

## A Theory for the Mobility of Ions of High Velocity

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The theories of Langevin and of Hassé and Cook for the mobility of ions in weak fields have been generalized to fields of any strength. The random energy of the ions is assumed to have a Maxwellian distribution, and the drift and random energies are both evaluated by momentum and energy balances.

**A**N ideal theoretical treatment of the mobility of ions in gases would consist in the solution of the Boltzmann integral equation,<sup>1</sup> in which the laws of continuity are applied to the motion of ions in phase space. A solution may some day be found through the equations published by Pidduck<sup>2</sup> in 1915. He transformed the Boltzmann equation into a Fredholm integral equation with a symmetrical kernel and was able to perform one of the six required integrations. In the absence of an exact solution, however, an approximate distribution function may be chosen, and the parameters contained in it may be so adjusted that the equation is satisfied in the mean. Any solution must comply with the laws of conservation of momentum and energy, and these may be taken as criteria. The energy of the ions may be resolved into two parts, the drift and random energies, and these may be taken as the parameters. For simplicity the analysis is confined to elastic impacts, to steady distributions, to uniform densities in coordinate space, to low ion concentrations, and to uniform fields.

An approximate function which differs from the equilibrium distribution by a small added term has been used by Langevin<sup>3</sup> in his theory of mobility. In this theory the random energy is set equal to the thermal energy of the molecules, and the drift energy is evaluated by a momentum balance. The theory is thus restricted to weak fields. It is generalized to fields of any strength by the adoption of a Maxwellian distribution for the random energy of the ions which is free of any restriction as to the amount of deviation

from equilibrium. The distribution is expressed by the equation

$$f_1 = \frac{n_1}{(2\pi m_1 k T_1)^{\frac{3}{2}}} \exp \left[ -\frac{(\mathbf{p}_1 - m_1 \mathbf{v})^2}{2m_1 k T_1} \right], \quad (1)$$

in which  $f_1$  is the density of ions in momentum space, and  $n_1$  is the density in coordinate space.  $m_1$  and  $\mathbf{p}_1$  are the mass and vector momentum of an ion.  $\frac{1}{2}n_1 m_1 v^2$  and  $\frac{3}{2}n_1 k T_1$  are the drift and random energies per unit volume, the sum of which is the total energy.

The molecules have the distribution of equilibrium. This is expressed by the equation

$$f_2 = \frac{n_2}{(2\pi m_2 k T_2)^{\frac{3}{2}}} \exp \left[ -\frac{\mathbf{p}_2^2}{2m_2 k T_2} \right], \quad (2)$$

in which  $f_2$  is the density of molecules in momentum space and  $n_2$  is the density in coordinate space,  $m_2$  and  $\mathbf{p}_2$  are the mass and vector momentum of a molecule, and  $T_2$  is the temperature of the gas.

The laws of conservation for steady motion are expressed by equating to zero the rates of change of the momentum and energy of the ions. In a field of intensity  $\mathbf{E}$  the ions take up momentum at the rate  $n_1 e \mathbf{E}$ , and energy at the rate  $n_1 e \mathbf{v} \cdot \mathbf{E}$ . They give up the momentum and energy

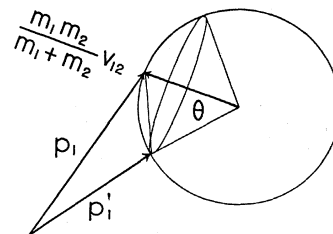


FIG. 1. The deflection of the ion by interaction with a molecule.

<sup>1</sup> L. Boltzmann, *Vorlesungen über Gastheorie*, Vol. I, p. 114; J. H. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, third edition, 1921), p. 210.

<sup>2</sup> B. F. Pidduck, *Proc. Lond. Math. Soc.* **15**, 89 (1915).

<sup>3</sup> P. Langevin, *Ann. de Chimie et de Physique* **8**, 245 (1905).

to the molecules of the gas at rates which may be evaluated by integration over momentum space of the product of the change in each quantity per collision and the frequency of collision.

In a particular interaction the ion and molecule approach each other with a relative velocity  $\mathbf{v}_{12}$ , and separate after impact with a relative velocity which has the same magnitude as  $\mathbf{v}_{12}$  but a different direction. The velocity of the ion itself is equal to the sum of the velocity of the center of mass, and the fraction  $m_2/(m_1+m_2)$  of  $\mathbf{v}_{12}$ . The velocity of the center of mass is invariant in a collision. The velocity of the ion after impact therefore lies on a sphere whose center is at the center of mass. The deflection of the ion is illustrated in Fig. 1. The change in momentum  $\mathbf{p}_1' - \mathbf{p}_1$  is equal to the product of the reduced mass  $m_1m_2/(m_1+m_2)$ , and the change in  $\mathbf{v}_{12}$ . The angle  $\theta$  through which  $\mathbf{v}_{12}$  is turned by impact is a function of the magnitude of  $\mathbf{v}_{12}$ , and of the distance  $\sigma$  between the asymptotes of the trajectories which the ion and molecule describe about the center of mass. The magnitude of the change in  $\mathbf{v}_{12}$  is equal to  $2v_{12} \sin \frac{1}{2}\theta$ .

If  $p_{11}$ ,  $p_{12}$  and  $p_{13}$  are Cartesian components of  $\mathbf{p}_1$ , the number of ions whose momenta lie in the element  $dp_{11}dp_{12}dp_{13}$  is equal to  $f_1 dp_{11}dp_{12}dp_{13}$ , and if  $p_{21}$ ,  $p_{22}$ , and  $p_{23}$  are components of  $\mathbf{p}_2$ , the number of molecules with momenta in the element  $dp_{21}dp_{22}dp_{23}$  is  $f_2 dp_{21}dp_{22}dp_{23}$ . After impacts between these ions and molecules the relative velocities are distributed symmetrically about

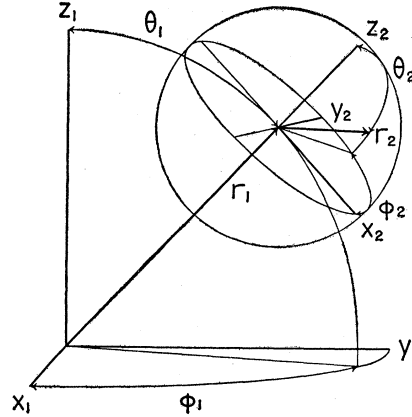


FIG. 2. Polar coordinates.

$\mathbf{v}_{12}$ , and added vectorially form a vector collinear with  $\mathbf{v}_{12}$ .  $\mathbf{p}_1' - \mathbf{p}_1$  may therefore be replaced in the integration by its component

$$-\frac{m_1m_2}{m_1+m_2}(1-\cos\theta)\mathbf{v}_{12}$$

along  $\mathbf{v}_{12}$ . Likewise, since  $\mathbf{p}_1'^2 - \mathbf{p}_1^2$  is identically equal to  $(\mathbf{p}_1' - \mathbf{p}_1) \cdot (\mathbf{p}_1' - \mathbf{p}_1 + 2\mathbf{p}_1)$ , it may be replaced in the integration by the expression

$$4\left(\frac{m_1m_2}{m_1+m_2}\right)^2 \sin^2 \frac{1}{2}\theta v_{12}^2 - 2\frac{m_1m_2}{m_1+m_2}(1-\cos\theta)\mathbf{p}_1 \cdot \mathbf{v}_{12}$$

Interactions in which  $\sigma$  lies in the range  $d\sigma$  occur with a frequency equal to the number of molecules in a prism of volume  $2\pi\sigma v_{12}f_1 dp_{11}dp_{12}dp_{13}d\sigma$ .

The completed momentum balance is therefore expressed by the equation

$$-\frac{m_1m_2}{m_1+m_2} \iiint \iiint \iiint f_1 f_2 \mathbf{v}_{12} Q(v_{12}) v_{12} dp_{11} dp_{12} dp_{13} dp_{21} dp_{22} dp_{23} + n_1 e \mathbf{E} = 0 \quad (3)$$

and the completed energy balance by the equation

$$\frac{m_2}{m_1+m_2} \iiint \iiint \iiint \iiint f_1 f_2 \left[ \frac{m_1m_2}{m_1+m_2} v_{12}^2 - \mathbf{p}_1 \cdot \mathbf{v}_{12} \right] Q(v_{12}) v_{12} dp_{11} dp_{12} dp_{13} dp_{21} dp_{22} dp_{23} + n_1 e \mathbf{v} \cdot \mathbf{E} = 0. \quad (4)$$

$Q(v_{12})$  is the diffusion cross section, and is defined by the equation

$$Q(v_{12}) = 2\pi \int (1 - \cos\theta) \sigma d\sigma.$$

Five of the six indicated integrations may be performed after transformation to polar coordinates. The required transformation is illustrated in Fig. 2 and is defined by the system of equations

$$\begin{aligned} p_{11} &= m_1 x_1 & p_{21} &= m_2(x_1 + x_2) & x_1 &= r_1 \sin \theta_1 \cos \phi_1 \\ p_{12} &= m_1 y_1 & p_{22} &= m_2(y_1 + y_2) & y_1 &= r_1 \sin \theta_1 \sin \phi_1 \\ p_{13} &= m_1 z_1 & p_{23} &= m_2(z_1 + z_2) & z_1 &= r_1 \cos \theta_1 \\ x_2 &= +r_2 \cos \theta_1 \cos \phi_1 \sin \theta_2 \cos \phi_2 - r_2 \sin \phi_1 \sin \theta_2 \sin \phi_2 + r_2 \sin \theta_1 \cos \phi_1 \cos \theta_2 \\ y_2 &= +r_2 \cos \theta_1 \sin \phi_1 \sin \theta_2 \cos \phi_2 + r_2 \cos \phi_1 \sin \theta_2 \sin \phi_2 + r_2 \sin \theta_1 \sin \phi_1 \cos \theta_2 \\ z_2 &= -r_2 \sin \theta_1 \sin \theta_2 \cos \phi_2 & & + r_2 \cos \theta_1 \cos \theta_2. \end{aligned}$$

$\mathbf{p}_1$  is expressed in terms of the position vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  by  $m_1 \mathbf{r}_1$ ,  $\mathbf{p}_2$  by  $m_2(\mathbf{r}_1 + \mathbf{r}_2)$ , and  $\mathbf{v}_{12}$  by  $-\mathbf{r}_2$ . The Jacobian of the transformation is  $m_1^3 m_2^3 r_1^2 r_2^2 \sin \theta_1 \sin \theta_2$ . To facilitate the integration, parameters may be inserted into the integrands of Eqs. (3) and (4), and the integrands may be expressed as partial derivatives with respect to these parameters of simpler functions. The integration may then be carried out first, and the partial differentiation last since the order is immaterial. The parameters are finally eliminated by setting them equal to unity.

The momentum balance is reduced by integration to the equation

$$-\frac{8}{\pi^{\frac{1}{2}}} \frac{(m_1 k T_2 + m_2 k T_1)}{(m_1 + m_2)} n_1 n_2 \Sigma_1 + n_1 e E = 0 \quad (5)$$

and the energy balance to the equation

$$-\frac{8}{\pi^{\frac{1}{2}}} \frac{n_1 n_2}{(m_1 + m_2)} v \left[ \frac{m_1 m_2}{m_1 + m_2} k (T_1 - T_2) \Sigma_2 + m_1 k T_2 \Sigma_1 \right] + n_1 e v E = 0. \quad (6)$$

$\Sigma_1$  and  $\Sigma_2$  are integrals. They are defined by the equations

$$\Sigma_1 = \int_0^\infty Q(\lambda) \frac{(2\lambda\xi \cosh 2\lambda\xi - \sinh 2\lambda\xi)}{(2\lambda\xi)^2} \exp(-\xi^2 - \lambda^2) \lambda^4 d\lambda \quad (7)$$

and

$$\Sigma_2 = 2 \int_0^\infty Q(\lambda) \frac{\sinh 2\lambda\xi}{(2\lambda\xi)^2} \exp(-\xi^2 - \lambda^2) \lambda^6 d\lambda. \quad (8)$$

$\xi$  and  $\lambda$  are defined by the equations

$$\xi^2 = \frac{m_1 m_2 v^2}{2(m_1 k T_2 + m_2 k T_1)} \quad (9)$$

and

$$\lambda^2 = \frac{m_1 m_2 v_{12}^2}{2(m_1 k T_2 + m_2 k T_1)}. \quad (10)$$

Langevin's general formula is recovered if  $v$  is made small.  $T_1$  becomes equal to  $T_2$ , and  $v$  is given by the equation

$$v = \frac{\pi e E [(m_1 + m_2)/m_1 m_2]^{\frac{1}{2}}}{(8/3) n_2 (2\pi k T_2)^{\frac{1}{2}} \int_0^\infty Q e^{-\lambda^2} \lambda^5 d\lambda}$$

The last integration may be performed once the cross section  $Q$  is known as a function of

the relative velocity  $v_{12}$ . The relation between  $Q$  and  $v_{12}$  would be disclosed by measurements of the scattering or retardation of ion beams. Unfortunately, the experimental data<sup>4</sup> now available are not sufficiently precise to warrant a quantitative calculation. In any case they represent qualitative evidence that  $Q$  decreases with increase in  $v_{12}$ .

Accurate theoretical values of  $Q$  have been calculated for two models, which may be used in conjunction with molecular force data from the equation of state. In the theory of Langevin,

<sup>4</sup> Cf. C. Ramsauer and O. Beeck, *Ann. d. Physik* **87**, 1 (1928); F. M. Durbin, *Phys. Rev.* **30**, 844 (1927); R. B. Kennard, *Phys. Rev.* **31**, 423 (1928); I. W. Cox, *Phys. Rev.* **34**, 1426 (1929); R. E. Holzer, *Phys. Rev.* **36**, 1204 (1930); J. S. Thompson, *Phys. Rev.* **35**, 1196 (1930); K. H. Bracewell, *Phys. Rev.* **54**, 639 (1938).

the ion and molecule are assumed to be rigid elastic spheres which attract each other with a force inversely proportional to the fifth power of the distance of separation. The attractive force is assumed to arise solely from polarization of the molecule by the field of the ion, and is expressed in terms of the dielectric constant  $\epsilon$  of the gas. The corresponding potential energy  $V$  is expressed in terms of the distance  $r$  by the equation

$$V = -\frac{\kappa_4}{r^4} = -\frac{(\epsilon-1)e^2}{8\pi n_2 r^4}.$$

In the theory of Hassé and Cook,<sup>5</sup> the rigid spheres are replaced by a repulsive force inversely proportional to the ninth power of the distance, and the equation for  $V$  becomes

$$V = \kappa_8/r^8 - \kappa_4/r^4.$$

The cross sections of the two models are functions of  $v_{12}$ , and of the energy coefficients  $\kappa_4$  and  $\kappa_8$ . They may be expressed in terms of the distance  $\sigma_{12}$ , at which the potential energy is zero. If the ion and molecule are rigid spheres,  $\sigma_{12}$  is the sum of the radii of the spheres, but if they repel with the inverse ninth power law, it is equal to  $(\kappa_8/\kappa_4)^{1/3}$ . For each model the ratio  $Q/\pi\sigma_{12}^2$  may be expressed as a separate function of the ratio  $\lambda/\mu$ , in which the parameter  $\mu$  is defined by either of the equations

$$1/\mu^2 = \frac{8\pi p \sigma_{12}^4 (m_1 k T_2 + m_2 k T_1)}{(\epsilon-1)e^2 k T_2 (m_1 + m_2)}$$

and

$$1/\mu^2 = \frac{\kappa_8 (m_1 k T_2 + m_2 k T_1)}{\kappa_4^2 (m_1 + m_2)},$$

in which  $p$  is the pressure of the gas. At low velocities,  $Q/\pi\sigma_{12}^2$  for both models varies inversely as  $\lambda/\mu$ . At high velocities, it approaches unity if the ion and molecule are rigid spheres, but diminishes inversely with the square root of  $\lambda/\mu$  if they repel with the inverse ninth power law. The quantity  $(\lambda/\mu)(Q/4\pi\sigma_{12}^2)$  has been tabulated as a function of  $\lambda/\mu$  by Hassé<sup>6</sup> for the model with rigid spheres, and the quantity

$(1/\sqrt{2})(\lambda/\mu)^{1/2}(Q/2\pi\sigma_{12}^2)$  has been tabulated by Hassé and Cook<sup>7</sup> at small values of  $\mu/\lambda$ , and  $(\lambda/\mu)(Q/4\pi\sigma_{12}^2)$  at large values for the model with an inverse ninth power law. Their results have been used in the evaluation of  $\Sigma_1$  and  $\Sigma_2$  by numerical integration.

For each model the ratios  $\Sigma_1/\pi\sigma_{12}^2$  and  $\Sigma_2/\pi\sigma_{12}^2$  may be expressed in terms of  $\mu$  and  $\xi$ . These are functions of both  $T_1$  and  $v$ , and  $T_1$  cannot be eliminated from Eqs. (5) and (6). The variables  $v$  and  $E$  are separated, however, and expressed in terms of  $T_1$  by the introduction of three parameters,  $A$ ,  $B$ , and  $C$ , which are defined and related by the three sets of equations

$$\begin{aligned} A &= \frac{1}{2}\mu\xi(\pi\sigma_{12}^2/\Sigma_1) \\ &= (v/E)\rho^{1/2}(\epsilon-1)^{1/2}\left(\frac{m_1}{m_1+m_2}\right)^{1/2} \\ &= (\rho v/eE)(8\pi\kappa_4/m_2)^{1/2}\left(\frac{m_1}{m_1+m_2}\right)^{1/2}, \end{aligned} \quad (11)$$

$$B = (1/\xi)^2 \frac{\Sigma_1}{\Sigma_2 - \Sigma_1} = \frac{2k(T_1 - T_2)}{m_2 v^2}, \quad (12)$$

$$C = \frac{\Sigma_1}{\Sigma_2 - \Sigma_1} = \frac{m_1 k (T_1 - T_2)}{m_1 k T_2 + m_2 k T_1}, \quad (13)$$

in which  $\rho$  is the density of the gas.

Values of  $A$ ,  $B$  and  $C$  for various values of  $\xi$  are tabulated as a function of  $1/\mu$ , in Table I for the model with rigid spheres, and in Table II for the model with an inverse ninth power law. Curves of  $A$  and  $B$  for various values of  $1/\mu$  are plotted against  $C$  in Figs. 3 to 6.  $\mu$  and  $C$  contain  $T_1$  but not  $v$  and  $E$ . The drift velocity  $v$  and the mobility  $v/E$  may therefore be calculated from the curves for a given value of  $T_1$ .

If  $1/\mu$  is set equal to zero, the theory of small ions is obtained. The parameter  $A$  has the value 0.5105 and  $B$  the value  $\frac{2}{3}$ . The drift velocity  $v$  is then expressed by the equation

$$v = \frac{(0.5105)E}{\rho^{1/2}(\epsilon-1)^{1/2}} \left(\frac{m_1+m_2}{m_1}\right)^{1/2}.$$

If  $\mu$  itself is set equal to zero, the attractive forces are eliminated, and  $\Sigma_1$  and  $\Sigma_2$  may be

<sup>5</sup> H. R. Hassé and W. R. Cook, Proc. Roy. Soc. **A125**, 196 (1929); Phil. Mag. **12**, 554 (1931).

<sup>6</sup> H. R. Hassé, Phil. Mag. **1**, 139 (1926).  $(\lambda/\mu)(Q/4\pi\sigma_{12}^2)$  is represented in his notation by  $y$ , and  $\lambda/\mu$  by  $z\lambda$ .

<sup>7</sup> Reference 5.  $(1/\sqrt{2})(\lambda/\mu)^{1/2}(Q/2\pi\sigma_{12}^2)$  is represented in their notation by  $I_1/2\pi$ ,  $\mu/\lambda$  by  $k$ , and  $(\lambda/\mu)(Q/4\pi\sigma_{12}^2)$  by  $Y_1$ .

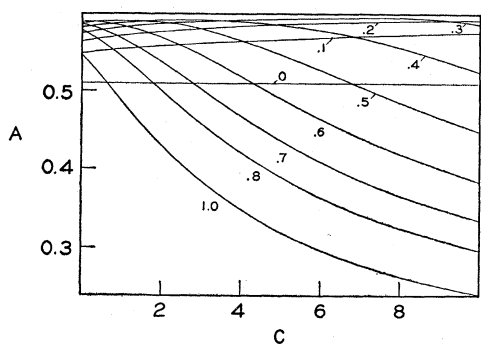


FIG. 3. The parameter *A* for the model with rigid spheres, at various values of  $1/\mu$ .

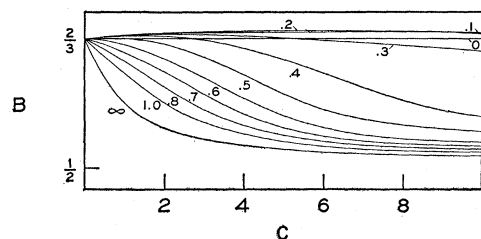


FIG. 4. The parameter *B* for the model with rigid spheres, at various values of  $1/\mu$ .

TABLE I. Parameters for the model with rigid spheres.

| $1/\mu$ | $\xi=1.0$ |       |       | $\xi=2.0$ |       |      |
|---------|-----------|-------|-------|-----------|-------|------|
|         | A         | B     | C     | A         | B     | C    |
| 0.1     | 0.553     | 0.669 | 0.669 | 0.561     | 0.673 | 2.69 |
| .2      | .570      | .670  | .670  | .579      | .674  | 2.70 |
| .3      | .581      | .669  | .669  | .589      | .672  | 2.69 |
| .4      | .588      | .669  | .669  | .592      | .667  | 2.67 |
| .5      | .591      | .667  | .667  | .584      | .650  | 2.60 |
| .6      | .588      | .663  | .663  | .559      | .628  | 2.51 |
| .7      | .577      | .657  | .657  | .523      | .611  | 2.44 |
| .8      | .559      | .649  | .649  | .486      | .592  | 2.37 |
| 1.0     | .509      | .636  | .636  | .416      | .574  | 2.30 |

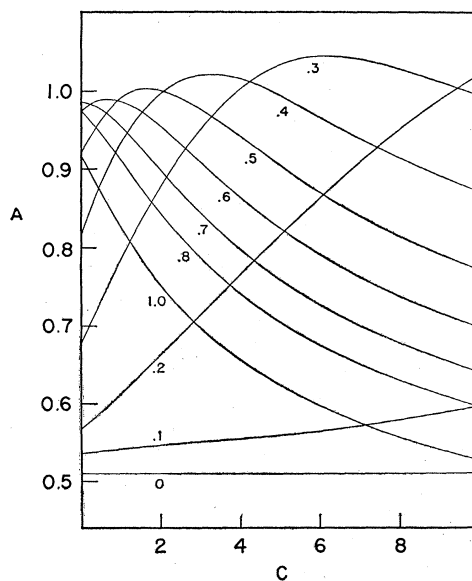


FIG. 5. The parameter *A* for the model with an inverse ninth power law, at various values of  $1/\mu$ .

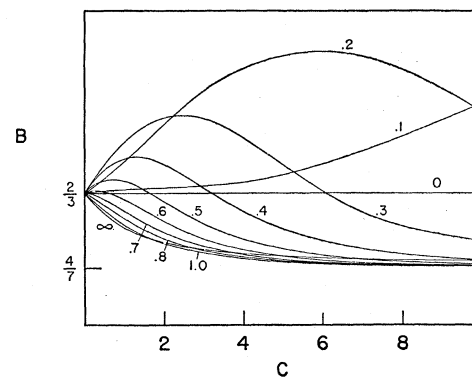


FIG. 6. The parameter *B* for the model with an inverse ninth power law, at various values of  $1/\mu$ .

TABLE II. Parameters for the model with an inverse ninth power law.

| $1/\mu$ | $\xi=1.0$ |       |       | $\xi=1.6$ |       |       | $\xi=2.0$ |       |      | $\xi=3.0$ |       |      | $\xi=4.0$ |       |       |
|---------|-----------|-------|-------|-----------|-------|-------|-----------|-------|------|-----------|-------|------|-----------|-------|-------|
|         | A         | B     | C     | A         | B     | C     | A         | B     | C    | A         | B     | C    | A         | B     | C     |
| 0.1     | 0.541     | 0.670 | 0.670 | 0.546     | 0.673 | 1.722 | 0.550     | 0.675 | 2.70 | 0.568     | 0.710 | 6.39 | 0.639     | 0.873 | 13.96 |
| .2      | .600      | .693  | .693  | .661      | .751  | 1.921 | .726      | .803  | 3.21 | .931      | .835  | 7.51 | 1.052     | .715  | 11.44 |
| .3      | .760      | .718  | .718  | .875      | .763  | 1.952 | .954      | .761  | 3.04 | 1.043     | .669  | 6.02 | .999      | .608  | 9.72  |
| .4      | .908      | .705  | .705  | .990      | .707  | 1.809 | 1.018     | .682  | 2.73 | .978      | .612  | 5.51 | .883      | .583  | 9.33  |
| .5      | .977      | .684  | .684  | 1.002     | .665  | 1.703 | .988      | .640  | 2.56 | .891      | .593  | 5.34 | .787      | .576  | 9.21  |
| .6      | .989      | .667  | .667  | .968      | .641  | 1.641 | .931      | .619  | 2.48 | .814      | .585  | 5.27 | .714      | .574  | 9.18  |
| .7      | .969      | .654  | .654  | .919      | .627  | 1.605 | .872      | .608  | 2.43 | .750      | .582  | 5.23 | .656      | .573  | 9.16  |
| .8      | .933      | .647  | .647  | .869      | .619  | 1.585 | .817      | .603  | 2.41 | .698      | .580  | 5.22 | .609      | .573  | 9.16  |
| 1.0     | .854      | .639  | .639  | .780      | .612  | 1.566 | .728      | .598  | 2.39 | .618      | .579  | 5.21 | .539      | .573  | 9.17  |

expanded into rapidly converging power series in  $\xi$ . In the case of rigid spheres the drift velocity  $v$  is given at small values of  $\xi$  by the equation

$$v = \frac{eE}{(8/3)n_2\sigma_{12}^2(2\pi kT_2)^{\frac{1}{2}}} \left( \frac{m_1+m_2}{m_1m_2} \right)^{\frac{1}{2}},$$

which represents one form of the conventional kinetic theory formula. For other values of  $\xi$  it is convenient to introduce a fourth parameter  $D_\infty$ , defined by the equations

$$D_\infty = \frac{1}{4}\pi^{\frac{1}{2}}\xi^2 \left( \frac{\pi\sigma_{12}^2}{\Sigma_1} \right) = (\rho v^2/eE)(\pi\sigma_{12}^2) \left( \frac{m_1}{m_1+m_2} \right).$$

Values of  $B$ ,  $C$ , and  $D_\infty$  are tabulated in Table III as a function of  $\xi$ .

On the other hand, if the repulsive force varies inversely as the ninth power of the distance,  $v$  is given at small values of  $\xi$  by the equation

$$v = \frac{eE}{(5.789)n_2(\kappa_8 kT_2)^{\frac{1}{2}}} \left( \frac{m_1+m_2}{m_1m_2} \right)^{\frac{1}{2}}.$$

For other values of  $\xi$ , it is convenient to introduce another parameter  $D_9$ , defined by the equations

$$D_9 = \frac{1}{4}\pi^{\frac{1}{2}}\mu^{\frac{1}{2}}\xi^{\frac{3}{2}}(\pi\sigma_{12}^2/\Sigma_1) \\ = (\rho v^{\frac{3}{2}}/eE)\pi(2\kappa_8/m_2)^{\frac{1}{2}} \left( \frac{m_1}{m_1+m_2} \right)^{\frac{3}{2}}.$$

Values of  $B$ ,  $C$  and  $D_9$  are tabulated in Table IV.

TABLE III. Parameters for rigid spheres with no attractive forces.

| $\xi$    | $B$           | $C$      | $D_\infty$ |
|----------|---------------|----------|------------|
| 0.0      | $\frac{2}{3}$ | 0.0      | 0.0        |
| .2       | 0.663         | 0.0265   | 0.132      |
| .4       | .654          | .1046    | .258       |
| .6       | .639          | .230     | .373       |
| .8       | .623          | .399     | .474       |
| 1.0      | .607          | .607     | .560       |
| 1.2      | .592          | .852     | .632       |
| 1.4      | .578          | 1.133    | .691       |
| 1.6      | .566          | 1.449    | .739       |
| 1.8      | .557          | 1.803    | .778       |
| 2.0      | .549          | 2.19     | .810       |
| 2.2      | .542          | 2.62     | .836       |
| 2.4      | .537          | 3.09     | .858       |
| 2.6      | .532          | 3.60     | .875       |
| 2.8      | .528          | 4.14     | .890       |
| 3.0      | .525          | 4.72     | .903       |
| 3.5      | .520          | 6.36     | .926       |
| 4.0      | .515          | 8.23     | .942       |
| $\infty$ | $\frac{1}{2}$ | $\infty$ | 1.000      |

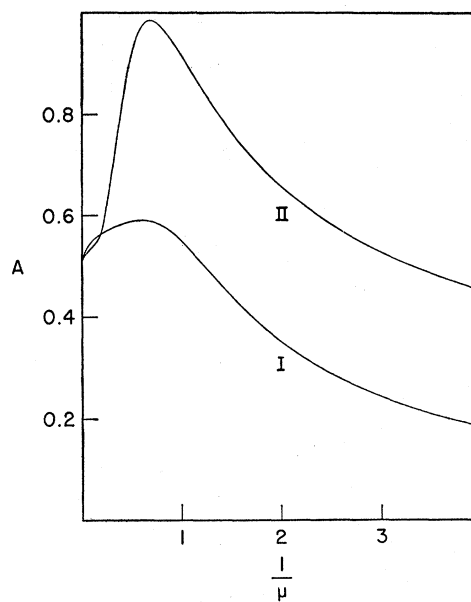


FIG. 7. The parameter  $A$  for weak fields. Curve I, Langevin's theory for rigid spheres; curve II, Hassé and Cook's theory for the inverse ninth power law.

When the drift velocity is small, the mobility is independent of field intensity. Values of  $A$  in this case have been tabulated by Hassé<sup>8</sup> as a function of  $1/\mu$  for the model with rigid spheres, and values of the quantity  $\frac{3}{16}\sqrt{2}(\mu^{\frac{1}{2}}/A)$  have been tabulated by Hassé and Cook<sup>9</sup> for the model

TABLE IV. Parameters for an inverse ninth power law with no attractive forces.

| $\xi$    | $B$           | $C$      | $D_9$ |
|----------|---------------|----------|-------|
| 0.0      | $\frac{2}{3}$ | 0.0      | 0.0   |
| .2       | 0.665         | 0.0266   | 0.342 |
| .4       | .660          | .1056    | .478  |
| .6       | .653          | .235     | .574  |
| .8       | .644          | .412     | .648  |
| 1.0      | .635          | .635     | .704  |
| 1.2      | .626          | .902     | .747  |
| 1.4      | .618          | 1.211    | .781  |
| 1.6      | .611          | 1.564    | .807  |
| 1.8      | .605          | 1.961    | .827  |
| 2.0      | .600          | 2.402    | .843  |
| 2.2      | .596          | 2.887    | .856  |
| 2.4      | .593          | 3.416    | .866  |
| 2.6      | .590          | 3.990    | .874  |
| 2.8      | .588          | 4.61     | .881  |
| 3.0      | .586          | 5.27     | .887  |
| 3.5      | .582          | 7.13     | .897  |
| 4.0      | .580          | 9.28     | .904  |
| $\infty$ | 4/7           | $\infty$ | .9284 |

<sup>8</sup> Reference 6.  $1/\mu$  is represented in his notation by  $\lambda$ .

<sup>9</sup> Reference 5.  $\frac{3}{16}\sqrt{2}(\mu^{\frac{1}{2}}/A)$  is represented in their notation by  $I(s)$ .  $1/\mu$  may be identified with their parameter  $s$ .

with an inverse ninth power law. Their results are reproduced in Fig. 7 for comparison. Curve I is a plot of  $A$  as a function of  $1/\mu$  for the model with rigid spheres, and curve II is the corresponding plot for the model with an inverse ninth power law.

As the drift velocity is increased, the parameter  $C$  approaches the ratio  $m_1/m_2$ ,  $1/\mu$  becomes large, and the parameters  $D_\infty$  and  $D_9$  approach the corresponding values in Tables III and IV. In the case of rigid spheres, the velocity then varies directly, and the mobility inversely as the square root of  $E/p$ . If the repulsive force obeys the inverse ninth power law, the velocity varies directly as the two-thirds power of  $E/p$ , and the mobility varies inversely as the cube root of  $E/p$ .

Although the theory is not exact, the general formulae should not be seriously in error.

Chapman,<sup>10</sup> Enskog,<sup>11</sup> and Pidduck<sup>2</sup> have shown that at low  $E/p$  the error is no greater than a few percent. Comparison with experiment,<sup>12</sup> however, indicates that the repulsive force varies with distance to a higher power than nine. The correct law may eventually be found through accurate measurements of the scattering and retardation of ion beams. The use of classical cross sections also introduces error at low velocities, and at low temperatures, but this is less important at high velocities where classical and quantum theories converge.

The writer takes pleasure in thanking Professor Leonard B. Loeb for several stimulating discussions of this subject.

<sup>10</sup> S. Chapman, Phil. Trans. **A217**, 115 (1917).

<sup>11</sup> D. Enskog, *Kinetische Theorie der Vorgänge in mässig verdünnten Gasen*, Inaugural Dissertation, Upsala, 1917.

<sup>12</sup> A. F. Pearce, Proc. Roy. Soc. **A155**, 490 (1936); A. V. Hershey, preceding paper.

## Antiferromagnetism in Some Manganous Compounds\*

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The temperature dependence (300°K to 40°K) of the magnetic susceptibility of the following  $Mn^{++}$  salts has been measured: MnO, MnS, MnSe, MnTe. A  $\lambda$ -point transition at low temperatures makes the susceptibility break away from a Weiss-Curie law and decrease with lowering temperatures. Each salt has its characteristic transition temperature, increasing with increasing molecular weight. Evidence for field dependence of the susceptibility and for magnetic hysteresis has been found. It seems likely that an exchange force is the cause of the transition from paramagnetism to antiferromagnetism.

### INTRODUCTION

THE paramagnetic susceptibility of salts usually obeys a Weiss-Curie law:  $\chi = C/(T - \Theta)$  where the constant  $C$  is the Curie constant,  $T$  the absolute temperature, and  $\Theta$  the point where the straight line  $1/\chi$  intersects the temperature axis. Deviations from this law have been observed in several salts<sup>1</sup> at low temperatures. The

experiments described in this paper are on the following  $Mn^{++}$  salts: MnO, MnS, MnSe, MnTe. At a temperature, characteristic for each salt, the susceptibility breaks away from the Weiss-Curie law and decreases with lowering of temperature.

Kelley<sup>2</sup> has measured the specific heat of Mn, MnSe, and MnTe; in the latter two compounds he has found a hump or abnormal specific heat. Measurements on MnO and MnS by Millar<sup>3</sup> and Anderson<sup>4</sup> each show a hump in the specific

\* The electrical conductivity as a function of temperature has been measured for these compounds. Details are described in a Letter to the Editor, Charles F. Squire, Phys. Rev., this issue.

<sup>1</sup> M. and B. Ruhemann, *Low Temperature Physics* (Cambridge, 1937), Chapter II.

<sup>2</sup> K. K. Kelley, J. Am. Chem. Soc. **61**, 203 (1939).

<sup>3</sup> R. W. Millar, J. Am. Chem. Soc. **50**, 1875 (1928).

<sup>4</sup> Anderson, J. Am. Chem. Soc. **53**, 476 (1931).