trapped by the isolated vacancies. Since the bleaching process described above, which is based on the recombination of vacancy pairs, is not available for the case of isolated vacancies, color centers involving such vacancies are permanent.

In terms of the above scheme, the following mechanism for the phenomena associated with electrolysis may be advanced. Under the influence of an electric field at elevated temperatures, the negative ions start to move toward the anode producing an excess of negative vacancies near the cathode, and conversely, the positive ions move toward the cathode producing positive vacancies near the anode. In order that the crystal be locally neutral, it is necessary that there be introduced at the cathode electrons equal in number to the excess negative vacancies and similarly holes in the electron band equal to the number of positive vacancies introduced at the anode. In general, the electrons and holes will be trapped in the vacancies, thus leading to color centers which spread from the cathode toward the anode. It is quite clear that the spreading reverses itself if the polarity of the field is reversed at any stage. If the direction of the field remains unchanged, the nature of the process changes when the positive vacancies in which holes have been trapped arrive at the cathode. When this happens, the condition of the electric neutrality is satisfied if electrons entering from the cathode combine with the holes trapped in the positive vacancies. This allows the newly created negative vacancies to be formed free of electrons, i.e., as color center precursors. As the negative vacancies containing the electrons diffuse toward the anode they are replaced by these precursors and in this fashion the color cloud is swept out toward the anode. The above discussion does not take into account the inhomogeneity of the electric field produced by the pointed cathode and also fails to explain the direct production of precursors and the increased susceptibility of a crystal in the metastable state for the production of nonpermanent centers.

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Motion of Gaseous Ions in a Strong Electric Field. II

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This paper continues an earlier one on the same subject. Its object is to elucidate the nature of the random motion of an ion about its drift. In Sec. F it is shown that this motion can be described as a diffusion with a diffusion tensor axially symmetric about the field. If the mean free time between the collisions of an ion with molecules is independent of speed, then explicit expressions may be deprived for the two diffusion coefficients; these expressions are written down without proof in Sec. G; they are connected with the mobility by a natural extension of the Einstein relation. In Sec. H, the longitudinal diffusion coefficient is computed numerically for the hard sphere model, high field, and mass ratio 1; the method of computation is the same as in Sec. D. Finally, it is shown in Sec. I how approximate formulas of wider validity can be inferred from the ones obtained.

IN the first paper of this series[11] the problem of the motion of ions through a gas was formulated under the assumption that the electric field was too large to be treated as a perturbation, as is often done. This problem was solved in the sense that the values of some simple velocity averages were worked out precisely while no attempt was made to write down the entire velocity distribution function. I believe that this type of approach will yield most answers of experimental interest. The actual formulation was restricted, however, to uniform ion densities. In this paper the problem of nonuniform densities will be tackled in the same spirit.

F. CHARACTER OF THE RANDOM MOTION OF IONS

It is intuitively reasonable to suppose that the drift velocity of ions is their most important property from the point of view of observation and that the random motion about this mean value is essentially a diffusion process. It will now be shown that this view is correct, provided the medium is thought of as anisotropic with the field direction as symmetry axis.

In order to prove this we modify Eq. (6) by assuming f to be a density in phase space, depending on space and time as well as velocity. If we adopt the notations

$$\partial/\partial\mathbf{r} \quad \text{and} \quad \partial/\partial\mathbf{c}$$

for the gradients in ordinary and velocity space, this formula reads

$$\partial f(\mathbf{c},\mathbf{r},t)/\partial t+\mathbf{a}\cdot\partial f(\mathbf{c},\mathbf{r},t)/\partial\mathbf{c}+\mathbf{c}\cdot\partial f(\mathbf{c},\mathbf{r},t)/\partial\mathbf{r}$$
$$=\int\int\{M(\mathbf{C}')f(\mathbf{c}',\mathbf{r},t)-M(\mathbf{C})f(\mathbf{c},\mathbf{r},t)\}\times\frac{1}{\tau(\gamma)}d\Pi_c d\mathbf{C}. \quad (64)$$

[11] Gregory H. Wannier, Phys. Rev. 83, 281 (1951). The two papers will be treated as forming together a single unit.

We now make the assumption that we deal with a distribution decaying at a constant small relative rate in some spatial direction. In zero approximation this distribution will displace itself with the drift velocity $\langle\mathbf{c}\rangle$. But in addition to this drift current there will be a current induced by the gradient which we propose to compute. We thus write the particle density $n(\mathbf{r}, t)$ in coordinate space in the form

$$n(\mathbf{r}, t)=n_0 \exp[\mathbf{k}\cdot(\mathbf{r}-\langle\mathbf{c}\rangle t)] \tag{65}$$

and the density in phase space

$$f(\mathbf{c}, \mathbf{r}, t)=n(\mathbf{r}, t)\{f(\mathbf{c})+f^*(\mathbf{c})\}. \tag{66}$$

In this expression $f(\mathbf{c})$ is the normalized unperturbed velocity distribution which results from Eq. (6). $f^*(\mathbf{c})$ is a correction to $f(\mathbf{c})$ which is caused by the presence of the density gradient. It follows from the definition of the problem that $f^*(\mathbf{c})$ makes no net contribution to the density, that is, that

$$\int f^*(\mathbf{c})d\mathbf{c}=0. \tag{67}$$

It will make a contribution to the current, however. The total current density $\mathbf{j}_t$ is given in terms of $f(\mathbf{c}, \mathbf{r}, t)$ by the formula

$$\mathbf{j}_t=\int f(\mathbf{c}, \mathbf{r}, t)\mathbf{c}d\mathbf{c}, \tag{68}$$

which upon substitution of (66) decomposes in two parts, stemming from $f(c)$ and $f^*(\mathbf{c})$, respectively. The first part just equals the product of density and drift velocity and thus is the expected drift current. The new current $\mathbf{j}$ induced by the density gradient thus arises from $f^*(\mathbf{c})$ and equals

$$\mathbf{j}=n(\mathbf{r}, t)\int f^*(\mathbf{c}, t)\mathbf{c}d\mathbf{c}. \tag{69}$$

In order to justify the assumptions (65) and (66) and, incidentally, to determine $f^*(\mathbf{c})$, these expressions must be substituted back into (64). After simplification with (6), the following equation results:

$$\mathbf{a}\cdot\frac{\partial f^*(\mathbf{c})}{\partial\mathbf{c}}+\int\int\{M(\mathbf{C})f^*(\mathbf{c})-M(\mathbf{C}')f^*(\mathbf{c}')\}\frac{d\Pi_c d\mathbf{C}}{\tau(\gamma)}$$
$$=-\mathbf{k}\cdot(\mathbf{c}-\langle\mathbf{c}\rangle)\{f(\mathbf{c})+f^*(\mathbf{c})\}. \tag{70}$$

This is an equation in velocity space only; the disappearance of the coordinates and the time proves the compatibility with (64) of the assumptions made in (65) and (66). In solving Eq. (70) we observe that our interest is only in diffusion, that is, the current resulting from a concentration gradient when treated in first-order perturbation. In this case both $\mathbf{k}$ and $f^*(\mathbf{c})$ are to be treated as small, and their product in (70) is to be neglected. The equation then becomes

$$\mathbf{a}\cdot\frac{\partial f^*(\mathbf{c})}{\partial\mathbf{c}}+\int\int\{M(\mathbf{C})f^*(\mathbf{c})-M(\mathbf{C}')f^*(\mathbf{c}')\}\frac{d\Pi_c d\mathbf{C}}{\tau(\gamma)}$$
$$=-\mathbf{k}\cdot(\mathbf{c}-\langle\mathbf{c}\rangle)f(\mathbf{c}). \tag{71}$$

The homogeneous prototype of this inhomogeneous equation is (6); arbitrary amounts of $f(\mathbf{c})$ could thus be added to a particular solution of (71) were it not for the orthogonality condition (67) which makes the solution definite.

The existence of the diffusion phenomenon follows easily from Eq. (71). $f^*(\mathbf{c})$ is a linear function of the three components k_x, k_y, and k_z with coefficients which do not depend on the density or its gradient, but only on the unperturbed velocity distribution $f(\mathbf{c})$; furthermore, the first two of these coefficients are equal. Hence, from (69) $\mathbf{j}$ comes out as a linear function of the three quantities $n(\mathbf{r}, t)k_x$, $n(\mathbf{r}, t)k_y$, $n(\mathbf{r}, t)k_z$; these are the components of the density gradient as is evident from (65); in addition, the multipliers of the first two components are equal. We may write therefore

$$\mathbf{j}=-(\mathfrak{D})\partial n/\partial\mathbf{r}, \tag{72}$$

where $(\mathfrak{D})$ is a tensor which is axially symmetric about the field direction; its two components, which we shall call the longitudinal diffusion coefficient $D_{||}$ and the transverse coefficient $D_\perp$, are computed entirely from the unperturbed velocity distribution $f(\mathbf{c})$. It is to be noted, however, that they contain the acting electric field as a parameter.

G. DIFFUSION FOR CONSTANT MEAN FREE TIME; GENERALIZED EINSTEIN RELATION

It is not surprising, in view of the successes achieved earlier, that explicit expressions can be derived for the two diffusion coefficients if the model of Secs. C and E. is adopted. The derivations, which proceed most easily by the classical method of Maxwell[12] rather than that of Sec. B, will be given in BSTJ.[4] The final result is

$$j_i=-\left[\frac{m+M}{M}\frac{\tau}{\langle 1-\cos\chi\rangle}\{\langle c_i c_k\rangle-\langle c_i\rangle\langle c_k\rangle\}\right]\frac{\partial n}{\partial x_k}. \tag{73}$$

Here tensorial notation has been employed in order to exhibit the tensor character of the square bracket, which, from (72), is just the diffusion tensor. If we substitute the explicit expressions (60), (62), and (63) for the velocity averages in (73), we get

$$D_{||}=\frac{(m+M)\tau kT}{mM\langle 1-\cos\chi\rangle}$$
$$+\frac{(m+M)^3a^2\tau^3\langle 2m(1-\cos\chi)^2+M\sin^2\chi\rangle}{mM^2\langle 1-\cos\chi\rangle^3\langle 4m(1-\cos\chi)+3M\sin^2\chi\rangle}, \tag{74}$$

[12] J. C. Maxwell, *Collected Papers* (Cambridge University Press, London, 1890), Vol. II, p. 40.

$$D_\perp=\frac{(m+M)\tau kT}{mM\langle 1-\cos\chi\rangle}+\frac{(m+M)^4a^2\tau^3\langle\sin^2\chi\rangle}{mM^2\langle 1-\cos\chi\rangle^3\langle 4m(1-\cos\chi)+3M\sin^2\chi\rangle}. \quad (75)$$

Special formulations for the isotropic model are obviously derivable from these. The formulas valid for the polarization force result by applying to them (30) and (31).

Equation (73) may be thought of as the natural extension of the Einstein relation to strong fields. This can be made explicit by writing it in the form

$$D_n/\text{mobility}=2\times(\text{mean random energy along } n)/e, \quad (76)$$

where n stands for one of the principal directions of the diffusion tensor. Equation (76) embraces both (73) and the Einstein relation. This means it is valid (a) for all interactions at low field and (b) for the mean free time case at all fields. An occasion to examine its validity beyond this range will present itself in the next section.

H. LONGITUDINAL DIFFUSION FOR THE CASE OF SECTION D

Diffusion offers a good test case to substantiate the claim made in Sec. D, namely, that specific quantities of experimental interest can be derived from the Boltzmann equation without working out the entire velocity distribution. Longitudinal diffusion was picked for computation, partly because its symmetry permits the use of the restricted expansion (11) rather than a more general expression, and partly because it looks as though the quantity is accessible to experimental measurement.[13]

For such a calculation the inhomogeneous equivalent of the equation system (17) is needed. This system is derived by following step by step the derivation of Sec. B, starting out from (71) which differs from (6) only in its inhomogeneous term. Skipping intermediate formulations corresponding to Eqs. (7), (8), and (14) we pass directly to the inhomogeneous form of the Eqs. (17), which reads

$$\begin{aligned}&a\nu(s+\nu+1)\{c^{s-1}P_{\nu-1}(\cos\vartheta)\}+a(\nu+1)(s-\nu)\\&\times\{c^{s-1}P_{\nu+1}(\cos\vartheta)\}-(2\nu+1)(1-I_{s,\nu})\\&\times\{c^sP_\nu(\cos\vartheta)/\tau(c)\}=k[\nu\langle c^{s+1}P_{\nu-1}(\cos\vartheta)\rangle\\&+(\nu+1)\langle c^{s+1}P_{\nu+1}(\cos\vartheta)\rangle-(2\nu+1)\langle c\cos\vartheta\\&\times\langle c^sP_\nu\cos\vartheta\rangle\rangle]. \quad (77)\end{aligned}$$

Here the curly brackets represent averages over $f^*(\mathbf{c})$, that is, corrections to the angular brackets which are caused by the density gradient. Equation (77) permit addition of an arbitrary amount of the pointed brackets to these curly ones, because the former satisfy the homogeneous equations (17). This indeterminacy is removed by (67).

Just as in Part I we do not have to solve the equation system (77) completely in order to find the value of the longitudinal diffusion coefficient. As previously, this is trivially true for the case of constant mean free time. Here Eq. (77) with $s=\nu=1$ yields the answer directly. We find, using (16),

$$-3\frac{M\langle 1-\cos\chi\rangle}{(M+m)\tau}\{c_z\}=k\cdot 3[\langle c_z^2\rangle-\langle c_z\rangle^2].$$

Because of (65), (69), and (72) this is the longitudinal part of (73) which is thus derived.

The computation of $D_{||}$ from (77) for other models demands the use of the method of Sec. D. The case of special interest is the hard sphere model for equal masses. Let us specialize the system (77) for this case. We render the velocity dimensionless by adopting (37); we abbreviate further

$$\langle w^sP_\nu(\cos\vartheta)\rangle=\langle s,\nu\rangle \quad (78)$$

and

$$\{w^sP_\nu(\cos\vartheta)\}=k\lambda\{s,\nu\}. \quad (79)$$

The extra complication in the definition of the curly brackets symbols is such that all external parameters disappear from the equation system (77), which now reads

$$\begin{aligned}&\nu(s+\nu+1)\{s-1,\nu-1\}+(\nu+1)(s-\nu)\{s-1,\nu+1\}\\&-(2\nu+1)(1-I_{s,\nu})\{s+1,\nu\}=\nu\langle s+1,\nu-1\rangle\\&+(\nu+1)\langle s+1,\nu+1\rangle-(2\nu+1)\langle 1,1\rangle\langle s,\nu\rangle. \quad (80)\end{aligned}$$

Equation (80) forms a system of linear relations among the curly bracket symbols. Their interconnection is the same as the one shown in Fig. 4; hence the procedure for solving the system is identical with the one in Sec. D. The normalization condition is replaced by (67), which reads in the present notation

$$\{0,0\}=0. \quad (81)$$

In the place of (38), (39), and (40) we find

$$\begin{aligned}\{4,0\}&=-(5/3)\langle 4,1\rangle+(5/3)\langle 1,1\rangle\langle 3,0\rangle\\&-(10/3)\langle 2,0\rangle-(20/3)\langle 2,0\rangle+10\langle 1,1\rangle^2. \quad (82a)\end{aligned}$$

$$\begin{aligned}112\{3,0\}-3\{7,0\}&=4\langle 7,1\rangle-4\langle 1,1\rangle\langle 6,0\rangle\\&+(56/5)\langle 5,0\rangle+(112/5)\langle 5,2\rangle-(168/5)\langle 1,1\rangle\langle 4,1\rangle\\&-(1344/25)\langle 3,1\rangle+(1344/25)\langle 3,3\rangle\\&+(448/5)\langle 1,1\rangle\langle 2,0\rangle-(448/5)\langle 1,1\rangle\langle 2,2\rangle. \quad (83a)\end{aligned}$$

$$\begin{aligned}54\{2,0\}-(295/28)\{6,0\}+(17/165)\{10,0\}&\\=-(17/135)\langle 10,1\rangle+(17/135)\langle 1,1\rangle\langle 9,0\rangle&\\-(17/36)\langle 8,0\rangle-(17/18)\langle 8,2\rangle+(17/12)\langle 1,1\rangle\langle 7,1\rangle&\\+6\langle 6,1\rangle-(21/5)\langle 6,3\rangle-(44/5)\langle 1,1\rangle\langle 5,0\rangle&\\+7\langle 1,1\rangle\langle 5,2\rangle+(54/5)\langle 4,0\rangle+(108/7)\langle 4,2\rangle&\\-(288/35)\langle 4,4\rangle-(162/5)\langle 1,1\rangle\langle 3,1\rangle&\\+(72/5)\langle 1,1\rangle\langle 3,3\rangle. \quad (84a)\end{aligned}$$

[13] The measurements of J. A. Hornbeck, Phys. Rev. **83**, 374 (1951), give a fluctuation in the mean drift which shows up in Fig. 5 for instance, by a rounding off of the vertical drop. One would expect this to be due to longitudinal diffusion of the ions.

The knowledge of the unperturbed velocity averages required by these equations is rather more extensive than was anticipated in Part I. Most of them are derivable from (41) and the coefficients following; for some the accuracy so obtained is insufficient because of cancellations in the equation system (17); these were obtained by extrapolation. The resultant numbers will be published in BSTJ.[4] Upon substitution the equations become

$$\{4, 0\} = -10.494, \tag{82b}$$

$$112\{3, 0\} - 3\{7, 0\} = 647.8, \tag{83b}$$

$$54\{2, 0\} - (295/28)\{6, 0\} + (17/165)\{10, 0\} = -566.4. \tag{84b}$$

The following step could perhaps be improved. We know in a general way that the diffusion correction to the velocity distribution is some sort of p-type function. What is needed, however, in this method is the correction to $h_0(w)$; beyond the knowledge implicit in (81), we know very little about it. In view of this ignorance the form (41) was adopted for this correction, with new undetermined coefficients p, q, r, s. This is undoubtedly a poor choice and explains the slower convergence observed here than in (42), (44), and (46). To start with the zero order is completely lost, because (81) yields a zero coefficient. We find in first order, using (81) and (82), $p^{(1)}=4.8842$, $q^{(1)}=-4.2689$, $r^{(1)}=s^{(1)}=0$; in second order, using (81), (82), and (83), $p^{(2)}=-10.542$, $q^{(2)}=+14.993$, $r^{(2)}=-4.408$, $s^{(2)}=0$; in the third order, using (81), (82), (83), and (84), $p^{(3)}=-0.8710$, $q^{(3)}=+1.1754$, $r^{(3)}=+1.0140$, $s^{(3)}=-0.5809$. The longitudinal diffusion coefficient results from these numbers by the use of (65), (69), and (72). With the notation of (79) the formula becomes

$$D_{||} = -a^{\frac{1}{2}}\lambda^{\frac{3}{2}}\{1, 1\}. \tag{85}$$

The average $\{1, 1\}$, in turn, is reducible to $\{3, 0\}$ by the appropriate equation (80). We find

$$\{1, 1\}^{(1)} = -0.3695, \tag{86a}$$

$$\{1, 1\}^{(2)} = -0.2075, \tag{86b}$$

$$\{1, 1\}^{(3)} = -0.2198. \tag{86c}$$

This extrapolates with reasonable certainty to

$$D_{||} = 0.22a^{\frac{1}{2}}\lambda^{\frac{3}{2}}. \tag{87}$$

To gain an appreciation of this result we can compare it with the guess that would have resulted from (76). The mobility concept is ambiguous for all but the cases discussed then. It would seem that the appropriate concept here is the differential mobility because comparison is made between a small density gradient and a small change in the applied field. Thus, we would interpret (78) to mean

$$D_{||} \approx \frac{\partial\langle c_z\rangle}{\partial a}[\langle c_z^2\rangle - \langle c_z\rangle^2], \tag{88a}$$

which, with (37), (43), and (47), becomes

$$D_{||} \approx 0.26a^{\frac{1}{2}}\lambda^{\frac{3}{2}}. \tag{88b}$$

The error of formula (76) is thus 18 percent, when compared to (87).

I. CONCLUDING REMARKS; GENERALIZED RELATIONSHIPS

The purpose of these two articles was to develop the theory of ionic motion sufficiently well so that the presence of a strong electric field is no longer felt to be an insuperable obstacle to the use of kinetic theory. Explicit formulas, such as (43) and (87), were worked out when the experimental situation seemed to indicate the need for it.[5,13] For a wider and less rigorous use, estimates, such as (21) and (76), were presented. In addition, there is in the formulas for constant mean free time information which yields to judicious treatment. For example, if we desire to know the drift velocity of an ion for the hard sphere model and high field, but arbitrary mass ratio, then we can start from (18) replacing the mean free time by a mean free path

$$\langle c_z\rangle \approx [(M+m)/M](a\lambda/c).$$

As usual in kinetic theory we interpret the c in the denominator as a root mean square value; then we can substitute from (21) and get the final formula

$$\langle c_z\rangle \approx (M+m)^{\frac{1}{2}}m^{\frac{1}{2}}M^{-\frac{1}{2}}a^{\frac{1}{2}}\lambda^{\frac{3}{2}}. \tag{89}$$

For ions in the parent gas this expression differs from (43) by only 4 percent. For electrons (89) checks the result of Druyvesteyn[2] to within 12 percent. Finally, for heavy ions in a light gas, where the answer can be worked out rigorously also,[4] Eq. (89) is exact. Thus, it qualifies as a reliable approximate formula.

Because of a shortage of space, certain proofs and topics have been omitted from these two articles. A more extensive account is to appear shortly in the *Bell System Technical Journal*.[4]

These two articles owe their existence to the stimulation of Dr. J. A. Hornbeck of this laboratory. In the course of his experiments he perceived the gap in the existing theory which this study is intended to fill.

J. ERRATA IN PAPER I[11]

The definition of $I_{s,\nu}$ given in Eq. (16) does not agree with the verbal statement on the page preceding. A factor $(M+m)^2/2Mm$ has to be added to the verbal definition of $I_{s,\nu}$.

In the formula lying between (19) and (20) a factor $\langle 1-\cos\chi\rangle$ has been omitted in the denominator.

In formula (32) the second M should be an N.

In formula (63) the factor M^2 in the denominator should read M.