Journal of Engineering Physics and Thermophysics, Vol. 69, No. 4, 1996

POTENTIAL ENERGY OF MAGNESIUM ATOM–HYDROGEN MOLECULE INTERACTION AND INTERDIFFUSION COEFFICIENT

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The potential energy of intermolecular interaction is calculated by the quantum-mechanical exchange perturbation theory. The results are used to calculate the diffusion coefficient for magnesium vapor in hydrogen. The calculations agree with the experimental results.

For subsequent calculation of the transfer coefficients, the potential energy of intermolecular interaction at medium and large intermolecular distances can be calculated using the quantum-mechanical exchange perturbation theory (EPT) [1-3]. In this theory, the approximate Schrödinger equation includes (by the antisymmetrization operator of the wave function of the system) the effect of weak overlap of electron shells at medium intermolecular distances. The overlap results in exchange interaction satisfying the Pauli exclusion principle for the electron distribution over the molecular orbitals. At large intermolecular distances the overlap of the shells disappears and the EPT coincides with the standard Rayleigh–Schrödinger perturbation theory, which results in polarization (dispersion for nonpolar molecules) interaction [1].

The authors of [4] give EPT results in a version [3] of the potential energy of the interaction between alkali and alkali-earth metal (magnesium included) atoms and helium atoms. In this case the interaction of valence electrons of metal atoms (one electron for alkali metals and two electrons for alkali-earth metals) with two electrons of a helium atom were explicitly taken into consideration. The effect of electrons from the metal-atom skeleton was included, using the pseudopotential method [5, 6]. Unsöld's approximation [7] was used in calculations of exchange-polarization and polarization interactions. The approximation consisted in introduction of the average effective energy of excited states. The potential interaction energies estimated by the EPT method agree with the values reported in the literature (found by complete nonempirical and semiempirical quantum-mechanical calculations).

The dependences of potential energy on the interatomic distance calculated within EPT are used in calculation of the interdiffusion coefficients of metal vapor (superheated metal vapors are almost monoatomic [9]) in helium within the Enskog–Chapman theory [8]. The calculated diffusion coefficients for magnesium vapor in helium agree with experimental values [10] found with Stefan's method (i.e., with the coefficients found from the rate of evaporation of metal into gas). The calculated diffusion coefficients for alkali metals in helium also agree with experimental data. From experimental data on evaporation of barium into helium, the pressure of saturated barium vapor (the vapor is saturated at the evaporation surface) as a function of temperature is found using a diffusion formula [8] and the potential energy calculated within EPT. The specified approximation formula for the found pressure values lying in the range of pressures reported in the literature [11-13] is given in [14] together with a formula for the diffusion coefficient.

We used the same EPT method in a version [3] for calculation of the potential energy of interaction between magnesium atoms and a biatomic hydrogen molecule (just as in [4], the ground state of the system is meant)*. In

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* Excited states of interacting atoms or molecules are included in calculation of exchange-polarization and polarization energies.

St. Petersburg State Technical University, St. Petersburg, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 4, pp. 582-588, July-August, 1996. Original article submitted June 27, 1994.

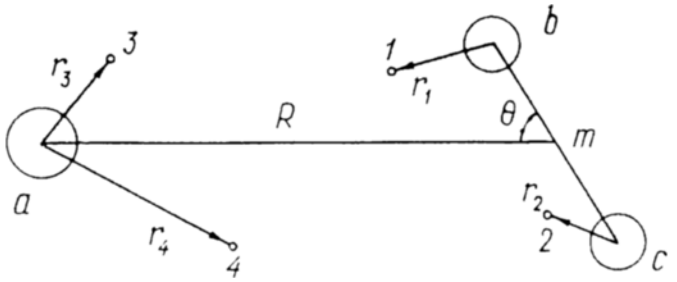


Fig. 1. Diagram of atoms and electrons in Mg-H_2 system: *a*, metal atom; *b* and *c*, hydrogen atoms in H_2 molecules; 1 and 2) electrons of hydrogen atom; 3 and 4) valence electrons of metal atom; r_n (n = 1, 2, 3, 4), electron coordinates; *m*, center of mass of H_2 molecules; *R*, distance between atom *a* and point *m*.

this case the calculation is substantially complicated in view of the fact that apart from the distance R (in [4] the internuclear distance, and now in the case of interaction with hydrogen, the distance between the nucleus of the metal atom and the center of mass of the biatomic H_2 molecule), one more parameter appears. This is the angle θ determined by the direction of collision (Fig. 1). In the ground state of the H_2 molecule the distance between the hydrogen nuclei is 1.4 atomic units. The electron wave function of the hydrogen molecule was written following Heitler–London [1]

$$\psi^{H_2} = \frac{1}{\sqrt{2(1+S^2)}}\,[\psi_b(1)\,\psi_c(2) + \psi_b(2)\,\psi_c(1)]\,\frac{1}{\sqrt{2}}\,[\alpha(1)\beta(2) - \alpha(2)\beta(1)].$$

In the above expression ψ_b and ψ_c are spatial wave functions of the electrons on hydrogen atoms b and c (Fig. 1); α and β are spin electron functions with opposite spin orientations; $S = \int \psi_b(1)\psi_c(1)d\tau_1$ is the overlap integral of the electron centered on hydrogen atoms b and c. Just as in other similar integrals of quantum mechanics, integration in this interval is carried out over the entire space; $d\tau_1$ is an element of the space of this electron marked by number 1. As usual, the numbers in parentheses in the space and spin functions indicate the space or spin coordinates of electrons in the adopted numbering.

Depending on the radius r (atomic units), the space function of the electron of the hydrogen atom b or c with reference points at the atomic nucleus has the form

$$\psi = 1/\sqrt{\pi}\,\exp(-r).$$

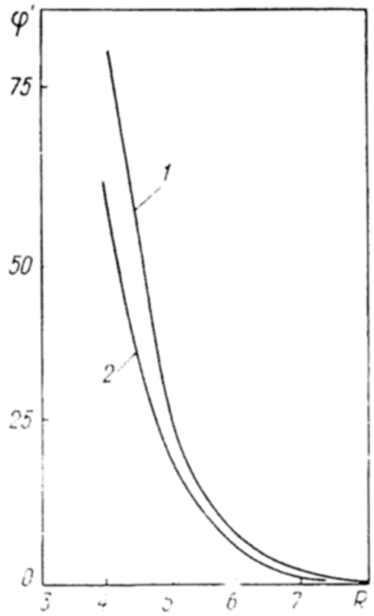
In calculations this Sleuter type function was approximated by a sum of Gaussian functions in which r is replaced by r^2 with the appropriate coefficient in the exponent. The same pseudopotentials and the corresponding wave pseudofunctions of valence electrons were chosen as in [4].

According to [3] the potential energy of intermolecular interaction is expressed as a series

$$\varphi(R) = E^{(10)} + E^{(12)} + E^{(20)} + E^{(22)} + \dots,$$

where the first superscript of the energy components $E^{(ik)}$ means the order of approximation along the perturbation operator and the second superscript is the same along the overlag integrals of valence electrons (in the present case, of magnesium and hydrogen atoms). In the series it is sufficient to take only the term of the exchange-polarization energy $E^{(22)}$. The other terms of the series, namely, $E^{(10)}$, $E^{(12)}$, and $E^{(20)}$ express electrostatic, exchange, and polarization (dispersion) energies, respectively.

The initial Schrödinger equation written in a Born–Oppenheimer approximation of stopped atomic nuclei includes the Coulomb energies of attraction of electrons of one molecule (or atom) to nuclei of another, repulsion of electrons, and repulsion of nuclei of different molecules. For the Mg-H_2 system, the perturbation operator has the form (in atomic units, a.u.):



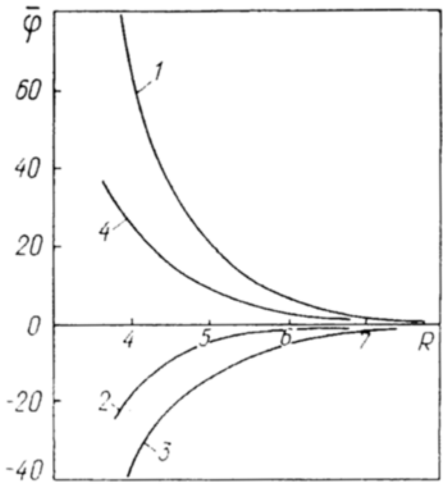


Fig. 2. Potential interaction energy $\varphi'_{\text{Mg-H}_2}$ (a.u. × 10^3) (electrostatic and exchange) following the exchange perturbation theory versus intermolecular distance R (a.u.); 1) $\varphi_{C_{\infty v}}(R)$; 2) $\varphi_{C_{2v}}(R)$.

Fig. 3. Total angle-averaged potential interaction energy $\bar{\varphi}$ (a.u. × 10^{-3}) of Mg-H_2 versus intermolecular distance R (a.u.)): 1) $\bar{\varphi}'(R)$ from formula (2); 2) polarization energy $C_6^{\text{Mg-H}_2}/R^6$; 3) $\bar{\varphi}''(R)$ from formula (3); 4) $\bar{\varphi}(R)$, total from formula (4).

$$\hat{V} = \sum_{j=1}^{N_b+N_c} \left[-\frac{Z_a}{r_{aj}} + U(r_{aj}) \right] - \sum_{i=1}^{N_a} \left[\frac{1}{r_{bi}} + \frac{1}{r_{ci}} \right] - \sum_{k=1}^{N_b+N_c} \sum_{m=3}^{M} \frac{1}{r_{km}} + Z_a \left(\frac{1}{R_{ab}} + \frac{1}{R_{ac}} \right), \tag{1}$$

where, as in Fig. 1, subscript a refers to the metal atom and subscripts b and c, to hydrogen atoms in the hydrogen molecule. For magnesium $N_a = 2$, $Z_a = 2$ (skeleton charge) and for hydrogen $N_b + N_c = 2$. The electron coordinates (radii) r_{aj}, r_{bi}, and r_{ci} have reference points at the nuclei of the metal (a) and hydrogen (b and c), r_{km} is the distance between k and m electrons (for magnesium in the double sum $M = 4$), R_{ab} and R_{ac} are the distances from the nucleus of the metal atom to the nuclei of the hydrogen atoms, $U(r_{aj})$ is the pseudopotential of the j valence electron of the metal.

The sums of electrostatic and exchange interaction energies $E^{(10)} + E^{(12)} = \varphi'(R)$ calculated for the Mg-H_2 system are shown in Fig. 2 versus the distance R at two values of the angle $\theta = 0$ ($C_{\infty v}$ symmetry) and $\theta = \pi/2$ (C_{2v} symmetry). In Fig. 3 one can see a curve of the angle θ-averaged $\varphi'(R)$ in accordance with the formula

$$\bar{\varphi}'(R) = \int_0^{\pi/2} \varphi'(R, \theta) \sin\theta d\theta \Big/ \int_0^{\pi/2} \sin\theta d\theta = \frac{1}{3}\varphi'_{C_{\infty v}}(R) + \frac{2}{3}\varphi'_{C_{2v}}(R), \tag{2}$$

obtained by integration of $\varphi(R, \theta)$ for Li-H_2 interaction from results of complete nonempirical quantum-mechanical calculations [15].

It should be also borne in mind that H_2 molecules rotate around the instantaneous axis that passes through the center of mass perpendicularly to the straight line connecting the hydrogen nuclei (which, in turn, undergo vibrations). Each rotational degree of freedom (a biatomic molecule has two degrees of freedom in accordance with the two angles determining the position of the instantaneous rotational axis) has, on the average, $1/2kT$ energy,

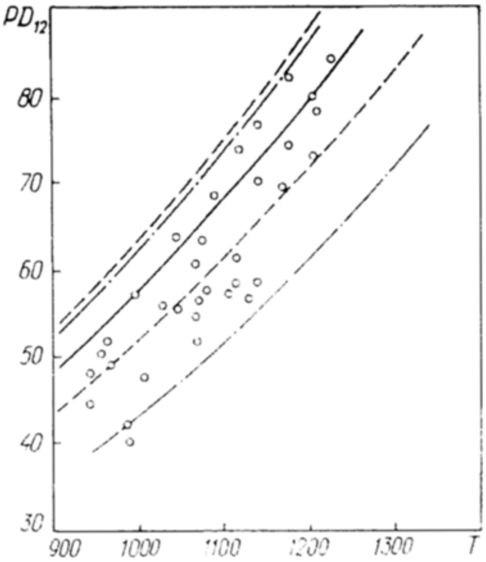


Fig. 4. Plot of PD_{12} (N/sec) versus temperature T (K); dots) experiment; solid curve) EPT calculation; dashed curves) ±10% deviation from calculation; dot-dash curves) ±18% spread of experimental points.

which, with the moment of inertia of the molecule known, determines the average frequency of rotation. In addition, H_2 molecules can be rotated by the action of a colliding atom [16]. Thus, the question of the most correct averaging of the potential energy of interaction between the atom and H_2 molecule (or any other biatomic molecule) is complicated and has not been answered completely. However, in the present case $\varphi'_{C_{\infty v}}(R, 0)$ and $\varphi'_{C_{2v}}(R, \pi/2)$ are not very large (Fig. 2) as regards the effect of collisions on the values of the integrals and averaging (2) can be considered sufficient for the required accuracy of results.

In the present EPT calculations for the Mg-H_2 system, the sum of the polarization and exchange-polarization energies $E^{(20)} + E^{(22)} = \varphi''(R)$ was not determined directly (unlike the calculations in [4] for the Mg-He system). We used calculation results of [4] with approximate scaling

$$\bar{\varphi}''_{\text{Mg-H}_2}(R) = \bar{\varphi}''_{\text{Mg-He}}(R)\, C_6^{\text{Mg-H}_2}/C_6^{\text{Mg-He}} . \tag{3}$$

The constant C_6 determines the first largest term (instantaneous-dipole-induced interaction) of the polarization attraction energy C_6/R^6 in a multipole expansion. For the system of magnesium and helium atoms $C_6^{\text{Mg-He}} = 22$ a.u. [17], but for the system of a magnesium atom and a hydrogen molecule the values of the analogous constant are not given. The Sleuter–Kirckwood formula can be used to estimate the angle-averaged $C_6^{\text{Mg-H}_2} \approx$ 73.5 a.u. Results of calculations from formula (3) are given in Fig. 3. In the same figure one can see a curve of the angle-averaged potential energy of interaction between a magnesium atom and a hydrogen molecule

$$\bar{\varphi}(R) = \bar{\varphi}'(R) + \bar{\varphi}''(R) . \tag{4}$$

In the range of up to R = 8 a.u. as a maximum, the energy $\bar{\varphi}(R)$ cooresponds to repulsion. Attraction occurs at larger intermolecular distances and the estimated depth of the potential well (corresponding to equilibrium of repulsion and attraction) does not exceed several Kelvins (in temperature units). Thus, for calculation of interdiffusion coefficients, the potential energy $\bar{\varphi}(R)$ can be approximated by the Born well-less repulsion potential

$$\bar{\varphi}(R) = B \exp(-R/\rho) , \tag{5}$$

where B and ρ are constants. Tables of collision integrals for this model potential are given in [18]. The products

$$PD_{12} = \frac{3}{16\pi} \frac{\sqrt{2\pi (kT)^3 m_{12}}}{Q_{12}^{(1,1)}(T)}$$

calculated with such an approximation and using the formula of a first approximation in the Enskog–Chapman kinetic theory for a mixture of uniatomic magnesium–hydrogen vapor are given in Fig. 4 together with experimental points. Experiments were carried out by Stefan's method on an experimental device described in [10, 19]. An alundum crucible with an internal diameter and height of about 17 and 34 mm,respectively (crucibles with a height of 65 mm were also used), was used as a diffusion cell. A melted (by heating) weighed amount at magnesium (a cylinder 5–10 mm high, shaped to fit the diameter of the crucible) was placed on the bottom of the crucible. The top section of the crucible was blown by hydrogen. Under the conditions of the experimental facility used, the hydrogen flow rate was 50–120 liter/h. This resulted in a more than one-hundred-fold decrease in the magnesium concentration at the crucible edge as compared with saturation at the evaporation surface. Meanwhile, no marked aerodynamic vortex appeared at the throat of the crucible. In the experiments the temperature ranged from 940 to 1230 K. The furnace was thermostated by an automatic control unit within 3–6°. The total pressure was close to atmospheric pressure (the product PD_{12} is independent of pressure). Depending on the set temperature, the experiment duration varied from 0.5 to 2 h, and was 4 h in one case, and in that this case 30 to 200 mg of magnesium evaporated. The loss of magnesium mass was determined by weighing the crucible before and after the experiment within 0.1 mg. In this case a correction was introduced for evaporation during heating and cooling of the diffusion cell, which was established by special experiments without maintaining steady-state conditions. When results were processed with Stefan's formula [10], and the pressure of saturated magnesium vapor was determined with the data of [9]. The total spread of experimental values was occassionally ±18%. However, it should be borne in mind that the experiments carried out at lower temperatures seem unreliable, because incompletely decomposed compounds with hydrogen [20] or admixtures in the gas can be formed on the magnesium surface. This can prevent evaporation of magnesium. In experiments on magnesium diffusion in inert gases (helium and argon) [10], the spread of experimental points was within ±10% with the exponent $n = 1.73$ in the temperature dependence.

In Fig. 4 one can see that the PD_{12} curve calculated by the EPT method agrees with the results of experiments carried out at higher temperatures with a spread within ±10%. For the calculated curve the exponent in the temperature dependence $PD_{12} = PD_{12}^0(T/T_0)^n$ is 1.75. Temperature T_0 is assumed to be 1030 K and the product of the total pressure by the diffusion coefficient is $PD_{12}^0 = 61.0$ N/sec at the given temperature.

NOTATION

P, total pressure of gas mixture; D_{12}, interdiffusion coefficient of binary mixture; k, Boltzmann constant; T, absolute temperature; m_{12}, dimensionless mass of two molecules; $Q_{12}^{(1,1)} = \sigma_{12}^2 \Omega_{12}^{(1,1)*}$, diffusion cross-section determined by collision integral; n, exponent in the temperature dependence of diffusion coefficient.

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