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DIFFUSION OF METASTABLE INERT GAS ATOMS IN THE SAME GAS

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The diffusion coefficient of metastable atoms of mobile gases in the gas itself, which is determined by the elastic scattering of the metastable atoms by the atoms in the ground state, is calculated in the Chapman–Enskog approximation. An asymptotic expression for the interaction potential between the atoms, which is valid for large distances between the nuclei, is used to determine the atomic elastic collision cross section.

1. IMPORTANT plasma characteristics (the rate of change of the degree of ionization of the plasma, or the rate of change of the population of definite excited states of the atom) produced in an inert gas are determined by the presence of metastable atoms. The lifetime of the metastable atoms relative to their departure to the walls, determined by the diffusion of these atoms in their own gas, was investigated in a large number of experiments.[1-5] In this paper we calculate the diffusion coefficient of a metastable atom in its own gas. The exchange interaction of the metastable atom of helium with the helium atom in the ground state was calculated earlier[6] by variational methods. It was established thereby that the diffusion cross section for the scattering of a metastable atom by an atom in the ground state, which determines the diffusion coefficient of the metastable atoms, corresponds at temperatures below 10^3 °K to elastic collision of the atoms. Thus, the determination of the diffusion coefficient of metastable atoms is connected with the determination of the interaction potential of the metastable atom and of the atom in the ground state. In the present paper, in the calculation of the diffusion coefficient, we use asymptotic expressions for the interaction potential of the atoms, which are valid at large distances between the atoms. Such an approach does not claim a higher accuracy in the calculation of the diffusion coefficient than is given by the use of interaction potentials obtained by the variational method. However, the asymptotic method is simple to use and makes it possible to calculate the diffusion coefficient of the metastable atom in any gas, whereas the use of the variational method is limited to the case of helium.

2. The asymptotic value of the potential of the exchange change interaction of an excited atom and an atom in the ground state in the limits when the distance R between them is large, is given by[7]

$$U_{\text{exc}}(R) = 2\pi\Phi^2(R)\left(L - {}^2\!/_3\,\alpha^{3/4}\beta^{1/2}\right), \tag{1}$$

where L is the length for scattering of the electron by the perturbing atom, α is the polarizability of the perturbing atom, $\Phi(R)$ is the wave function of the weakly-bound electron at the location of the perturbing atom, so that R is the distance between the nuclei, $\gamma^2/2$ is the binding energy for the valence electron of the metastable atom, $\beta = \sqrt{\gamma^2 - 2/R}$. We are using a system of atomic units in which $\hbar = m = e^2 = 1$.

The wave function of a weakly bound electron, which is mainly concentrated in the Coulomb field of the atomic remainder, has at large distances r from the nucleus the form

$$\Phi(r) = \frac{A r^{1/\gamma - 1}}{\sqrt{4\pi}} e^{-r\gamma}, \qquad A = \frac{(2\gamma)^{1/\gamma}\gamma}{\sqrt{\Gamma(1/\gamma + l + 1)\,\Gamma(1/\gamma - l)}}, \tag{1a}$$

where $l < 1/\gamma$ is the orbital angular momentum of the valence electron.

An important role in the case of heavy atoms of noble gases is played by the long-range interaction

$$U_{\text{l.r.}} = -\frac{C}{R^6}, \tag{2}$$

where the van der Waals interaction constant C for the atom in the ground state and the excited atom is[7]

$$C = \alpha\langle r^2\rangle, \tag{2a}$$

where α is the polarizability of the atom in the ground state, $\langle r^2 \rangle$ is the square of the orbit of the weakly-bound electron of the excited atom.

Formulas (1) and (2) for the interaction potentials of the atoms in the ground and excited states can be used as the basis for the calculation of the diffusion coefficients of metastable atoms. In the case of helium, at internuclear distances that are significant for the diffusion coefficient, the long-range interaction turns out to be small compared with the exchange interaction, and can be neglected.

Table I gives the potential (in atomic units) of the interaction between a metastable helium atom and a helium atom in the ground state; in our case the exchange potential was calculated with the aid of the asymptotic formula (1), whereas in the paper of Buckingham and Dalgarno[6] it was calculated by the Heitler-London method, and in other papers[8-11] by a variational method. In the paper of Buckingham and Dalgarno,[6] the metastable helium atom was considered in the independent-electron approximation, so that the $He(2^3S) + He(1^1S)$ and $He(2^1S) + He(1^1S)$ interactions turned out to be the same.

3. The calculations of Buckingham and Dalgarno[6] for the He(2S) + He(1S) pair show that at thermal energies the effective cross section for the transfer of excitation is smaller by one order of magnitude than the elastic-scattering cross section, so that the diffusion is determined entirely by the elastic scattering. The diffusion coefficient in the first Chapman–Enskog approximation is connected with the elastic cross section

Table I.

Collision partners	R	Asymptotic value $U_{exc}(R)$	$\frac{{}^3\Sigma_u+{}^3\Sigma_g}{2}$ from [6]	$\frac{{}^1\Sigma_u+{}^1\Sigma_g}{2}$ from [6]	${}^3\Sigma_u$ from [9]	${}^3\Sigma_u$ from [8]	${}^1\Sigma_u$ from [10]	${}^1\Sigma_u$ from [11]
He (2^3S) in He	4	0.0148	0.0158		0.0132	0.004		
	5	0.0062	0.0071		0.0051	0.004		
	6	0.0024	0.00316		0.0032			
	7	0.0009	0.00186					
	8	0.0003	0.00057					
	9	0.0001	0.00023					
	10	0.00004	0.00008					
He (2^1S) in He	4	0.0186		0.0158				0,00183
	5	0.0092		0.0071			0.00547	0.00701
	6	0.0042		0,00316			0.004	0.00538
	7	0,0018		0.00186.				
	8	0.0008		0.00057			0,00165	0,00183
	9	0.0003		0,00023				
	10	0.0001		0.00008			0,00038	0.000601

by the relation[12]

$$D_1=\frac{3\sqrt{\pi T}}{8NM^{1/2}\bar{\sigma}},\qquad \bar{\sigma}=\frac{1}{2}\int_0^\infty \sigma^*(x)e^{-x}x^2\,dx,\qquad x\equiv\frac{Mv^2}{4T},\tag{3}$$

where N is the density of the atoms, T the gas temperature, M the mass of the nuclei, σ^* the diffusion cross section for elastic collision of the atoms, and v the relative collision velocity of the atoms.

The second Chapman–Enskog approximation leads to a value of D which differs by only 1–2% from the value in the first approximation, so that (3) is a good approximation.

4. At thermal energies, the interaction of the He(2S) + He(1S) pair corresponds to repulsion, as follows from (1), since the length for the scattering of an electron by a helium atom is positive. We estimate the elastic-scattering cross section from the relation $\sigma = \pi R_0^2$; $U(R_0) = \epsilon$ (for absolutely hard spheres), and ϵ is the collision energy. It turns out that the value of R_0 at thermal collision energies greatly exceeds the characteristic atomic dimensions, and the U(R) dependence is very strong when $R \sim R_0$, so that there exists a small parameter

$$(\gamma R_0)^{-1}\cong|U(R_0)\,/\,U'(R_0)R_0|\ll 1,$$

which can be used to determine the corrections $\sim(\gamma R_0)^{-1}$ to $\sigma = \pi R_0^2$.

The diffusion scattering cross section of a particle in a centrally-symmetrical field is

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

where l is the collision angular momentum, δ_l the scattering phase, and k the particle momentum.

In the case of thermal energies, the main contribution to the cross section is made by collisions with large momenta

$$l\sim\mu R_0 v\gg 1,\tag{5}$$

where μ is the reduced mass of the nuclei, and v is the relative velocity of their collision.

To determine δ_l for large values of l, we break up the region of distances R from the particle to the center into two, $R < r_0$ and $R \geq r_0$, where r_0 is the classical turning point ($r_0(\rho = 0) = R_0$, ρ is the classical impact parameter). In solving the Schrödinger equation in the first region we used the fact that $r_0 \gg 1$, so that the interaction potential U(R) changes more strongly than the centrifugal potential. Then in the region $R < r_0$ the wave function depends in the same manner on the quantity $(R - r_0)$ at all values of the angular momentum l. The diffusion cross section (4) can therefore be calculated by using the classical formula for δ_l:

$$\delta_l=k\int_{r_0}^{\infty}\left[\sqrt{1-\frac{U}{\varepsilon}-\frac{(l+1/2)^2}{k^2r^2}}-1\right]dr+\frac{\pi}{2}\left(l+\frac{1}{2}\right)-kr_0.\tag{6}$$

We have found that the classical approximation for the calculation of the diffusion equation is valid if condition (5) is satisfied. This condition is weaker than the condition for the applicability of the quasiclassical approach for the calculation of the phases:

$$k\,/\,\gamma\sim l\,/\,R_0\gamma\gg 1.\tag{7}$$

We represent the diffusion cross section in the form of an expansion in powers of $(R_0\gamma)^{-1}$ and confine ourselves to the first term in this expansion. To this end, we write down the classical scattering angle $\chi = \pi - 2\varphi$ in the form

$$\varphi=\arcsin\frac{\rho}{r_0}+\Delta\varphi,\qquad \Delta\varphi=\int_{r_0}^{\infty}\left[\left(1-\frac{\rho^2}{r^2}-\frac{U}{\varepsilon}\right)^{-1/2}-\left(1-\frac{\rho^2}{r^2}\right)^{-1/2}\right]\frac{\rho\,dr}{r^2}.\tag{8}$$

The quantity $\Delta\varphi \sim (R_0\gamma)^{-1} \ll 1$. We expand the diffusion cross section in powers of $\Delta\varphi$:

$$\sigma^*=\pi\int_0^{\infty}(1-\cos\chi)\,d(\rho^2)=2\pi\int_0^{\infty}\left[1-\frac{\rho^2}{r_0^2}-\frac{2\rho}{r_0}\sqrt{1-\frac{\rho^2}{r_0^2}}\,\Delta\varphi\right]d(\rho^2).\tag{9}$$

We transform $\Delta\varphi$ into

$$\Delta\varphi=2\rho\sqrt{1-\frac{\rho^2}{r_0^2}}\frac{dr_0}{d(\rho^2)}-2\rho\frac{d}{d(\rho^2)}\int_{r_0}^{\infty}\left[\sqrt{1-\frac{\rho^2}{r^2}-\frac{U}{\varepsilon}}-\sqrt{1-\frac{\rho^2}{r^2}}\right]dr.\tag{10}$$

To determine the first term of the expansion of $\Delta\varphi$ in powers of $(R_0\gamma)^{-1}$, we calculate the integral in (10), assuming that the change of the difference under the integral sign is due only to the change of the exponent of the potential U(r), i.e., assuming $\rho^2/r^2 \approx p^2/r_0^2$. Then

$$\int_{r_0}^{\infty}\left[\sqrt{1-\frac{\rho^2}{r^2}-\frac{U}{\varepsilon}}-\sqrt{1-\frac{\rho^2}{r^2}}\right]dr\approx-\frac{q}{\gamma}\sqrt{1-\frac{\rho^2}{r_0^2}},$$

$$q=\int_0^1\frac{1-\sqrt{1-x}}{x}\,dx=2-\ln 4=0{,}614.\tag{11}$$

Table II.

Atom	Metastable level	L	α	First ionization potentials, eV	Excitation energy of given level, eV	γ	A
He	2^3S 2^1S	1.14 1.14	1.39 1.39	24.581 24.581	19,81 20,61	0.59 0.54	0.94 0.81
Ne	$^3P_2$	0.14	2,76	21.56	16.51	0.61	0.97
Ar	$^3P_2$	—1.4	11.1	15.76	11,57	0.55	0.83
Kr	$^3P_2$	—3.1	16.8	14.0	9.91	0.55	0.83
Xe	$^3P_2$	—5.7	27,2	12,13	8.32	0,53	0,77

We change over in (9) to integration with respect to dr_0, finding $d(\rho^2)/dr$ with the aid of the equation that determines the classical turning point r_0. We then finally obtain with the aid of (11) and (10) for the diffusion cross section, accurate to $(R_0\gamma)^{-1}$ inclusive,

$$\sigma^* = \pi R_0^2\left(1+\frac{0.23}{\gamma R_0}\right) \approx \pi R_1^2, \quad R_1 = R_0\left(1+\frac{0.23}{2\gamma R_0}\right). \tag{12}$$

Averaging (12) over the Maxwellian distribution of the relative collision velocities, we obtain, taking into account the weak logarithmic dependence of σ^* on the collision velocity v

$$\bar{\sigma} = \sigma^*(2.4\, v_T) \equiv \pi R_2^2, \quad U(R_2)\,/\,T = 5.1. \tag{13}$$

5. Formulas (3) and (13) make it possible to determine the diffusion coefficient of metastable atoms in the case of helium, when the long-range interaction of the atoms is small. For atoms of other noble gases, an important role is played, besides the exchange interaction, also by the van der Waals interaction, so that the interaction potential of the atoms is the sum of potentials (1) and (2):

$$U = U_{\text{exc}} - C\,/\,R^6. \tag{14}$$

Both terms in (14) are negative ($L < 0$), so that the interaction of the atoms is pure attraction, which increases sharply with decreasing distance. Therefore the interaction potential of the atoms (14) is best approximated by the expression $U = -C_n/R^n$, with the diffusion cross section differing little from the cross section for the capture of the atom by the metastable atom[13]

$$\sigma^* = \frac{\pi n}{n-2}\left[\frac{C_n(n-2)}{2E}\right]^{2/n}. \tag{15}$$

Averaging this expression over the Maxwellian distribution, we obtain for the average scattering cross section contained in (3)

$$\bar{\sigma} = \pi R_1^2, \quad U(R_1)\,/\,T = 5(n+2)\,/\,n^2, \tag{16}$$

where $n = R_1U'(R_1)/U(R_1)$.

Formulas (3) and (16) make it possible to determine the diffusion coefficients of the metastable atoms of neon, argon, krypton, and xenon in their own gas.

Table II lists the values of the parameters needed for the calculation of the diffusion coefficient.

Table III lists the calculated values of the averaged diffusion cross section for different values of the gas temperature, and also the values of the diffusion coefficients determined on the basis of formulas (3), (13), and (16) at a pressure p = 1 mm Hg for inert gases. The calculated diffusion coefficients are compared with the experimental values D_{exp}.

Table III.

Atom	T, °K	$\bar{\sigma}$, 10^{-15} cm^2	D, cm^2/sec	D_{exp}
He(2^3S)	500	2.7	710	
	300	3.2	460	470±25 [2] 410 [3]
	150	4.0	260	
	77	4.8	160	130 [3] 200 [1]
	64	5.1	140	190 [1]
	40	5.7	100	
	20	6,6	60	100 [1]
He(2^1S)	500	3,3	570	
	300	4,0	370	440±50 [2]
	150	5.0	210	
	75	6,2	120	
	40	7.2	75	
	20	8,6	45	
Ne($^3P_2$)	77	6,0	56	60 [3]
	40	7,2	33	
	20	8.7	19	
Ar($^3P_2$)	300	8,0	64	54 [3] 45±4 [4] 67.5 [5]
	273	8.2	54	
	150	9,7	34	
	77	11,6	20	
	40	13,4	13	
	20	15,5	8	
Kr($^3P_2$)	500	8.1	51	
	300	9,4	38	
	150	11.3	20	
	77	13.2	12	
	40	15.5	8	
Xe($^3P_2$)	500	10,1	33	
	273	11.7	21	13±1 [4]
	150	13.5	13	
	77	16,0	8	
	40	18,5	5	
	20	22,0	3	

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