DIFFUSION AND MOBILITY OF IONS IN A GAS

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INTRODUCTION

THE diffusion and mobility of ions are important parameters characterizing the motion of ions in a gas. These parameters enable us to describe the motion of an ion in a gas over long periods of time (compared to the average time interval between collisions) in the presence of an external electric field and in its absence. Since diffusion and mobility are determined by the collisions of an ion with particles of a gas the value of these parameters, their dependence on the gas temperature, and also the dependence of the mobility on the intensity of the electric field give us the possibility of investigating the nature of the elementary act of collision of an ion with a gas particle and the cross section for this process.

The mobility of ions in gases has been a topic for investigation over a period of several decades. The case that has been investigated in greatest detail is the case of low intensity of the external electric field [1-6] when the velocity acquired by an ion over a mean free path under the influence of the electric field is much smaller than its average velocity. In this case the mobility of the ion K is related to the diffusion coefficient D by the Einstein relation [7]

$$K = \frac{eD}{T} \qquad (1)$$

(e is the charge of the ion, T is the gas temperature), so that a measurement of the mobility enables one also to determine the diffusion of the ions in the gas. Of independent interest are the cases of intermediate and high intensities of the electric field which are realized in a gas discharge and in an electrostatic generator. For example, it is specifically a measurement of the mobility at high fields [8] that first provided the possibility of correctly establishing the dependence of the cross section for resonance charge exchange on the velocity and of determining the magnitude of this cross section at low collision velocities for a number of inert gases.

Mobility of ions in gases has been discussed in a number of reviews and monographs [1-6,9-11]. In writing the present review we have utilized the more complete information on the mobility of ions obtained recently.

FORMULATION OF THE PROBLEM AND GENERAL METHODS FOR CALCULATING THE MOBILITY

In order to obtain the mobility of ions in a gas it is necessary to take into account the effect of collisions of the ions with the atoms of the gas on their directed motion in an electric field. For this purpose it is convenient to utilize the kinetic equation for the velocity distribution function for the ions. In this chapter we investigate the kinetic equation for the velocity distribution function for the ions and discuss the approximate methods commonly used to solve it. In obtaining the kinetic equation we shall assume that the density of ions in the gas is considerably lower than the density of the gas particles N. Then the presence of the ions in the gas will not upset the Maxwellian velocity distribution of the neutral particles of the gas, and it is possible to neglect collisions between the ions in writing down the kinetic equation. If we restrict ourselves to elastic collisions of ions with gas particles, then the velocity distribution function for the ions f(v) in a gas in a constant electric field of intensity F satisfies the kinetic equation [12,13]

$$\frac{eF}{M} \frac{\partial f(\mathbf{v})}{\partial \mathbf{v}} = N \int [f(\mathbf{v}') \varphi(v_1')$$

$$- f(\mathbf{v}) \varphi(v_1)] g |a(\chi, g)|^2 d \cos \chi \, d\Phi \, d\mathbf{v}_1. \qquad (2)$$

Here $\varphi(\mathbf{v}) = (m/2\pi T)^{3/2} \exp(-mv^2/2T)$ is the Maxwellian distribution function for the gas particles, T is the gas temperature, M and m are the masses of an ion and of a gas particle, $\mathbf{v}$ and $\mathbf{v}_1$ are the velocities of the ion and of the gas particle before the collision; $\mathbf{v}'$ and $\mathbf{v}_1'$ are their velocities after the collision, as the result of which scattering occurs which is characterized by the scattering angles χ and Φ in the center of mass system; $a(\chi, g)$ is the scattering amplitude, $g = |\mathbf{v} - \mathbf{v}_1|$ is the relative velocity for a collision between an atom and an ion.

We multiply Eq. (2) on the left by Mv_x (the x axis is directed along the field) and integrate over velocity space. Utilizing the relation

$$\frac{1}{2\pi} \int_0^{2\pi} d\Phi (v_x' - v_x) = \frac{1}{2\pi} \frac{m}{m+M} \int_0^{2\pi} (g_x' - g_x) d\Phi = \frac{mg_x}{m+M} (1 - \cos \chi)$$

(g' is the relative velocity after the collision), we obtain the formula [12]:

$$\frac{eF}{\mu N} = \int f(\mathbf{v}) \varphi(v_1) g g_x \sigma^*(g) \, d\mathbf{v} \, d\mathbf{v}_1, \qquad (3)$$

where $\mu = mM/(m + M)$ is the reduced mass, $\sigma^*(g) = \int (1 - \cos \chi) \, d\sigma = \int |a(\chi, g)|^2 (1 - \cos \chi) \times d\Phi d \cos \chi$ is the transport cross section for the scattering of an ion by a gas particle. For low intensity of the electric field the distribution function for the ions differs little from the Maxwellian distri-

bution function. With an accuracy up to the first term in the expansion in powers of eF the distribution function for the ions has the form

$$f(\mathbf{v}) = \varphi(v)[1 + h(v)\,v\cos\theta],\qquad(4)$$

where θ is the angle between $\mathbf{v}$ and $\mathbf{F}$, and this form of the expansion of the distribution function follows directly from the kinetic equation (2). The drift velocity of the ions w and their mobility K can be expressed in terms of the function $h(v)$:

$$w = \int v_x f(\mathbf{v})\,d\mathbf{v} = \frac{1}{3}\int v^2 \varphi(v)\,h(v)\,d\mathbf{v};\qquad K = \frac{w}{F}.\qquad(5)$$

The exact value of the function $h(v)$ can be obtained by solving the kinetic equation. Usually the mobility is obtained by means of the Chapman-Enskog method [14] which, in spite of its simplicity, usually gives a result close to the exact one. The Chapman-Enskog method is associated with an expansion of $h(v)$ in terms of suitable Sonine polynomials and is particularly simple in the case of evaluating ionic mobility. The first Chapman-Enskog approximation corresponds to the assumption that $h(v) = \text{const}$. If the value of this constant is obtained by substituting (4) into (3), then from formula (5) we obtain for the ionic mobility K_I and for the drift velocity w_I

$$K_I = \frac{3\pi^{1/2}e}{8N(2T\mu)^{1/2}\bar{\sigma}},\qquad w_I = K_I F,\qquad(6)$$

where

$$\bar{\sigma} = \frac{1}{2}\int_0^\infty \sigma^*(x)\,e^{-x}x^2\,dx,\qquad x = \frac{\mu v^2}{2T},\qquad(6a)$$

v is the relative velocity for the collision of an ion with a gas particle.

Usually mobility is expressed relative to a particle density of $N = 2.69 \times 10^{19}\,\text{cm}^{-3}$ which corresponds to a pressure of 1 atm at a gas temperature of 0°C. If in formula (6) the temperature T is measured in degrees Kelvin, the reduced mass μ is measured in units of the proton mass, and the average cross section in units of πa_0^2 ($0.88 \times 10^{-16}\,\text{cm}^2$), then this formula assumes the form [5]

$$K = \frac{2,1\cdot 10^4}{\bar{\sigma}\,(\mu T)^{1/2}}\frac{\text{cm}}{\text{sec}}\Big/\frac{\text{volt}}{\text{cm}}.\qquad(7)$$

The second approximation of the Chapman-Enskog method yields [12]

$$w = w_I(1 + \Delta),$$

$$\Delta = \frac{\frac{2}{5}\left(m\dfrac{d\ln\Omega}{dT}\right)^2}{m^2 + 3M^2 + 2mM\dfrac{\sigma^{(2)}}{\bar{\sigma}}},\qquad\text{where}\qquad \Omega = \sqrt{\frac{2T}{M}}\,\bar{\sigma},$$

$$\sigma^{(2)} = \int (1 - \cos^2\chi)\,d\sigma.\qquad(8)$$

In order to determine the degree of accuracy of the result obtained in the Chapman-Enskog approximation we shall compare formulas (6) and (8) with the exact result in those cases when an exact solution is possible.

1) If $M \gg m$, i.e., the ionic mass is much greater than the mass of the gas particles, then $\Delta \sim (m/M)^2 \ll 1$, and the result (6) is asymptotically exact in the limit $m/M \to 0$.

2) In the case of mobility of ions in a gas composed of the same atoms, when $m = M$, and the cross section for resonance charge exchange depends weakly on the velocity and considerably exceeds the cross section for elastic scattering ($\chi = \pi$), we obtain $\Delta = 1/40$. The discrepancy between formula (6) and the result obtained by solving the kinetic equation [15] exactly is approximately of the same amount. In Table I we give the ratio of the exact value of the function $h(v)$ to that obtained in the first Chapman-Enskog approximation.

3) In the case $M \ll m$ the situation coincides with that which occurs in considering an electron moving in a constant electric field in a gas. In this case the kinetic equation can be solved [14,16-20] by expanding the distribution function in terms of the small parameter $M/m \ll 1$. If the potential for the interaction between an ion and a gas particle is given in the form $U = cR^{-n}$, then the ratio of the exact solution for the drift velocity to that obtained in the first approximation of the Chapman-Enskog method (6) will turn out to be equal to

$$\frac{w}{w_I} = \frac{16}{9\pi}\Gamma\left(3 - \frac{2}{n}\right)\Gamma\left(2 + \frac{2}{n}\right).\qquad(8a)$$

The correction associated with taking into account the second Chapman-Enskog approximation (8) is equal to

$$\Delta = \frac{1}{10}\left(1 - \frac{4}{n}\right)^2.$$

A comparison of the result of the second approximation in the Chapman-Enskog method with the exact result is made in Table II (the data are taken from [10]).

Until now we have been investigating the first term in the expansion of the mobility and of the drift velocity in powers of $eF/TN\sigma^*$. The mobility at low field intensities taking into account the first two terms of the expansion has the form [12,21]

$$K = K_0 + K_2 F^2 + \cdots\qquad(9)$$

For high electric field intensity

$$\frac{eF}{TN\sigma^*} \gg 1\qquad(10)$$

the drift velocity of the ions turns out to be much greater than the thermal velocity of the ions and of the gas particles. In this case the relative velocity of collision between an ion and a gas particle coincides with the velocity of the ion, and relation (3) assumes the form

$$\frac{eF}{\mu N} = \int f(\mathbf{v})\,v v_x \sigma^*(v)\,d\mathbf{v}.$$

Table I

$v\sqrt{\dfrac{2T}{M}}$	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
$h/h_{Ch.E}$	1.51	1.44	1.39	1.31	1.22	1.15	1.05	0.98	0.91	0.89	0.86

Table II

n	∞	12	6	4	2
(8a)	1.132	1.056	1.013	1	1.132
$1+\Delta$	1.100	1.044	1.011	1	1.100

Since in the limiting case under consideration the only parameter having the dimension of a velocity on which the distribution function depends is the drift velocity, it follows from the last relation that $eF/\mu N \sim w^2 \sigma^*(w)$. Therefore, if the law for the dependence of the cross section on the velocity $(U = cR^{-n})$ has the form $\sigma^*(v) \sim v^{-4/n}$, then we have

$$ w \sim \left(\frac{eF}{\mu N}\right)^{\frac{n}{2(n-2)}}, \qquad K \sim \frac{1}{F}\left(\frac{eF}{\mu N}\right)^{\frac{n}{2(n-2)}}. \qquad (11) $$

Formula (11) gives the qualitative dependence of the mobility on the field intensity in the limit of high field intensity. More exact expressions for the ionic mobility at large values of the field intensity can be obtained by solving the kinetic equation for a specific form of the scattering of ions by gas particles, and this has been carried out in a number of cases in [13,15,22-24].

EXPERIMENTAL METHODS FOR MEASURING IONIC MOBILITY

We consider the methods available for measuring the mobility and the diffusion of ions in a gas. The most exact of the old methods of measuring mobility, which gave the most information on the mobility of ions and which is still being used at present, is Tyndall's method [1,25].

Figure 1 shows a block diagram of an apparatus which is typical for this method [26]. At the moment when the first pulse is applied the grids x_2 and x_3 are opened and the ions penetrate into the drift region between the grids x_3 and x_4. At the moment the second pulse is applied the grids x_4 and x_5 are opened. If the time between the two pulses (which can be varied under the conditions of this experiment) coincides with the time of passage of the ions through the drift region a maximum is observed in the current measured by the collector. The sources of ions in the experiments on the measurement of ionic mobility are provided by a gas discharge, by ultraviolet radiation or by α particles if the mobility of ions is being measured in a gas of the same substance, or by a heated filament onto which an appropriate salt has been deposited if one measures the mobility of ions in a different gas.

Tyndall's method is less accurate compared to other modern methods for measuring ionic mobility in a gas. Nevertheless, it is the only method in use at present which enables one to measure the mobility of ions in a foreign gas since it utilizes a continuously acting source.

The development of pulse techniques has enabled one to measure by a direct method the mobility of ions in a gas of the same substance [26-28].

The method consists of measuring the time interval after which a decrease is observed in the current arising as a result of a pulse of ionization near the cathode. The circuit in which the current is measured contains a gaseous gap, while the pulse of ionization which leads to the production of electrons and ions near the cathode is produced either as a result of irradiating the cathode or with the aid of a glow discharge. The time after which a decrease is observed in the current in the circuit is determined by the time taken by the ions to traverse the drift region. If two kinds of ions are formed near the cathode two decreases in the current are observed in the circuit, and the accuracy of the method is sufficiently great to enable one to separate ions of different types if their mobilities differ by not less than 10%.

Modern methods of measurement of ionic mobilities in a gas utilize one of the methods described
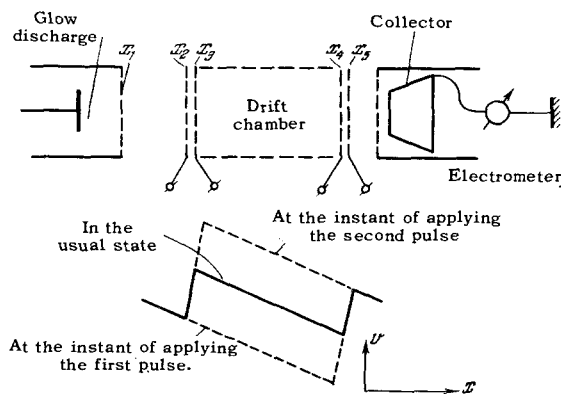

FIG. 1. Block diagram of Tyndall's apparatus and the potential distribution in it.

above supplemented by various improvements. The most important of these improvements is the combination of a drift chamber with a mass spectrometer[29-30] and this in the case of not too low drift velocities enables one to determine directly the kind of ions to which the measured mobility corresponds.

The most exact method of determining the diffusion coefficient for ions in a gas of the same substance is based on studying the decay of a plasma in the case when conditions for ambipolar diffusion are satisfied.

We assume that in a finite volume a weakly ionized plasma is produced in which ions of one kind are present. Then the flux of ions j_+ and the flux of electrons j_- will turn out to be equal to

$$j_- = -D_-\nabla n_- - K_-Fn_-, \quad j_+ = -D_+\nabla n_+ + K_+Fn_+, \quad (12)$$

where K_+, K_- are the mobilities of the ions and the electrons, D_+, D_- are the diffusion coefficients for these particles, and n_+, n_- are their densities. The intensity of the electric field F which arises as a result of the action of the space charge satisfies the Poisson equation

$$\text{div } F = 4\pi(n_+ - n_-)e. \quad (12a)$$

In the case when ambipolar diffusion occurs the value of this field is sufficiently great so that the densities and the currents of the ions and of the electrons are close to one another. If one assumes that the temperature T of the ions and of the electrons coincides with the temperature of the gas, and if one utilizes the Einstein relation (1) one obtains in this case for the particle current ($j_- \approx j_+$, $n = n_- \approx n_+$):

$$j = -\frac{D_-K_+\nabla n_- + D_+K_-\nabla n_+}{K_- + K_+} = -2D_+\nabla n. \quad (13)$$

The result (13) is valid if the condition $|n_+ - n_-| \ll n$ is satisfied. It follows from (12a) ($|n_+ - n_-|$ $\sim (F/4\pi L)e$) and from (12) ($eF \sim T/L$) that ambipolar diffusion occurs when

$$L \gg r_D = \sqrt{\frac{T}{8\pi ne^2}},$$

where L is the characteristic dimension of the plasma, and r_D is the Debye-Hückel radius.

The experimental method of obtaining the coefficient which is based on ambipolar diffusion is associated with measuring the time dependence of the density of the electrons in the plasma decaying after the cessation of the discharge[31-33]. The weakly ionized plasma is produced in a resonator. The change in the resonance frequency of the resonator is measured, which is associated with the presence of plasma in the resonator, and it is proportional to the free electron density. The high degree of accuracy of measuring the frequency shift enables one to determine the relative density of the electrons as it varies over several orders of magnitude. The result so obtained is compared with the solution of the diffusion equation

$$\frac{\partial n_-}{\partial t} = -2D_+\Delta n_- \quad (14)$$

under boundary conditions corresponding to the resonator being utilized. As a result of such a comparison the diffusion coefficient for the ions in the gas is determined.

The method based on ambipolar diffusion guarantees that the measurements will have the highest degree of accuracy, but according to the idea of this method it can be utilized only in the case when ions of one kind predominate in the discharge. This method was utilized to measure the diffusion of inert gas ions in the same gas. In an inert gas both atomic ions are formed of the type He^+ and also molecular ions of the type He_2^+, with the molecular ions being formed as a result of triple collisions of atomic ions with gas atoms, so that the ratio between the number of atomic and molecular ions depends on the gas density. Therefore by varying the density of the inert gas one can create conditions when either atomic or molecular ions are predominantly formed in the discharge, and one can then measure the diffusion coefficient corresponding to a given kind of ions.

MOBILITY OF IONS IN A DIFFERENT GAS

In the case of motion of ions in a different monatomic gas the distribution function for the ions is determined primarily by the elastic scattering of the ions by atoms. If in this case the main contribution to the cross section is made by collisions with large impact parameters in which the scattering is associated with the polarization interaction between the ion and the atom the scattering cross section is inversely proportional to the relative velocity of the collision and does not differ appreciably from the cross section for polarization capture. It follows from (3) that if the elastic scattering cross section is inversely proportional to the velocity then

$$w = \frac{eF}{\mu\nu}, \quad K = \frac{e}{\mu\nu}, \quad (15)$$

where $\nu = Ng\sigma^*(g)$ is the collision frequency. Apparently in the case of polarization interaction between an ion and an atom the mobility of the ion depends neither on the field intensity nor on the temperature. The case of polarization interaction between an ion and an atom investigated in the papers of Langevin[34] and Hasse[35] has been investigated in detail in the review by Dalgarno et al.[3] If at the same time the polarization capture and small angle scattering are taken into account this leads to the following formula for the diffusion scattering cross section:

$$\sigma^* = 2.21\pi\sqrt{\frac{\alpha e^2}{\mu g^2}}. \quad (16)$$

Here μ is the reduced mass of the ion and the atom and α is the atomic polarizability. Substitution of

Table III. Polarizability and dipole moments of atoms and molecules of gases.

Gas	Dipole moment (Debye)	Dipole moment (Debye)	Gas	Polarizability (at. un.)	Polarizability (at. un.)
He	0	1.39	NO	0.16	11.5
Ne	0	2.76	HCl	1.03	17.4
Ar	0	11.1	HBr	0.79	23.6
Kr	0	16.8			
Xe	0	27.2			
			CO_2	0	17.5
			Cl_2	0	54.6
H_2	0	5.52	H_2O	1.84	9.8
D_2	0	5.39	N_2O	0.17	19.7
O_2	0	10.6	H_2S	1.02	24.4
N_2	0	11.8	SO_2	1.62	25.6
CO	0,1	13.1			

Table IV. Polarizability of atoms in the ground state

Atom	Polarizability (at. un.)	References	Method of determination	Atom	Polarizability (at. un.)	References	Method of determination
H	4.5	37	I	Mg	130	48	VII
Li	165	38	II	K	281	38	II
	150±13	40	III		260±27	40	III
	135±20	41	IV		250±30	41	IV
	183	43	V		230±12	42	III
	110±20	46	VI		300	43	V
Be	45	47	VII	Ca	130—156	45	II
	30	50	VII	Rb	296	38	II
	31	49	VII		257±27	40	III
B	34.5	39	VII		270±34	41	IV
C	14.2	39	VII	Sr	340	42	III
N	7.65	44	V	Cs	158—218	45	II
	8.8	39	VII		363	38	II
O	5.2	44	V		325±40	40	III
F	27.5	39	VII		355±44	41	IV
Na	166	38	II		285±14	42	III
	145±14	40	III	Ba	410	43	V
	135±17	41	IV		420±40	46	VI
	182	43	V	Hg	210—310	45	II
Mg	35—60	45	II		37		VIII

I — quantum mechanical calculation.
II — calculation on the basis of a spectrum and atomic oscillator strengths.
III — method of electrical deflection of a beam.
IV — method of a gradient balance of an electric and a magnetic field.
V — optical Stark effect.
VI — electron microscope.
VII — calculation by the Hartree-Fock method.
VIII — measurement of the dielectric permittivity of a gas.

(16) into (15) gives for the mobility of the ion corresponding to the atomic density $N = 2.69 \times 10^{19}$ cm^{-3}[3]:

$$K = \frac{35,9}{\sqrt{\alpha\mu}} \frac{cm^2}{V\text{-sec}}, \qquad (17)$$

where the reduced mass is expressed in units of the proton mass, and the polarizability α in atomic units. The values of the polarizability of atoms and molecules of certain gases* and also dipole moments of these molecules are given in Table III [36]. In Table IV are given values of the polarizability of a number of atoms and an indication is given of the methods on the basis of which these quantities had been obtained. In Table V a comparison is made of the experimentally measured values of the mobility of gases at room temperature with those calculated by means of formula (17). The experimental values of the mobility of the ions of alkali metals are taken from [1,52,53], those for Ne$^+$ are taken from [54], and those for the negative oxygen ion are taken from [55]. In Table VI the experimentally measured values of the mobility of molecular ions of inert gases in the same gas are compared with those obtained by means of formula (17). Theoretical values of the mobility are quoted without citing the references.

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*The polarizability of a molecule is a tensor. In Table III the average value of this parameter is listed.

Table V. Ratio of the experimentally measured mobility at
room temperature to that calculated by formula (17).

Ion \ Gas	He	Ne	Ar	Kr	Xe	H_2	N_2	CO
Li^+	1.27	1.17	1.06	1.07	1.06	1.02	0.89	0.58
Na^+	1.38	1.24	1.07	1.06	1.09	1.13	0.97	0.82
K^+	1.35	1.28	1.08	1.10	1.07	1.14	0.98	0.89
Rb^+	1.29	1.26	1.08	1.08	1.07	1.14	0.99	0.90
Cs^+	1.19	1.18	1.07	1.08	1.07	1.15	0.99	0.90
NO^+	1.12		1.25			1.36	1.12	
O_3^-	0.75	0.88	0.89	0.88	0.76	0.91	0.90	

Table VI. Mobility of molecular ions of inert gases in the same
gas at room temperature.

He_2^+ (20)		Ne_2^+ (6)	Ar_2^+ (2.1)	Kr_2^+ (1.16)	Xe_2^+ (0.74)
20.9 [1 *]	16.2 [64]	6.5 [28, 59, 64]	2.65 [28]	1.1—1.2 [27]	
20.3 [28]	16.4 [65]	5.8 [57 **]	1.79 [57 **]		
19 [58]	16.7 [66]	5.8 [58]	1.9 [58, 64, 68]	1.21 [28]	0.67—0.77 [27]
20.3 [59]		7.5 [60]	2.7 [59]		0.79 [28]
20.3 [60]		6.1 [67]	2.6 [60]		
16.2 [61]		6.4 [131]			
16.7 [62]					
16.2 [63]					

*)In these papers the He_2^+ ion is incorrectly classified as He^+, as was shown
in [69].

**)Values are with reference to a density corresponding to 0°C and 1 atm.

As follows from Table V the polarization potential
gives not a bad description of the interaction of an
ion with an atom in those cases when its value is of
the order of magnitude of the gas temperature. For
large distances R between the ion and the atom the
long range potential describing their interaction has
the form

$$V = -\frac{\alpha}{2R^4} - \frac{b}{R^6} + \ldots, \qquad b > 0, \qquad (18)$$

where the first term corresponds to the polarization
interaction, and the second term corresponds to the
sum of the interactions of the dipole of the ion with
the dipole of the atom and of the charge of the ion
with the quadrupole moment of the atom. If we use
the long range interaction potential (18) and assume
that over the range of distances where the interaction
potential is of the order of magnitude of the tempera-
ture the second term in (18) is small compared to the
first one we obtain [3] for the ionic mobility the ex-
pression

$$K = K_0 \left[1 + \frac{2b}{3\alpha} \left(\frac{2T}{a\pi} \right)^{1/2} \right]^{-1}, \qquad (19)$$

where K_0 is the mobility of the ion (17) correspond-
ing to the polarization interaction potential. The
values of the coefficient b in the case of the interac-
tion of ions of alkali metals with atoms of inert gases
and with certain gas molecules have been calculated
by Margenau [56]. As calculations have shown for

these pairs the difference between (19) and (17) at
room temperature is small (thus, for example, for
the pair Li^+ – He it is equal to 1.3%, and for the
pair Li^+ – Xe it amounts to 0.5%).

The deviation of the value of the ionic mobility
from the value given by formula (17) is related to the
short range exchange interaction between an ion and
an atom. In the case of the interaction between ions
of alkali metals and inert gas atoms which possess
closed electron shells the exchange interaction leads
to repulsion. Therefore in the case of the motion of
ions of alkali metals in inert gases the presence of
an exchange interaction between the ions and the
atoms leads to a reduction in the effective cross
section for the scattering of the ions, and conse-
quently to an increase in the mobility compared to
the value (17) obtained in the case of a polarization
interaction.

Definite information on the interaction between an
ion and an atom can be obtained from the tempera-
ture dependence of the mobility at low field intensity.
We assume that for distances between an ion and an
atom at which the potential representing the interac-
tion between an ion and an atom is of the order of
magnitude of the temperature this potential can be
approximated by the expression $U \sim R^{-n}$. Then at
low field intensity the dependence of the mobility on
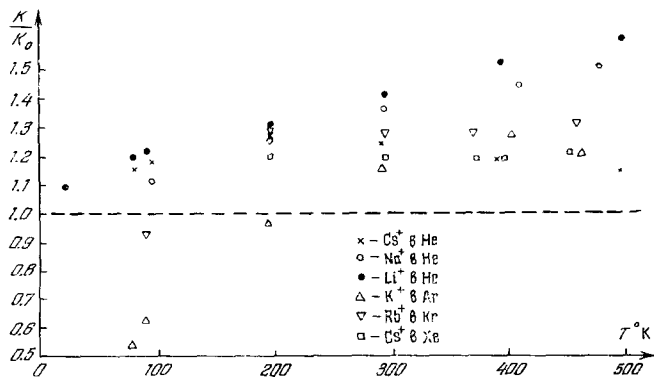the temperature, as follows from (6), has the form:

FIG. 2. Ratio of the experimentally measured ionic mobility to that calculated by means of formula (17) at different temperatures.

Table VII

System	γ	$\epsilon\,(10^{-2}\mathrm{eV})$	r_m (Å)	r_0 (Å)	C (Å²) empir.	C (Å²) theoret.
Li⁺ — He	0.10	4.74	2.22	1.94	0.73	0.78
Na⁺ — He	0.15	4.03	2.35	2.06	1.30	1.17
Cs⁺ — He	0.42	1.40	3.36	2.96	10.9	7.03
K⁺ — Ar	0.2	12.1	3.00	2.63	3.00	2.85
Rb⁺ — Kr	0.2	11.9	3.34	2.93	3.72	3.72
Cs⁺ — Xe	0.2	10.6	3.88	3.40	5.02	5.52
He₂⁺ — He	0.25	9.9	1.93	1.70	1.66	2.29
Ne₂⁺ — Ne	0.4	1.0	4.3	3.80	16	

$K \sim T^{(2/n)\,-\,(1/2)}$. Figure 2 compares the ratio of the experimentally measured mobility of the ions of alkali metals in inert gases [57,70-72] to the value calculated by means of formula (17) at different temperatures. As may be seen, the comparison usually yields $n \lesssim 4$, i.e., due to the exchange interaction the effective attraction increases as the ion approaches the atom slower than in the case of polarization interaction. The exchange interaction depends exponentially on the distance between the atoms so that its contribution to the interaction potential between atomic particles increases sharply as the distance between them diminishes.

The effect of the exchange interaction on the potential describing the interaction between an ion of an alkali metal and an inert gas atom can be determined if we study the dependence of the ionic mobility on the intensity of the electric field at high fields. In the case when the effective potential for the interaction between an atom and an ion is given by $U \sim R^{-n}$ the mobility of the ion at high values of the field intensity F is related to the field intensity by the expression $K \sim F^{(4-n)/2(n-2)}$. Since the experimentally measured mobility of ions of alkali metals in an inert gas [1] increases with increasing field intensity for high fields, then $n \lesssim 4$.

Thus, from the experimental data on the measurement of the value of the mobility of the ions of alkali metals in inert gases, and also from the dependence of the mobility on the gas temperature and on the intensity of the electric field one can establish certain properties of the effective potential describing the interaction between an ion and an atom. Over the range of distances between an ion and an atom where the value of this potential is of the order of the average energy of the ions in the gas this potential does not differ much from the polarization potential, and this difference is associated with the short range exchange interaction between the ion and the atom. In the case of the interaction between ions of alkali metals and atoms of inert gases the exchange inter-

action leads to a repulsion. In this case utilizing experimental data on the mobility of ions in the gas one can calculate the value of the exchange interac- action for the range of distances between an ion and an atom indicated above. Thus, in [21] the potential for the interaction between an ion and an atom was represented in the form

$$V = \frac{\epsilon}{2}\left[(1+\gamma)\left(\frac{r_m}{r}\right)^{12} - 4\gamma\left(\frac{r_m}{r}\right)^6 - 3(1-\gamma)\left(\frac{r_m}{r}\right)^4 \right].$$

Here $3\epsilon(1-\gamma)r_m^4$ is the atomic polarizability, while two other relations for the parameters in this potential in the case of a number of interacting pairs of ions and atoms were determined by comparing the experimentally measured values of the mobility at different temperatures [1,57,59,70-72] with the values calculated with the aid of this potential. The results are shown in Table VII. In this table the values are given of the coefficient of the term involving r^{-6} $C = 4\gamma r_m^2/3(1-\gamma)$ as calculated by Margenau [56] by a quantum mechanical method (the theoretical value), and also as obtained from the condition that the experimental and the theoretical values of the mobility at different temperatures should agree (the empirical value). The distance r_0 is determined by the relation $V(r_0) = 0$.

MOBILITY OF IONS IN THE SAME GAS

The mobility of ions in the same gas consisting of atoms is related in an essential manner to the resonance charge exchange between an ion and an atom. As a result of the resonance charge exchange the electron which is initially associated with one atomic core goes over to another atomic core. After a collision between an ion and an atom as a result of which resonance charge exchange occurs the ion moves along the trajectory of the atomic particle which was neutral before the collision. Therefore a resonance charge exchange leads to the scattering of an ion even in the case when the colliding ion and atom move along straight line trajectories and affects in a significant manner the diffusion of ions in the same gas.

The probability of resonance charge exchange can be determined in the following manner. The eigenstates of the quasimolecule consisting of an ion and the

corresponding atom can be divided in virtue of the symmetry of the problem into even (g) and odd (u) states depending on the property of the corresponding wave function of preserving or altering their sign under a reflection of electrons with respect to the symmetry plane (the plane perpendicular to the axis joining the nuclei and; bisecting the distance between them). For large distances between the atoms the eigenfunctions of the quasimolecule have the form $\psi_{g,u} = (1/\sqrt{2})(\psi_1 \pm \psi_2)$, where the functions ψ_1 and ψ_2 correspond to finding the electron near the first or near the second atomic core respectively in the given state. The eigenfunctions of the quasimolecule satisfy the Schrödinger equation: $\hat{H}\psi_{u,g} = \epsilon_{u,g}\psi_{u,g}$ where ϵ_u and ϵ_g are the energy levels of the quasimolecule which depend on the distance between the nuclei treated as a parameter. When the distance between the ion and the atom is infinitely large the energy of the quasi molecule $\epsilon_u = \epsilon_g$ and coincides with the electron energy of the isolated atom.

For the impact parameters of the collisions between ions and atoms which determine the cross section for resonance charge exchange it is possible to neglect the inelastic transitions between the states of the quasimolecule. In this case the wave function of the system satisfying the Schrödinger equation $i\hbar\partial\Psi/\partial t = H\Psi$ and corresponding to finding the electron before the collision near the first atomic core ($\Psi|_{t=-\infty} = \psi_1$) has the form

$$\Psi = \frac{1}{\sqrt{2}}\psi_g e^{-i\int_{-\infty}^{t} \epsilon_g dt'} + \frac{1}{\sqrt{2}}\psi_u e^{-i\int_{-\infty}^{t} \epsilon_u dt'}$$

On the basis of this relation and utilizing the orthogonality of the wave functions of the quasimolecule for infinite separation between the nuclei $\langle \psi_1|\psi_2 \rangle = 0$, $\langle \psi_1|\psi_1 \rangle = \langle \psi_2|\psi_2 \rangle = 1$ we obtain for the probability of resonance charge exchange[73,74]

$$w = |\langle \psi_2|\Psi|_{t=\infty}\rangle|^2 = \frac{1}{4}\left| e^{-\int_{-\infty}^{+\infty}\epsilon_g dt} - e^{-\int_{-\infty}^{+\infty}\epsilon_u dt}\right|^2 = \sin^2\zeta(\rho),$$

$$\zeta(\rho) = \int_{-\infty}^{+\infty}\frac{(\epsilon_u - \epsilon_g)}{2} dt,$$

where ρ is the impact parameter for the collision.

In order to find the mobility of ions in the same gas we calculate the diffusion cross section for the scattering of an ion by an atom taking resonance charge exchange into account. According to the definition of the diffusion scattering cross section we have

$$\sigma^* = \int_0^\infty 2\pi\rho\, d\rho\, [(1-\cos\chi)\cos^2\zeta + (1-\cos\chi')\sin^2\zeta],$$

where χ is the scattering angle in the center of inertia system for the nucleus with which the ion was initially associated, χ' is the angle in the system of the center of inertia between the direction of the velocity of this nucleus prior to the collision and the

direction of the velocity of the other nucleus after the collision; the angle χ' characterizes the scattering of the ion in the case when resonance charge exchange occurs. Since $\chi + \chi' = \pi$ and according to the definition of the resonance charge exchange cross section we have $\sigma_{res} = \int_0^\infty 2\pi\rho\, d\rho\sin^2\zeta$, we have

$$\sigma^* = \int_0^\infty 2\pi\rho\, d\rho\, [(1-\cos\chi)\cos^2\zeta + (1+\cos\chi)\sin^2\zeta]$$

$$= 2\sigma_{res} + \int_0^\infty 2\pi\rho\, d\rho\,(1-\cos\chi)\cos 2\zeta. \qquad (20)$$

Thus, if we can neglect elastic scattering compared to resonance charge exchange, or if this scattering is associated with polarization capture, then[75]

$$\sigma^* = 2\sigma_{res}. \qquad (21)$$

The second term in formula (20) is determined by small angle scattering for impact parameters for collisions in which resonance charge exchange does not take place ($\zeta = 0$). This term is always smaller than the first one. Even in the limit of low velocities when charge exchange occurs as a result of the capture of the ion and the first term in formula (20) is equal to the cross section for the capture σ_{cap}, the second term, in accordance with (16), is equal to $0.105\sigma_{cap} = 0.21\pi(\alpha/2\epsilon)^{1/2}$ where α is the atomic polarizability, ϵ is the energy of the atom and of the ion in the center of inertia system.

If the elastic scattering cross section is small compared to the charge exchange cross section then in the case when the electron undergoing the transition is in an s-state the connection between the charge exchange cross section $\pi R_0^2/2$ and the relative velocity of the collision of the ion and the atom is given by the relation[76]

$$0.28\frac{v}{v_0} = A^2 S\left(\frac{\pi}{2\gamma}\right)^{1/2}\left(\frac{R_0}{a_0}\right)^{\frac{2}{\gamma}-\frac{1}{2}} e^{-\frac{R_0}{a_0}\gamma-\frac{1}{\gamma}}. \qquad (22a)$$

If the electron undergoing the transition is in a p-state then the cross section for resonance charge exchange averaged over the direction of the angular momentum of the electron is determined by the relation

$$\sigma = \frac{\pi}{2}\left[R_0 - \frac{2}{\gamma} + \frac{\pi}{\gamma}\sqrt{\frac{3}{2R_0\gamma}}\right]^2,$$

$$0.28\frac{v}{v_0} = 3A^2 S\left(\frac{\pi}{2\gamma}\right)^{1/2}\left(\frac{R_0}{a_0}\right)^{\frac{2}{\gamma}-\frac{1}{2}} e^{-\frac{R_0}{a_0}\gamma-\frac{1}{\gamma}}. \qquad (22b)$$

Here ($me^4\gamma^2/2\hbar^2$) is the binding energy of the electron in the atom, $a_0 = \hbar^2/me^2$ is the Bohr radius, $v_0 = e^2/\hbar$, and the constant A is related to the asymptotic behavior of the electron wave function of the atom, so that the radial electron wave function normalized to unity is given at large distances r between the electron and the nucleus by

$$\Psi = Aa_0^{-3/2}\left(\frac{r}{a_0}\right)^{\frac{1}{\gamma}-1}\exp\left(-\frac{r}{a_0}\gamma\right).\qquad(23)$$

The quantity S characterizes the state of the electron in the atom. Thus, if an ion on the basis of which an atom is formed has spin equal to zero, then S = 1, if the spin of the ion is equal to $\frac{1}{2}$, and the spin of the atom is equal to zero, then S = $\frac{1}{2}$.

In formulas (22a)—(22b) the elastic scattering of ions by atoms is neglected. If the elastic scattering associated with the polarization interaction between ions and atoms ($V = -\alpha e^2/2R^4$) is significant, then the charge exchange cross section is given by the expression[77]

$$\sigma_{res}=\begin{cases}\frac{\pi R_0^2}{2}\left[1-\frac{V(R_0)}{E}\right], & v_0 > v_1,\\[2mm]\pi\left(\frac{\alpha e^2}{2E}\right)^{1/2}, & v_0 < v_1,\end{cases}\qquad(24)$$

where the velocity v_1 is determined by the relation

$$R_0(v_1)=\left(\frac{\alpha e^2}{\mu v_1^2}\right)^{1/4}.\qquad(24a)$$

Here $\pi R_0^2(v)/2$ is the charge exchange cross section obtained by neglecting elastic scattering and determined by formulas (22), α is the atomic polarizability, $\pi(2\alpha e^2/E)^{1/2}$ is the cross section for the polarization capture of an ion by an atom, and E is the kinetic energy of the ion and of the atom in the center of inertia system.

Substituting (24) and (21) into (6a) we obtain for the transport cross section averaged over the Maxwellian distribution of the ions an expression analogous to that found in[78] in which, however, the cap-

ture of ions by atoms is taken into account incorrectly:

$$\frac{1}{2}\bar{\sigma}=\sigma_{res}(2.24v_T)\,e^{-z}\left(1+z+\frac{z^2}{2}\right)+\frac{\pi^2\alpha e^2 e^{-z}(1+z)}{16T\sigma_{res}(1.75v_T)}$$
$$+\frac{\pi}{2}\left(\frac{\alpha e^2}{2T}\right)^{1/2}\left[\frac{3\sqrt{\pi}}{4}\Phi(\sqrt{z})-e^{-z}\left(z+\frac{3}{2}\right)\right],\qquad(25)$$

where $z = v_1/v_T$, $v_T =\sqrt{2T/M}$, M is the mass of the ion and of the atom, while v_1 is determined by the relation (24a). In brackets it is shown for what value of the relative velocity of collision the resonance charge exchange cross section is taken.

In the limit $z \rightarrow 0$, when we can neglect the elastic scattering compared to resonance charge exchange we obtain from (25) and (6)

$$K=\frac{0.331e}{N(MT)^{1/2}\sigma(2.24v_T)}.$$

This result corresponding to the Chapman-Enskog approximation differs little from the value obtained by means of an exact numerical solution of the kinetic equation for the distribution function of the ions in the limit of low intensity of the external electric field and of small elastic scattering cross section[13]

$$K=\frac{0.341e}{N(MT)^{1/2}\sigma_{res}(2.13v_T)}.$$

In the limit $z \rightarrow \infty$ when the scattering of an ion is associated with the polarization capture of the ion by an atom the result obtained with the aid of (24) and (6a) differs little from that given by formula (17). It is convenient to rewrite formula (24) in the following form in order that with its aid we would obtain correct values of the mobility in the limits of large and small z:

Table VIII. Mobility of atomic ions of inert gases in the same gas

Temperature \ Gas	He	Ne	Ar	Kr	Xe
300°	11.3 10.5 [28, 63, 82] 10.8 [58, 59] 10.2 [60] 10.7 [61, 64] 10.4 [66] 9.6 [67]	4.3 4.0 [28, 82] 4.4 [58] 4.2 [59] 3.9 [60, 67] 4.1 [64]	1.64 1.6 [28, 59, 64] 1.63 [58] 1.4 [60] 1.84 [68] 1.38 [79] 1.54 [80]	0.91 0.9—0.95 [27] 0.9 [28] 0.87 [57 *)] 1.01 [81]	0.62 0.6—0.65 [27] 0.58 [28] 0.61 [57 *)] 0.55 [81]
195°	12.8 12.1 [59] 11.1 [67]	5.0 4.5 [59] 4.2 [67] 4.3 [135]	1.83 1.95 [59]		
77°	15.4 13.5 [59] 13.8 [67]	6.2 5.2 [59,67]	2.12 2.2 [59] 1.88 [79]		

*)Values have been reduced to a density corresponding to 0°C and 1 atm.

$$\frac{1}{2}\bar{\sigma} = \frac{40}{41}\sigma_{res}(2.13v_T)e^{-z}\left(1+z+\frac{z^2}{2}\right) + \frac{\pi^2\alpha e^2 e^{-z}(1+z)}{16T\sigma_{res}(1.75v_T)}$$

$$+\frac{\pi}{2}\left(\frac{\alpha e^2}{2T}\right)^{1/2}\left[\frac{3\sqrt{\pi}}{4}\Phi(\sqrt{z})-e^{-z}\left(z+\frac{3}{2}\right)\right]$$

$$+0.14\frac{\pi}{2}\left(\frac{\alpha e^2}{2T}\right)^{1/2}. \tag{26}$$

In Table VIII the experimentally measured mobility of atomic ions of inert gases in the same gas is compared with that calculated by means of formulas (26) and (6). The theoretical value of the mobility is given in the table without citing references. Here the cross section for the resonance charge exchange of a helium ion was calculated on the basis of formula (22a), while in the case of ions of other inert gases formula (22b) was utilized.

In almost all these cases one can utilize for the average cross section the expansion (26) for small z

$$\frac{1}{2}\bar{\sigma} = \frac{40}{41}\sigma_{res}(2.13v_T) + \frac{\pi^2\alpha e^2}{16T\sigma_{res}(1.75v_T)} + 0.14\left(\frac{\alpha e^2}{2T}\right)^{1/2} \tag{26a}$$

In Table IX obtained on the basis of formula (26a) the result is compared with the experimental value of the mobility of metallic ions in the same gas. The cross section for the resonance charge exchange is calculated by means of formula (21a). The value of the coefficient A for mercury turns out to be equal to 5.5 ± 0.5, as was found by means of joining the asymptotic value of the wave function of the electron (23) with the result of the calculation in the Hartree-Fock approximation [89] over the range of distances between the electron and the nucleus $5.3a_0 < r < 8.7a_0$. The initial data for the remaining pairs, just as in the case of inert gases, were taken from [76].

Specific calculations of the mobilities of ions in the same gas were carried out in [90,91] for He⁺, and in [92] for He⁺⁺ in He, in [93] for Ne⁺ in Ne, and Ar⁺ in Ar and in [94] for H⁻ in H and also for a number of pairs in the review by Dalgarno [4]. It should be noted that in these references in evaluating the resonance charge exchange cross section the required difference between the terms of the quasi-molecule composed of an ion and an atom for large distances between them was evaluated by the variational method. However, as was shown in [95,96] in this case the variational method is inapplicable, and this affects the correctness of the results of the references cited above.

In the case of high values of the intensity of the external electric field for not very low gas temperatures when one can neglect the elastic scattering of ions by atoms, the kinetic equation for the distribution function of the ions is easily solved, and the mobility of the ions is independent of the gas temperature [13],

$$K = \left(\frac{2e}{\pi MF\sigma N}\right)^{1/2}, \tag{27}$$

where the charge exchange cross section is taken for a velocity of collision $1.34(eF/NM\sigma)^{1/2}$. For medium values of the intensities of the electric field $eF/TN\sigma_{res} \sim 1$ in the case when one can neglect the elastic scattering of an ion by an atom the kinetic equation for the velocity distribution function of the ions can be solved by the variational method [13] and the drift velocity of the ion found in this manner can be well approximated by the expression

$$w = \sqrt{\frac{2T}{M}}\beta\cdot0.48[1+0.13\beta^2]^{-1/4}, \tag{28}$$

where $\beta = eF/2TN\sigma[(2T/M)^{1/2}(4.5+1.8\beta)^{1/4}]$. It should be noted that although in expressions (27)—(28) the velocity at which the resonance charge exchange cross section is taken depends on the drift velocity, and consequently, on the intensity of the electric field, nevertheless, similar relations can be easily solved because of the small dependence of the cross section on the velocity.

In Fig. 3 the drift velocity of He⁺, Ne⁺, Ar⁺ in the same gas calculated by means of formula (28) is compared with the experimental data of Hornbeck [58]. In Fig. 4 a similar comparison is carried out for Kr⁺ and Xe⁺ using the measurements of Varney [27] and of Munson and Tyndall [57]. The same figure also

Table IX. Mobility of metallic ions in vapors of the same atoms (cm²/V sec)

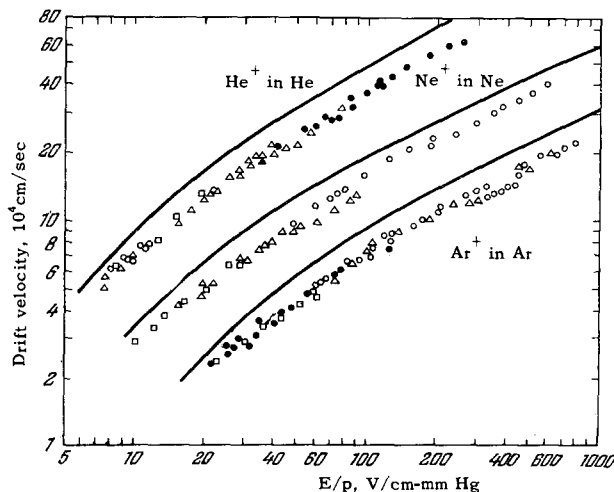| Hg	Rb	Cs
T = 350° K 0.26 0.30 [83]; 0.24 [84] 0.29 [85]; 0.22 [86]	T = 620—660° K 0.125—0.132 0.075 [88] 0,18 [133]	T = 300° K 0.12; 0.4 [87] T = 630° K. 0,091, 0.075 [99], 0,12 [133] T = 1400° K. 0.064 0,066 [132]

FIG. 3. Comparison of formula (28) with the experimental data on Hornbeck [58] for the drift velocity of ions of inert gases in the same gas.

gives the dependence of the drift velocity of Cs^+ in cesium vapour on the intensity of the electric field which was also calculated in accordance with formula (28).

MOBILITY OF MOLECULAR AND COMPLEX IONS IN THE GAS

Until now we have considered the motion of an ion in an atomic gas when only elastic scattering and resonance charge exchange between an ion and an atom are possible. It turns out that the relations obtained above remain valid also in the case of the motion of an ion in a molecular gas if in the collision of an ion with the molecule only one type of ions is produced[97]. In this case as a result of polarization capture of an ion by a molecule a compound molecule is formed which lives sufficiently long compared to the characteristic times of oscillation of the atoms in the molecule. If this compound molecule can break up into an ion and a molecule in a unique manner the diffusion cross section for the transition is determined as before by polarization capture and formula (7) turns out to be valid. This circumstance was utilized by us in Table V in compiling which we assumed that formula (17) is valid for molecular ions and gases consisting of molecules.

More complex is the case when several different types of ions are formed in the gas. Thus, in the case of motion of inert gas ions in the same gas both atomic and molecular ions are present*. Molecular ions of inert gases can be initially formed as a result of collisions of excited atoms of inert gases with their atoms[98]. The formation of molecular ions from

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*It is interesting that in inert gases more than one sort of molecular ions can be formed. Experimentally this was found in helium [66,82,134] and in argon [80]. The most stable molecular ion corresponds to the combination of an atomic ion and an inert gas atom both in their ground states. As analysis shows [135] in the case of helium in addition to such an ion $He_2^+(^2\Sigma_u^+)$ another stable ion is $He_2^+(^4\Sigma_u^+)$ which is formed when a helium ion approaches its metastable atom $He(2^3S)$. The dissociation energy of this ion exceeds 1 eV, so that its lifetime in the gas with respect to dissociation due to collisions with atoms is sufficiently great. The probability for the transition of a molecular ion to the ground electronic state as a result of a change in spin is exceedingly small, since this process corresponds to a collision of a molecular ion with atoms whose spin and orbital angular momenta are both equal to zero. Therefore the metastable molecular ion under consideration is stable. Since in the collision of a metastable molecular ion of helium with an atom (in contrast to the case of a collision of a molecular ion in the ground electronic state) no exchange of atoms occurs the cross section for the collision of a metastable molecular ion with an atom is smaller than in the case of a collision of a molecular ion existing in its ground state. Therefore the mobility of a metastable molecular ion is higher than that of a molecular ion in the ground state. Evidently metastable molecular ions can exist in all inert gases.
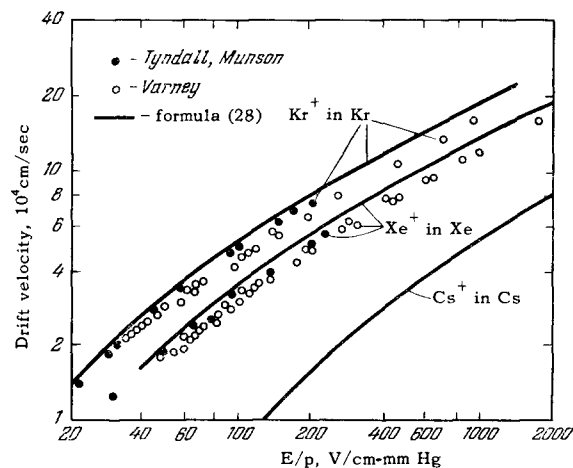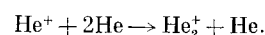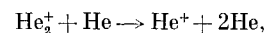

FIG. 4. Comparison of the experimental data of references [27,57] with the results of calculations according to formula (28).

atomic ones occurs as a result of triple collisions

$$He^+ + 2He \longrightarrow He_2^+ + He.$$

Since the reverse process is determined by binary collisions

$$He_2^+ + He \longrightarrow He^+ + 2He,$$

the ratio between the numbers of atomic and molecular ions which are in equilibrium with the gas depends on the gas density. At high gas densities molecular ions predominate in it, at low densities atomic ions predominate. This situation is utilized in the experimental method of measuring the mobility of ions of inert gases based on ambipolar diffusion (cf., II). By varying the gas density one achieves the predominance of one type of ions so that the diffusion of this type determines the rate of decay of the plasma.

The case considered above when two types of ions exist in the gas with one of them formed as a result of triple collisions has characteristic features. In this case the time for the transition of an atomic ion into a molecular one – the lifetime of the atomic ion – is long and in order of magnitude is equal to the time of collision between an ion and an atom multiplied by the ratio of the volume per atom to the volume occupied by this atom. If the number of atomic and molecular ions is of the same order of magnitude the lifetime of the molecular ion is great since the probability is small that the relative energy of the colliding ion and an atom will exceed the dissociation energy of the ion. Therefore in the measurement of the mobility a situation is possible when the lifetime of the ions greatly exceeds the time of motion of the ions in the drift chamber T_{dr}. In such a case the mobility of each kind of ions can be measured independently. In the opposite limiting case $\tau_{1,2} \ll T_{dr}$ the average mobility

$$K = \frac{K_1\tau_1 + K_2\tau_2}{\tau_1 + \tau_2}, \qquad T_{dr} \gg \tau_{1,2}, \qquad (29)$$

is measured so that $K_{1,2}$ is the mobility of the given kind of ions, and $\tau_{1,2}$ is the lifetime for these ions.

We now obtain the value of the coefficient of transformation k_c of an atomic ion into a molecular one as a result of triple collisions with gas atoms. We define the coefficient for the transformation of an atomic ion into a molecular one by the relation

$$\frac{dN^+_{mol}}{dt}\Big|_{t=0} = k_c N^+_{at} N^2_a,$$

where N^+_{at}, N^+_{mol}, and N_a are respectively the densities of atomic and molecular ions and of atoms. It is assumed that at the initial instant of time molecular ions are absent.

For the determination of the coefficient of transformation of ions we shall use Thomson's theory[136] which was developed for the evaluation of the coefficient of recombination of a positive and a negative ion as a result of collisions with neutral gas particles. In the problem under consideration the formation of a molecular ion corresponds to a simultaneous collision of an atomic ion with two atoms such that as a result of this collision one of the atoms takes away from the ion the excess kinetic energy so that the ion turns out to be in a bound state with the other atom. The molecular ion produced as a result of such a collision turns out to be in an excited vibrational state. Subsequent collisions of the ion with gas atoms remove the vibrational excitation from the molecular ion.

In the process of a triple collision of an atomic ion and of two atoms we neglect the interaction between the atoms compared to the polarization interaction between an atom and an ion $\alpha e^2/2R^4$ (α is the atomic polarizability, R is the distance between the ion and the atom). In order that the ion could transfer to the atom an energy of the order of the gas temperature T which initially characterizes both the ion and the atom it is necessary for them to collide with an impact parameter b determined by the relation $\alpha/b^4 \sim T$. The frequency of formation of a bound state between an atom and an atomic ion as a result of triple collisions is a product of the frequency of the penetration of the atom into the critical region $N_a \bar{v} b^2$ and the collision probability $N_a b^3$ at that moment for the ion with another atom which takes away the excess energy. Here N_a is the density of atoms, $\bar{v}$ is the average velocity of collision of an ion with an atom; the size of the critical region in which the interaction between an ion and an atom is of the order of their kinetic energy and within which it is possible for the ion to be captured by the atom is of order b. From the relations obtained above we obtain the dependence of the coefficient for the transformation of atomic ions into molecular ones on the parameters of the atom and on the gas temperature[137]:

$$k_c = \text{const} \left(\frac{\alpha e^2}{M}\right)^{1/2} \left(\frac{\alpha e^2}{T}\right)^{3/4} \tag{30}$$

In deriving this formula we assumed that the dis-

sociation energy for the molecular ion is considerably higher than the gas temperature and for distances for which the potential for the interaction between the atom and the ion is of the order of magnitude of the temperature their interaction is described by the polarization law. Under such assumptions the capture of an atom by an atomic ion is primarily determined by the polarization interaction between them, and also by the interaction between the atom and the ion carrying away the excess energy. Therefore the coefficient for the transformation of atomic ions into molecular ones is expressed only in terms of the parameters appearing in formula (30), so that the constant in this formula does not depend on the type of atoms. In this case formula (30) refers to the process

$$2X + X^+ \rightarrow X^+_2 + X. \tag{31}$$
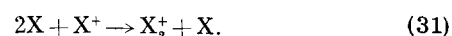
The most complete information on the coefficient for the transformation of atomic ions into molecular ones was obtained in the case of helium. The value of the coefficient of the transformation in units of 10^{-31} cm^6 sec^{-1} for helium ions at a temperature of 300°K is equal to 0.62 according to the measurements Phelps and Brown[138], to 0.35 according to Kretschmer and Petersen[139], to 1.08 according to Beaty and Patterson[140], to 1.05 according to Oskam and Mittelstadt[141], to 1.15 according to Hackam and Lennon[142], to 1.09 according to Niles and Robertson[143], to 1.12 according to Beaty and Patterson[144]. The calculation of the coefficient of transformation for helium ions carried out by Bates leads at the temperature indicated above to the value 1.6 $\times 10^{-31}$ cm^6 sec^{-1}. If on the basis of the results given above the coefficient for the transformation of helium atoms at a temperature of 300°K is taken to be equal to 1.1×10^{-31} cm^6 sec^{-1}, then the constant in formula (30) should be set equal to 42:

$$k_c = 42 \left(\frac{\alpha e^2}{M}\right)^{1/2} \left(\frac{\alpha e^2}{T}\right)^{3/4}. \tag{32}$$

The coefficient for the transformation of the ions of neon calculated by means of formula (32) 1.15 $\times 10^{-31}$ cm^6 sec^{-1} differs from the experimentally measured one[140] 0.58×10^{-31} cm^6 sec^{-1}. The coefficient for the transformation of argon ions obtained by Kretschmer and Petersen[139] 1.5×10^{-31} cm^6 sec^{-1} and also the coefficient of transformation for helium atoms 0.35×10^{-31} cm^6 sec^{-1} do not agree with formula (32). But the ratio between these quantities which in accordance with measurements is equal to 4.2 and which on the basis of formula (32) should be equal to 4.25, is in good agreement. The value of the coefficient for the transformation of mercury ions estimated by Biondi[136] $\sim 10^{-31}$ cm^6 sec^{-1} at a temperature of 400°K disagrees with the result obtained on the basis of formula (32) 4.7×10^{-31} cm^6 sec^{-1}.
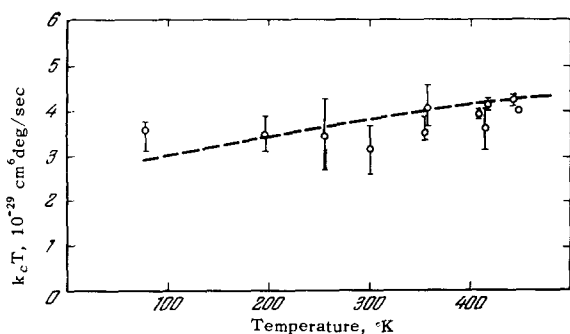
Figure 5 shows the dependence of the coefficient

FIG. 5. Dependence of the coefficient of transformation k_c of atomic He$^+$ ions into molecular ones on the temperature of the gas.

for the transformation of helium atoms on the temperature as measured by Niles and Robertson[143]. As can be seen, the relation $k_c \sim T^{-3/4}$ agrees satisfactorily with experiment. Niles and Robertson[143,147] have obtained the relation $k_c \sim T^{-1}$ utilizing the hard sphere model for the colliding particles in investigating the process inverse to (31), and obtaining the coefficient for the transformation of ions from the rate of the process inverse to (31). It should be noted that the result of Niles and Robertson is associated with model assumptions, while formula (32) is valid if the potential describing the interaction of an ion and an atom agrees with the polarization interaction in that region where the value of this potential is of the order of magnitude of the temperature. The last assumption is well satisfied at room temperature. In this case the polarization potential turns out to be of the order of magnitude of the temperature at distances between the ion and the atom which are large compared to the dimensions of the atom. The exchange interaction between an ion and an atom is considerably smaller here than the polarization interaction.

We consider the transformation of atomic ions into molecular ones which occurs when ions and atoms of different kinds participate. We investigate the following processes:

$$X^+ + 2Y \rightarrow XY^+ + Y, \tag{33a}$$
$$X^+ + X + Y \rightarrow X_2^+ + Y, \tag{33b}$$
$$X^+ + X + Y \rightarrow XY^+ + X. \tag{33c}$$
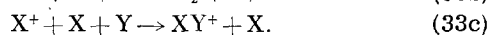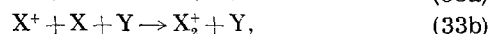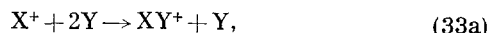
The processes (33) differ from (31) by the fact that particles of different mass participate in the collision so that the transfer energy is proportional to the square root of the ratio of the masses and the initial energy. Let μ be the mass of particle Y, and M the mass of particle X, with $M \geq \mu$. In calculating the process (33a) according to the Thomson formula we find that the critical radius b is determined as before by the relation $\alpha_Y e^2/b^4 \sim T$, but the cross section σ for the collision of particles X and Y corresponding to an exchange of energy $\sim T$ should be sought from the relation $\sigma \sim \rho^2$, $(\alpha_Y e^2/\rho^4) \times (\mu/M)^{1/2} \sim T$. As a result of this we obtain for the

coefficient of conversion of ions corresponding to process (33a) ($k_c \sim \sqrt{T/\mu b^3 \sigma}$):

$$k_c = 42 \left(\frac{\mu}{M}\right)^{1/4} \left(\frac{\alpha_Y e^2}{T}\right)^{3/4} \left(\frac{\alpha_Y e^2}{\mu}\right)^{1/2}. \tag{34a}$$

In obtaining this we have utilized the requirement that in the limit $\mu \rightarrow M$ the result should go over into formula (32)*.

Utilizing the same method we obtain for the coefficient of conversion of ions in the case of processes (33b) and (33c)

$$k_c = 42 \left(\frac{\mu}{M}\right)^{1/4} \left(\frac{\alpha_X e^2}{T}\right)^{3/4} \left(\frac{\alpha_Y e^2}{\mu}\right)^{1/2}, \tag{34b}$$

$$k_c = 42 \left(\frac{\alpha_Y e^2}{T}\right)^{3/4} \left(\frac{\alpha_X e^2}{M}\right)^{1/2}. \tag{34c}$$

The rate for the process (33) was measured by Biondi[146] for the triple collision Hg$^+$ + Hg + He $\rightarrow$ Hg$_2^+$ + He and the conversion coefficient at a temperature of 100°K turned out to be equal to 1.7 $\times 10^{-31}$ cm^6 sec^{-1}. Calculations according to formula (34b) yield 1.5×10^{-31} cm^6 sec^{-1}. Oskam[148] has measured the conversion coefficient for an atomic neon ion in the collision of a helium atom with neon and obtained the result 3×10^{-30} cm^6 sec^{-1} which differs by more than an order of magnitude from the theoretical one.

We consider the mobility of ions in a gas which containes polar molecules. In this case polar molecules can combine with an ion forming a complex ion. The appearance of complex ions will affect in a significant manner the mobility of ions in the gas.

The most careful experimental study of this phenomenon was carried out in the papers by Tyndall and co-workers[100-102] in the case of motion of ions of alkali metals in an inert gas to which an admixture of water vapor was added. The most interesting experimental fact established in this series of papers consists of the formation of only one kind of complex ions[100] in each of the cases investigated. This stable complex ion contains several water molecules. The lifetime of the complex and of the simple ion is usually smaller than the drift time of the ion during the measurement of the mobility, so that the mobility of the ion is determined by formula (29). In Table X a comparison is made of the mobility of an ion of an alkali metal in an inert gas with that of the complex ion formed using it as a base[100].

Just as in the case of molecular ions the lifetime of the complex ion is reduced as a result of increasing the gas temperature or the intensity of the elec-

*This is not quite exact, since in the case of process (31) the scattering of both atoms by the ion is correlated with each other. But if the masses of the atoms are considerably different their scattering by the atom occurs independently. Moreover, a definite role in the process (31) is played by the resonance charge exchange. But these circumstances cannot significantly alter the coefficient of proportionality.

Table X. Mobility of ions of alkali metals (and of complex ions formed on the basis of these ions and water molecules) in inert gases at 20°C and 1 atm

Gas Ion	He		Ne		Ar		Kr		Xe	
	simple	complex	simple	complex	simple	complex	simple	complex	simple	complex
Li⁺	25.6	11.70	11.8	5.28	4.99	2.26	3.97	1.46	3.04	0.98
Na⁺	24.2	11.15	8.7	5.25	3.23	2.26	2.34	1.43	1.80	0.94
K⁺	22.9	11.85	8.0	5.26	2.81	2.19	1.98	—	1.44	0.92
Rb⁺	21.4	12.80	7.18	5.38	2.40	2.10	1.57	1.37	1.10	0.87
Cs⁺	19.6	13.40	6.50	5.48	2.23	2.18	1.42	—	0.97	0.83

tric field, since in this case the probability is increased that the energy of motion of the colliding complex ion and the gas particle will exceed the dissociation energy of the complex ion. On the other hand, the lifetime of the simple ion associated with its transition into a complex ion is decreased by increasing the density of the gas and of the water vapor since in this case there is an increase in the probability of triple collisions with the participation of water vapor in the course of which complex ions are formed. Therefore, just as in the case of molecular ions, complex ions predominate at low temperatures, low fields and high densities of gas and water vapor. In the opposite limiting case the ion spends most of the time in the state of a simple ion. These regularities have been confirmed experimentally [100-102]. Thus, Fig. 6 gives the dependence of the mobility of ions of lithium in argon on the intensity of the electric field for different concentrations of water vapor. From this diagram it can be seen that at low fields complex ions predominate, while at high fields simple ions predominate and the transition from one kind of ions to the other one occurs at lower values of the field intensity when the admixture of water vapor is reduced.

The relative number of complex ions with a given number of water molecules which is formed in the gas in the absence of the electric field can be found by statistical methods if the parameters of the com-
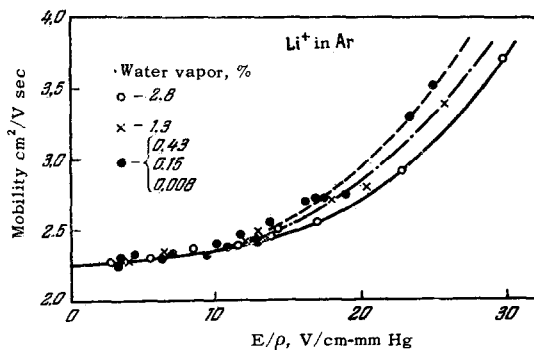
plex ions are known [101]. A simple method for estimating the number of polar molecules in a complex ion which is stable at a given temperature and a given density of the gas in the admixture was proposed by Bloom and Margenau [103].

A measurement of the mobility of ions of alkali metals in water vapor [102] in the limit of low fields shows that the mobility of complex ions in water vapor has a weak dependence on the element and amounts to 0.725 cm²/V sec for lithium, 0.715 for sodium, 0.705 for potassium, 0.700 for rubidium and 0.695 for cesium.

The appearance of complex ions in the gas can be demonstrated in the study of the dependence of the mobility of ions in a mixture of gases on the percentage composition of the mixture. If the ion does not form complex ions with any of the components of the mixture the mobility of the ion in the mixture will be expressed in terms of the mobility in each of the gases K_1, K_2 and the concentration of the gases C_1, $1 - C_1$ in accordance with Blank's law [104]

$$K = \frac{K_1 K_2}{K_1 C_1 + K_2 (1 - C_1)} . \tag{35}$$

A deviation from Blank's law is associated with a

FIG. 6. Mobility of lithium ions in argon with an admixture of water vapor. Mobility of Li⁺ in pure argon is 5 cm²/V sec.
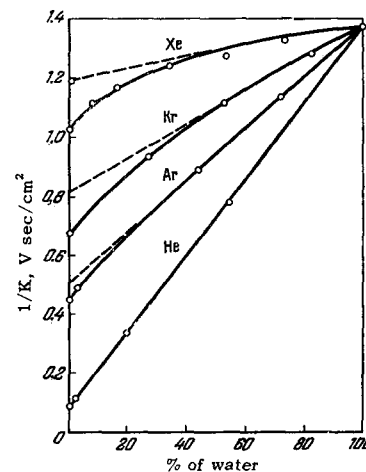

FIG. 7. Mobility of lithium ions in a mixture of an inert gas and water vapor. Dotted line corresponds to Blank's law.

violation of the assumption utilized in obtaining (35) that the mobility of an ion in one of the components of the mixture is independent of the concentration of the other component. Therefore a violation of Blank's law is associated with the formation of complex ions. Figure 7 shows the dependence of $1/K$ for a lithium ion moving in a mixture of an inert gas and water. The value of $1/K$ which satisfies Blank's law and is linear with respect to the concentrations of the components is shown in this diagram by a dotted line.

The presence of an admixture of polar molecules is not necessarily required for the formation of complex ions. Thus, David and Munson [105] have observed the formation of complex ions accompanying the motion of lithium ions in xenon at room temperature. In this case the maximum deviation from Blank's law amounted to $\sim 4\%$.

FORMATION OF IONS IN MOLECULAR GASES

Of practical interest is the study of the kind of ions formed in molecular gases under given experimental conditions (temperature, gas pressure and intensity of the electric field). The most detailed information in the study of this problem can be obtained by utilizing an apparatus for the measurement of the mobility of ions which is associated with a mass spectrometer [29,30]. Such an apparatus enables one to determine the types of ions which exist in the gas under given conditions. A measurement of the relative content of each kind of ions enables one to obtain information on the chemical reactions of the ion with the gas molecules as a result of which ions of a different sort are produced.

If the ions move in the gas and enter into a chemical reaction with the gas molecules only infrequently, the mobility of each kind of ion can be measured independently. Usually the converse relation holds
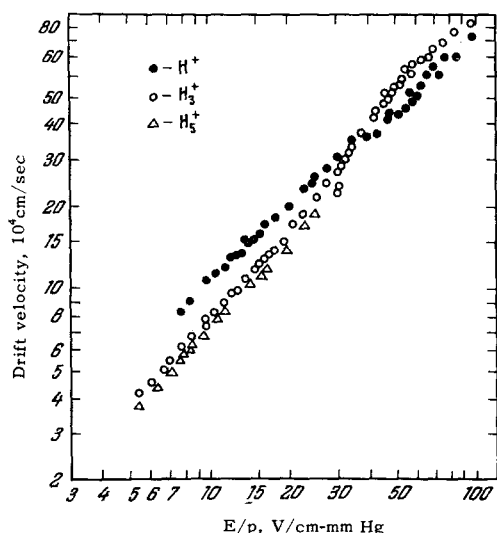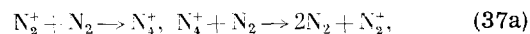
$$T_{\mathrm{dr}} > \tau \qquad (36)$$
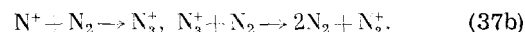
(τ is the characteristic time for entering into a chemical reaction, T_{dr} is the drift time), so that if under given experimental conditions there exist several kinds of ions in the gas, then as a result of the chemical reaction the ion has time to alter its nature many times during the drift. In this case the drift velocity of the ion should not depend on the type of ion which leaves the drift chamber. Figure 8 shows the dependence on the field intensity of the drift velocity of ions formed in hydrogen, and Fig. 9 shows the same dependence for N^+, N_3^+ and N_2^+, N_4^+ ions in nitrogen [106]. An indication is given as to the kind of ions that are formed at the exit from the drift region. As may be seen from these figures condition (36) turns out to be quite acceptable.

The problem of the composition of ions formed in gases and of transitions between the different kinds of ions has been elucidated most fully in the case of nitrogen [1,30,52,106–118,149,150], of hydrogen [1,29,68,114,119–130] and of oxygen [108,151–161]. In molecular nitrogen under ordinary condition the following ions are formed [107]: N^+, N_2^+, N_3^+, and N_4^+. The most important reactions corresponding to transitions from one kind of ions to another are considered to be [108]

$$N_2^+ + N_2 \rightarrow N_4^+, \quad N_4^+ + N_2 \rightarrow 2N_2 + N_2^+, \qquad (37a)$$

and [109]

$$N^+ + N_2 \rightarrow N_3^+, \quad N_3^+ + N_2 \rightarrow 2N_2 + N_2^+. \qquad (37b)$$

The reactions (31) correspond to the assumption that
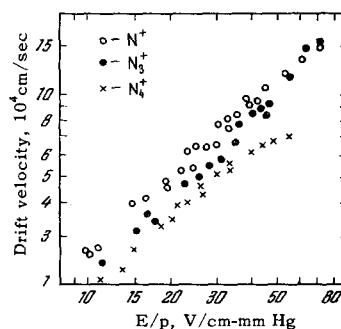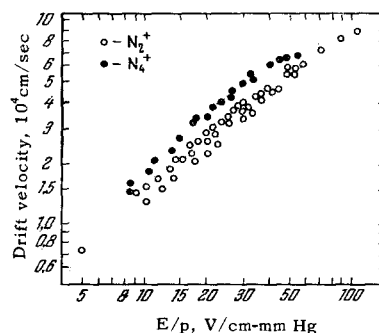

FIG. 8. Mobility of ions formed in hydrogen [29].

FIG. 9. Drift velocity of nitrogen ions in nitrogen [106].
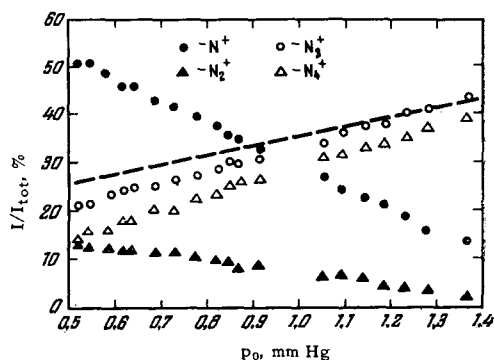
FIG. 10. Relative intensity of the flux of ions in nitrogen [30].

FIG. 11. Drift velocity of nitrogen ions in nitrogen at different temperatures.

in nitrogen there exist two independent pairs of ions N^+, N_3^+, and N_2^+, N_4^+, so that the chemical reaction of an ion with a molecule of nitrogen with a transition from one pair of ions to the other pair is of low probability, since it requires the breaking of the binding of the N_2 molecule and is energetically disadvantageous. Actually, the binding between ions within each pair is quite significant, but the neglect of transitions between the pairs is not justified. An analysis of the experimental results shows that the generally accepted point of view on the mechanism of the reactions between the pairs (37) turns out to be unjustified. Figure 10 gives the relative flux density of nitrogen density. If the complex ions (N_3^+, N_4^+) were formed in two-particle collisions of the ordinary ion (N^+, N_2^+) with a nitrogen molecule, as is assumed in (31), the relative yield of ions would not depend on the gas density for a constant gas temperature and electric field intensity. Moreover, if the transition between the ions of different pairs would be of low probability the total flux of N_2^+, N_4^+ ions (the dotted line in Fig. 10), and also of N^+, N_3^+ ions would not vary as the gas density is varied. An analysis of Fig. 10 shows that the complex ions (N_3^+, N_3^+) are formed as a result of triple collisions of simple ions (N^+, N_2^+) and nitrogen molecules with transitions existing between the ion pairs N^+, N_3^+ and N_2^+, N_4^+. The transition between the ions N_2^+, and N_3^+ was observed in [110], and between the ions N^+ and N_2^+ which determine the composition of ions in nitrogen at high temperatures was observed in [150].

From an analysis of Fig. 9 one can deduce that the binding of the ions N_2^+ and N_3^+ is to the greatest extent responsible for the transitions between the given ion pairs.

In molecular hydrogen there can exist slow H^+, H_3^+, and H_5^+ ions [29]. The molecular ion H_2^+ easily enters into the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H + 1.17$ eV, and is, therefore, not observed in molcular hydrogen. The H_3^+ ion is formed from the H^+ ion, and the H_5^+ ion is formed from the H_3^+ ion apparently as a result of triple collisions with hydrogen molecules. At room temperature the frequency of exchange between the
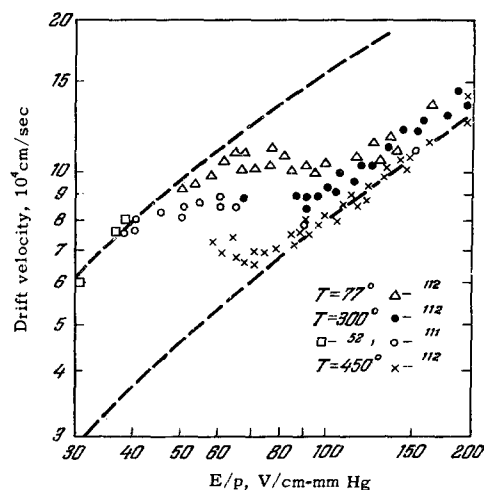
H_3^+ and H_5^+ ions is higher than between the H^+ and H_3^+ ions.

In molecular oxygen the stable positive ions are O^+, O_2^+, and O_3^+ [108,151-154], and also the O_4^+ ion the dissociation energy of which amounts to 0.2 ev [155]. In contrast to the cases of hydrogen and nitrogen in oxygen there can be formed the stable negative ion O_2^- [156-161]. At low gas temperatures in molecular oxygen one also observes the negative ion O_4^- the dissociation energy of which amounts to 0.06 ± 0.02 eV [161].

When condition (36) is satisfied a measurement of the mobility referred to a given sort of ions at the exit has no meaning. The mobility of ions in this case depends on the ratio between the number of ions of each kind formed in the gas, and, consequently, depends on the gas density. When condition (36) is violated the measured mobility is also related to the method of production of the primary ions. Failure to take into account the facts enumerated above leads to contradictory information on the mobility of ions in the gas since in obtaining the mobility in this case its dependence on the gas density is neglected. Thus, Sinnot [128] obtains for the mobility of helium ions in helium a result which is close to the result of Biondi and Chanin, while the mobilities of hydrogen ions in hydrogen obtained using the same apparatus [126,128] show a considerable discrepancy.

The composition of ions formed in gases obeys the same regularities which were discussed in the preceding chapter. Specifically, the complex ions have a large binding energy compared to the simple ions and predominate at low temperatures, low intensities of the electric field and high gas densities. A graphical confirmation of this regularity can be seen in Fig. 11 which gives the dependence of the mobility of nitrogen ions in nitrogen on the intensity of the fields for different temperatures [11,112]. It can be seen that at low

field intensities the mobility corresponds to one type of ions, and at high field intensities to another type with the transition from complex ions to simple ones taking place at lower field intensities as the temperature of the gas is increased.

If in the gas there exists an admixture of particles of low electron binding energy so that the reaction of the gas ions with the molecules of the admixture is energetically favorable the composition of the ions existing in the gas can be significantly changed. This requires high gas purity in the case of measuring the mobility of ions in the same gas with a large ionization potential. At the same time the property described above can be utilized as a method of creating ions of the admixture in order to obtain the mobility of these ions in a gas consisting of molecules with a high ionization potential[1].

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