reason, it appears that H_2^- is not involved. The existence of H_1^- remains a possibility. Calculations, such as were made for H_2^- to compare electron affinities, are not possible since the concentration of H_1 is unknown.

The pressure independent component is much too large to explain[12] in terms of a radiative recombination process. Dissociative recombination, as suggested by Bates,[13] can very well account for the observed data.

The author wishes to express his gratitude to Professor S. C. Brown and to Professor W. P. Allis of Massachusetts Institute of Technology for stimulating discussions and to Mr. K. W. Rau for expert assistance.

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[12] D. R. Bates, Phys. Rev. **77**, 718 (1950).

[13] D. R. Bates, Phys. Rev. **78**, 492 (1950).

PHYSICAL REVIEW VOLUME 84, NUMBER 3 NOVEMBER 1, 1951

Diffusion as Hydrodynamic Motion

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(Received July 16, 1951)

A phenomenological definition of diffusion in a binary mixture suggests a description of the motion by a hydrodynamic equation which contains a frictional force proportional to the relative diffusion velocity. Plausible assumptions give a set of hydrodynamic equations for any gaseous mixture, which may include charged molecules in a magnetic field. The equations determine the diffusion velocities in terms of the applied forces, the pressure gradients, and the binary diffusion coefficients. The same equations are also derived from kinetic theory in the first diffusion approximation. In higher approximations where thermal diffusion first appears, the equations are no longer valid.

In a previous paper[1] the motion of electrons and ions through a neutral gas in a magnetic field was analyzed with hydrodynamic equations in which frictional forces represented the retarding action of the gas. A phenomenological definition of diffusion suggested the frictional force, and its dependence on both diffusion velocity and diffusion coefficient.[2] Thus diffusion velocities could be related to the forces acting on each type of ion without the difficult ideas of mean free path and collision frequency. The present paper has three purposes: to state assumptions necessary for applications of the phenomenological definition; to extend previous equations, limited to ion densities small compared to the gas density, to any gaseous mixture;[3] and to test the conclusions by the second approximation of kinetic theory,[4] a procedure which shows that there is no simple way to include thermal diffusion.

Let p_r, ρ_r, and n_r be the pressure, mass density, and number density of the rth species of molecules in a mixture of N species. Each gas is assumed to obey the ideal gas law, $p_r = n_r kT$. To define the diffusion coefficient D_{rs}, suppose the mixture consists of the two species r and s at a uniform temperature and uniform total pressure, $p = p_r + p_s$. Let the mean molecular velocities $\langle \mathbf{c}_r \rangle_{\text{Av}}$ and $\langle \mathbf{c}_s \rangle_{\text{Av}}$ at a point $\mathbf{r}$, t be measured in a reference frame such that $n_r\langle \mathbf{c}_r \rangle_{\text{Av}} + n_s\langle \mathbf{c}_s \rangle_{\text{Av}} = 0$. We assert as an experimental fact that the diffusion current is then given by

$$n_r\langle \mathbf{c}_r \rangle_{\text{Av}} = -D_{rs}\partial n_r/\partial \mathbf{r}. \tag{1}$$

For the coefficients so defined, $D_{rs} = D_{sr}$, which can be seen by applying the definition to the species s. To remove the restriction to a special reference frame it is only necessary to express $\langle \mathbf{c}_r \rangle_{\text{Av}}$ in terms of the velocity difference $\langle \mathbf{c}_r \rangle_{\text{Av}} - \langle \mathbf{c}_s \rangle_{\text{Av}}$; $\langle \mathbf{c}_r \rangle_{\text{Av}} = n_s(n_r + n_s)^{-1}(\langle \mathbf{c}_r \rangle_{\text{Av}} - \langle \mathbf{c}_s \rangle_{\text{Av}})$. If, at the same time, n_r is replaced by p_r through the ideal gas law, Eq. (1) may be written

$$-\partial p_r/\partial \mathbf{r} = \theta_{rs}(\langle \mathbf{c}_r \rangle_{\text{Av}} - \langle \mathbf{c}_s \rangle_{\text{Av}}), \tag{2a}$$

$$\theta_{rs} \equiv kTn_r n_s(n_r + n_s)^{-1}(D_{rs})^{-1}. \tag{2b}$$

Equation (2), which is equivalent to Eq. (1), may be applied in any reference frame for both terms are invariant to Galilean transformations.

The form of Eq. (2) suggests an equilibrium of hydrodynamic forces since the negative pressure gradient is the force exerted on a fluid in a unit volume by the fluid outside that volume. The right-hand member has the appearance of a frictional force, for it is proportional to and oppositely directed to the relative velocity of the

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[1] M. H. Johnson and E. O. Hulburt, Phys. Rev. **79**, 802 (1950).

[2] A. Einstein introduced such a force in his well-known theory of Brownian motion. Thereafter it has been repeatedly used in the theory of electrolytes. A. Schlüter, Z. Naturforsch. **5a**, 72 (1950); **6a**, 73 (1951), has based a treatment of gaseous diffusion on the concept of frictional forces. He introduced the forces and evaluated the frictional coefficients in a different way than that followed in reference 1 and in the present paper. The hydrodynamic equations he obtained, explicitly given in his second paper for a mixture of two ionized and one neutral component in the presence of external fields, are essentially the same as Eq. (6) above.

[3] For a preliminary report, see M. H. Johnson, Phys. Rev. **82**, 298 (1951).

[4] S. Chapman and G. T. Cowling *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, England (1939), Chaps. 7, 8, 9, and 18. We shall use the notation and units of this book. For symbols we have sometimes incompletely defined, the list of symbols at the beginning of the book should be consulted, where page references to all definitions will be found.

two fluids. Moreover, with this interpretation the force exerted by species *r* on species *s* is equal in magnitude and opposite in direction to that exerted by *s* on *r*, which can be seen by writing Eq. (2) for species *s*. Hence we assume that Eq. (2) represents an equilibrium of hydrodynamic forces; the left side is the self-force of molecules *r* and the right side is the force exerted by molecules *s* on molecules *r*.

Our final assumption may now be stated: if a force between two groups of molecules is specified by physical parameters of the two groups, it is not altered by the presence of molecules foreign to both groups. For example, by applying this hypothesis to the force between molecules of species *r* inside and outside a unit volume, the self-force is $-\partial p_r/\partial \mathbf{r}$ whatever may be the mixture containing the species *r*. Likewise, the frictional force exerted by molecules of species *s* on molecules of species *r* is $\theta_{rs}(\langle \mathbf{c}_r\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}})$, where θ_{rs} is given by Eq. (2b), whatever gases comprise the mixture.

The last hypothesis determines the dependence of D_{rs} on the number densities. In the foregoing binary mixture (r, s), arbitrarily divide molecules *r* into two groups of number densities n_r' and n_r'', with $n_r'+n_r''=n_r$. Considering the mixture as one of three components, we have

$$-\partial p_s/\partial \mathbf{r}=\theta_{sr}'(\langle \mathbf{c}_s\rangle_{\mathrm{Av}}-\langle \mathbf{c}_r'\rangle_{\mathrm{Av}})+\theta_{sr}''(\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}-\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}),\quad (3a)$$

$$-\partial p_r'/\partial \mathbf{r}=\theta_{rs}'(\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}})+\theta_{rr}(\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}-\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}),\quad (3b)$$

$$-\partial p_r''/\partial \mathbf{r}=\theta_{rs}''(\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}})+\theta_{rr}(\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}-\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}).\quad (3c)$$

Adding the last two equations,

$$-\partial p_r/\partial \mathbf{r}=\theta_{rs}'(\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}})+\theta_{rs}''(\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}}).\quad (4)$$

But Eq. (3a) and Eq. (4) must be identical with the force equilibrium for the binary mixture (r, s). That requires

$$(\theta_{sr}'-n_r'\theta_{sr}/n_r)\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}+(\theta_{sr}''-n_r''\theta_{sr}/n_r)\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}=0\quad (5)$$

for arbitrary values of $\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}$ and $\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}$ since, with n, n_r' and n_r'' fixed, two of the velocities $\langle \mathbf{c}_s\rangle_{\mathrm{Av}}$, $\langle \mathbf{c}_r'\rangle_{\mathrm{Av}}$ and $\langle \mathbf{c}_r''\rangle_{\mathrm{Av}}$ can be made to assume any preassigned value by adjusting the three pressure gradients. Equation (5) can be satisfied if, and only if, θ_{sr}/n_r does not depend on n_r. A similar division of species *s* shows θ_{sr}/n_s cannot depend on n_s. Hence θ_{rs}/n_rn_s cannot depend on the number densities or, by Eq. (2b), $D_{rs}(n_r+n_s)$ cannot depend on the number density of either species.

Consider a mixture of *N* components in which molecules *r* have a charge e_r and mass m_r. The various forces in the dynamical equilibrium for molecules *r* are: the self-force, $-\partial p_r/\partial \mathbf{r}$; a frictional force, $\theta_{rs}(\langle \mathbf{c}_r\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}})$, for each species $s (s\neq r)$; an external force, $\rho_r\mathbf{F}_r$, which may be partly gravitational and partly electrical in origin; the ampere force $n_re_r\langle \mathbf{c}_r\rangle_{\mathrm{Av}}\times\mathbf{H}$ on the electric current, produced by the motion of the charges, in a magnetic field $\mathbf{H}$; and finally the force of inertial reaction, $-\rho_r\mathbf{a}$, which must be included according to d'Alembert's principle if the gas as a whole has an acceleration $\mathbf{a}$. Collecting all terms, the hydrodynamic equations for the equilibrium of forces become

$$-\partial p_r/\partial \mathbf{r}+\rho_r(\mathbf{F}_r-\mathbf{a})+n_re_r\langle \mathbf{c}_r\rangle_{\mathrm{Av}}\times\mathbf{H}=\textstyle\sum_s \theta_{rs}(\langle \mathbf{c}_r\rangle_{\mathrm{Av}}-\langle \mathbf{c}_s\rangle_{\mathrm{Av}}).\quad (6)$$

There are *N* such equations which may be solved for the *N* velocities in terms of the pressure gradients and the external forces. Equation (6) may be applied in any reference frame for it is invariant to galilean transformations. Thus $\langle \mathbf{c}_r\rangle_{\mathrm{Av}}$ may be replaced by the mean peculiar velocity, $\langle \mathbf{C}_r\rangle_{\mathrm{Av}}=\langle \mathbf{c}_r\rangle_{\mathrm{Av}}-\mathbf{c}_0$, provided we use the electromagnetic field, $\mathbf{E}$ and $\mathbf{H}$, proper to the reference frame in which $\mathbf{c}_0=\rho^{-1}\sum_s \rho_s\langle \mathbf{c}_s\rangle_{\mathrm{Av}}=0$.

The hydrodynamic equations solve a variety of problems. For example, to obtain conductivities of an ionic mixture, the terms on the left side of Eq. (6) which do not contain $\mathbf{E}$ or $\mathbf{H}$ may be omitted. If the equations are then solved for the velocities, the total electric current, $\mathbf{j}=\sum_s n_se_s\langle \mathbf{c}_s\rangle_{\mathrm{Av}}$, is obtained as a linear vector function of $\mathbf{E}$. The coefficient of $\mathbf{E}$ is the conductivity dyadic.

We now turn to kinetic theory. The second approximation to the distribution function[5] is $f_r^{(0)}(1+\phi_r)$ where $f_r^{(0)}$ is the maxwell function,

$$f_r^{(0)}=n_r(m_r/2\pi kT)^{\frac{3}{2}}\exp(-m_rC_r^2/2kT),\quad (7)$$

and ϕ_r satisfies the equation,

$$\frac{D_0f_r^{(0)}}{Dt}+\mathbf{C}_r\cdot\frac{\partial f_r^{(0)}}{\partial \mathbf{r}}+\left(\mathbf{F}_r-\frac{D_0\mathbf{c}_0}{Dt}\right)\cdot\frac{\partial f_r^{(0)}}{\partial \mathbf{C}_r}+\frac{e_r}{m_r}f_r^{(0)}(\mathbf{C}_r\times\mathbf{H})\cdot\frac{\partial \phi_r}{\partial \mathbf{C}_r}=-\textstyle\sum_s I_{rs}(\phi_r+\phi_s),\quad (8a)$$

$$I_{rs}(\phi_r+\phi_s)\equiv\int\int f_r^{(0)}f_s^{(0)}(\phi_r+\phi_s-\phi_r'-\phi_s')k_{rs}d\boldsymbol{\kappa}d\mathbf{c}_s.\quad (8b)$$

The solution of Eq. (8) has the form,

$$\phi_r=\mathbf{D}_r\cdot\mathbf{C}_r,\quad (9)$$

where $\mathbf{D}_r$ is a linear vector function of the pressure gradients, the forces $\mathbf{F}_s$ and the temperature gradient; the coefficients depend on $\mathbf{H}$ and on the magnitude of $\mathbf{C}_r$. With Eq. (9), the diffusion currents become

$$n_r\langle \mathbf{C}_r\rangle_{\mathrm{Av}}=\int f_r^{(0)}\mathbf{C}_r\phi_rd\mathbf{c}_r=\tfrac{1}{3}\int f_r^{(0)}C_r^2\mathbf{D}_rd\mathbf{c}_r.\quad (10)$$

The solution of the integral equations for $\mathbf{D}_r$, which

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[5] T. G. Cowling, Proc. Roy. Soc. (London), A **183**, 453 (1945); see reference 4, Chap. 18.

present a formidable mathematical problem, have been given by Cowling[4] when $\mathbf{D}_r$ does not depend on the velocity, i.e., in the first diffusion approximation. To this order, terms containing the temperature gradient drop out and there is no thermal diffusion.

The hydrodynamic equations may be regarded as a momentum balance. Similar relations are obtained from kinetic theory by multiplying Eq. (8) by $m_r\mathbf{C}_r d\mathbf{c}_r$ and integrating over $d\mathbf{c}_r$. The first term vanishes because it contains $\mathbf{C}_r$ only as a scalar. The second term becomes $(\partial/\partial\mathbf{r})\cdot\langle\mathbf{CC}\rangle_{\mathrm{Av}}=(\partial/\partial\mathbf{r})\cdot\mathbf{p}^{(0)}=\partial p_r/\partial\mathbf{r}$. The third and fourth can be integrated by parts so that the whole equation becomes

$$-\frac{\partial p_r}{\partial\mathbf{r}}+\rho_r\left(\mathbf{F}_r-\frac{D_0\mathbf{c}_0}{Dt}\right)+n_re_r\langle\mathbf{C}_r\rangle_{\mathrm{Av}}\times\mathbf{H}=\textstyle\sum_s\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r),\qquad(11\mathrm{a})$$

with

$$\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r)\equiv\int m_r\mathbf{C}_rI_{rs}(\phi_r+\phi_s)d\mathbf{c}_r.\qquad(11\mathrm{b})$$

The integral $\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r)$ is the momentum per unit volume transferred by collisions from molecules r to molecules s. Identifying $D_0\mathbf{c}_0/Dt$ with $\mathbf{a}$, the left side of Eq. (11a) is the same as the left side of Eq. (6). Hence the second approximation to kinetic theory leads to the same expressions for the hydrodynamic forces even in the case that the thermal gradient is not zero.

When $\mathbf{D}_r$ does not depend on C_r Eq. (10) becomes

$$\langle\mathbf{C}_r\rangle_{\mathrm{Av}}=(kT/m_r)\mathbf{D}_r.\qquad(12)$$

There is then a simple connection between $\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r)$ and the velocities, for we have

$$\begin{aligned}\Delta_{rs}{}^{(1)}&(m_r\mathbf{C}_r)\\&=\int\int\int f_r{}^{(0)}f_s{}^{(0)}m_r\mathbf{C}_r[\mathbf{D}_r\cdot(\mathbf{C}_r-\mathbf{C}_r{}')\\&\qquad+\mathbf{D}_s\cdot(\mathbf{C}_s-\mathbf{C}_s{}')]k_{rs}d\boldsymbol{\kappa}d\,\mathbf{c}_rd\,\mathbf{c}_s\\&=\int\int\int f_r{}^{(0)}f_r{}^{(0)}m_r\mathbf{C}_r(\mathbf{C}_r-\mathbf{C}_r{}')d\boldsymbol{\kappa}d\,\mathbf{c}_rd\,\mathbf{c}_s\\&\qquad\cdot(\mathbf{D}_r-m_r\mathbf{D}_s/m_s)\\&=\int\int\int f_r{}^{(0)}f_s{}^{(0)}m_r\mathbf{C}_r(\mathbf{C}_r-\mathbf{C}_r{}')d\boldsymbol{\kappa}d\,\mathbf{c}_rd\,\mathbf{c}_s\\&\qquad\cdot(\langle\mathbf{C}_r\rangle_{\mathrm{Av}}-\langle\mathbf{C}_s\rangle_{\mathrm{Av}})(m_r/kT).\qquad(13)\end{aligned}$$

As $\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r)$ is a linear vector function of $\langle\mathbf{C}_r\rangle_{\mathrm{Av}}-\langle\mathbf{C}_s\rangle_{\mathrm{Av}}$ which does not depend on $\mathbf{D}_r$ or $\mathbf{D}_s$, all reference to species other than r or s has disappeared from Eq. (13). The momentum transferred from molecules r to molecules s is independent of the mixture, in accord with the final hypothesis made in deriving Eq. (8). Moreover the right side of Eq. (13) must have the known value for a binary mixture, that is

$$\begin{aligned}\Delta_{rs}{}^{(1)}&(m_r\mathbf{C}_r)\\&=(kT(n_r+n_s)^{-1}n_rn_s/[D_{rs}]_1)(\langle\mathbf{C}_r\rangle_{\mathrm{Av}}-\langle\mathbf{C}_s\rangle_{\mathrm{Av}}),\qquad(14)\end{aligned}$$

where $[D_{rs}]_1$ is the first approximation to the binary diffusion coefficient. Inserting Eq. (4) into Eq. (11a) we obtain Eq. (8) if it is understood that $[D_{rs}]_1$ be used in Eq. (2b). The hydrodynamic equations are therefore equivalent to the first diffusion approximation.[6]

If $\mathbf{D}_r$ depends on C_r, $\Delta_{rs}{}^{(1)}(m_r\mathbf{C}_r)$ becomes a linear vector function of all the velocities and of the temperature gradient; each coefficient is a complicated integral which depends on all the components in the mixture. Consequently the right side of Eq. (11a) cannot be resolved into a sum of terms, each of which refers to an isolated binary mixture, so that it no longer has the same form as the right side of Eq. (6). In higher diffusion approximations the simple connection between momentum transfer and diffusion velocities, Eq. (14), is lost and the hypothesis underlying the right side of Eq. (6) is not valid. Since thermal diffusion appears only if $\mathbf{D}_r$ depends on C_r, it is not possible to describe thermal diffusion by adding a sum of binary terms proportional to the temperature gradient to right side of Eq. (6).

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[6] I am indebted to Professor Cowling for the observation that Eq. (6) may be derived from Eq. (37) of his 1945 paper (see reference 5) by multiplying the latter equation by $\mathbf{d}_s$ and summing over s, thus establishing the equivalence.