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MOBILITY OF HEAVY IONS IN A GAS

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1. In the present work the motion of ions in a constant electric field in a gas is investigated, the mass of whose molecules m is much smaller than the ion mass M. It is assumed that the ion density is much smaller than the density of gas molecules, so that collisions of ions with one another may be neglected.

The motion of heavy ions in a gas in an electric field in the case when the drift velocity of the ion is much smaller than the thermal velocity of the molecules was investigated by Kihara ([1]). He found that in this case the ion velocity distribution function in the electric field retains the character of a Maxwellian distribution shifted by the magnitude of the drift velocity. In the present work a broader range of values of the ion drift velocity is considered, and a general formula is found relating the drift velocity of a heavy ion to the electric-field strength, with allowance for elastic scattering of the ion by gas particles. At the same time, the simple method for finding the drift velocity in the case under consideration makes it possible to find the relation between the drift velocity and the electric-field strength when transitions between vibrational and rotational molecular levels play an important role in collisions of the ion with molecules.

A substantial simplification of the problem considered is due to the small width of the ion velocity distribution function. This width is determined either by the mean thermal velocity of the ions or by the mean change in the ion velocity in one collision with a molecule. The first quantity is small in comparison with the thermal velocity of the molecules; the second is of order $\frac{m}{M}g$, where g is the relative collision velocity. Thus, the width of the ion velocity distribution function is much smaller than the mean relative collision velocity of the ion and the molecule. This circumstance makes it possible to determine the drift velocity of a heavy ion in a gas of light molecules without solving the kinetic equation for the ion distribution function.

2. The kinetic equation for the ion velocity distribution function $f(\mathbf{v})$, for the case when the ion density is much smaller than the density of the gas particles, has the form ([1,2])

$$\frac{eE}{M}\frac{\partial f}{\partial v_x} = \int [f(\mathbf{v})f^{(0)}(v_1) - f(\mathbf{v}')f^{(0)}(v_1')]\, |a(\chi, g)|^2 \, d\cos\chi \, d\varphi \, d\mathbf{v}_1. \quad (1)$$

Here E is the electric-field strength, which is directed along the x-axis; $\mathbf{v}, \mathbf{v}_1$ are the velocities of the ion and of the gas molecule; $\mathbf{v}', \mathbf{v}_1'$ are their velocities after the collision; g is the relative velocity of the ion and molecule; χ, φ are the angles of scattering of the ion by the molecule in the center-of-inertia system; $a(\chi, g)$ is the amplitude of elastic scattering of the ion by the molecule. The Maxwellian velocity distribution function of the atoms is

$$f^{(0)}(v_1) = N\left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv_1^2/2T},$$

so that N is the density of gas molecules and T is the gas temperature.

Multiplying equation (1) by Mv_x and integrating over the ion-velocity space, we obtain on the left the force acting on the ion from the electric field, and on the right—from the medium ([1]):

$$eE = M\int f(\mathbf{v}) f^{(0)}(v_1)(v_x' - v_x)|a(\chi, g)|^2 g\, d\cos\chi\, d\varphi\, d\mathbf{v}\, d\mathbf{v}_1 =$$

$$= \mu \int f(\mathbf{v}) f^{(0)}(v_1) g g_x \sigma^*(g)\, d\mathbf{v}\, d\mathbf{v}_1. \qquad (2)$$

Here $\mu = mM/(m+M) \approx m$ is the reduced mass of the ion and molecule; $\sigma^*(g) = \int (1-\cos\chi)|a|^2\, d\cos\chi\, d\varphi = \int (1-\cos\chi) d\sigma$ is the transport cross section; the ion distribution function $f(\mathbf{v})$ is normalized to unity. In deriving (2), the relation

$$\frac{1}{2\pi}\int_0^{2\pi} (\mathbf{v} - \mathbf{v}')\, d\varphi = \frac{m}{m+M}\frac{1}{2\pi}\int_0^{2\pi} (\mathbf{g} - \mathbf{g}')\, d\varphi = \frac{mg}{M+m}(1-\cos\chi),$$

was used, where $\mathbf{g}'$ is the relative velocity of the ion and atom after the collision.

We shall now use the fact that the width of the ion velocity distribution function is either of the order of the thermal velocity of the ions, or $\sim (m/M)g$, where g is the relative collision velocity of the ion and molecule. In the case when the ion drift velocity is much greater than the thermal velocity of the ions, we make in (2) the substitution $f(\mathbf{v}) = \delta(\mathbf{v} - \mathbf{w})$, where $\mathbf{w} = \int \mathbf{v} f(\mathbf{v})\, d\mathbf{v}$ is the drift velocity of the ion directed along the field. We find

$$\frac{eE}{\mu N} = \left(\frac{m}{2\pi T}\right)^{3/2} \int e^{-mv_1^2/2T} g_{xg} \sigma^*(g)\, d\mathbf{v}_1, \qquad (3)$$

where $\mathbf{g} = \mathbf{w} - \mathbf{v}_1$. Integrating (3) over the angles, we rewrite this relation in another form:

$$\frac{eE}{\mu N} = \frac{e^{-mw^2/2T}}{w^2}\left(\frac{2T}{\pi m}\right)^{1/2}\int_0^\infty e^{-mg^2/2T} g^2\, dg\, \sigma^*(g)\left[\frac{mwg}{T}\,\mathrm{ch}\,\frac{mwg}{T} - \mathrm{sh}\,\frac{mwg}{T}\right]. \tag{4}$$

In the case when the ion drift velocity is much smaller than the thermal velocity of the gas molecules, we replace the relative collision velocity in formula (2) by the velocity of the gas molecule. We obtain the result of Kihara ([1]):

$$w = 3\sqrt{\pi}\, eE(2T/m)^{5/2} \Big/ 8\mu N \int_0^\infty e^{-mg^2/2T} g^5 \sigma^*(g)\, dg. \tag{5}$$

It is not difficult to show that, in the case when the ion drift velocity is much smaller than the thermal velocity of the gas molecules, formula (4), when expanded in the small parameter mwg/T, goes over into (5). Therefore, although relations (3), (4) were obtained under the assumption that the ion drift velocity is much greater than its mean thermal velocity, they are valid for any ion drift velocity. These relations uniquely determine the dependence of the drift velocity of a heavy ion in a gas of light molecules on the electric-field strength, taking into account elastic scattering of ions by gas molecules.

3. Let us consider the limiting cases of formulas (3), (4). If the ion drift velocity is much smaller than the thermal velocity of the gas molecules, formulas (3), (4) go over into (5), and the ion mobility $K = w/E$ does not depend on the field strength.

In the case when the transport cross section is inversely proportional to the relative collision velocity, i.e., the collision frequency $\nu = Ng\sigma^* = \text{const}$, we obtain from (3)

$$w = eE/\mu\nu, \qquad K = e/\mu\nu. \tag{6}$$

Formula (6) coincides with the general formula for the mobility (1) for the case when $\sigma^* \sim 1/g$.

For a large value of the drift velocity $g \approx w$, and from (3) we find the relation between the drift velocity and the field strength in this case

$$eE/\mu N = w^2 \sigma^*(w). \tag{7}$$

The last result can be obtained in a simpler way on the basis of the fact that the momentum of a heavy particle changes little upon collision with gas particles. Indeed, in this case the equation of motion of the ion has the form

$$\frac{dP_x}{dt} = eE - \int \Delta P_x N w\, d\sigma = eE - \mu N w^2 \sigma^* = 0,$$

whence relation (7) follows directly. Here $\Delta P = \mu w(1 - \cos\chi)$ is the change in the ion momentum upon collision with a light particle in the case when the ion velocity w, which changes little upon collision, determines the relative collision velocity.

4. Formulas (3)–(7) were obtained taking into account only elastic scattering of the ion by a molecule. They are easily generalized to the case when excitation of the internal degrees of freedom of the molecule is significant. Thus, if one assumes that the interaction potential of the ion with the molecule does not depend on the vibrational and rotational state of the molecule, and that the distribution of molecules over these states does not depend on the electric-field strength, then in formulas (2)–(7) the transport cross section $\sigma^*(g)$ should be replaced by

$$\sigma^*_{\text{el}}(g) + \frac{1}{Z} \sum_{\substack{n,m \\ n \neq m}} c_n e^{-E_n/T} \left\{ \sigma^*(g, n \to m) + \right.$$

$$\left. + \left[1 - \sqrt{1 + \frac{2(E_n - E_m)}{\mu g^2}} \right] \sigma(g, n \to m) \right\}.$$

Here $\sigma^*_{\text{el}}(g)$ is the transport cross section for elastic scattering; $\sigma^*(g, n \to m)$, $\sigma(g, n \to m)$ are the transport and total classical cross sections of an inelastic transition of the molecule from state n to m upon collision with an ion with relative velocity g; E_n, E_m are the excitation energies of the given state of the molecule; c_n is the statistical weight of this state, $Z = \sum_n c_n e^{-E_n/T}$ is the statistical sum.

Excitation of the rotational and vibrational degrees of freedom of a molecule plays an essential role in the motion of a heavy atomic ion in a gas of light molecules. Therefore, measurement of the ion drift velocity as a function of the gas temperature and of the electric-field strength can provide definite information about the excitation cross section of the vibrational and rotational degrees of freedom of the molecule upon collision with a heavy atomic ion.

Thus, a relation has been established between the electric-field strength and the drift velocity of a heavy ion in a gas of light molecules. The result obtained can be used to determine the transition cross section for the vibrational and rotational degrees of freedom of the molecule upon its collision with a heavy atomic ion, from the experimentally measured dependence of the ion drift velocity on the temperature of the gas of light molecules and on the electric-field strength.

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CITED LITERATURE

1. T. Kihara, Rev. Mod. Phys., **25**, 844 (1953).

2. G. H. Wannier, Bell Syst. Techn. J., **32**, 170 (1953).

Note: Figure translations are in progress. See original paper for figures.