CALCULATION OF DIFFUSION COEFFICIENTS OF TWO-ELECTRON METALS IN INERT GASES AND MOLECULAR HYDROGEN

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Calculation of diffusion coefficients for two-electron metal (i.e., those with two valence electrons) vapors in helium, argon, and molecular hydrogen is considered.

Calculation of the diffusion coefficients of metal vapors* in gases (as well as that of other transport coefficients) can be carried out using Enskog-Chapman kinetic theory formulas [1]. However use of conventional empirical approaches for determining the parameters of the potential energy of molecular interaction (and use of arbitrary combination rules) can lead to unexpected errors. For example, for mixtures of alkali metal vapors with inert gases such calculations, as is shown by a number of verification attempts, as a rule lead to values 1.5-2 times lower than experimentally determined diffusion coefficients. For inert gas mixtures of metals with two valence electrons both lowered and elevated (up to 1.5 times) values of the diffusion coefficient may be obtained. Meanwhile, the potential energy of molecular interaction can be determined reliably by solving the Schrodinger equation in the Borne-Oppenheimer approximation of "halted" cores [2], after which the value of D_{12} can be found more accurately. Thus, calculation of the diffusion coefficients of alkali metal vapors in inert gases with the first approximation of Enskog—Chapman theory

$$PD_{12} = \frac{3k^{3/2}(N_A/\pi)^{1,2}}{8} \frac{\sqrt{T^3(M_1+M_2)/(2M_1M_2)}}{\sigma^2\Omega_{12}^{(1,1)^*}(T^*)} \tag{1}$$

using the interaction potential energy determined from the quantum mechanical solution (established in both nonempirical [3-5] and semiempirical [6-10] calculations) leads to good agreement with experimental data [11]. Moreover, as was shown in [11], agreement with experiment can also be achieved with use of a more approximate quantum mechanical theory [12, 13] involving introduction of an empirical parameter for the inert gases. This method also proves convenient for mixtures of bivalent metal vapors not only with inert gases, but also with molecular hydrogen, which will be considered in greater detail below. Initially we will compare with experiment the results of calculations based on the more precise quantum mechanical solutions.

Calculation of the potential energy of interaction of a magnesium atom with helium atoms (with explicit consideration of all electrons of both the metal and the gas) was carried out in [14] by a nonempirical quantum mechanical method with consideration of configuration interaction**. Another study [15] performed this calculation for a wider region of interatomic (internuclear) distances with consideration of configuration interaction as well. In this calculation only the two valence electrons of the magnesium were considered explicitly. To consider the effects of inner electrons non-empirical pseudopotentials dependent on the orbital quantum number ℓ (ℓ-dependent pseudopotentials) were used [16]. For identical nuclear states the results of [14, 15] practically coincide (Fig. 1). The depth of the potential well defined approximately in [15] (the major calculations were performed for smaller interatomic distances) comprised 21 K at $R \approx 9.8$ atomic units. Due to the relatively shallow depth of the well (ε/k is

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*Metal vapors, especially superheated ones, are practically monatomic.
**That is, with consideration of the series of excited electronic states of the Mg—He quasi-molecule, which permits refining the interaction in close-lying and neighboring states, including the ground state, and determination of the long-distance dispersion interaction.

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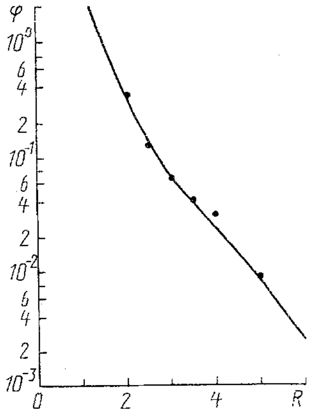

Fig. 1. Potential energy of interaction between magnesium and helium atoms: solid line, $\phi(R)$ from calculations of [15]; points, calculation of [14]. ϕ, R, atomic units.

small in comparison to temperatures of the order of thousands of K), to approximate the potential curve we will use a well-free Borne repulsive potential

$$\varphi(R) = B \exp(-R/R_0), \tag{2}$$

where B and R_0 are constants. Tables of collision integrals for this potential are presented in [17]. Results of calculating PD_{12} for mixtures of magnesium vapor with helium with Eq. (1) are presented in Table 1. From this table one can see the good agreement between calculated and experimental [18] PD_{12} values (see also Fig. 2).

Semiempirical quantum mechanical calculations of the potential energy of interaction between bivalent metals and inert gases were presented in [19, 20]. In [19] the Baylis method [21], suitable for the case of heavy gases (Ar, Kr, Xe) considered therein, was used. This is a method which uses ℓ-independent Gombas pseudopotentials [22], based on a statistical model of the atom. We will use a similar method for calculating the interaction with heavy inert gases. Table 1 shows results of PD_{12} calculations with Eq. (1) for a mixture of cadmium vapor with argon using the interaction potential energy of [19], approximation formula (2) (although in the given case potential well depth is about 380 K for $R \approx 6/6$ atomic units). We again see satisfactory correspondence between calculation and experiment [18].

In [20] a calculation of the potential energy of interaction of bivalent metal atoms with atoms of light inert gases (He, Ne) was presented. Due to the small number of electrons in such atoms use of the statistical theory is limited. Therefore ℓ-dependent pseudopotentials are used, considering the actual features of electron shell construction. As in a number of other studies (for example, [23]) terms are included directly in the Hamiltonian to consider empirical data on electron interaction with inert gas atoms, as well as spectroscopic data for the metal ions. Table 1 shows results of PD_{12} calculations with Eq. (1) using potential energy values calculated in [20] for interaction of magnesium, cadmium, and mercury atoms with helium atoms, approximated with Eq. (2) for interatomic distances. It is evident from the table that for Mg—He and Cd—He mixtures the calculated results agree very well with experiment. However for the mixture Hg—He the agreement is unsatisfactory. Table 1 gives PD_{12} values found in this manner for Mg—Ne, Cd—Ne, and Hg—Ne mixtures. However for these mixtures the comparison was formed not with experimental values, but rather PD_{12} values established by generalization of experimental data on other mixtures [24]. It is evident that the agreement is good for Mg—Ne and Cd—Ne mixtures, but lacking for Hg—Ne. The marked divergence of the PD_{12} values from experimental values for this mixture as well as Hg—He can apparently be explained by elevation of the interaction potential values of [20] for mixtures of mercury vapor with neon and helium. This was noted by the authors of [20] themselves in regard to Hg—Ne. For the mixture Hg—He the elevation of the calculated potential is confirmed by comparison with the potential reconstructed from data on atomic beam scattering.

We will now turn to calculating diffusion coefficients of monatomic metal vapors in molecular hydrogen. Upon interaction of a metal atom with a biatomic molecule the potential energy depends not only on coordinate R (in the given case the distance from the metal atom core to

TABLE 1. Calculated PD_{12} Values Found Using Results of Semiempirical Calculations of Atomic Interaction Energy (d, ratio of calculated PD_{12} values to experimental (or found by generalization))

Mixture	T, K	PD_{12}, N/sec	d
Mg—He [15]	1030	41,4	1,02
Mg—He [20]	1030	40,3	1,00
Mg—Ne [20]	1030	19,7	0,91
Hg—He [20]	470	10,9	0,74
Hg—Ne [20]	470	4,8	0,78
Cd—He [20]	780	25,0	1,04
Cd—Ne [20]	780	10,3	0,94
Cd—Ar [19]	780	7,8	1,15

the center of the straight line joining the cores in the biatomic molecule (Fig. 3)) but also the angle θ between that line and the vector R. Yet another parameter for the potential energy is the inter-core distance, which we will only consider in calculations of diffusion, the given distance comprising $r_{H_2} = 1.4$ atomic units. The mean (over angle θ) potential $\overline{\phi}(R)$ can be defined by the following expression

$$\overline{\varphi}(R)=\frac{1}{3}\varphi(R,\ \theta=0)+\frac{2}{3}\varphi\left(R,\ \theta=\frac{\pi}{2}\right), \tag{3}$$

where $\phi(R,\ \theta = 0)$ and $\phi(R,\ \theta = \pi/2)$ are the potentials for the two closest types of system symmetry, corresponding to the indicated θ values.

Equation (3) follows from the fact that in three-dimensional space twice as many collisions occur on the frontal configuration ($\theta = \pi/2$) as on the side ($\theta = 0$). The expression was tested by integration over the angle θ of the potential function $\phi(R,\ \theta)$, approximating the numerical results of the theoretical study for the system $Li—H_2$ [25]. In the present study nonempirical calculations were carried out using two sets of base wave functions (limited and more complete). Coulomb and exchange energy were calculated by the Hartree-Fock method and a more complete calculation considering multiconfiguration interaction. For the potential energy of interaction of alkali metal atoms (Li, Na, K, Rb, Cs) with a hydrogen molecule a semi-empirical calculation was also carried out [26] for $\theta = 0$ and $\theta = \pi/2$ using ℓ-dependent pseudopotentials by the method employed in [23]. However for the system $Li—H_2$ the results of [26] diverge intensely from the more accurate data of [25]. Nonempirical calculations for potential energy for the system $Na—H_2$ were performed by the Hartree—Fock method in [27] for $\theta = 0$ and $\theta = \pi/2$. In the latter case the calculations considered multiconfiguration interaction. Resting upon the results of [25, 27], we may, as in [11], use asymptotic quantum mechanical theory [12, 13] to calculate the interaction of a metal atom with a hydrogen molecule. The electron scattering length of molecular hydrogen required in such calculations can be taken as $L = 1.27$ atomic units [28]. If we take the integration radius (problem parameter about the hydrogen molecule $\rho = 0.2$ atomic units in the asymptotic expression used in [11]:

$$\varphi_{\text{exc}}(R)=2\pi(L+\rho)(\beta'\rho+1)\exp(\beta'\rho)\Phi^2(R)/(1-\beta'L), \tag{4}$$

then exchange energy as calculated by that expression corresponds to results of the calculations of [25, 27] averaged over angle θ with the aid of Eq. (3) (Fig. 4). We consider the results of these studies without consideration of the long-distance action of the lithium and sodium atoms on the hydrogen molecule. Such calculations basically define the exchange interaction energy, as does Eq. (4). The agreement obtained permits using this expression with the indicated $\overline{\phi}_{\text{exc}}(R)$ value to determine the average exchange energy of atomic interaction of bivalent metals with a hydrogen molecule. For two-electron metals (i.e., atoms with two equivalent valence electrons) in Eq. (4) we must introduce a factor $\omega = 2$ [11], which develops when a Rak genealogical scheme is used [13]. To estimate the long-distance attractive energy (which transforms to dispersive at large distances) one can use the approximate recalculation formula

$$\overline{\varphi}_{\text{at}}^{M-H_2}(R)=\overline{\varphi}_{\text{at}}^{Na-H_2}(R)\,C_6^{M-H_2}/C_6^{Na-H_2}, \tag{5}$$

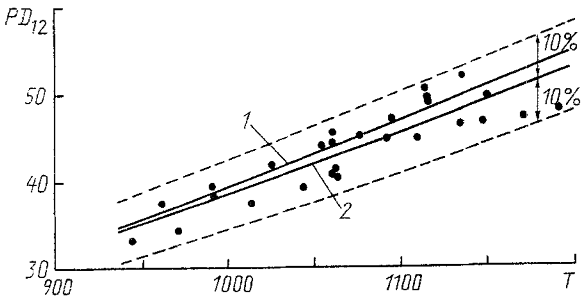

Fig. 2. Comparison of diffusion coefficient values for magnesium—helium mixture calculated with nonempirical interaction potential [15] (curve 1) and experiment [18] (points); curve 2, averaged line. PD_{12}, N/sec, T, K.

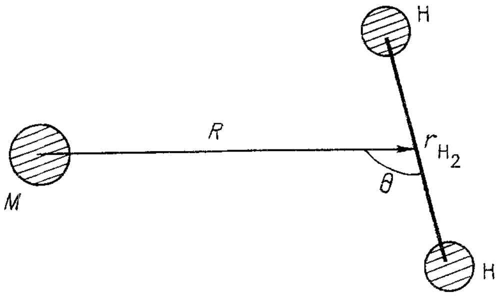

Fig. 3. For calculation of the interaction potential of a metal atom (M) with a biatomic homomolecule (H—H).

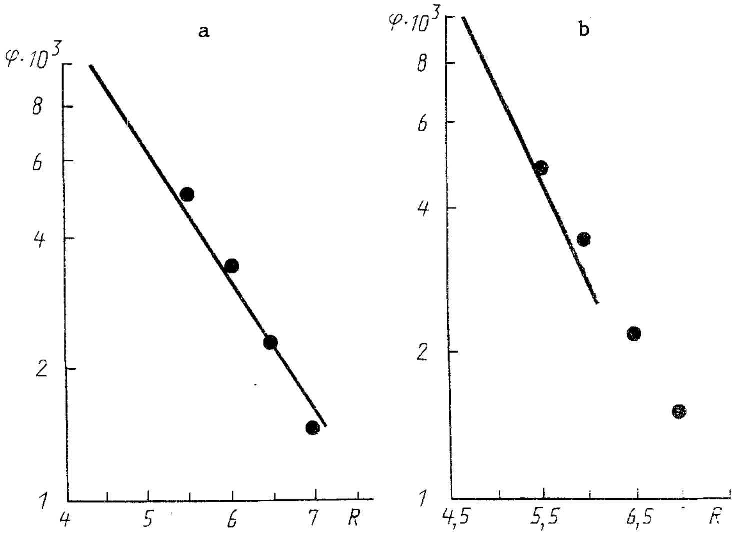

Fig. 4. Potential interaction energy with hydrogen molecule: a) lithium atom (solid line, calculation of [25]; points, asymptotic calculation); b) sodium atom (solid line, calculation of [27]; points, asymptotic calculation).

where $\bar{\phi}_{\mathrm{at}}^{\mathrm{Na-H_2}}(R)$ is the difference between the interaction energies of Na and H_2 averaged over angle calculated in [27] with and without consideration of configuration interaction. In the absence of values of the dispersion constant C_6 in the reference literature those may be calculated using the Slater—Kirkwood method [2]. The net (by Eq. (4) with introduction of the factor $\omega = 2$ and by Eq. (5)) potential interaction energies for the systems Mg—H_2, Zn—H_2, and Cd—H_2 were approximated by Eq. (2). Results of further PD_{12} calculations with

TABLE 2. Calculated (with use of asymptotic potentials) Values of PD_{12} for Mixture of Metal Vapor with Molecular Hydrogen (d is ratio of calculated values of PD_{12} to experimental ones)

Mixture	T, K	PD_{12}, N/sec	d
Mg—H_2	1030	56,9	1,04
Zn—H_2	880	46,0	1,02
Cd—H_2	780	36,8	1,15

Eq. (1) are presented in Table 2. The comparison with the experimental data of [29] shown there shows satisfactory correspondence.

NOTATION

P, mixture pressure; D_{12}, mutual diffusion coefficient in binary mixture; k, Boltzmann's constant; N_A, Avagadro's number; M_1 and M_2, molecular masses of components; T, absolute temperature; σ, geometric parameter of molecular (atomic) interaction potential energy ϕ; $T^* = kT/\varepsilon$, reduced temperature; ε, potential well depth; $\Omega_{12}^{(1,1)*}(T^*)$, reduced collision integral; R, distance between centers of mass of interacting molecules (atoms); θ, angle between molecule axis and straight line joining its center of mass to the core of interacting metal atom; ϕ_{exc}, exchange molecular (atomic) interaction energy; $\beta' = \sqrt{2I_1 - 2/R}$, I_1 is single ionization potential of the metal atom; Φ(R), asymptotic wave function of metal atom valence electron.

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HEAT AND MASS TRANSFER IN HYDROGEN SORPTION—DESORPTION IN METAL-HYDRIDE POWER-PLANT COMPONENTS

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A mathematical model which describes the dynamics of hydride-accumulator operation, taking account of the laws of heat and mass transfer and the reaction kinetics of hydrogen sorption—desorption, is developed. Estimates of the accuracy of the approximate analytical solutions are given. A generalization of the quasi-steady method of solving the Stefan problem is obtained.

The hydrides of intermetallide compounds (IMC) — for example, $LaNi_5$, FeTi, etc. — are capable of reversible sorption and desorption of a large quantity of hydrogen. To optimize the operating conditions and construction of hydride accumulators, it is expedient to use mathematical modeling. In [1], a mathematical model of heat transfer in the hydride layer was proposed, and an approximate analytical solution was obtained under the assumption that sorption—desorption occurs at constant temperature (frontal model). In [2], a model taking account of heat and mass transfer was proposed; in [3], a model also taking account of the kinetics of hydrogen sorption—desorption was considered.

The mathematical model here outlined is obtained on the basis of the laws of mass and energy conservation in differential form [4] and the equations of reaction kinetics, and is more general than those considered previously.

The following assumptions are made in its formulation:

1) heat transfer occurs on account of heat conduction of the hydride and convection in the filtration of free hydrogen in the hydride pores;

2) the filtration of hydrogen occurs in viscous conditions;

3) the change in hydrogen content in the hydride is due to two factors: the sorption—desorption reaction and the diffusion of bound hydrogen in the hydride.

The mathematical model includes the following equations:

mass conservation of free hydrogen (continuity) taking account of the equation of state of an ideal gas for free hydrogen

$$\frac{M_{H_2}}{R_{gas}}\frac{\partial}{\partial\tau}\left(\frac{\Pi p_{H_2}}{T}\right)=hd_{me}^2\operatorname{div}\left(\frac{\Pi^3}{(1-\Pi)^2}\frac{p_{H_2}}{\mu_{H_2}T}\operatorname{grad}p_{H_2}\right)-\frac{M_{H_2}}{2}\frac{\rho_h}{M_h}\left(\frac{d\varkappa}{d\tau}-\operatorname{div}(D_H\operatorname{grad}\varkappa)\right); \quad (1)$$

energy conservation (heat transfer)

$$\left(c_h\rho_h+c_{H_2}\frac{M_{H_2}}{R_{gas}}\Pi\frac{p_{H_2}}{T}\right)\frac{\partial T}{\partial\tau}=\operatorname{div}(\lambda_h\operatorname{grad}T)+\frac{Q\rho_h}{2M_h}\left(\frac{d\varkappa}{d\tau}-\right. \quad (2)$$

$$\left.-\operatorname{div}(D_H\operatorname{grad}\varkappa)\right)+\beta hd_{me}^2\frac{M_{H_2}}{R_{gas}}c_{H_2}\frac{\Pi^3}{(1-\Pi)^2}\frac{p_{H_2}}{\mu_{H_2}T}(\operatorname{grad}p_{H_2},\ \operatorname{grad}T);$$

the kinetic equation of hydrogen sorption—desorption

$$\frac{d\varkappa}{d\tau}=K\exp\left(-\frac{e}{R_{gas}T}\right)\left[\frac{p-p_d(T,\varkappa)}{p_d(T,\varkappa)}\right](\varkappa_{max}-\varkappa). \quad (3)$$

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