Hartree—Fock electron functions and are unconditional (nonoscillating) at shorter distances. When the pseudopotential has been introduced the law of electron-core attraction becomes $-Z_a/r + U(r)$. In our calculations we use the pseudopotentials and valenace electron pseudofunctions from [13], where they are given as expansions in the Gaussian functions. A characteristic feature of the Gaussian functions is that they depend exponentially on the squared distance to the electron.

The problem is formulated in the Born—Oppenheimer approximation, while the Hamiltonian of a system of two atoms is represented as the sum of the Hamiltonians of the isolated atoms and the perturbation operator V. In the atomic system of units

$$\hat{V}=\sum_{j=1}^{N_b}\left(-\frac{Z_a}{r_{aj}}+U(r_{aj})\right)-\sum_{i=1}^{N_a}\frac{Z_b}{r_{bi}}+\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\frac{1}{r_{ij}}+\frac{Z_aZ_b}{R}.$$

Subscript a pertains to the metal atom; b to the helium atom; i and j correspond to electrons of atoms a and b, respectively; $Z_b = N_b = 2$.

The perturbation operation written takes into account the Coulomb interaction of helium electrons with the core of the metal and isolated valence electrons of the metal with the helium nucleus, as well as valence electrons of the metal atom and electrons of the helium atom, the metal core, and the helium nucleus. An operator for the transposition of electrons between atoms is introduced into the wave function of the system to incorporate the exchange repulsive interaction of atoms at intermediate distances, when the electron orbitals overlap [2, 10, 14].

We carry out specific calculations using an EPT technique [14] (the varius versions of the EPT, as a rule, lead to identical results up to the second approximation inclusively and subsequent approximation make an insignificant contribution to $\varphi(R)$ [2]). In [14] the interatomic potential is written as the series

$$\varphi(R) \equiv E-(E_a+E_b)=E^{(10)}+E^{(12)}+E^{(20)}+E^{(22)}+\ldots, \tag{2}$$

where E is the total energy of the system; and E_a and E_b are the energies of isolated atoms. The first superscript at the terms of the expansion on the right side of (2) denotes the order of the approximation in the perturbation operator and the second superscript, in the overlap integral of the wave functions of the metal valence electrons and the helium electrons.

The first two terms in the expansion (2) are calculated from the formulas

$$E^{(10)}=\int \Psi_0 \hat{V} \Psi_0 d\tau,$$

$$E^{(12)}=-\int (\hat{P}_1\Psi_0)\hat{V}\Psi_0 d\tau + E^{(10)}\int (\hat{P}_1\Psi_0)\Psi_0 d\tau,$$

where Ψ_0 is the product of the wave functions Ψ_0^a and $\Psi_0{}^b$ of isolated atoms; $\hat{P}_1$ is an operator which acts on Ψ_0 by transposing valence electrons between interacting atoms (one electron in each transposition). The integration is carried out over the entire configuration space of the isolated electrons, where $d\tau = \prod_{j=1}^{N_a+N_b} d\tau_i$ is a differential element of this space. The term $E^{(10)}$ has the connotation of electrostatic energy and $E^{(12)}$ is the exchanged energy. The approximation of Unsöld [15] is used to calculate the third and fourth terms in (2) as

$$\begin{gathered}
E^{(20)}=-\frac{1}{\Delta E}\left[\int \Psi_0 \hat{V}^2 \Psi_0 d\tau-\left(\int \Psi_0 \hat{V} \Psi_0 d\tau\right)^2\right], \\
E^{(22)}=-\frac{1}{\Delta E}\left[-\int (\hat{P}_1\Psi_0)\hat{V}^2\Psi_0 d\tau+\int (\hat{P}_1\Psi_0)\Psi_0 d\tau \int \Psi_0 \hat{V}^2 \Psi_0 d\tau-2E^{(10)}E^{(12)}\right]
\end{gathered} \tag{3}$$

where $E^{(20)}$ is the polarization energy and $E^{(22)}$ is the exchange-polarization energy. The mean Unsöld energy ΔE is chosen so that at large distances $E^{(20)}$ calculated from Eq. (3) would coincide with the first term of the asymptotic expansion of $E^{(20)}$ obtained in perturbation theory without exchange. This term has the form $-C_6/R^6$; values of the constant C_6 are given in [16].

The wave functions Ψ_0^a and $\Psi_0{}^b$ of isolated atoms are expressed by Slater determinants. The determinant consists of the products of the spin functions and pseudofunctions of the valence electrons for the metal atom [13] while for the helium atom it consists of two electron orbitals, whose spatial part is represented in our calculations as an expansion in 20 Gaussian functions [16, 17]. The integrals are calculated from the formulas of [17]. As in [11], we use approximate formulas to calculate the integrals, which contain the squared perturbation operator.

The results of EPT calculations of $\varphi(R)$ are shown in Figs. 1 and 2, where they are compared with the data of nonempirical and semiempirical calculations [3, 5, 7, 8]. As we see, the agreement is good (the deviations range from 1 to 20%). The sole exception are the results for a Be–He pair of atoms: the discrepancy with the results of [7] reaches 50%. This discrepancy, however, can be explained by the fact that, as already mentioned, [7] did not include the configurational interaction and the results are too high.

The atomic interaction potential energies, calculated by the EPT method as well as taken from the literature [3, 5, 7, 8], were approximated by the Born potential

$$\varphi(R)=B\exp(-R/\rho),$$

where B and ρ are constants. This is possible since EPT calculations of $\varphi(R)$ showed that for the cases under consideration the potential wells are not deep (several degrees). The values found for ε and R_{min} are close to those obtained in other calculations. For example, for a Mg–He pair of atoms, according to our calculations as well as the calculations of [5], $\varepsilon = 1\cdot 10^{-5}$ a.u. ≈ 3 K and $R_{min} = 10.5$ a.u.

Values of the cross section $Q_{12}{}^{(1,1)}$ as a function of $\alpha = \ln(B/kT)$ for the Born potential are given in [18]. The calculated values of the diffusion coefficient and the exponent

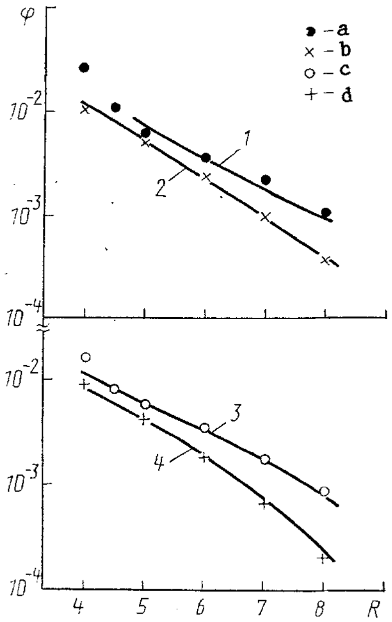

Fig. 1

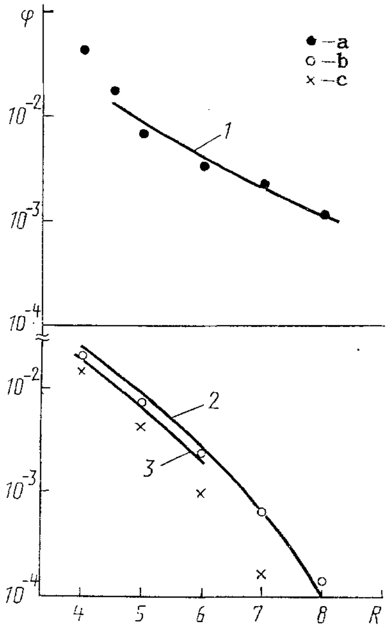

Fig. 2

Fig. 1. Comparison of the potential energy (a.u.) of atomic interaction, calculated by the EPT method [a) Rb–He, b) Na–He, c) K–He, and d) Li–He], with the results of nonempirical [3] (Li–He, curve 4) and semiempirical calculations [8] (Rb–He, curve 1, Na–He, curve 2 and K–He, curve 3). R, a.u.

Fig. 2. Comparison of the potential energy (a.u.) of atomic interaction, calculated by the EPT method [a) Cs–He, b) Mg–He, and c) Be–He], with the results of semiempirical calculations [8] (Cs–He, curve 1) and nonempirical calculations (data of [5] for Mg–He, curve 2 and data of [7] for Be–He, curve 3). R, a.u.

TABLE 1. Calculated EPT Values of PD_{12}, n, and the Ratio of the EPT Values of PD_{12} to Those Calculated from Nonempirical and Semiempirical Potentials (d_1) and to the Experimental Values (d_2)

Mixture	T, K	PD_{12}, N/sec	d_1	d_2	n
Li—He	1210	88,4	0,96[3]	—	1,97
Na—He	655	20,8	1,01[8]	0,95[19]	1,95
	473	11,1		1,04[20]	
K—He	723	19,5	0,91[8]	0,75[20] 0,93[21]	1,95
Rb—He	720	18,2	0,97[8]	—	1,94
Cs—He	723	16,7	0,95[8]	0,82[22]	1,95
Be—He	2430	280,3	1,10[7]	—	1,82
Mg—He	1030	44,0	0,99[5]	1,09[23]	1,82
Ca—He	1280	49,2	—	—	1,88
Sr—He	1230	40,5	—	—	1,88
Ba—He	1290	38,7	—	—	1,88

of n($PD_{12} \sim T^n$) from the atomic interaction potential energies, obtained by the EPT method, are shown in Table 1. The table also compares the values obtained for PD_{12} with those cacualted from nonempirical and semiempirical potentials [3, 5, 7, 8]. The discrepancies are small and are 10% in the worst case (Be–He). Comparison of the EPT calculated values of PD_{12} with the available experimental data shows that the deviation does not exceed the band of experimental error [19-23]. The above-mentioned agreement indicates that the calculated values of PD_{12} are rather reliable.

We also carried out experiments on the diffusion of monoatomic barium vapor in helium by the Stefan method on equipment described in [23]. To eliminate the interaction of the molten barium with the diffusion tube walls the tube was made of tantalum (diameter 14 mm,

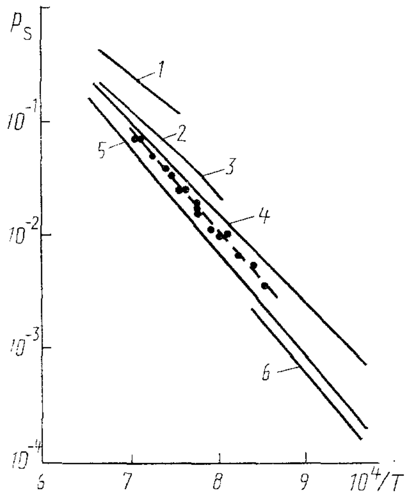

Fig. 3. Temperature dependence of the barium saturated vapor pressure p_s (Pa): 1) data of [24], 2) [25], 3) [26], 4) [27], 5) [28], and 6) [29]. The points denote the values of p_s obtained by processing experiments on barium vapor diffusion in helium; the dashed line represents their approximation dependence. $10^4/T$, 1/K.

height 55 mm). The temperature range of the experiments was 1170-1420 K. If the data on the evaporation of a metal is to be processed in order to determine the diffusion coefficient, it is necessary to have the values of the pressure p_s of its saturated vapor. The published data on barium p_s (some are given in Fig. 3), however, differ greatly. When available data are used in processing diffusion experiments the resulting values of D_{12} differ by a factor of up to three. In addition the difference in the slopes of the temperature dependences p_s affects the exponent n of the temperature dependence of D_{12}. For example, the use of p_s from [27] and from [28] results in values of n that differ threefold. Accordingly, we reproduced the value of p_s for barium by processing the diffusion experiments, using the values of D_{12} calculated by the EPT method. The approximated dependence (confidence coefficient 0.95) in the temperature range from 1170 to 1420 K has the form

$$\lg p_s = (5.25 \pm 0.26) - \frac{9020 \pm 460}{T}$$

(p_s, Pa). The results are shown in Fig. 3. The reproduced values of p_s lie between the results of [27] and [28].

As a whole the calculations carried out show that fairly reliable results are obtained when EPT is used to compute the potential energy of the atomic interaction of alkali and alkali-earth metals with helium for subsequent determination of the diffusion coefficient.

NOTATION

P is the pressure of the gas mixture; D_{12} is the binary diffusion coefficient; k is the Boltzmann constant; T is the temperature; m_{12} is the reduced mass; R is the distance between the centers of mass of the interacting atoms; Z_a is the charge of the core of the metal atom; $Z_b = 2$ is the charge of the core of the helium atom; N_a is the number of valence electrons in the metal atom; $N_b = 2$ is the number of electrons of the helium atom; $r_{\alpha k}$ is the distance from the center of mass α of the atom to the electron k ($\alpha = a$, b; k = i, j); C_6 is the constant of long-range interaction; ε is the depth of the well of the atomic interaction potential energy; and R_{min} is the distance to the point of minimum atomic interaction potential energy.

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