SOVIET PHYSICS JETP VOLUME 26, NUMBER 3 MARCH, 1968

DIFFUSION OF METASTABLE HELIUM ATOMS IN HELIUM GAS AT LOW TEMPERATURES

I. Ya. FUGOL' and P. L. PAKHOMOV

Physico-technical Institute of Low Temperatures, Academy of Science, Ukrainian S.S.R.

Submitted April 19, 1967

Zh. Eksp. Teor. Fiz. **53**, 866–873 (September, 1967)

The temperature dependence of the diffusion coefficient D and the diffusion cross section Q_d of metastable helium atoms in a gas of normal helium atoms is investigated. Q_d and D are calculated theoretically by employing the Poshusta-Matsen continued interaction potential. The diffusion coefficients are determined experimentally at 300, 77, 64, 20 and 4°K. The results confirm the existence of long range repulsion between atoms due to the existence of a peak on the potential curve for interaction between normal and metastable atoms.

1. INTRODUCTION

THE process of scattering of metastable helium atoms in a gas of normal atoms is one of the effects for which a classical description is unsuitable. When the atoms in question come close together, there exist two interaction potentials, V_S and V_A, which differ in the character of the symmetry of the wave function of the system with respect to exchange of nuclei. The need for taking into account two potential energies and symmetry effects leads to a disparity between the quantum and classical cross sections. Experimental data on collisions of metastable atoms can serve as a direct confirmation of the importance of quantum symmetry effect.

A study of the scattering and of the diffusion of metastable atoms of helium is also of considerable interest in view of the unusual character of the interaction between the normal and metastable helium atoms. The potential of the symmetrical wave function V_S describes only repulsion. The potential of the antisymmetrical state V_A has a number of singularities. At short distances ($r \approx 2a_0$, a_0 - Bohr radius) the atoms are attracted, and a bound molecular state ${}^3\Sigma_u^+$ exists. With increasing distance, the attraction gives way to long-range repulsion. A maximum ("hump") of repulsion appears on the potential-energy curve. The long-range part of the potential $V_A(r)$ is shown in Fig. 1.

Detailed calculations of the potential energy of interaction were first made by Buckingham and Dalgarno[1] (curve 1 for V_A). More consistent calculations with an exact allowance for the Van-der-Waals interaction were made by Poshusta and Matsen[2] (curve 2). The maximum height of the repulsion "hump," according to their data, is lower than that obtained in[1], and amounts to approximately 0.1 eV at a distance $r \approx 4.5a_0$ between the atoms. There is a noticeable difference also in the asymptotic behavior of the potentials at large r: the Poshusta and Matsen (PM) potential decreases more rapidly than the Buckingham and Dalgarno potential (BD).

Connected with the quantum character of the scattering and with the form of the potential curve of the interaction are the singularities of the diffusion of the metastable helium atoms. In this paper we describe the results of measurements of the coefficient of diffusion of metastable He^4 atoms in a decaying helium plasma in a wide range of temperatures from 4 to 300°K. The experimental data are compared with the theoretical calculations of the diffusion cross section.

2. DIFFUSION CROSS SECTION AND DIFFUSION COEFFICIENT

In this section we describe the results of a theoretical calculation of the cross section and the diffusion coefficient for the case of scattering of metastable and normal He^4 atoms. These calculations were made using an empirical interaction potential V_A, which has been constructed by us and which is a continuation of the PM potential to lower colliding-atom energies. At temperatures below 300°K, the scattering is from the long-range repulsion potential. The dashed lines of Fig. 1 show the values of the colliding-atom energy corresponding to the temperatures 300, 77, and 20°K. The intersection of the dashed lines with the potential-energy curve characterizes the effective radius of the scattering potential for these temperatures. We see that for temperatures below 300°K the effective scattering radius exceeds $6a_0$.

The BD potential was calculated up to distances $12a_0$; its asymptotic form at large distances is the same for both the symmetrical and the antisymmetrical cases, and obeys the exponential law

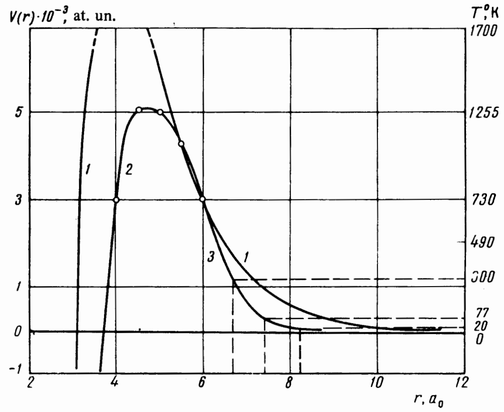

Fig. 1. Energy of long-range repulsion of metastable and normal helium atoms ($V_A(r)$). 1 – BD potential, 2 – PM potential, 3 – continued empirical potential. (The temperature scale is recalculated from the corresponding atom energy using the diffusion velocity $v_d = (10\kappa T/m)^{1/2}$, where m/2 is the reduced mass).

$$V_{S,\,A}(r) \sim ar^2e^{-1.18r} \pm bre^{-1.87r}, \tag{1}$$

where r is the distance in a_0 units. Starting with a distance $8a_0$, the second term becomes negligible and V_S and V_A practically coincide. Buckingham and Dalgarno calculated the diffusion cross section Q_d using the potential 1 of Fig. 1.

The PM potential was calculated only up to a distance $6a_0$. In our calculations we used the values of the empirical potential $V_A(r)$ obtained by asymptotically continuing the PM potential to $9a_0$. We assume that V_S and V_A are equal already at $r = 7a_0$. The continued potential is constructed in such a way that it coincides with the PM potential at values of r in the interval $5-6a_0$, and follows an exponential law at larger r:

$$V_{S,\,A} \sim Ar^2e^{-Br}. \tag{2}$$

The coefficients for the continued potential are A = 21.115 and B = 2.04 (in atomic units). The potential constructed in this manner has smaller scattering radii at low energies of the colliding atoms (curve 3 of Fig. 1).

The diffusion cross section Q_d was calculated by means of the formula

$$Q_d = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_l - \delta_{l+1}), \tag{3}$$

where $k = mv/2\hbar$ is the wave vector, v is the relative velocity, m/2 is the reduced mass of the helium atom, and δ_l is the phase of the scattering of the partial wave with number l. The general expression (3) turns out to be valid in this case, too, the only difference being that the even and odd phases are determined respectively by the interaction potentials V_S and V_A.

A detailed examination of the scattering of atoms with identical nuclei is contained in the papers of Massey and Smith[3] and Buckingham and Dalgarno[4]. It must be noted, however, that Buckingham and Dalgarno used in their theoretical paper[4] a formula for the diffusion cross section Q_d with a coefficient which is half as large. This decreased the results of the corresponding numerical calculations of Q_d. In comparing the $Q_d(v)$ dependence for different interaction potentials we shall double throughout the values of[4] for the diffusion cross section.

The scattering phase shifts which enter in formula (3) were calculated with the aid of the well-known Jeffries formula[5]

$$\delta_l = \int^{\infty} dr\left[k^2 - \frac{m}{\hbar^2}V(r) - \frac{(l+{}^1/_2)^2}{r^2}\right]^{1/2} - \int^{\infty} dr\left[k^2 - \frac{(l+{}^1/_2)^2}{r^2}\right]^{1/2}, \tag{4}$$

where $V(r) = V_S(r)$ for the even phases and $V(r) = V_A(r)$ for odd phases. The lower limit of integration is the largest root of the integrand. Formula (4) is valid in the quasiclassical approximation, the conditions for the applicability of which, as is well known, are

$$\rho \gg \lambda\!\!\!^{-} = \hbar/mv, \quad \rho V \gg \hbar v. \tag{5}$$

Here ρ is the radius of the scattering potential, and V is of the order of magnitude of the potential in that region. For the interaction potentials of normal and metastable helium, which are shown in Fig. 1, the quasiclassical conditions are satisfied up to velocities $v = 4 \times 10^4$ cm/sec, which corresponds approximately to $T \approx 15°$K.

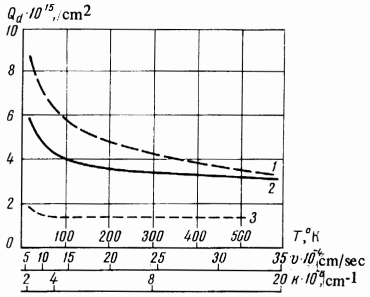

Fig. 2. Diffusion cross section for the scattering of metastable and normal helium atoms. 1 – Theoretical BD dependence (values decreased by one half); 2 – curve calculated with continued PM potential; 3 – diffusion cross section for normal helium atoms (data of Bendt [6]).

The integration in (4) was carried out graphically for definite values of k in the interval from $k = 2 \times 10^8$ cm^{-1} (T = 20°K) up to $k = 2 \times 10^9$ cm^{-1} (T = 600°K). The cross section $Q_d(v)$ was calculated by using the obtained phase shifts. Figure 2 shows the calculated dependence of the diffusion cross section for the scattering of metastable and normal helium atoms. Curve 1 represents the data of Buckingham and Dalgarno[4] multiplied by two, and curve 2 the values of $Q_d(v)$ calculated by us using the continued PM potential with a smaller effective radius.

According to the kinetic theory of Chapman and Enskog, the diffusion coefficient D is expressed in terms of the diffusion cross section as follows:

$$D = \frac{3\pi}{32}\left(\frac{16\varkappa T}{\pi m}\right)^{1/2}\frac{1}{n\bar{Q}_d}. \tag{6}$$

Here $\bar{Q}_d$ is the averaged diffusion cross section, which is equal to

$$\bar{Q}_d = \left(\frac{m}{4\varkappa T}\right)^3 \int_0^{\infty} dv\, v^5 Q_d(v) \times \exp\left(-\frac{mv^2}{4\varkappa T}\right), \tag{7}$$

n is the particle density, v the velocity, and $m = 6.6 \times 10^{-24}$ g the helium-atom mass. As seen from (6), the integrand

$$f(v) = v^5 \exp(-mv^2/4\varkappa T)$$

has a maximum at a value of v equal to the characteristic diffusion velocity

$$v_d = (10\varkappa T/m)^{1/2}. \tag{8}$$

If the cross section $Q_d(v)$ is constant or depends little on the velocity, then the quantity $Q_d(v)$ can be taken outside the integral sign in (7) at the point $v = v_d$. Therefore the diffusion velocity determines the temperature scale on going from the $Q_d(v)$ dependence to $Q_d(T)$ (see Fig. 2).

The temperature dependence of the distribution coefficient was determined from formulas (6) and (7). We note that both dependences in Fig. 2 can be sufficiently well approximated in the temperature interval from 4 to 900°K by a simple curve of the type

$$Q_d(v) = \alpha + \beta/v. \tag{9}$$

The $Q_d(v)$ curve corresponding to the BD potential is well described by formula (9) with coefficients

$$\alpha = 2.6 \cdot 10^{-15}\ \text{cm}^2 \qquad \beta = 4 \cdot 10^{-10}\ \text{cm}^3/\text{sec} \tag{10}$$

The $Q_d(v)$ curve for the potential with the smaller effective radius is approximated by formula (9), in which

$$\alpha = 2.6\cdot 10^{-15}\ \text{cm}^2, \qquad \beta = 2\cdot 10^{-10}\ \text{cm}^3/\text{sec} \tag{11}$$

Substituting (9) in expressions (7) and (6) we get

$$Dn = \frac{3\pi}{32}\frac{(16\varkappa T/\pi m)^{1/2}}{[\alpha + {}^3/_4\beta(16\varkappa T/\pi m)^{-1/2}]} \tag{12}$$

We introduce the value of the reduced pressure[1], equal to $P = P_0\cdot 300/T$, where $p_0 = n\kappa T$ is the true pressure at the temperature T. Then

$$DP = 0.31\cdot 10^{-16} Dn\ (\text{cm}^2\text{sec}^{-1}\ \text{mm Hg}). \tag{13}$$

The so calculated temperature dependence of the coefficient DP corresponding to the two potentials, is shown in Fig. 3.

3. EXPERIMENT

The diffusion coefficient of the metastable helium atoms was determined by investigating the decay kinetics of the metastable state 2^3S of He in its own excited gas. It was shown in [7,8] that at sufficiently low pressures and low gas densities, not exceeding $n = 6 \times 10^{16}\ \text{cm}^{-3}$, the disintegration of the metastable atoms proceeds principally as the result of their diffusion to the walls of the vessel. The change in the concentration M(t) of the metastable atoms is described by a diffusion equation with a diffusion coefficient D

$$\partial M/\partial t = -D\Delta M. \tag{14}$$

The change in the concentration averaged over the volume is given by the exponential relation

$$M(t) = M_0 \exp\left(-\frac{D}{\lambda^2}t\right), \tag{15}$$

where M_0 is the initial concentration of the metastable helium atoms, and λ is the "diffusion length." For a cylindrical vessel of radius R and length L we have $\lambda = [(2.4/R)^2 + (\pi/L)^2]^{-1/2}$; for a spherical vessel $\lambda = R/\pi$.

The experimental conditions in the measurement of the diffusion coefficient were as follows: A helium plasma was produced in a glass vessel. The helium was excited by an electrodeless method with the aid of a pulsed high-frequency generator which produced rectangular pulses of duration 0.1—0.01 msec and repetition frequency 25 Hz. The lifetimes of the metastable atoms in the decaying plasma were several milliseconds at the end of the high-frequency pulse. All the measurements were made 150 μsec following the end of the excitation.

The concentration of the metastable atoms in the state 2^3S was determined from the resonance absorption of the 3889 Å line from an external source. At small optical densities, the concentration is proportional to the integral absorption of the resonance line: $M \propto \Delta I/I$[7].

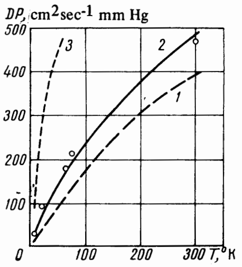

Fig. 3. Temperature dependence of the diffusion coefficient DP of metastable helium atoms in a gas of normal atoms. 1 – calculated dependenc with BD potential; 2– calculated curve with continued PM potential; points – experimental results; 3 – temperature dependence of the diffusion coefficient of normal helium atoms (data of Bendt [6]).

The low-temperature measurements were made in metallic cryostats. The discharge vessel was placed inside the metallic cryostat directly in the cryogenic liquid (nitrogen, hydrogen, or helium), so that the vessel-wall temperature coincided with the temperature in the cryostat. The distribution of the temperature inside the volume of the discharge vessel with gaseous helium can be estimated with the aid of the heat-conduction equation. If the excitation is accompanied by the transfer to the vessel of a power w (W/cm³) uniformly distributed over the entire volume, then this equation is written in the form

$$\Delta T = w/K, \tag{16}$$

where K is the coefficient of thermal conductivity of the helium. The solution of (16) for a sphere of radius R is

$$T = T_0 + \frac{w}{6K}(R^2 - r^2) \tag{17}$$

(T_0 is the wall temperature). The temperature change averaged over the volume is

$$\bar{T} - T_0 = wR^2/15K. \tag{18}$$

If the heat supplied during the time of the pulse does not exceed $W = w(4\pi R^3/3) \approx 0.3$ W, then the gas temperature differs from the discharge-vessel wall temperature by not more than 2—3°K even when T = 4°K and P = 0.2 mm Hg ($K = 4 \times 10^{-4}$ W/cm-deg).

With respect to the temperature of the metastable atoms we can state that on the whole they are close to the gas temperature, since the elastic collisions cause the metastable atoms to be in thermal equilibrium with the normal atoms. Indeed, the time of relaxation between the metastable and normal atoms is of the order of $\tau = (nvQ)^{-1}$, where $Q \approx 5 \times 10^{-15}\ \text{cm}^2$ is the scattering cross section, $n \approx 0.66 \times 10^{16}\ \text{cm}^{-3}$ is the density of the helium atoms, and $v \gtrsim 2 \times 10^4$ cm/sec is the velocity of the atoms. It follows therefore that the characteristic values of τ do not exceed several microseconds.

In the study of the diffusion of metastable atoms we investigated cylindrical discharge vessels (R = 2 cm, L = 1.6 cm), connected with the gas system, and also sealed closed spherical bulbs of radius 2.5 cm.

Let us stop to discuss the estimate of the pressure in the bulbs at low temperature. For closed vessels, this question does not arise, since the particle density $n = p_{300}/300\kappa$ is constant in them, and the reduced pressure P is always known. But if the vessels are connected to the external gas system, then a pressure drop can be produced along the joining tube, when the mean free path becomes comparable with the tube diameter d. This case is possible at T = 4°K and P < 1 mm Hg. The true pressure in the bulb is then not equal to the pressure measured in the system that communicates with the bulb. The maximum discrepancy due to the thermal effusion can be by a factor of 8 when d < L ($p_{300} = p_4(300/4)^{1/2}$). In intermediate

---

[1] We shall use henceforth reduced pressures throughout.

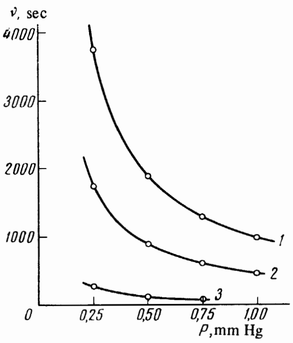

Fig. 4. Diffusion collision frequency $\nu = D/\lambda^2$ vs. reduced pressure ($\lambda^{-2} = 2$). 1 – hyperbola DP = 940, T = 340°K; 2 – hyperbola DP = 420, T = 77°K; 3 – hyperbola DP = 56, T = 4°K; points - experimental results.

cases, when d ~ L, the Knudsen formula can be used to calculate the pressure. An inaccurate determination of the pressure in open vessels at 4°K has led to an erroneous figure for the diffusion cross section in the brief note[8]. In the present investigation, all the measurements in open vessels at 4°K were additionally monitored by means of experiments with sealed bulbs.

4. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The disintegration of the metastable 2^3S helium atoms was investigated at 300, 77, 64, 20, and 4°K. The observed M(t) dependences for these temperatures in the reduced-pressure interval 0.2–1 mm Hg are exponential. Their slope on a semilogarithmic scale is inversely proportional to the pressure and, in accord with formula (15), represents the diffusion collision frequency $\nu = D/\lambda^2$. Figure 4 shows a plot of $\nu(P)$ at 4, 77, and 300°K. The curves are described by the hyperbolas Dp = const. The hyperbolic dependence of D on P serves as an additional control indicating that the disintegration of the metastable atoms occurs during the course of the diffusion.

The values of DP for the metastable atoms are shown in Fig. 3. The value of DP measured at 300°K coincides within the limits of errors (10%) with the data of Phelps[9,10]. At 77°K, the results diverge somewhat. A value DP = 130 cm^{-2} sec^{-1} mm Hg is given in[9], whereas we obtained at 77°K the value DP = 200 cm^{2}sec^{-1} mm Hg. The experimental data at the low temperatures (64, 20, and 4°K) were obtained first. Our measured values of the diffusion coefficient fit well the calculated curve obtained by using the continued potential of Poshusta and Matsen (see Fig. 3).

The diffusion coefficient of the metastable helium atoms differs greatly from the value of D for the normal atoms and is characterized by a different temperature dependence. The peculiarities of the diffusion of metastable atoms become more clearly manifest when the effective diffusion cross sections are compared.

Bendt[6] measured the diffusion coefficient $D(3 \rightarrow 4)$ of the isotope He^3 in He^4. Using the formula

$$D(\mathrm{He}^4) = \left(\frac{2m_3}{m_3 + m_4}\right)^{1/2} D(3 \rightarrow 4) \tag{19}$$

Bendt calculated the values of the self-diffusion coefficient D(He^4). It is obvious, that the value of D(He^4) obtained in this manner does not take into account the quantum symmetry effects and is determined at high temperature by the geometrical self-diffusion cross section

$$Q_{\mathrm{geom}} = \pi a^2 \approx 1.35\cdot 10^{-15}\ \mathrm{cm}^2, \tag{20}$$

where a/2 = 1.04 Å is the radius of the helium atom. Figure 2 shows the dependence of Q_{geom} according to Bendt's data.

The diffusion cross section of metastable atoms differs from the geometrical cross section, first, in magnitude (it exceeds the geometric cross section) and, second, in the temperature dependence (a strong increase with decreasing temperature). At high temperatures (T ~ 900°K) the cross section reaches $Q_d = 2.6 \times 10^{-15}$ cm^2, which is almost double the geometric cross section of the normal atoms (20). It is of interest to see to what measure these differences are connected with the influence of the symmetry effect—the transfer of excitation from one atom to another during the collision process. The cross section for resonant excitation transfer was calculated in[4] and measured in[11]. At the present time there is still no full agreement between calculation and experiment. Nonetheless it can be regarded as established that the scattering with excitation transfer becomes significant only in the temperature region $T \approx 1000$°K. Therefore the quantity Q_d calculated for 900°K should contain a contribution from the resonant excitation transfer. At temperatures $T \approx 300$°K, the transfer of excitation is made difficult by the presence of a maximum on the potential curve $V_A(r)$. The value of the transfer cross section Q_{tr} becomes then smaller than 10^{-16} cm^2 and does not play any role in the diffusion of the metastable atoms.

The strong temperature dependence of the diffusion cross section is due to the form of the potential curve $V_A(r)$. The increase of the diffusion cross section with decreasing temperature is the result of the increase of the effective radius for the elastic scattering of the atoms (see Fig. 1). The obtained experimental data for the temperature dependence of the diffusion coefficient confirm the presence of a long-range repulsion between the normal and metastable helium atoms and agree with the interaction potential of Poshusta and Matsen.

Thus, at high temperatures, when the energy of the colliding particles is comparable with the height of the "hump" on the potential V_A, the diffusion of metastable atoms is determined by quantum symmetry effects (resonant excitation transfer). At low temperatures, the excitation transfer does not play any role, and the observed increase of the diffusion cross section reflects the existence of a long-range repulsion between atoms.

---

[1] R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. **A213**, 327 (1952).

[2] R. D. Poshusta and F. A. Matsen, Phys. Rev. **132**, 307 (1963).

[3] H. S. W. Massey and R. A. Smith, Proc. Roy. Soc. **A142**, 142 (1933).

[4] R. A. Buckingham and A. Dalgarno, ibid. **A213**, 506 (1952).

[5] N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions, Oxford, 1933.

[6] P. J. Bendt, Phys. Rev. **110**, 85 (1958).

[7] I. Ya. Fugol', P. L. Pakhomov, and Yu. F. Shevchenko, Opt. Spektrosk. **21**, 741 (1966).

[8] P. L. Pakhomov and I. Ya. Fugol', ZhETF Pis. Red. **3**, 389 (1966) [JETP Lett. **3**, 254 (1966)].

[9] A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1203 (1953).

[10] A. V. Phelps, ibid. **99**, 1307 (1955).

[11] F. D. Colegrove, L. D. Schearer, and G. K. Walters, ibid. **135**, 352 (1964).

Translated by J. G. Adashko
98