SOVIET PHYSICS JETP VOLUME 34, NUMBER 6 JUNE, 1972

Electron Mobility in Dense Gases

L. A. Palkina, B. M. Smirnov, and O. B. Firsov

Institute of High Temperatures, USSR Academy of Sciences

Submitted July 20, 1971

Zh. Eksp. Teor. Fiz. **61**, 2319–2325 (December, 1971)

A relation is established between the densities of electrons and negative ions moving in a gas in an external field, in the presence of statistical equilibrium between them. The change of the mobility of the electrons in the gas with increasing gas density is determined for a constant ratio of the electric field intensity to the gas density, if this change is due to the formation of a negative ion. An analysis is carried out of the experimental and theoretical data on the dependence of the electron mobility on the gas density for a constant ratio of the field strength to the gas density.

1. As measurements of the mobility of electrons in a gas at low density of electrons and high density of gas molecules[1-7] (the gas pressure of the order of several dozen atmospheres) have shown, the mobility of the electrons[1)] in certain gases depends not only on the ratio of the electric field intensity E to the density of gas molecules N, but also on the density of the molecules itself. This indicates the formation in dense gases, in the course of electron drift, of negative molecular ions in stable or auto-ionizing states.[8,9] Capture of electrons by gas molecules with successive decay of the negative ions slows the drift motion of the electrons through the gas. Frommhold[8] reduced the experimental data on electron mobility in molecular hydrogen and nitrogen with account of this fact. He considered the possibility of electron capture in hypothetically composed resonant states whose energies are of the order of the energy of the molecular rotation levels. Kouri[9] considered the possibility of empirical calculation of such resonance energies. However, Frommhold's reduction included but one parameter, the width of the auto-ionizing levels of the negative ion of the molecule, and this led to an indeterminacy in the results. In contrast with this, in the present paper we establish a relation between the change of the electron mobility with increasing gas density, only one parameter of the negative ion—the binding energy; of the electron in the atom. The results are used to reduce the experimental data on the electron mobility in a gas at high pressures.

2. We shall consider the directional motion of an electron in a gas when it can form a bound state with the gas molecules in the course of its motion. Inasmuch as the mobility of a negative ion is much less than the mobility of a free electron, we can assume that the motion of the electron takes place only in that moment of time when it does not form a bound state with the gas molecule. Therefore, the observable value of the electron mobility K_e is equal to

$$K_e = K_0 W_e, \tag{1}$$

where K_0 is the value of the mobility in the limit of low gas density, and W_e the probability that the electron is free. We introduce the probability W_i of finding the electron in a bound state, forming a negative ion with the gas molecule. By definition,

$$W_e + W_i = 1. \tag{2}$$

We shall assume that as an electron moves in the gas between electrons it can frequently take part in the formation of a negative ion. Under real experimental conditions, in the observation of the effect under consideration, this is satisfied with a great deal to spare. Here we can use the laws of statistical physics to find the value of W_e. To be precise, $W_e/W_i = N_e/N_i$, where N_e, N_i are the equilibrium densities of electrons and negative ions and are established in the gas in the presence of statistical equilibrium.

3. We establish the connection between the density of the electrons and negative ions in the gas in the presence of statistical equilibrium. The negative ion can be found both in auto-ionizing and in stable bound states, i.e., the binding energy; of the electron with the molecule in the formation of the negative ion can be either positive or negative. We shall assume that the particle energy distribution functions $f(\epsilon)$ are given and in the general case are different from Maxwellian. They are normalized by the condition

$$\int_0^\infty f(\varepsilon)\,\varepsilon^{1/2}\,d\varepsilon = 1. \tag{2'}$$

In the presence of statistical equilibrium, the relation between the equilibrium values of the densities N_e and N_i is found from the condition that the number, per unit volume and per unit time, of the transitions connected with the formation and destruction of negative ions as the result of collisions with molecules, be the same:

$$N_e N_m^2 \int_{\varepsilon_0}^{\infty}\int_0^{\varepsilon-\varepsilon_0} f_m(\varepsilon-\varepsilon_0-\varepsilon')\sqrt{\varepsilon-\varepsilon_0-\varepsilon'}\,f_e(\varepsilon')\sqrt{\varepsilon'}\,\gamma(\varepsilon-\varepsilon_0-\varepsilon',\varepsilon')\,d\varepsilon\,d\varepsilon'$$

$$= N_m N_i \int_{\varepsilon_0}^{\infty}\int_0^{\varepsilon-\varepsilon_0} f_i(\varepsilon)\,\sigma(\varepsilon,\varepsilon')\sqrt{2\varepsilon/\mu}\,\sqrt{\varepsilon}\,d\varepsilon\,d\varepsilon'. \tag{3}$$

Here N_m is the density of the gas molecules, μ the reduced mass of the nuclei, and f_e, f_m, f_i are energy distribution functions for the electrons and for the relative motion of the molecule + molecule and molecule + negative ion systems, respectively. Further, in Eq. (3), $\sigma(\epsilon, \epsilon')d\epsilon'$ is the cross section for destruction of the negative ion in molecular collisions if their c.m.s. collision energy is equal to ϵ and the energy of the liberated electron is the range from ϵ' to $\epsilon' + d\epsilon'$; $\gamma(\epsilon - \epsilon_0 - \epsilon', \epsilon')$ is the constant of the reverse process—the triple collision of two molecules with energies of relative motion $(\epsilon - \epsilon_0 - \epsilon')$ and an electron with energy ϵ'. As a

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[1)] The mobility of the electrons is referred to a single value of the gas density.

result of the reverse process, the electron forms a bound state with one of the molecules (ϵ_0 is the binding energy of the electron with the molecule, and can be either positive or negative); here the resultant negative molecular ion and the second molecule fly off with energy ϵ in the center-of-mass system. The constant γ is measured in units of cm^6/sec.

The relation between the constant γ of triple formation of the negative ion and the negative-ion destruction cross section σ is established from the detailed balancing principle. If the system is in thermodynamic equilibrium, then the particle distribution function in Eq. (3) is Maxwellian and the relation between the densities of the particles is determined from Saha's formula:

$$\frac{N_e N_m}{N_i} = \frac{g_e g_m}{g_i} \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} e^{-\varepsilon_0/T}, \tag{4}$$

where g_e, g_m, and g_i are the statistical weights of the electron, molecule, and negative ion, corresponding to their electronic states, T is the temperature of the system, and m is the mass of the electron. Using this in Eq. (3), we obtain the relation between the constants of the direct and reverse processes:

$$\sqrt{(\varepsilon - \varepsilon_0 - \varepsilon')\varepsilon'}\,\gamma(\varepsilon - \varepsilon_0 - \varepsilon', \varepsilon') = \frac{g_i}{g_e g_m} \frac{2\pi^2\hbar^3}{m^{3/2}\mu^{1/2}} \varepsilon\sigma(\varepsilon, \varepsilon'). \tag{5}$$

This allows us to represent Eq. (3) in the form

$$F \equiv \frac{N_i}{N_e N_m} = \frac{g_i}{g_e g_m} \frac{\sqrt{2}\pi^2\hbar^3}{m^{3/2}} \int_{\varepsilon_0}^{\infty} d\varepsilon \int_0^{\varepsilon-\varepsilon_0} f_m(\varepsilon - \varepsilon_0 - \varepsilon')\varepsilon\sigma(\varepsilon, \varepsilon') f_e(\varepsilon')\,d\varepsilon'$$
$$\times \left[\int_{\varepsilon_0}^{\infty} d\varepsilon \int_0^{\varepsilon-\varepsilon_0} f_i(\varepsilon)\varepsilon\sigma(\varepsilon, \varepsilon')\,d\varepsilon'\right]^{-1}. \tag{6}$$

In this formula, the limits of integration correspond to the case in which $\epsilon_0 > 0$, i.e., a stable negative ion is formed. In the case of the auto-ionizing state of the negative ion ($\epsilon_0 < 0$), the quantity ϵ changes from zero to infinity. In this case, Eq. (6) is greatly simplified, because the decay of the negative ion takes place spontaneously, without the participation of the molecule. Therefore, $\sigma(\epsilon, \epsilon')$ does not depend on ϵ and moreover, the energy ϵ' of the liberated electron is close to the energy $\epsilon_a = -\epsilon_0 > 0$ of the auto-ionizing state, so that the integral $\int \sigma(\epsilon, \epsilon')d\epsilon'$ converges near $\epsilon' = \epsilon_a = -\epsilon_0$. We then obtain, in the case of the auto-ionizing state of the negative ion,

$$F \equiv \frac{N_i}{N_e N_m} = \frac{g_i}{g_e g_m} \frac{\sqrt{2}\pi^2\hbar^3}{m^{3/2}} f_e(\varepsilon_a). \tag{7}$$

In the presented formula, the electron energy distribution function is normalized by the condition (2′). In the case of a Maxwellian energy distribution of the electrons Eqs. (6) and (7) transform into the Saha formula.

4. Inasmuch as it can be assumed from the laws of statistical physics that the probabilities W_e and W_i of finding the electron in a free or bound state are proportional respectively to the densities N_e and N_i of the electrons and negative ions, which are in statistical equilibrium under these conditions, we get for the electron mobility, taking this and relations (1) and (2) into account,

$$K_e = \frac{K_0}{1 + N_m F(\bar{\varepsilon})} \approx K_0(1 - N_m F(\bar{\varepsilon})), \tag{8}$$

because under the experimental conditions the denominator of this formula differs but little from unity. Here $F(\bar{\epsilon})$ represents the right side of relations (6) and (7) and does not depend on the density of the gas ($\bar{\epsilon}$ is the characteristic energy of the electrons).

We can use the distribution function in the Lorentz approximation[10] for the energy distribution function of the electrons $f_e(\epsilon')$; this takes into account the presence of a constant electric field in the gas and elastic collisions of the electron with the gas molecules. It is valid in the fundamental region of energies of the electron and takes the form (see[10])

$$f_e(\varepsilon') = C \exp\left[-\int_{\varepsilon_a}^{\varepsilon'} \frac{d\varepsilon'}{T + e^2E^2M/3m^2\nu_{el}^2}\right], \tag{9}$$

where C is the normalization constant, E the intensity of the electric field, $\nu_{el} = Nv\sigma_{el}$ the frequency of elastic collisions of the electron with the gas molecules of mass M, v the velocity of the electron, and σ_{el} the cross section of elastic collision of the electron with the molecule. If the collision frequency ν_{el} does not depend on the velocity of the electron, then $f = C \exp((\epsilon_a - \epsilon)/\bar{\epsilon})$ and according to Eq. (7)

$$F(\bar{\varepsilon}) = \left(\frac{m\bar{\varepsilon}}{2\pi\hbar^2}\right)^{-3/2} \exp\left\{-\frac{\varepsilon_a}{\bar{\varepsilon}}\right\} \frac{g_i}{g_e g_m}. \tag{10}$$

Here the characteristic energy of the electrons $\bar{\epsilon}$ is determined by measuring the coefficient D of electron diffusion across the field and the electron mobility K_0 on the basis of the relation

$$\bar{\varepsilon} = eD / K_0, \tag{11}$$

e is the charge of the electron.

The relation (10) is valid for any dependence of the collision frequency on the electron velocity for small field intensities, when the characteristic energy is equal to the gas temperature T. In this case, the value of $F(\bar{\epsilon})$ can be found with the help of the Saha formula (4). For high field intensities ($\bar{\epsilon} \gg T$) the numerical factor in Eq. (10) changes for arbitrary dependence of ν_{el} on v. In particular, if the collision frequency is proportional to the velocity of the electron, then

$$f_e(\varepsilon') = C \exp\left[\frac{\varepsilon_a^2 - \varepsilon'^2}{\pi\bar{\varepsilon}^2}\right],$$

and Eq. (10) takes the form

$$F(\bar{\varepsilon}) = 0.615 \frac{g_i}{g_e g_m} \left(\frac{m\bar{\varepsilon}}{2\pi\hbar^2}\right)^{-3/2} \exp\left[-\frac{1}{\pi}\left(\frac{\varepsilon_0}{\bar{\varepsilon}}\right)^2\right]. \tag{12}$$

5. We now use the results obtained for $F(\bar{\epsilon})$ to find the energy of the negative ion on the basis of the measured values of the dependence of the electron's mobility on the gas density for a fixed ratio E/N. According to the result, at a sufficient experimental accuracy in the case of the considered mechanism of mobility decrease, and in the presence of only one auto-ionizing state of the negative ion, the value ϵ_0 should be the same in all cases. Tables I–III give the values of this quantity for the ions H_2^-, N_2^- and CO_2^-, obtained by reducing the measurements of the drift velocity of the electrons as a function of E/p and p ($p = N_m T$ is the gas pressure) at a gas temperature T = 293°K in molecular hydrogen,[2,3] nitrogen[2,3] and carbon dioxide gas.[5] For the other molecular gases, in which a dependence of the drift velocity on the gas pressure at constant values of E/p was observed, the experimental data were unreliable. The measured values of $eD/K_0 = f(E/p)$ for the consid-

Table I. Excitation energy of the auto-ionizing state of H_2^-

V/cm torr	$\bar{\varepsilon}$ eV [4]	ε_a, eV	
		p = 31350 torr	p = 16950 torr
0,03	0.031	0.18—0.13	0.17—0.12
0,04	0.033	0,19—0.13	0.18—0.13
0.08	0.042	0,24—0.17	0,22—0.16
0.16	0.058	0.30—0,22	0.30—0,22
0.24	0.076	0.40—0.29	0,40—0.31
0.32	0.093	0,47—0.35	0.46—0.35
0.8	0,2	0.84—0.68	0.86—0,69

Table II. Excitation energy of the auto-ionizing state of N_2^-

V/cm torr	$\bar{\varepsilon}$ eV [11]	ε_a, eV	
		p = 29350 torr	p = 14782 torr
0.04	0.052	0,28—0.20	0.28—0.20
0.06	0.073	0,40—0.29	0.41—0.29
0,08	0,087	0.49—0,35	0.50—0.35
0.1	0.1	0,65—0.43	0.62—0.40
0.15	0.14	0.67—0.51	0,67—0.51
0.2	0.195	0.85—0.68	0,87—0.69
0,3	0,29	1.12—0.95	1.12—0.98
0.5	0,4	1.47—1.27	1,53—1.30
0.8	0.53	1,55—1.47	1,66—1.53

ered gases were taken from the work of Crompton[4] and the book of McDaniel.[11]

In the reduction of the experimental data we assumed that there is only a single state of the negative ion. The reduction made use of Eqs. (10) and (12), i.e., the limiting dependences of the cross section for elastic collisions of the electron with the molecule on the collision velocity ($\sigma_{el} \sim 1/v$, const) were incorporated in the distribution function of the electrons with respect to the energy. It is these limiting dependences which determine the region of tabulated values of ϵ_a. Inasmuch as the excitation energy of the auto-ionizing state of the negative ion of the molecule does not depend on the conditions of the experiment used to obtain this quantity, the values given in each table should correspond to one and the same number. The scatter of these numbers characterizes both the accuracy of the experiment and the validity of the theory used to reduce the experiment. The experimental errors were not taken into account in finding the energies of the negative ions. It should be noted that the sensitivity of the result to the accuracy of the introduced data increases sharply with increasing electron energy.

As follows from the data given in the tables, the negative ions of the molecules that are formed in each of the studied molecular gases by the electron motion are found in the auto-ionizing state. It is most probable that these auto-ionizing states arise upon excitation of the rotational or vibrational states of the molecule by collision with the slow electron. As the result of such a collision, the electron is captured by the molecule and stays in a bound state until it undergoes the reverse transition. If the auto-ionizing states of the negative ion have such a nature, then the considered pressure dependence of the electron mobility should appear in molecular gases and should not be observed in atomic gases.

Table III. Excitation energy of the auto-ionizing state of CO_2^-

	p, torr		
	25 000	20 000	16 000
ϵ_a, eV*	0.22—0.28	0.18—0.23	0.14—0.15

*E/p = 5 V/cm-torr, T = 0.202 eV.

6. Another mechanism of the pressure dependence of the electron mobility was considered by Yakubov.[12] This mechanism is due to the simultaneous scattering of the electron by several gas particles. At a low gas temperature, equal to the electron temperature, where the result obtained by Yakubov is valid, this mechanism leads to the following value of the function F(T), which enters in Eq. (7), for low values of the gas density N_m:

$$F_{Ya} = 0.64\sigma_{el}\,\hbar/\sqrt{mT}. \tag{13}$$

This mechanism produces a decrease in the electron mobility with increasing gas density, as does the mechanism connected with negative ion formation. But, in contrast to the case of negative ion formation considered by Yakubov,[12] the mechanism of change of the electron mobility with gas pressure should appear in the same fashion both for atomic and molecular gases. At low gas densities, it corresponds to the expansion of the mobility in the small parameter $\hbar\sigma_{el}N_m/\sqrt{mT}$, whereas the small parameter of the mobility expansion is equal to $(\hbar/mT)^{3/2}N_m$ at low gas densities for the case considered by us. It follows then that the effect of negative ion formation on the electron mobility can appear at lower gas densities than the simultaneous scattering of the electron by several gas molecules if the energy of the auto-ionizing state is small.

Comparing the expressions for the function F in Eq. (7), obtained on the basis of Eq. (13) for the mechanism of simultaneous scattering of the electron by several molecules (F_a) and on the basis of Eq. (6) for the mechanism of negative ion formation (F_{neg}), in the region of low temperatures, where the result of Yakubov is valid, we have

$$\frac{F_{Ya}}{F_{neg}} = 0.04\frac{m\sigma_{el}}{\hbar^2}T\exp\left\{\frac{\varepsilon_a}{T}\right\}. \tag{14}$$

This ratio is small for not very large ϵ_a/T. Inasmuch as the ratio ϵ_a/T can be established from experimental data, this experiment lets us decide which of the considered mechanisms of the pressure dependence of the electron mobility applies in specific cases. At the present time, the accuracy of the experimental results is insufficient to answer this question uniquely. For example, it has been established experimentally[3] that there is no pressure dependence of the electron mobility in helium and argon at $p \lesssim 50$ atm. In these cases, no negative ion is formed, so that this dependence should be associated with the simultaneous scattering by several molecules. However, an estimate of the effect according to Yakubov's formula shows that the effect does not greatly exceed the accuracy of the experiment in this case. The data of Tables I and II for hydrogen and nitrogen agree better with the Yakubov mechanism than with the one considered here. We shall assume that a more careful measurement of the mobility in molecular gases will allow us to establish the reason for the effect of the pressure on the mobility and, if this is connected with negative ion formation, it will enable us to determine reliably the parameters of the auto-ionizing state of the negative ion.

7. We now discuss the dependence of the excitation energy of the auto-ionizing state ϵ_a and the properties of the auto-ionizing state of the negative ion on the gas density. We shall consider the region of low gas densities

$$N_m R_0^3 \ll 1, \tag{15}$$

where R_0 is a quantity of the order of the dimensions of the molecule. Upon satisfaction of this condition, the interaction potential of the molecules is exponentially ($\sim \exp[-R_0 N_m^{1/3}]$) small in comparison with the characteristic atomic quantity. The shift in the excitation energy of the auto-ionizing state of the negative ion is of the same order, because this energy change is due to the interaction of the negative ion with the surrounding molecules in the region of coordinates where the molecule is concentrated. The change in the excitation energy of the auto-ionizing state is in the greatest degree due to the shift in the boundary of the continuous spectrum, which is determined by the interaction of the electron with the surrounding molecules. For example, in the case of short-range interaction of the electron with the molecules, this shift is equal to[13] $2\pi a_0^2 L N_m$, where L is the scattering length of an electron by the molecule. Inasmuch as the excitation energies of the auto-ionizing state ϵ_a are small, this effect begins to appear at low gas densities.

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Translated by R. T. Beyer
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