

PROCESSES OF ELASTIC SCATTERING OF METASTABLE

HELIUM ATOMS IN HELIUM GAS

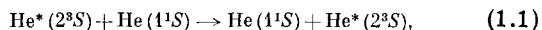
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Usp. Fiz. Nauk 97, 429-452 (March, 1969)

1. FEATURES OF ELASTIC SCATTERING OF METASTABLE 2^3S HELIUM ATOMS

THE elastic scattering of excited helium atoms in a gas of normal atoms has many features connected, first, with quantum symmetry effects and, second, with the unusual character of the interaction of the atoms. Helium itself is among those few objects for which theoretical calculation exist, so that a quantitative comparison of theory and experiment is possible. In this review we analyze the total and diffusion scattering cross sections, and also the process of scattering of metastable atoms



which is accompanied by excitation transfer. In this process, the excitation is transferred from one identical nucleus to the other without energy exchange of relative translational or internal motion between the individual atoms. Therefore scattering in accordance with the scheme (1.1) can be regarded as a modification of the elastic-scattering process.

The elastic scattering of metastable atoms in their own gas is characterized by two interaction potentials V_S and V_A . They pertain to two different states of the system of normal and metastable atoms, and differ in the character of the symmetry of the system wave function relative to permutation of identical nuclei. The antisymmetrical potential V_A corresponds to the antisymmetrical wave function of the system and has a minimum that results in the existence of the helium molecule He_2^* (the asterisk denotes the excited state). The molecular term of this antisymmetrical state is $2^3\Sigma_u^+$. The symmetrical potential V_S is pure repulsive, and the state has the symmetry of the term $2^3\Sigma_g^+$. The presence of two interaction potentials is essentially the consequence of quantum symmetry effects, and therefore the process of scattering of metastable helium atoms, generally speaking, cannot be described by the classical theory. The quantum theory of collisions between identical atoms was first developed by Massey and co-workers.^[1-5] The processes of elastic scattering of metastable and normal helium atoms were theoretically analyzed by Buckingham and Dalgarno.^[6] The calculation of the elastic-scattering cross sections for the isotopes He-4 and He-3 is given in^[7-8]. The diffusion scattering cross section of metastable atoms of inert gases was considered also by B. M. Smirnov et al.^[9] on the basis of the asymptotic expression for the interaction energy of the excited atom and the atom in the ground state, in the limit of large distances between them.

Another feature of the metastable helium molecule

He_2^* is the presence of a maximum on the potential-energy curve $V_A(R)$ at relatively large distances between the nuclei ($R = 4.5a_0$ and $a_0 = 0.53 \times 10^{-8}$ cm is the Bohr radius). This maximum is due to competition of exchange forces of different types. The interaction potentials of the normal and excited atoms were calculated by Buckingham and Dalgarno^[10] and were later refined in^[11,12]. It must be emphasized that the magnitude of the maximum on the $V_A(R)$ curve is small (it amounts to a fraction of an electron volt) and is determined by the difference between two large exchange energies—the electron-exchange energy in the atoms and the energy of simultaneous exchange of an electron and a nucleus. Therefore the results of calculations of the long-range repulsion are quite sensitive to the form of the wave functions. As a result of the approximate character of the calculation, both the very existence of a long-range repulsion and the law governing the variation of the potential at large distances require experimental confirmation and refinement.

For the study of the long-range interaction, particular interest attaches to experiments on the elastic scattering of metastable and normal atoms at low temperatures.

The first experimental determination of the coefficient of diffusion of the metastable helium atoms in their own gas at 300° K belongs to Ebbinghaus.^[13] Using an indirect method, Biondi^[14] also obtained the value of the diffusion coefficient at room temperature. A direct experimental measurement of the diffusion coefficient at room and nitrogen temperatures was performed by Phelps and Molnar.^[15,16] The diffusion of the metastable atoms of helium-4 and helium-3, in the entire temperature interval from 4.2° K to 300° K, was investigated in^[17,7,8]. The total scattering cross section of the excited helium atoms was measured by the molecular-beam method in^[18-22]. The cross section of the process (1.1) with excitation transfer was first measured by Colegrove et al.^[23] at room temperature. In a wide temperature interval, the cross section for the excitation transfer was investigated by the same authors in^[24]. Greenhow^[25] also measured this cross section at room temperature. Bendt^[26] determined the self-diffusion coefficient of normal He-3 atoms in He-4 in the temperature interval from 2° to 500° K. Bendt's data make it possible to calculate the geometrical self-diffusion cross section of normal helium atoms.

In this review we discuss and compare the results of theoretical and experimental investigations of the cross sections of the elastic processes from the point of view of reconstructing the potential of interaction between metastable and normal helium atoms.

2. FUNDAMENTAL RELATIONS OF THE QUANTUM THEORY OF SCATTERING

The scattering cross sections of different processes are determined by the scattering amplitude f . The quantum-mechanical expression for the amplitude f should be determined with allowance for the symmetry properties of the colliding atoms. The quantum theory of the scattering of identical atoms in the unexcited state is contained in the well known works of Massey et al.^[1-5] We present the results of calculations of the amplitude and of the differential scattering cross section for exciting and normal atoms in the presence of two interaction potentials.^[3,6] In the collision between excited and normal helium atoms, the principle of identity of the particles is applicable only to the nuclei. In the case of He-4, whose nuclei have no spin and are described by Bose-Einstein statistics, the wave function of the system Φ_{B-E} should be symmetrical with respect to permutation of the nuclei, i.e.,

$$\Phi_{B-E} = \Phi_+, \quad (2.1)$$

The index “+” denotes symmetrization of the wave function with respect to the coordinate of the nuclei. A similar relation holds also for the scattering amplitudes of these functions. The scattering probability is proportional to the differential cross section

$$|f_{B-E}|^2 = |f_+|^2, \quad (2.2)$$

where f_+ is the scattering amplitude of the function Φ_+ .

In the case of He-3, the nuclei of which have spin $1/2$ and obey Fermi-Dirac statistics, the total wave function Φ_{F-D} is antisymmetrical with respect to permutation of the nuclei. This function is constructed in the usual manner from products of spin and coordinate functions:

$$\Phi_{F-D} = \chi_+ \Phi_+ + \chi_- \Phi_-, \quad (2.3)$$

where χ_+ and χ_- are spin functions that are symmetrical and antisymmetrical with respect to the nuclei, and Φ_- is a coordinate function which is antisymmetrical with respect to permutation of the nuclei. According to Mott and Massey,^[4] the differential cross section for the scattering of unpolarized He-3 atoms is expressed in terms of the amplitudes f_+ and f_- by the formula

$$|f_{F-D}|^2 = \frac{1}{4} |f_+|^2 + \frac{3}{4} |f_-|^2. \quad (2.4)$$

In the presence of two interaction potentials, $V_S(R)$ and $V_A(R)$, the total wave function Φ of a system of identical atoms can be represented in the form^[6]

$$\Phi = \varphi_S \psi_S(R) + \varphi_A \psi_A(R); \quad (2.5)$$

here φ_S and φ_A are wave functions describing the electrons in the atoms at a fixed position of the nuclei, and φ_S and φ_A are symmetrical and antisymmetrical with respect to the permutation of the nuclei. The functions $\psi_S(R)$ and $\psi_A(R)$ describe the relative motion of the nuclei (ψ_S is symmetrical and ψ_A antisymmetrical with respect to the nuclei), and satisfy the Schrödinger equations with interaction potentials $V_S(R)$ and $V_A(R)$, respectively:

$$[\Delta + k^2 - M\hbar^{-2}V_{S,A}(R)] \psi_{S,A} = 0; \quad (2.6)$$

here

$$k = \frac{Mv}{2\hbar} \quad (2.7)$$

is the wave number of the relative motion of the helium atoms with mass M and relative velocity v .

The scattering amplitude of the functions ψ_S and ψ_A are connected in the usual manner with the scattering phases of the partial waves:

$$f_S(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) [\exp(2i\beta_l) - 1] P_l(\cos\theta), \quad (2.8)$$

$$f_A(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) [\exp(2i\gamma_l) - 1] P_l(\cos\theta). \quad (2.9)$$

The scattering phases β_l and γ_l correspond to the potential $V_S(R)$ of the symmetrical state and to the potential $V_A(R)$, respectively.

Knowing the scattering amplitudes $f_S(\theta)$ and $f_A(\theta)$, it is easy to find the amplitudes $f_+(\theta)$ and $f_-(\theta)$. To this end it is necessary to symmetrize the wave function, namely, it is necessary to take for $f_+(\theta)$ the symmetrical part of the total scattering amplitude

$$f_S(\theta) + f_A(\theta) \quad (2.10)$$

and for $f_-(\theta)$ the antisymmetrical part. The permutation of the nuclei corresponds to replacement of the scattering angle θ by $\pi - \theta$. The symmetrical (antisymmetrical) part of the amplitude $f_S(\theta)$ is

$$\frac{1}{2} [f_S(\theta) \pm f_S(\pi - \theta)], \quad (2.11)$$

and the symmetrical (antisymmetrical) part of the amplitude $f_A(\theta)$ is

$$\frac{1}{2} [f_A(\theta) \mp f_A(\pi - \theta)]. \quad (2.12)$$

The change of the sign in front of the second term in (2.4) is due to the antisymmetry of the electronic wave function φ_A relative to the permutation of the nuclei. We obtain consequently for the amplitudes f_{\pm} the formula

$$f_{\pm}(\theta) = \frac{1}{2} \{ [f_S(\theta) + f_A(\theta)] \pm [f_S(\pi - \theta) - f_A(\pi - \theta)] \}. \quad (2.13)$$

The square of the modulus of these amplitudes can be represented in the form

$$|f_{\pm}(\theta)|^2 = \frac{1}{4} [|f_S(\theta) + f_A(\theta)|^2 + |f_S(\pi - \theta) - f_A(\pi - \theta)|^2] \pm S(\theta), \quad (2.14)$$

where $S(\theta)$ are the interference terms containing products of the type $f_{S,A}(\theta)f_{S,A}(\pi - \theta)$. It is known^[4] that the scattering amplitudes $f_S(\theta)$ and $f_A(\theta)$ have “sharp” maxima at small values of θ , i.e., the functions $f_{S,A}(\theta)$ and $f_{S,A}(\pi - \theta)$ do not overlap, and their product is close to zero. For this reason, the interference terms can be neglected, and the differential cross sections $|f_+(\theta)|^2$ and $|f_-(\theta)|^2$ turn out to be the same. Consequently, the differential cross sections for the scattering of the metastable atoms of helium-4 and helium-3 are equal to each other:

$$|f(\theta)|^2 = |f_{B-E}|^2 = |f_{F-D}|^2 = \frac{1}{4} [|f_S(\theta) + f_A(\theta)|^2 + |f_S(\pi - \theta) - f_A(\pi - \theta)|^2]. \quad (2.15)$$

The first term in (2.15) can be regarded as the probability of direct elastic scattering of the excited and normal atoms; the second term is due to the difference between the potentials V_S and V_A , and describes the process of scattering with excitation transfer (1.1).

Knowledge of the differential scattering cross section makes it possible to express the total cross section, the diffusion cross section, and the excitation-transfer cross section in terms of the scattering phases.

The total cross section Q is given by the formula

$$Q = 2\pi \int_0^\pi d\theta \sin \theta |f(\theta)|^2 = 4\pi k^{-2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l, \quad (2.16)$$

where the even phases $\delta_{2l} = \beta_{2l}$ are determined by the potential V_S and the odd phases $\delta_{2l+1} = \gamma_{2l+1}$ are determined by the potential V_A .

The diffusion (transport) cross section is

$$Q_d = 2\pi \int_0^\pi d\theta \sin \theta (1 - \cos \theta) |f(\theta)|^2 = 4\pi k^{-2} \sum_{l=0}^{\infty} (l+1) \sin^2 (\delta_l - \delta_{l+1}). \quad (2.17)$$

The excitation transfer cross section Q_{tr} is determined by that part of the differential scattering cross section (2.15) which is connected with the difference between the interaction potentials and the permutation of the nuclei (the second term in (2.15)). The differential excitation-transfer cross section is

$$|f_{tr}(\theta)|^2 = \frac{1}{4} |f_S(\pi - \theta) - f_A(\pi - \theta)|^2. \quad (2.18)$$

The transfer cross section T_{tr} is given by

$$\begin{aligned} Q_{tr} &= 2\pi \int_0^\pi d\theta \sin \theta |f_{tr}(\theta)|^2 = \frac{\pi}{2} \int_0^\pi d\theta \sin \theta |f_S(\theta) - f_A(\theta)|^2 \\ &= \pi k^{-2} \sum_{l=0}^{\infty} (2l+1) \sin^2 (\beta_l - \gamma_l). \end{aligned} \quad (2.19)$$

All the cross sections (Q , Q_d , and Q_{tr}) are uniquely determined by the scattering phases β_l and γ_l , which are connected in turn with the form of the interaction potentials V_S and V_A .

3. INTERACTION POTENTIALS

The potentials of interaction between the metastable and normal atoms in the $^3\Sigma_u^+$ and $^3\Sigma_g^+$ states were calculated by Buckingham and Dalgarno in the first order of perturbation theory with the aid of the Heitler-London method. They obtained the following formula for the interaction energy:

$$V_{S,A} = \frac{H^{(1)} - 2H^{(2)} \pm (H^{(3)} - 2H^{(4)})}{I^{(1)} - 2I^{(2)} \pm (I^{(3)} - 2I^{(4)}), \quad (3.1)$$

where $H^{(1)}$ is the average energy of the Coulomb interaction between the electrons and the nuclei, $H^{(2)}$ is the energy of the exchange interaction due to the electron exchange, $H^{(3)}$ is the exchange energy due to the exchange of nuclei, and $H^{(4)}$ is the exchange energy in the case of simultaneous exchange of electrons and nuclei; $I^{(k)}$ are the corresponding normalization integrals. Values of $H^{(k)}$ and $I^{(k)}$ as functions of the distances between the nuclei are given in [10]. The term with $H^{(3)}$ is due to the pure nuclear exchange, significant only at small distances, and leads to the appearance of a minimum at $R \approx 2a_0$. It can be neglected in the region $R > 2a_0$. At the same distances, on the other hand, the Coulomb energy $H^{(1)}$ is much smaller than the electron exchange energy $2H^{(2)}$, owing to the strong screening of the nuclei by the electrons. The difference between the potentials V_S and V_A at $R > 2a_0$ is due to the term $H^{(4)}$. For the symmetrical potential, the terms $H^{(2)}$ and $H^{(4)}$

add up and produce a repulsion interaction. For the antisymmetrical potential, the competition between these two terms, which enter with opposite signs, leads to the appearance of a maximum of the long-range repulsion. According to the calculations of Buckingham and Dalgarno, the height of the "hump" of the maximum at $R = 4h_0$ amounts to 0.29 eV. The decrease of the long-range repulsion potentials is described by the function

$$V_{S,A}(R) \sim aR^2 \exp\left(-1.18 \frac{R}{a_0}\right) \pm bR \exp\left(-1.87 \frac{R}{a_0}\right). \quad (3.2)$$

Starting with the distance $7a_0$, the second term in (3.2) is negligible (the value of $H^{(4)}$ in (3.1) is negligibly small) and the potentials V_S and V_A practically coincide. In this region, the potentials are likewise well approximated by a power-law dependence in the form

$$V_{S,A}(R) = \text{const} \cdot R^{-6}. \quad (3.3)$$

Figure 1 shows plots of these interaction potentials as functions of R . In the same paper, Buckingham and Dalgarno discussed second-approximation corrections to the interaction energy due to the Van der Waals forces. The Van der Waals forces play an important role at distances $R > 4a_0$, and are determined by the polarizability of the atoms. Since the polarizability of the metastable atoms is not known with sufficient accuracy, Buckingham and Dalgarno plotted potential curves for two values of the Van der Waals energy, -10^{-6} and $-20R^{-6}$ (in atomic units*). Using $-20R^{-6}$, the maximum of the repulsion turned out to equal 0.146 eV and to be located at $R = 4.25h_0$.

The work by Buckingham and Dalgarno attracted considerable interest and simulated further theoretical investigations. The most detailed calculations of the interaction potentials were undertaken by Matson and his coworkers. [11,12] Unlike [10], they used a variational calculation method. It was confirmed in [11] that the potential curve $V_A(R)$ has a maximum, the height of which was estimated to be 0.19 eV at $R = 4.5a_0$. The authors of [11] attribute the deviation from the results of Buckingham and Dalgarno to the use of a better approximation for the wave functions. In a later paper,

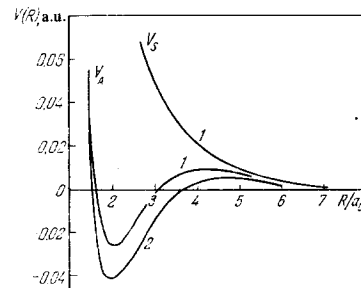


FIG. 1. Potentials of the interaction between the metastable (2^3S) and normal (1^1S) helium atoms: 1—potentials calculated by Buckingham and Dalgarno in the first approximation (B-D) [6]; 2—potential $V_A(R)$ according to Poshusta and Matson (P-M) [12].

*The atomic unit of energy is $e^2/a_0 = 27.21$ eV, and the unit of length is $a_0 = 0.53 \times 10^{-8}$ cm.

Poshusta and Matson^[12] gave refined values of $V_A(R)$ up to $R = 6a_0$. According to^[12], the height of the maximum is 0.138 eV at $R = 4.5a_0$.* Figure 1 shows the interaction potential of Poshusta and Matson. We note that the height of the maximum, estimated in^[10] with allowance for the second approximation for $V_A(R)$, agrees fairly well with the calculation of Poshusta and Matson.^[12] Quite recently, Dalgarno and his co-workers made a new calculation of the static polarizability of the helium atoms in the states 1^1S , 2^3S and others.^[39] Using the results of these calculations, they found that the constant of the Van der Waals interaction $-CR^{-6}$ between the metastable and the normal atoms of helium is $C = 29.1$ a.u. This value of the constant C is larger than those employed in the calculation of the interaction potentials $V_S(R)$ and $V_A(R)$ in^[10]. The increase of the Van der Waals interaction should lead to a certain lowering of the potential curve of the interaction in the region of large distances, compared with the potential in^[10]. The asymptotic behavior of the interaction energy of the metastable and normal atoms of the inert gases at large distances was considered by B. M. Smirnov et al.^[27,9,40] The interaction energies as given by various authors are listed in the table.

Interaction energy of metastable (2^3S) and normal helium atoms as given by various authors (in units of 10^{-3} a.e. = 0.0272 eV)

R , un. of a_0	V_A				V_S	
	B-D [10], first approximation	P-M [12]	Asymptotic P-S-Ch [9]	Empirical po- tential [8]	B-D [10]	Empirical po- tential [8]
4.0	10.35	3.2	13	3.2	21.43	21
4.5		5.1		5.1		
5.0	6.11	5.05	5.4	5.05	8.1	8.1
5.5		4.3		4.3		5.4
6.0	3.00	3.2	2.1	3.2	3.3	3.3
6.5				1.6		1.75
7.0	1.33		0.78	0.6	1.4	0.6
7.5				0.25		0.25
8.0	0.57		0.28	0.1	0.6	0.1
8.5				0.05		0.05
9.0	0.23		0.1		0.23	
10.0	0.08		0.04		0.08	

The existence of a maximum of long-range repulsion for helium was at first unexpected. Recently, however, similar repulsion maxima were theoretically predicted also for other excited atoms of the helium and hydrogen molecules.^[28,29] The presence of such a maximum is apparently possible also for excited states of the neon molecule.^[30] It can be assumed that the potential barrier on the interaction curve exists also for excited states of many molecules consisting of identical atoms.

4. EMPIRICAL POTENTIAL. CALCULATION OF THE CROSS SECTIONS OF ELASTIC PROCESSES

The potential barrier hinders the formation of the He_2^* molecule and exerts a strong influence on the processes of scattering of metastable and normal atoms. It is therefore important to have reliable data on the

* It should be pointed out that the height of the maximum is given in the plot and in the tables of^[12] as 0.138 eV, whereas the text lists a different value, 0.08 eV.

magnitude of the long-range repulsion. Owing to the approximate character of the theoretical calculations, great interest attaches to the solution of the "inverse" problem—the reconstruction of the potential curve from the experimental data.

In very rough outlines, the idea of reconstructing the potential consists in the following: The scattering cross section at a given average energy (temperature) is obtained from the experimental data. The magnitude of the cross section depends on the scattering radius a , and the particle energy depends on the height of the potential at this value of the radius. Knowing the dependence of the cross section and the energy (temperature), it is possible to obtain the potential curve. Obviously, this method can be used to reconstruct only the repulsion potentials. Actually, on the other hand, the repulsion potential cannot be reconstructed in such a simple manner. This is connected primarily with the fact that the repulsion has a nonlocal character: the scattering is connected with an entire region on the potential curve. The nonlocality is manifest already in the very single act of scattering, in the form of a change of the particle velocity as a result of the interaction. In addition, the nonlocality is due to the particle velocity distribution, and in the quantum case to the uncertainty principle. In fact, for the construction of the potential it is necessary, using some heuristic considerations, to choose a potential function such that the cross sections calculated with its aid and their temperature dependences agree with experiment. In the case of helium, the theoretically calculated potentials are in a semiquantitative agreement with experiment. The experimental data make it possible to correct and refine the interaction potential.

The long-range repulsion potentials $V_A(R)$ and $V_S(R)$ were reconstructed from the temperature dependence of the diffusion coefficient and the diffusion cross section in our paper.^[7,8] The constructed empirical potential in the region of large distances ($R > 4a_0$) is shown in Fig. 2; the corresponding values of the energy are listed in the table. The empirical potential V_A in the region of the maximum differs from the potential of Buckingham and Dalgarno (B-D) and coincides with the data of

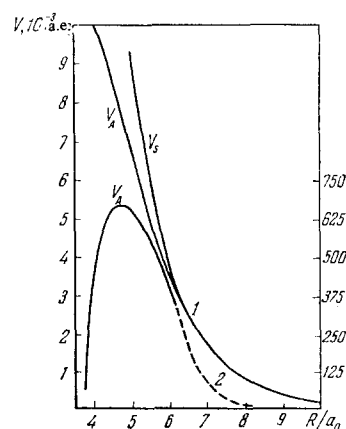


FIG. 2. Long-range part of the $He(2^3S) - He(1^1S)$ interaction potential: 1—the Buckingham and Dalgarno potential; 2—empirical potential. The temperature scale on the right is calculated from the relation $\mu v_d^2 = 2V(R)$, where $\mu = M/2$ is the reduced mass and $v_d = (5\kappa T/\mu)^{1/2}$ is the diffusion velocity.

Poshusta and Matson (P-M). The empirical potential can be represented with good accuracy by the asymptotic form (when $R < 6a_0$)

$$V_A(R) \sim AR^2 \exp(-2,04R). \quad (4.1)$$

$A = 21,12 \text{ a.u.}$

or

$$V_A(R) \sim CR^{-12}, \quad C = 75 \text{ a.u.}$$

Here R is expressed in units of a_0 . The empirical potential at larger distances decreases more steeply than the B-D first-approximation potential. Experiments show that the difference between V_A and V_S is not significant when $R > 7a_0$. The potential V_S for $R < 6a_0$ was chosen in accordance with the B-D second-approximation calculation.

The use of the diffusion cross section for the reconstruction of the potential is convenient because the quantum diffraction effects are likewise much less pronounced in the diffusion than in the total cross section. This is connected with the fact that small scattering angles make no noticeable contribution to the diffusion cross section, owing to the factor $(1 - \cos \theta)$ (see (2.17)). In addition, the role of the quantum symmetry effects connected with excitation transfer is small at low temperatures, when the difference between the potentials $V_A(R)$ and $V_S(R)$ is small compared with each of them. For the total cross section and the excitation transfer cross section, the quantum effects are more important.

We proceed now to calculate the elastic scattering cross sections, using the empirical potential. We start from the formulas of the quantum theory of scattering. Although the diffusion cross section can be calculated classically, for the sake of uniformity, we shall calculate all the cross sections, Q , Q_d , and Q_{tr} , by means of the quantum formulas (2.16), (2.17), and (2.19). The scattering phases will be determined from the Jeffries quasiclassical formulas:^[4]

$$\delta_l = \int_0^\infty dR \left[k^2 - \frac{M}{\hbar^2} V(R) - \frac{(l+1/2)^2}{R^2} \right]^{1/2} - \int_0^\infty dR \left[k^2 - \frac{(l+1/2)^2}{R^2} \right],$$

where $V(R) = V_S(R)$ for the phases β_l and $V(R) = V_A(R)$ for the phases γ_l . The lower limit of integration is the largest root of the integrand. Expression (4.2) is valid in the quasiclassical approximation, whose applicability conditions, as is well known, is

$$a \gg \lambda = \frac{\hbar}{Mv}, \quad aV(a) \gg \hbar v; \quad (4.3)$$

Here a is the radius of the scattering potential, and $V(a)$ is of the order of magnitude of the potential in this region. For the interaction potentials of the normal and metastable helium, shown in Fig. 2, the quasiclassical conditions are satisfied up to velocities $v \approx 4 \times 10^4$ cm/sec, which corresponds approximately to $T \approx 20^\circ \text{ K}$.

The integration in (4.2) was carried out graphically for definite values of k in the interval from $k = 1 \times 10^8 \text{ cm}^{-1}$ ($E = 0.038 \times 10^{-3} \text{ a.u.}$) to $k = 1 \times 10^9 \text{ cm}^{-1}$ ($E = 3.8 \times 10^{-3} \text{ a.u.}$). Figure 3 shows a plot of the phase against the number at different energies E . We see that at high energies ($E \sim 10^{-3} \text{ a.u.}$) a difference appears between the phases γ_l and β_l for different potentials. At low energies, only several of the first few phases are of appreciable magnitude. The number l of phases that are

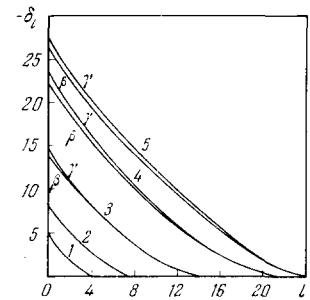


FIG. 3. Dependence of the scattering phases on the number at different energies $E = \hbar^2 k^2 / M$ (in a.u.)

essential for the scattering is approximately equal to the number of partial waves subtended by the characteristic scattering radius, i.e.,

$$l \approx ka. \quad (4.4)$$

Therefore, in calculating the cross sections at low energies, we can confine ourselves to several phases, whereas at high energies the number of phases increases.

The known scattering phases for the empirical potentials were used to calculate the total scattering cross section Q (2.16), their diffusion cross section Q_d (2.17), and the excitation-transfer cross section Q_{tr} (2.19). The plots of all these cross sections against the energy are shown in Fig. 4. The total and diffusion cross sections have rather large values: Q ranges from 0.6×10^{-14} to $0.9 \times 10^{-14} \text{ cm}^2$, and Q_d from 0.3×10^{-14} to $0.7 \times 10^{-14} \text{ cm}^2$. Such appreciable scattering cross sections are a reflection of the existence of a long-range repulsion between the metastable and normal helium atoms. The increase of the cross sections with decreasing energy is connected with the increase of the effective radius of the scattering potential. The total and diffusion cross section curves can be approximated with sufficient accuracy, for large velocities, by a formula of the type

$$Q = \alpha + \frac{\beta}{v}, \quad (4.5)$$

where v is the relative velocity, $v = 2\hbar k / M$.

For the total cross section we have

$$\alpha = 5.2 \cdot 10^{-15} \text{ cm}^2, \quad \beta = 2.8 \cdot 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (4.6)$$

For the diffusion cross section, the interpolation coefficients are equal to

$$\alpha_d = 2.6 \cdot 10^{-15} \text{ cm}^2, \quad \beta_d = 2 \cdot 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (4.7)$$

We note that an interpolation of the type (4.5) for the total cross section is satisfactory when $v \geq 2 \times 10^5 \text{ cm/sec}$; the calculated values of $Q(v)$ at low velocities increase more slowly than in accordance with formula (4.5). For low velocities ($v < 2 \times 10^8 \text{ cm/sec}$), the dependence of the total cross section on the velocity $Q(v)$ is approximated much better by a power-law function of the type

$$Q = C_1 v^{-0.18} (\text{km/sec}), \quad C_1 = 8 \cdot 10^{-15} \text{ cm}^2 \quad (4.8)$$

The interpolation (4.5) for the diffusion cross section is sufficiently good even at low velocities, owing to the more rapid increase of Q_d with increasing velocity (see Fig. 4). The quantities α are the limiting values of the scattering cross sections at high velocities.

The excitation-transfer cross section begins to in-

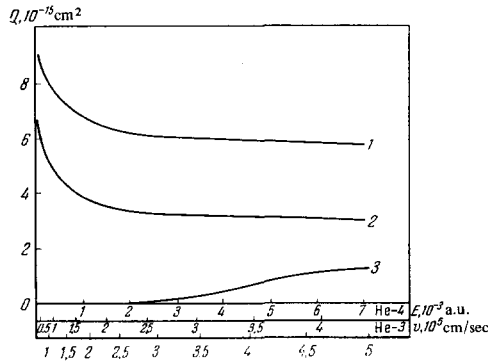


FIG. 4. Cross sections for the scattering of metastable (2^3S) and normal helium atoms: 1—total cross section Q ; 2—diffusion cross section Q_d ; 3—excitation-transfer cross section Q_{tr} .

crease at energies above 0.6×10^{-3} a.u., and is much smaller than the diffusion and total cross sections. This is a reflection of the quality of the potentials V_S and V_A at large distances, owing to the presence of a ‘‘hump’’ on the potential V_A . The value of Q_{tr} reaches a maximum at energies on the order of 4×10^{-3} a.u. (~ 0.1 eV); in this case $Q_{tr} \approx 1.3 \times 10^{-15} \text{ cm}^2$.

The different cross sections are connected by simple limiting relations at low and high energies. In the region of low values of k , the principal role is played by s -scattering ($l = 0$). In formulas (2.16) and (2.17) it is necessary to retain only the first terms with $l = 0$. The zeroth phase δ_0 is asymptotically equal to $\delta_0 = -ka$, where a is the effective scattering radius at extremely low energies. From (2.16) and (2.17) we obtain the following limiting relations for the total and diffusion cross sections:

$$Q = Q_d = 4\pi a^2, \tag{4.9}$$

i.e., as $k \rightarrow 0$ ($ka \ll 1$), the total and diffusion cross sections become equal. For the considered potentials V_A and V_S , the condition $ka \ll 1$ is satisfied at atom velocities $v \ll 10^4$ cm/sec. The excitation-transfer cross section in this energy region is certainly equal to zero, since the phases β_l and γ_l are the same.

Starting with velocities of the order of $v \gtrsim 10^5$ cm/sec, another limiting case $ka \gg 1$ is satisfied. All the partial waves with $l \leq ka$ contribute to the scattering. To determine the connection between the limiting values of the cross sections Q , Q_d , and Q_{tr} , the analysis can be carried out in the approximation of rectangular barriers with effective radii $a_A(v)$ and $a_S(v)$, which depend on the particle velocity. At large values of ka , the scattering phases β_l and γ_l are large compared with unity (Fig. 5). Let us consider the limiting value of the total cross section (2.16). The squares of the sine functions in these expressions can be replaced by their mean values $\frac{1}{2}$, and the summation over l can be replaced by integration. The upper integration limit is ka_S for even phases and ka_A for odd ones. As a result we obtain

$$Q = \pi (a_S^2 + a_A^2). \tag{4.10}$$

The limiting value of the diffusion cross section can be calculated analogously in that energy region where not only the phases themselves are large, but also phase differences of the type $\beta_l - \gamma_{l+1}$ are much larger than

unity; then

$$Q_d = \frac{\pi}{2} (a_S^2 + a_A^2). \tag{4.11}$$

Formula (4.11) is valid if

$$k |a_S - a_A| \gg 1. \tag{4.12}$$

Indeed, for a rectangular area, the phases are asymptotically equal to $\delta_l = -ka - l\pi/2$, and the differences are $\delta_l - \delta_{l+1} = \pi/2 \pm k(a_S - a_A)$. Therefore relation (4.11) may be violated in the energy region where the difference between the potentials is small. Where the inequality (4.12) is satisfied, the following connection exists between the cross sections Q and Q_d :

$$Q = 2Q_d. \tag{4.13}$$

Finally, in the energy region where the condition (4.12) is satisfied, we obtain for the transfer cross section

$$Q_{tr} = \frac{\pi}{4} (a_S^2 + a_A^2) = \frac{1}{2} Q_d \pm \frac{1}{4} Q. \tag{4.14}$$

The limiting relations (4.14) show that the diffusion cross section is twice as large as the excitation-transfer cross section and half as large as the total cross section. As is well known, the difference between Q and Q_d is connected with quantum effects—the contribution of small-angle scattering to the total cross section. Relations (4.14) are valid at particle energies both larger and smaller than the height of the ‘‘hump’’ on the potential V_A . However, the effective scattering radius a_A decreases at an energy exceeding the height of the ‘‘hump.’’ As seen from Fig. 4 and from the interpolation coefficients (4.6) and (4.7), the limiting relations (4.14) are well satisfied for all three cross sections. Indeed, at large values of k we get $Q = 5.2 \times 10^{-15} \text{ cm}^2$, $Q_d = 2.6 \times 10^{-15} \text{ cm}^2$, and $Q_{tr} = 1.3 \times 10^{-15} \text{ cm}^2$.

We have also performed numerical calculations using the potential of Buckingham and Dalgarno. The results for the diffusion and excitation-transfer cross sections agree with the corresponding calculations of [6]*. The cross sections are Q_d and Q_{tr} with the B-D potential, as expected, were larger than the cross sec-

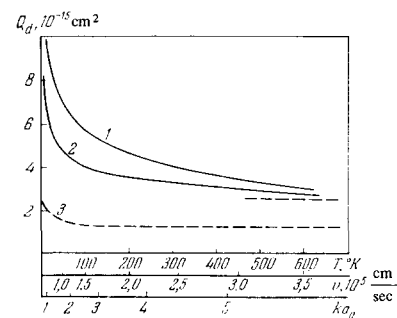


FIG. 5. Diffusion scattering cross section Q_d : 1—calculation with B-D potential; 2—calculation with empirical potential; 3—geometric self-diffusion cross section (from [26]).

*The formula used in [6] to calculate the cross section Q_d had a coefficient half as large as in (2.17). This decreased the results of the corresponding numerical calculations. In the comparison of the $Q_d(v)$ dependence for the different interaction potentials, we have doubled the data of [6] for the differential cross section throughout.

tions calculated with the empirical potential, but their energy dependences turned out to be similar. A check has revealed appreciable discrepancies both in the values of the total cross section Q and in the energy dependence $Q(v)$. Apparently, an error was made in the numerical calculations of the total cross section in [6]. This probably explains why the limiting values of the cross sections as given by [6] do not satisfy relations (4.14). Figure 5 shows the diffusion cross sections calculated for the Buckingham and Dalgarno potential and for the empirical potential. For comparison, the same figures shows the diffusion cross section of normal helium atoms as given by Bendt. [28]

5. EXPERIMENTAL INVESTIGATION OF THE DIFFUSION OF METASTABLE HELIUM-4 ATOMS AND HELIUM-3 ATOMS IN A GAS OF NORMAL ATOMS

The diffusion cross section can be determined by an experimental study of the diffusion. The diffusion coefficient of the metastable atoms is determined by measuring the kinetics of the decay of the metastable state 2^3S in the afterglow of discharge in helium. At sufficiently low pressures and low gas densities, the destruction of the metastable atoms proceeds mainly as a result of their diffusion to the vessel walls. The change in the metastable-atom concentration $M(t)$ is described by a diffusion equation with a coefficient D

$$\frac{\partial M}{\partial t} - D\Delta M = 0. \quad (5.1)$$

We shall assume that deactivation of the metastable state takes place on the surface of the discharge vessel, so that the following boundary condition is valid

$$M_{\text{sur}} = 0. \quad (5.2)$$

The time variation of the volume-average concentration is exponential

$$M(t) = M_0 \exp\left(-\frac{D}{\lambda^2} t\right), \quad (5.3)$$

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

The concentration of the metastable atoms in the state 2^3S is measured by determining the resonant absorption of the 3889 Å line from an external source. At low optical densities, the concentration is proportional to the integral absorption of the resonant line, viz., $M \sim \Delta I/I_0$, where I_0 is the intensity in the absence of absorption and $\Delta I = I_0 - I$ is the magnitude of the absorption. The experimental setup and other details of the experiment are described in [7, 31, 32].

The accuracy of the experimental results that follow is determined by the errors in the measurement of the total absorption ($\pm 5\%$) and by the uncertainty of the gas temperature ($\pm 5-8\%$ at low temperatures and $\pm 3\%$ at room temperature). So large a temperature inaccuracy is connected with the heating of the gas during the time of the excitation pulse. Therefore the average error in the determination of D amounts to approximately $\pm(5-10)\%$, and a somewhat smaller value of the diffusion coefficient is more probable.

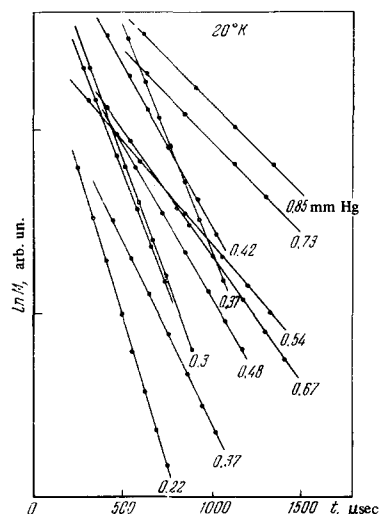


FIG. 6. Time dependence of the metastable atom concentration M (in the afterglow), $T = 20^\circ\text{K}$, the pressures are indicated in relative units $P = P_{300} T/300$ mm Hg.

The destruction of the metastable atoms was investigated in helium-3 and in helium-4 in the temperature interval 300–4° K and in the pressure interval 0.2–5 mm Hg. (The pressures are given in the relative units $P = P_{300} T/300$ throughout.) Under these conditions, the observed experimental plots of $M(t)$ in the afterglow are exponential curves. This is illustrated in Fig. 6, which shows plots of $M(t)$ in a semilogarithmic scale at liquid-hydrogen temperature and at different pressures. The slopes of the straight lines have the meaning of the diffusion collision frequency ν . In accordance with (5.3), the value of ν is connected with the diffusion coefficient by the relation

$$\nu = \frac{D}{\lambda^2}. \quad (5.4)$$

The correctness of such an interpretation of the experimental data is confirmed also by the fact that the dependence of the argument of the exponential on the pressure corresponds to the dependence of the diffusion coefficient on P . Figure 7 shows the dependence of the collision frequency of the pressure at different temperatures for helium-3 and helium-4. The experimental points lie on hyperbolas $\nu P = \text{const}$, i.e., for each temperature one determines a $DP = \text{const}$. The values of these constants are listed in the caption of Fig. 7. This method was used to measure the temperature dependence of DP for helium-3 and helium-4. Figure 8 shows this dependence. The experimental points fit a power-law curve of the type

$$D \propto T^q, \quad q = 0.65 \pm 0.06. \quad (5.5)$$

The diffusion coefficients for helium-3 and helium-4 differ in the entire investigated temperature interval by a constant factor

$$\frac{D(\text{He-3})}{D(\text{He-4})} = 1.15. \quad (5.6)$$

This factor is equal to the square root of the isotope-mass ratio.

Let us proceed to a discussion of the experimental

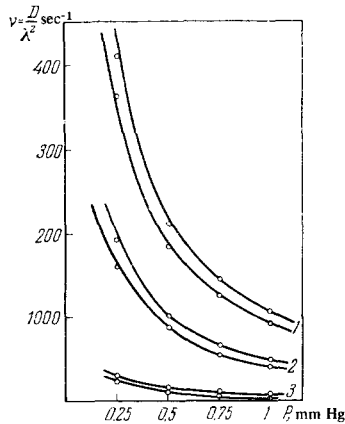


FIG. 7. Pressure dependence of the diffusion collision frequency (in relative units $P = P_{300}T/300$) for helium-3 (upper curves) and helium-4 (lower curves) ($\lambda^2 = 0.5 \text{ cm}^2$). 1 - $T = 300^\circ\text{K}$, $DP = 540$ (He-3), $DP = 470$ (He-4); 2 - $T = 77^\circ\text{K}$, $DP = 250$ (He-3), $DP = 210$ (He-4); 3 - $T = 4^\circ\text{K}$, $DP = 32.5$ (He-3), $DP = 28$ (He-4). \circ - experimental data, curves - for $DP = \text{const}$.

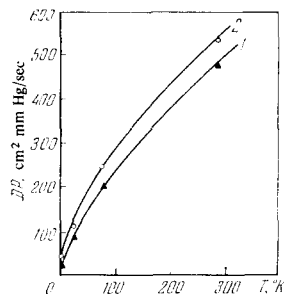


FIG. 8. Temperature dependence of the diffusion coefficient of metastable helium-3 and helium-4 atoms in their own gas. \circ, \blacktriangle - experimental data; curves - $D \propto T^{2/3}$; 1 - He-4, 2 - He-3.

data and to a comparison with the theoretical results on the diffusion cross section. According to the kinetic theory of Chapman and Enskog (see [33]) the diffusion coefficient D is expressed in terms of the diffusion cross section in the following manner:

$$D = \frac{3\pi}{32} \left(\frac{16\kappa T}{\pi M} \right)^{1/2} \frac{1}{N \bar{Q}_d(T)}; \quad (5.7)$$

here N is the particle density and $\bar{Q}_d(T)$ is the average diffusion cross section, equal to

$$Q_d(T) = \left(\frac{M}{4\kappa T} \right)^3 \int_0^\infty dv v^3 Q_d(v) \exp\left(-\frac{Mv^2}{4\kappa T}\right). \quad (5.8)$$

As seen from (5.8), the integrand

$$f(v) = v^3 \exp\left(-\frac{Mv^2}{4\kappa T}\right) \quad (5.9)$$

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

$$v_d = \left(\frac{10\kappa T}{M} \right)^{1/2}. \quad (5.10)$$

If the cross section $Q_d(v)$ is constant or depends little on v , then the quantity $Q_d(v)$ (5.8) can be taken outside the integral sign at the point $v = v_d$ (or at the energy $E_d = 5\kappa T/2$). Therefore the diffusion velocity determines the temperature scale on going over from the $Q_d(v)$ dependence to $\bar{Q}_d(T)$ (this temperature scale is shown in Figs. 2 and 5).

Using the interpolation formula (4.5) for the diffusion cross section $Q_d(v)$, we obtain

$$\bar{Q}_d(T) = \alpha_d + \frac{3}{4} \beta_d \left(\frac{16\kappa T}{\pi M} \right)^{-1/2}. \quad (5.11)$$

Expression (5.11), accurate to several per cent, coincides with the value of $Q_d(v)$ at $v = v_d$. Substituting the average value $\bar{Q}_d(T)$ in (5.7), we get the formula

$$DN = \frac{3\pi}{32} \frac{(16\kappa T/\pi M)^{1/2}}{\alpha_d + 0.75\beta_d (16\kappa T/\pi M)^{-1/2}}. \quad (5.12)$$

If we express the concentration N in terms of the relative pressure P and compare the values of the numerical constants, then (5.12) can be represented in the form

$$DP = 0.31 \cdot 10^{-16} DN = \frac{36.5T}{5.75 + T^{1/2}}, \quad (5.13)$$

where T is in degrees Kelvin. Expression (5.13) makes it possible to calculate the theoretical temperature dependence of the diffusion coefficient for the empirical potential. The interpolation formula (4.5) for the cross section Q_d with a B-D potential (see Fig. 5) has the coefficients $\alpha_d = 2.6 \times 10^{-15} \text{ cm}^2$ and $\beta_d = 4 \times 10^{-10} \text{ cm}^3/\text{sec}$. In this case the temperature dependence of the diffusion coefficient is described by the expression

$$DP = \frac{36.5T}{11.5 + T^{1/2}}. \quad (5.14)$$

Figure 9 shows a comparison of the experimental results obtained by various workers with the calculated temperature dependences of the diffusion coefficient. We see that our experimental data agree well, within the limits of experimental error, with those calculated on the basis of the empirical potential. The quantity $DP = 470 \text{ cm}^2/\text{sec mm Hg}$, measured by Phelps [16] at room temperature, does not differ from our data. The values obtained in an earlier paper [15] are $DP = 410 \text{ cm}^2 \text{ sec}^{-1} \text{ mm Hg}$ for 300°K and $DP = 130 \text{ cm}^2/\text{sec mm Hg}$ for 77°K . The last two values of DP are much lower than the values measured by us. As indicated by Phelps, the values of DP obtained later in [16] are more reliable. The values obtained for DP by Ebbinghaus and Biondi at 300°K

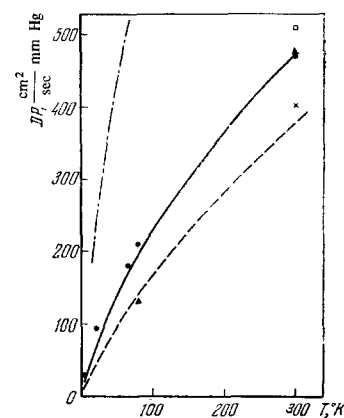


FIG. 9. Comparison of the calculation and experiment on the diffusion of metastable helium-4 atoms. Solid curve - calculation for the empirical potential $V(R)$ in accordance with formula (5.13); dashed - calculation for B-D potential in accordance with formula (5.14); dash-dot - for normal atoms (from [26]); \bullet - our experimental data [5]; \blacktriangle - data of Phelps [15, 16]; \times - experiment by Ebbinghaus [13]; \square - the results of Biondi [14].

differ from ours by 10–15%, which is within the limits of the experimental errors indicated by these authors.

It follows evidently from Fig. 9 that the Buckingham and Dalgarno first-approximation potential can not explain the entire aggregate of the experimental data on the diffusion of metastable atoms in their own gas at low temperatures. In essence, it was just these discrepancies that made it necessary to construct the empirical potential, which was chosen such as to reconcile the experimental and theoretical values of DP in the entire investigated temperature interval.

From the already indicated experimental fact that the diffusion coefficients of the isotopes helium-3 and helium-4 are inversely proportional to $M^{1/2}$, it can be concluded that the average cross sections $\overline{Q_d}(T)$ are equal (see (5.7)). This in turn is evidence of the equality of the cross sections $Q_d(E)$ of the two isotopes at the same energies (but not at the same velocities). By the same token, this confirms the theoretical conclusion (2.15), namely that the differential scattering cross sections $|f(\theta)|^2$ are equal in the case of collisions of atoms whose nuclei obey different statistics. In addition, it follows from this experimental fact that the interaction potentials for both isotopes can be regarded as the same. The latter conclusion is quite natural, since the interaction potentials are determined principally by the exchange and the Van der Waals interactions, which do not depend on the mass of the nucleus. Thus, experiments with helium-3 afford a satisfactory experimental confirmation of the correctness of the empirical potential.

Bendt^[26] measured the diffusion coefficient $D(3 \rightarrow 4)$ of the isotopes helium-3 and helium-4. Using the formula

$$D(\text{He-4}) = \left(\frac{2M_3}{M_3 + M_4} \right)^{1/2} D(3 \rightarrow 4) \quad (5.15)$$

he calculated the self-diffusion coefficient $D(\text{He-4})$. Obviously, the quantity $D(\text{He-4})$ calculated in this manner does not take into account the quantum symmetry effects, and is determined at high temperatures by the geometrical self-diffusion cross section

$$Q_g = \pi d^2 \approx 1.35 \cdot 10^{-15} \text{ cm}^2, \quad (5.16)$$

where $d/2 = 1.04 \text{ \AA}$ is the radius of the helium atom. Figure 8 shows a plot of Q_g , and Fig. 9 a plot of $(DP)_g$ in accordance with the data of Bendt. 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 stronger increase with decreasing temperature). At high temperatures ($T \sim 600^\circ \text{ K}$) we have $Q_d = 2.6 \times 10^{-15} \text{ cm}^2$, which is almost double the geometrical cross section of normal atoms (5.16).

6. ANALYSIS OF THE EXPERIMENTAL AND THEORETICAL RESULTS FOR THE TOTAL CROSS SECTION

The empirical interaction cross section reconstructed from diffusion experiments can be verified also against other experiments: against measurements of the total cross section and of the excitation-transfer cross section. In this chapter we discuss the theoret-

ical and experimental results for the total scattering cross section of metastable helium atoms 2^3S with normal helium atoms 1^1S . We must point out immediately the appreciable quantitative differences between the experimental data obtained by different authors, which differ both from experiment to experiment and with the calculation results.

Until recently, practically the only calculation available was that of Buckingham and Dalgarno, who used their own potential in first approximation. It is difficult to understand why, but it turned out that the numerical values of the total cross section in^[6] are incorrect even for the potential (B-D) calculated by the authors themselves. Therefore the interpolation formula for the total cross section is a function of relative velocity, given by the authors in^[6], was likewise incorrect. This is all the more annoying, since the results of their calculations were subsequently used by many experimenters to compare their data with theory. We have repeated the calculations of the total cross section $Q(v)$ for the B-D potential using the scattering phase shifts given in^[6]. Figure 10 shows the results of all the calculations in the experiments. Curve 3 represents the data of Buckingham and Dalgarno, curve 2 the results of our calculations with the same potential, and curve 1 the dependence of the total cross section of the velocity for the empirical potential. It is seen from Fig. 10 that the discrepancy between curves 2 and 3 is quite appreciable, especially at large velocities. As was indicated in Ch. 4, the various cross sections of the elastic processes are connected, in the limit of large velocities, by limiting relations (4.14). The total cross section from curve 2 at velocity $4.2 \times 10^5 \text{ cm/sec}$ does not satisfy these relations. Indeed, according to Buckingham and Dalgarno, at $v = 4.2 \times 10^5 \text{ cm/sec}$ we have $Q = 14.5 \times 10^{-15} \text{ cm}^2$, $Q_d = 2.5 \times 10^{-15} \text{ cm}^2$, and $Q_{tr} = 1.3 \times 10^{-15} \text{ cm}^2$, i.e., the total cross section differs from the diffusion cross section not by a factor of 2 but by a factor of 6. In addition, the dependence of $Q(v)$ in accordance with curve III contradicts the law governing the variation of the B-D potential in the long-range repulsion region.

According to the well known paper by Massey and Mohr,^[3] the total scattering cross sections depend on

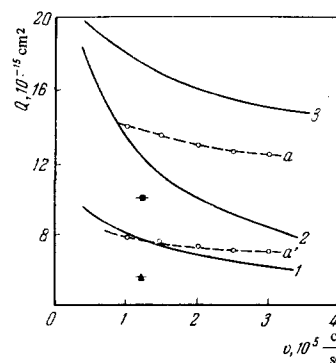


FIG. 10. Comparison of the calculation results with experiment of the total scattering cross section of metastable helium-4 atoms. Solid lines—calculated $Q(v)$ curves; 1—for empirical potential; 2—for B-D potential according to our calculation; 3—calculation of Buckingham and Dalgarno. O, ●, ▲—experimental values; a—O—data of Rothe et al. [21], ●—data of Stebbings [18] and Hasted [19], ▲—data of Richard and Muschlitz [20], a'—O—data of Rothe decreased by a factor $\sqrt{\pi}$.

the velocity in accordance with the law

$$Q(v) = \text{const} \cdot v^{-2/(n-1)}, \quad (6.1)$$

If the interaction potential decreases in accordance with a power law

$$V(R) \sim R^{-n}. \quad (6.2)$$

This conclusion was obtained from a quantum analysis and is valid with good accuracy. As indicated in Ch. 3 (see formula (3.3) in Fig. 1), when $R \gtrsim 7a_0$ the B-D potential can be approximated by power-law function with $n = 6$. Therefore, at velocities $v < 5 \times 10^5$ cm/sec the cross section $Q(v)$ for the B-D potential should decrease like $v^{-0.4}$. This law is satisfied for curve 2 and is not satisfied for curve 3.

The discrepancy between curves 2 and 1 is connected with the differences in the interaction potentials—the height of the hump and the law governing the decrease of the long-range repulsion. For curve 1, in accordance with the empirical-potential approximation ($V_{S,A}(R) \sim R^{-12}$), the variation of $Q(v)$ obeys the law

$$Q(v) = 8 \cdot 10^{-15} \left(\frac{10^5}{v} \right)^{0.182}. \quad (6.3)$$

The total elastic-scattering cross sections were measured with the aid of the molecular-beam method.^[18-22] Such experiments should be carried out at sufficiently large angular resolution of the apparatus, in order to register the contribution made to the total cross section by the small-angle scattering. By resolution is meant that minimal scattering angle θ_0 , registered in the given instrument as the angle of deflection of the atom as a result of the collision act. Massey and Burhop^[5] indicate that the error in the determination of the total cross section does not exceed 10% if $\theta_0 = 3.6^\circ$ (at room temperature). The directly determined quantity is the mean free path $\bar{\lambda}$ of the metastable atom, determined from the beam attenuation. Knowing the free path $\bar{\lambda}$, we can determine the average value

$$\bar{Q} = \frac{1}{N\bar{\lambda}}, \quad (6.4)$$

where N is the density of the scattering gas of normal atoms. The average value \bar{Q} is connected with the effective total cross section $Q(v)$ in a rather complicated manner, since the average cross sections include actually a double averaging—over the particle velocities in the beam and in the scattering gas. The character of the averaging depends on the ratio of the particle velocities in the beam and in the gas, and also on the behavior of the scattering cross section itself as a function of the velocity. If the cross section does not depend on the velocity, then the reduction of the experimental data can be carried out by means of the procedure described by Massey and Burhop^[5] (see also^[34]). For a power law potential of the form (6.2), a reduction method was proposed by Berkling et al.^[35] To obtain the true cross section $Q(v)$ by means of this procedure it is necessary to use the relation

$$Q(v) = \frac{\bar{Q}(u/v)^{2/n-1}}{F(n, x)}, \quad (6.5)$$

where u is the velocity of the monochromatic beam, $x = u/(2\kappa T/M)^{1/2}$ is the ratio of the velocity u to the most probable gas velocity; the function $F(n, x)$ is tab-

ulated in^[35]; at large n and x ($x \gtrsim 2$), the function $F(n, x)$, is close to unity.

The points of Fig. 10 represent the experimental values of $Q(v)$, processed with the aid of the procedure (6.5) at $n = 12$. The results of Stebbings^[18] and Hasted^[19] practically coincide: $\bar{Q} = 14.9 \times 10^{-15}$ cm² and $Q(v) = 10.5 \times 10^{-15}$ cm² ($F(12, 1) = 1.4$). The resolution in the experiments of^[18,19] was approximately 1° . The data of Richard and Muschlitz^[20] were obtained with a mean resolution 6.5° . The experimental value is $\bar{Q} = (7.5 \pm 0.5) \times 10^{-15}$ cm², and after reduction $Q(v) = 5.5 \times 10^{-15}$ cm². Quite good resolution ($\theta_0 = 1'$) was attained in the experiments of Rothe et al.^[21,22] Unfortunately, the authors did not give the measured values of \bar{Q} . Insofar as can be judged from the formula given in their article,^[22] the experiments were reduced by a formula that differs from (6.5) by a factor $\sqrt{\pi} = 1.77$. Consequently Fig. 10 shows the data of the indicated experiments (curve a), and also the values of $Q(v)$ reduced by a factor $\sqrt{\pi}$ (curve a'). The values of $Q(v)$ given in the paper of Rothe et al.,^[21] can also be regarded after reduction as overestimated on the basis of the following considerations. The total scattering cross section should not exceed double the diffusion cross section. At room temperature, the results of different authors give a reliable value of the quantity $DP = 470$ cm²/sec mm Hg, from which we get $Q_d = 3.5 \times 10^{-15}$ cm². These values correspond to a relative velocity $v = v_d = 2.5 \times 10^5$ cm/sec. Consequently, the total cross section Q for this velocity cannot exceed 7×10^{-15} cm². The total cross section given by Rothe et al.^[21] at this velocity is $Q = (12.7 \pm 0.3) \times 10^{-15}$ cm². This is precisely larger by $\sqrt{\pi}$ times than the maximum estimate of the total cross section for this velocity.

It is seen from Fig. 10 that once the data of^[21] are corrected by a factor of $\sqrt{\pi}$ (curve a'), they agree well with the results of calculations of the total cross section on the basis of the empirical potential (curve 1). It must also be assumed that the data of Richard and Muschlitz^[20] are in satisfactory agreement with the calculation for the empirical potential, inasmuch as the angular resolution of their instrument was insufficient to measure completely the small-angle scattering. Therefore the total cross section obtained in these experiments is overestimated. The data of Stebbings^[18] and Hasted^[19] differ somewhat from the calculations. The reasons for these discrepancies are not clear. Thus, with the exception of the data of^[18,19], all the results of the later experiments are in good agreement with the calculation of the total cross section $Q(v)$ on the basis of the empirical potential.

7. COMPARISON OF THEORY AND EXPERIMENT FOR THE EXCITATION-TRANSFER CROSS SECTION

The excitation transfer is connected with the change of symmetry of the state of the colliding atoms as a result of scattering. The cross section of this process differs from zero only in the case when the interaction potentials V_S and V_A are different. The value of the transfer cross section and its dependence on the velocity are determined by the form of the potential curves. According to O. B. Firsov,^[41] the excitation transfer

probability W is proportional to $\sin^2 \Omega t$, where Ω is the transfer frequency and $t \sim a/v$ is the characteristic interaction time, with $\Omega \sim \Delta V/\hbar$, where ΔV is the difference between the potentials V_S and V_A . The probability W should be averaged over the characteristic scattering region. Therefore the dependence of W on the velocity should be

$$W \approx \sin^2 \left(\frac{\Delta V a}{\hbar v} \right). \quad (7.1)$$

If ΔV depends little on velocity, then the transfer cross section increases with decreasing particle energy, and has a maximum when $v \rightarrow 0$. A similar situation occurs, for example, in collisions between hydrogen atoms or in the case of resonant charge exchange of ions, when the two interaction potentials V_S and V_A have different signs at large distances and their difference changes slowly.

If ΔV changes rapidly as a function of velocity, then the dependence of the transfer cross section on v can be different. In the interaction between metastable and normal helium atoms, both potentials have the same sign at large distances, and their difference decreases sharply with distance and tends to zero. For this reason, the energy difference integrated over the characteristic scattering region $\Delta V a$ decreases much more rapidly than the velocity raised to the first power. In this case, the transfer cross section also tends to zero as $v \rightarrow 0$. In the region of large velocities, which correspond to small distances between the interacting atoms, the difference of the potential energies of the two states of the system is relatively large, and depends little on the velocity. The energy of the colliding particles exceeds in this case the height of the potential barrier, and the latter no longer influences the character of the dependence of the transfer cross section on the velocity. At high energies, Q_{tr} will again decrease. Consequently, in the presence of a long-range repulsion on the potential $V_A(R)$, the excitation transfer cross section has a broad maximum at energies on the order of the height of the repulsion "hump." The maximum value of Q_{tr} is the limiting value of this cross section in relations (4.14).

Figure 11 shows the calculated dependences of the excitation transfer cross section on the energy. The solid curve pertains to the empirical potential. The

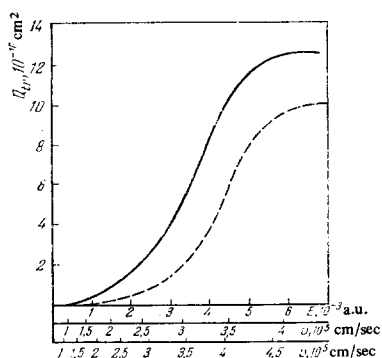
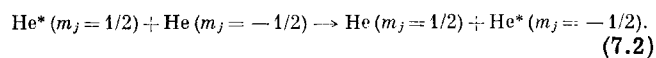


FIG. 11. Calculated plots of the excitation transfer cross section vs. velocity. Solid curve—for empirical potential; dashed curve—for B-D potential with allowance for the second-approximation correction $-20R^{-6}$ a.u. (the upper velocity scale is for He-4, the lower for He-3).

dashed curve represents the results of the calculation of Q_{tr} , performed by Buckingham and Dalgarno^[10] for their potential with allowance for the Van der Waals correction $-20R^{-6}$ A.u. At low energies, Q_{tr} tends to zero, since the potentials V_S and V_A practically coincide (see the table on p. 000). With increasing energy of the atoms, the transfer cross section increases as a result of the discrepancy between the potential curves. The higher the maximum on the potential curve V_A , the smaller the difference between V_A and V_S at the given colliding atom particle energy. Therefore the excitation transfer cross section turns out to be smaller for the B-D potential, which has a higher maximum, than for the empirical potential. The difference between the cross sections Q_{tr} at low energies is due to the difference between the asymptotic behaviors of the interaction potentials.

The cross section for excitation transfer from the metastable atom to the normal one was measured by Colegrove and co-workers^[23,24] and by Greenhow.^[25] The method used by them makes it possible to measure the averaged cross section of excitation transfer only for atoms with nonzero nuclear angular momentum—for helium-3. The gist of the method consists in the following. A high-frequency discharge is used to produce excited metastable atoms. The excited gas is in a magnetic field and is eliminated by a polarized resonant emission line (10,830 Å) from an external source with helium-4. Owing to the equality of the frequencies of the transitions $2^3S-2^3P_{1,3}$ (in helium-4) and $2^3S_1-2^3S_0$ (in helium-3), it is possible to effect optical pumping of the metastable helium-3 atoms in states with different projections of the total angular momentum m_j . The optical pumping produces a nonequilibrium population at these sublevels. In the case of right-polarized light, in particular, the levels with $m_j = +\frac{1}{2}$ become enriched. The lifetime τ of the metastable nonequilibrium states is determined by the collisions with the normal atoms, which produce the excitation transfer. In the case of collisions with normal atoms having momentum projections $-\frac{1}{2}$ or $+\frac{1}{2}$, electron excitation exchange takes place without a change in the nuclear momentum. Thus, after collision with a normal atom with $m_j = -\frac{1}{2}$, a metastable atom with $m_j = -\frac{1}{2}$ appears instead of a metastable atom with $m_j = +\frac{1}{2}$. The scheme of this process can be written in the form



In other words spin flip takes place as a result of the reaction (7.2). Therefore the line width of the nuclear magnetic resonance between levels with $m_j = \frac{1}{2}$ and $m_j = -\frac{1}{2}$ is determined by the cross section of the process (7.2), i.e., by the cross section of the excitation transfer.

The line width Δf of nuclear magnetic resonance for the sublevels of the metastable atoms was measured in^[23-25]. The value of Δf is connected with the excitation transfer cross section Q_{tr} by the formula

$$\Delta f \approx \frac{1}{\pi \tau} = \frac{N \bar{v} Q_{tr}}{\pi}, \quad (7.3)$$

where N is the density of the normal atoms, and the bar denotes averaging over the velocities. Generally speaking, other inelastic collisions causing destruction of metastable states, as well as the inhomogeneity of the

magnetic field, also contribute to the line width. Estimates show that the other inelastic processes play no noticeable role under the conditions of the experiments of [23-25], and the inhomogeneity of the magnetic field can lead to an overestimate of \bar{Q}_{tr} . By using a modulation technique, Colegrove et al. [23,24] succeeded in eliminating the broadening of the resonance line due to the field inhomogeneity. In [24] they measured $v\bar{Q}_{tr}$ in a wide temperature interval from 4° to 500° K. These data are shown in Fig. 12, together with the errors. For room temperature, the value of $v\bar{Q}_{tr}$ was obtained also by Greenhow. [25] His data exceeded the values of $v\bar{Q}_{tr}$ measured in [24] by a factor 1.5. These discrepancies may be connected with the influence of the magnetic-field inhomogeneity.

For a comparison of experiment with theory, the value of $v\bar{Q}_{tr}$ was calculated for the cross sections $Q_{tr}(v)$ listed in Fig. 11. The numerical calculation was based on the formula

$$\frac{\bar{v}Q_{tr}}{\pi} = \frac{1}{2} \left(\frac{M}{\pi kT} \right)^{3/2} \int_0^{\infty} dv v^3 Q_{tr}(v) \exp \left(-\frac{Mv^2}{4kT} \right). \quad (7.4)$$

The comparison results are shown in Fig. 12. We see that the experimental values are in satisfactory agreement with calculation based on the empirical potential. Even the corrected Buckingham and Dalgarno potential leads to greater deviation from experiment. Thus, experiments on the excitation-transfer cross section confirm convincingly the correctness of the chosen empirical potential.

8. CONCLUSION

Let us summarize the experimental and theoretical investigations of the elastic scattering of metastable helium atoms in helium gas. Measurement of the diffusion coefficient D in the temperature interval 300-4° K yields a much smaller quantity for the metastable atoms than for the normal helium atoms. The temperature dependence $D(T)$ follows approximately the $T^{2/3}$ law, showing by the same token that the diffusion cross section changes with temperature approximately like $T^{-1/6}$. Owing to the fact that, of all the elastic processes, diffusion is least sensitive to quantum effects (to small-angle scattering), classical similarity considerations can be employed to establish the connection with the interaction potential. The result is that the asymptotic form of the potential should be close to R^{-12} , and the

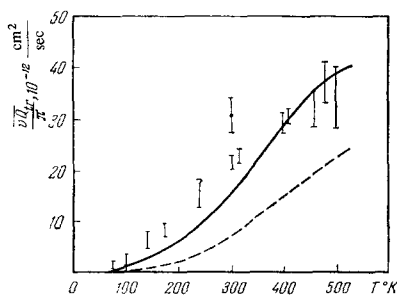


FIG. 12. Comparison of the experimental and calculated values of the averaged quantity $v\bar{Q}_{tr}/\pi$. Solid curve—calculation for the empirical potential; dashed curve—for the B-D potential. Vertical segments—experimental data with allowance for the errors (from [24]), ●—data of [25].

potential itself is repulsive. A comparison of experiments on the diffusion of helium-3 and helium-4 leads to the important conclusion that the interaction potentials and the differential scattering cross sections of isotopes having different statistics are identical. This agrees with the theoretical prediction that the differential cross sections of the two isotopes are equal. An experimental study of the total elastic-scattering cross section also shows that the cross section is large. Singularities were also observed in the excitation transfer cross section. Instead of the usually observed maximum at low velocities and the monotonic decrease of Q_{tr} with velocity, the excitation transfer cross section in helium at low temperatures is unusually small, increasing only at high temperatures and reaching a maximum at $T \sim 700-800^\circ\text{K}$. In other words, quantum symmetry effects are anomalously small at low energies ($E \lesssim 300^\circ\text{K}$).

The entire aggregate of the experimental data can be explained not only qualitatively but also quantitatively on the basis of the quantum theory of scattering and a correct choice of the interaction potential. The usual potential with attraction at large distances does not make it possible even to describe qualitatively the process of diffusion and excitation transfer. The already noted singularities of the elastic scattering of metastable helium atoms are in agreement with the presence of a maximum of a long-range repulsion on the potential $V_A(R)$. The existence of such an unusual potential was predicted by Buckingham and Dalgarno on the basis of theoretical calculations based on the Heitler-London method. However, the results of this calculation are quite approximate, especially at large distances. As noted by Gor'kov and Pitaevskii, [36] the asymptotic form of the potentials for the hydrogen molecule, obtained by the Heitler-London method, has a slower dependence than R than the exact form. The results of [36] can be regarded as a theoretical indication that in the case of the helium molecule the true asymptotic interaction is likewise steeper than that calculated by the Heitler-London method. [10] From this point of view, the results of the calculation by Poshusta and Matsen, [12] carried out with the aid of a variational method, are more reliable. However, the latter were not carried out in the asymptotic region $R > 6a_0$. At the same time, the elastic-scattering processes in the temperature interval 500-4° K are determined by the potential at large distances $R \sim (5-10)a_0$. Using the theoretical calculations, the interaction potential in the asymptotic region was reconstructed on the basis of the experimental data on diffusion. The reconstructed empirical potential coincides in the region of the long-range repulsion maximum with the Poshusta and Matsen potential and agrees approximately with the asymptotic calculation of B. M. Smirnov et al. [9] for $R > 6a_0$. The height of the maximum on the $V_A(R)$ curve is 5.1×10^{-3} a.u., and is located at $R = 4.5a_0$. At distances $R > 6a_0$, the potential decreases like $V_A(R) \approx 75 R^{-12}$ a.u. The potential $V_S(R)$ was chosen such that when $R < 6a_0$ it coincides with the potential $V_S(R)$ calculated by Buckingham and Dalgarno with allowance for the Van der Waals correction, and when $R > 7a_0$ the potential $V_S(R)$ coincides with the asymptotic form of the empirical potential $V_A(R)$. If these potentials are used for the calculation of the cross sections, then all the experimental data on the magnitude and temperature

dependence of the diffusion cross sections of helium-3 and helium-4, the total cross section, and the excitation-transfer cross section, without exception, are in good quantitative agreement with the theoretical calculation.

The existence of a repulsion barrier at large distances makes it possible to establish simple approximate limiting relations (4.14) between the different cross sections; these are confirmed by experiment. The limiting relations between the total and diffusion cross sections are satisfied already at velocities 2.5×10^5 cm/sec, which corresponds to interaction at distances smaller than $6a_0$. The limiting value of the excitation transfer cross section is reached in the region of the repulsion maximum.

It should be noted that the existence of a "hump" is confirmed also by experiments on elastic scattering of metastable atoms in their own gas.^[15,16,37] The maximum of the long-range repulsion, besides the interaction of the triplet metastable 2^3S atoms with the normal ones considered in this paper, was theoretically predicted^[10] for the potentials of the singlet metastable helium molecule. An indirect experimental confirmation of the existence of such a maximum for singlet metastable atoms was obtained in^[38]. An analogous long-range repulsion was predicted theoretically for some other excited states of the helium molecule, of the hydrogen molecule,^[28,29] and also apparently for neon. Repulsion maxima can exist also on plots of the energy of the interaction between metastable helium atoms and excited atoms of other noble gases. This may pertain, for example, to the reaction of helium atoms in the states 2^3S or 2^1S with neon (this process plays an important role in an He-Ne gas laser) and also to the series of Penning processes.

The method proposed here for reconstructing the interaction potential from the experimental data can be applied to all similar systems with long-range repulsion.

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Translated by J. G. Adashko