

## Measurements of the Mobility of Potassium Ions at High Field Intensity and Low Pressure

ALLEN V. HERSHEY

*University of California, Berkeley, California*

(Received July 12, 1939)

The mobility of potassium ions in the gases  $H_2$ , He,  $N_2$ , and A has been measured by the Townsend method, in which a beam of ions is deflected by a magnetic field. When the mobility is reduced to 760 mm of mercury and  $20^\circ C$  it should be expressible as a function of the ratio of electric intensity  $E$  to the pressure  $p$ . This is true at the highest pressures investigated but not at the lowest, apparently because of a breakdown in the method. At small values of  $E/p$  the results agree to within a few percent with the measurements by the Tyndall and Powell method. As  $E/p$  is increased, the mobility is at first constant. It then rises, passes through a peak, and finally falls. Pronounced peaks appear in the curves for  $H_2$ ,  $N_2$ , and A but not for He. The mobility is constant only in weak fields

where the ions and molecules interact with a frequency which is independent of the drift velocity of the ions. The rise in mobility with increase in  $E/p$  may be interpreted as the result of a decrease in the effectiveness of the forces of attraction between the ions and molecules. As the drift velocity exceeds the thermal velocities of the molecules, the collision frequency becomes greater, and the mobility finally falls. Langevin's theory of mobility may be generalized to express the variation with  $E/p$ . It is in qualitative agreement with the experimental results, but fails to account for more than a suggestion of the peaks. They are accounted for, however, by a generalization of Hassé and Cook's theory. The experimental data are bracketed by the two theories.

### INTRODUCTION

MEASUREMENTS of the mobility of ions of high velocity have been prevented in the past by experimental difficulties. It has not been possible to control the high frequency alternating potentials which are required by both the square wave and the electrical shutter methods. On the other hand, only constant potentials are required by the Townsend<sup>1</sup> method, and reliable data should be obtainable by its use.

The Townsend method consists in deflecting a beam of ions in a uniform electric field by an orthogonal magnetic field. The ion beam is received by three coplanar collecting plates which are separated by narrow slits. To obtain the magnetic intensity corresponding to a known deflection, the field is adjusted until the ion beam is centered over first one slit, and then the other. The use of two slits makes unnecessary an accurate knowledge of the position of the source of ions. The relation between mobility, deflection, and magnetic intensity does not explicitly contain the electric intensity.

Townsend and Bailey<sup>2</sup> have shown that the drift velocity of electrons may be expressed as a function of the ratio of electric intensity  $E$  to

pressure  $p$ , and numerous investigators<sup>3</sup> have demonstrated that the drift velocity of normal ions is inversely proportional to the pressure from a few mm of mercury to many atmospheres. Ions of high velocity are therefore to be found at large values of  $E/p$ . A limitation on the range of measurement is set by the sparking potential of the gas. The value of  $E/p$  at which a glow discharge occurs is known<sup>4</sup> to increase with decrease in pressure. The mobility of potassium ions in the gases  $H_2$ , He,  $N_2$ , and A has accordingly been investigated at low pressures by the Townsend method.

The investigation of mobility in a given gas is restricted to low pressure by the magnitude of the available magnetic field, but if the pressure is too low, the ions must travel too great a distance before they reach a terminal energy. On the other hand, if the apparatus is evacuated, it may be used to measure the ratio  $e/m$  of the ions under investigation.

### APPARATUS AND PROCEDURE

Details of the glass chamber with which the measurements were made are shown in Fig. 1.

<sup>1</sup> J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. **A88**, 336 (1913).

<sup>2</sup> J. S. Townsend and V. A. Bailey, Phil. Mag. **42**, 874 (1921); **44**, 1033 (1922); **46**, 657 (1923).

<sup>3</sup> A. F. Kovarik, Proc. Roy. Soc. **A86**, 154 (1912); A. J. Dempster, Phys. Rev. **34**, 53 (1912); McLennan and Keys, Phil. Mag. **30**, 484 (1915); W. Todd, Phil. Mag. **25**, 163 (1913).

<sup>4</sup> Paschen, Ann. d. Physik **37**, 69 (1889).

The ions were emitted at  $F$  in the form of a beam by a heated platinum filament which had been coated with Kunsman's<sup>5</sup> catalyst. The heated filament constituted a source of error since it maintained a density gradient in the gas. Error also arose from the finite distance through which the ions were accelerated. An attempt was made to eliminate both errors by mounting the source on a slide so that the ions could be made to traverse various distances in the gas. If the errors were constant, it should have been possible to cancel them out by making measurements at two different positions of the filament. Motion of the slide was transmitted through the wall of the chamber by an electromagnetic device at  $A$  in Fig. 1.

The electric field was maintained constant by an Evans<sup>6</sup> stabilizer. It was maintained uniform by a series of brass guard rings. Electrical connections to each ring were lead directly out through the wall of the chamber by separate tungsten to glass seals, so that the gas would have as little opportunity to break down as possible. The space occupied by the field was closed at  $F$  by a disk mounted on the slide. The filament occupied a slot in the disk and was coplanar with its surface. To avoid distortion of the field, the slide was always located in such a position that the face of the disk was coplanar with the median plane of the adjacent guard ring. The electric field was not uniform in the immediate vicinity of the edge of each guard ring, and the amount of deviation was estimated. It was less than one percent up to within one-half centimeter from the edge. The effectiveness of the guard rings as a shield against external fields was also investigated. Estimation of the greatest possible penetration of field showed that any distortion at the center of the chamber was negligible.

The ion beam was divided into sections by the three collecting plates 1, 2, and 3 in Fig. 1, which were coplanar with the last guard ring. The plates were all cut to the same width, so that the currents to two adjacent plates would be equal, if the beam were centered over the slit between them. The outer plates were fitted with projections to catch any ions that missed the center plate. Thus at low pressures the beam was divided by the edge

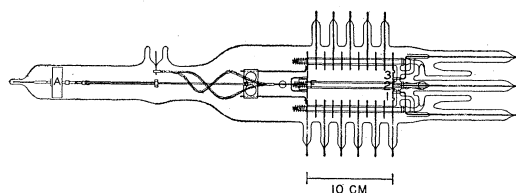


FIG. 1. The mobility chamber.

of the center plate. At high pressures, however, the ions followed the lines of force, and the beam was divided at the center of the slit between the plates. The division lines for intermediate pressures were found by a step by step integration of the equation of motion. The field of force was derived from the potential of a deep slot cut in a plane conductor. In  $H_2$  and He at the lowest pressure investigated, the effective width of the center plate was equal to the true width for all values of  $E/p$ , and at the next intermediate pressure, for large values of  $E/p$ . At higher pressures in  $H_2$  and He, and at all pressures in  $N_2$  and A the effective width was equal to the distance between the centers of the slits, and exceeded the true width by four percent.

The currents to two adjacent collecting plates were compared by observing with an electrometer, the rate at which they charged free conductors. Details of the electrometer connections are shown in Fig. 2. The center plate was connected to one pair of quadrants, and one outer plate to the other pair. The idle plate was grounded. Complications from fluctuations in the ion emission of the filament were avoided by the use of a null method. Before measurement the system was so adjusted that the electrometer needle would remain stationary if the currents were equal. The coefficients of capacity and induction of the four conductors 1, 2, 3 and 4 in Fig. 2 were evaluated by a series of experiments in which selected conductors were charged, and the charges were then shared. The coefficients were adjusted by trial until they satisfied the conditions for balance. Allowance was made for the slow drift of the electrometer which resulted from leakage and radioactive contamination.

The magnetic field was maintained constant by a Thyatron regulator.\* The intensity was

<sup>5</sup> C. H. Kunsman, J. Frank. Inst. 203, 635 (1927).

<sup>6</sup> R. D. Evans, Rev. Sci. Inst. 5, 371 (1934).

\* The use of a sensitive method of control in this regulator made possible the omission of mechanical stages. A description may be published later.

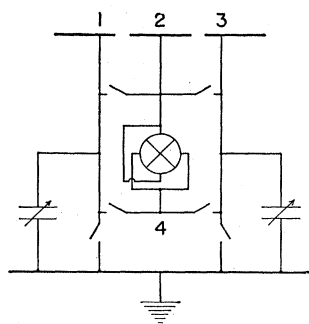


FIG. 2. Electrometer connections.

measured with a flip coil circuit whose electrical properties could be calculated accurately from geometrical dimensions. The field between the poles of the electromagnet was explored to determine the amount of deviation from uniformity. In the space occupied by the ion beam the deviation did not exceed one percent.

The gas pressure was measured with a pair of McLeod gages, each of which covered a different range. The gages registered only the partial pressure of the noncondensable component of the gas. The condensable component, mercury vapor, was excluded from the chamber by a liquid-air trap. The mean free path of the molecules of the gas was small by comparison with the dimensions of the system. The vapor pressure of mercury at the temperature of the gages was therefore added to the gage pressures to obtain the nearly uniform total pressure. The correction amounted at most to only a few percent.

The temperature was obtained with a thermometer just outside of the chamber. Heating of the gas inside by the filament set up a temperature gradient along the axis of the chamber. The temperature was estimated by a heat transfer analysis and corrections to the thermometer readings were calculated for a point midway between the filament and the collector system. They were tested on a discarded chamber into which thermocouples had been inserted. The corrections varied with pressure from  $1^\circ$  to  $2.5^\circ$  in  $H_2$ , and from  $1^\circ$  to  $3.5^\circ$  in He, but in  $N_2$  and Ar they amounted to  $1^\circ$ .

All gases were obtained from commercial tanks and were purified. The hydrogen was passed first through a trap filled with copper at  $350^\circ$ , then one with potassium hydroxide. These did not

remove traces of nitrogen which the hydrogen may have contained. The helium was passed over a liquid-air trap filled with charcoal, and was then exposed to a calcium arc to remove any traces of hydrogen or methane. The argon was also exposed to the calcium arc. The nitrogen was passed first through a trap filled with copper oxide, then one with copper, both at  $350^\circ$  to remove any traces of ammonia, oxygen, or oxides of nitrogen. The manufacturers of the gases claimed the purity of the hydrogen to be 99 percent; of the helium, 95 percent; of the argon, 99 percent; and of the nitrogen, 99.5 percent.

The chamber was baked out at  $300^\circ$  before insertion between the pole pieces of the electromagnet. The pressure recovered at a rate less than  $10^{-4}$  mm of mercury per day. The chamber was continuously separated from the rest of the system by the liquid-air trap. Readings were taken with the filament located at 5 cm and at 10 cm from the collector system. The magnetic field was adjusted in each experiment to bring the electrometer needle nearly to rest, and the electrometer rate was noted. The magnetic intensity was measured with two consecutive flips of the flip coil and the average was obtained. The direction of motion of the electrometer needle was reversed by a slight shift in field, and the measurements were repeated. The field was reversed and the procedure was repeated for the other slit. That magnetic intensity was found by graphical interpolation, which would have made the electrometer drift at the same rate as it drifted in the absence of any ion current.

During the investigation of mobility, the molecular weight of the ions was checked occasionally, by measurements of the deflection of the beam in a vacuum. Measurements were first attempted with a sodium catalyst, but were upset by traces of potassium contamination. A pure potassium catalyst was finally prepared, which emitted ions with a molecular weight of  $40 \pm 1$ .

#### METHOD OF ANALYSIS

An ideal theoretical interpretation of the experimental data would require a knowledge of the steady-state distribution in phase space of ions under the influence of electric and magnetic

fields. The interpretation may be simplified, however, in the case of heavy ions in light gases. The ions lose only a small fraction of momentum in each collision with a molecule, and almost continuous resistance is exerted upon them by the gas. They should therefore drift with a velocity  $\mathbf{v}$ , which is governed approximately by the vector equation

$$\mathbf{f} = e\mathbf{E} + (e/c)\mathbf{v} \times \mathbf{H} - (e/k)\mathbf{v} = m\dot{\mathbf{v}}. \quad (1)$$

In this equation the total force  $\mathbf{f}$  is equated to the sum of the electric force  $e\mathbf{E}$ , the magnetic force  $(e/c)\mathbf{v} \times \mathbf{H}$ , and the resistance  $-(e/k)\mathbf{v}$ . When the ions reach the terminal velocity, the acceleration  $\dot{\mathbf{v}}$  vanishes, and the velocity  $\mathbf{v}$  makes with the electric intensity  $\mathbf{E}$  an angle  $\theta$ , which is related to the magnetic intensity  $H$  and the mobility  $k$  by the equation<sup>1</sup>

$$\tan \theta = Hk/c. \quad (2)$$

If  $H$  is expressed in gauss,  $k$  is obtained in  $(\text{cm})^2/(\text{sec.})(\text{volt})$  by the substitution of  $10^8$  for  $c$ . In the absence of a magnetic field,  $k$  is equal to the ratio  $v/E$ .

The ions describe a curved path as they leave the source, but at a distance they pick up the terminal velocity and the ion beam should approach a straight line. A curved beam is illustrated with great exaggeration in Fig. 3. If two points on the beam are known, and a straight line is drawn between them, the direction of the line is, by Rolle's theorem, the direction of the beam at some point between. The further the points are from the source, the more nearly is the direction defined by the mobility. If  $x$  and  $y$  are the Cartesian coordinates of the displacement of the ion, and the  $x$  axis is taken parallel to the electric field, the straight line may be expressed by the equation

$$\tan \theta = y/(x - x_0) = Hk/c,$$

in which  $x_0$  is the coordinate of the point of intersection of the line and the axis of the chamber. Measurement of  $H$  for two values of  $x$  would make possible the elimination of  $x_0$ . If  $x_1$  and  $x_2$  are the two values of  $x$ , and  $H_1$  and  $H_2$  are the corresponding field intensities,  $x_0$  and  $k$  are ex-

pressed by the equations

$$x_0 = \frac{x_2 H_2 - x_1 H_1}{H_2 - H_1}, \quad (3)$$

$$k = \frac{yc(H_1 - H_2)}{(x_2 - x_1)H_1 H_2}. \quad (4)$$

For a given value of  $x$ ,  $y$  is a linear function of  $H$ . Changes in  $y$ ,  $H_1$ , and  $H_2$  which correspond to deflections of the beam from one slit to the other may therefore be substituted for the variables themselves. The values of  $k$  which are given by Eq. (4) may also be obtained by a linear extrapolation to  $1/x = 0$  in a plot of  $yc/xH$  against  $1/x$ .

In a vacuum those ions that start from rest describe a cycloid. The equation of the cycloid may be found in terms of Cartesian coordinates from scalar equations equivalent to Eq. (1). Omission of terms containing  $k$ , integration, substitution of initial conditions, elimination of the time, and expansion in a power series lead to the equation

$$y = \frac{2}{3}x^{\frac{3}{2}} \left( \frac{eH^2}{2mc^2E} \right)^{\frac{1}{2}} + \frac{1}{5}x^{5/2} \left( \frac{eH^2}{2mc^2E} \right)^{\frac{3}{2}} + \dots, \quad (5)$$

with which the ratio  $e/m$  may be computed by successive approximations. In a vacuum also, uncertainty in the position of the ion source may be eliminated by two measurements. Eq. (5) may be modified by the substitution of  $x - x_0$  for  $x$ , and  $x_0$  may be eliminated from numerical equations containing experimental values of  $x_1$ ,  $x_2$ ,  $H_1$ , and  $H_2$ .

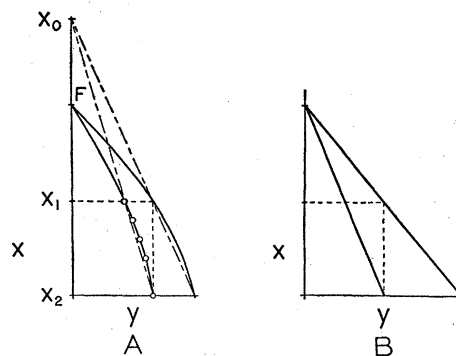


FIG. 3. The shape of the ion beam for two positions of the filament; A, if  $y$  and  $H$  were proportional; B, if the beam were straight.  $H_1 = 1.53H_2$ .  $K^+$  in A;  $p = 0.1$  mm;  $E/p = 112$ .

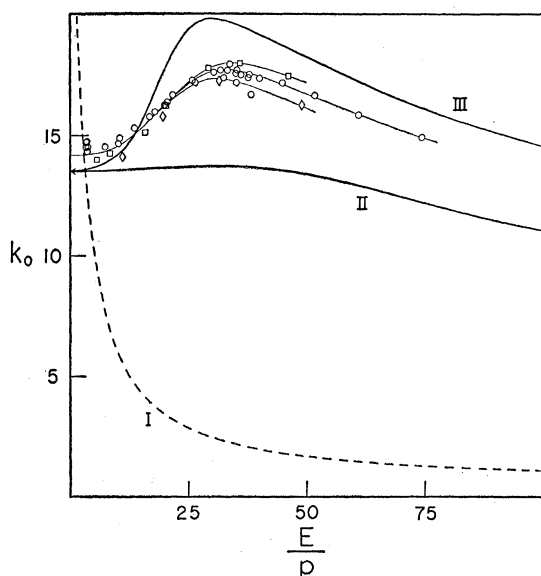


FIG. 4. The mobility of  $K^+$  in  $H_2$ .  $\diamond$ , 0.25 mm;  $\circ$ , 0.85 mm;  $\square$ , 2.7 mm.

#### THE MOBILITY

Values of the mobility have been calculated from the experimental data by Eq. (4), and have been reduced to 760 mm of mercury, and  $20^\circ C$  by the perfect gas law. The reduced mobility  $k_0$  is plotted against  $E/p$  in Figs. 4 to 7.  $k_0$  is expressed in  $(cm)^2/(\text{sec.})(\text{volt})$ ,  $E$  in  $(\text{volt})/(\text{cm})$  and  $p$  in mm of mercury. Experimental values of the drift velocity  $v$  at  $20^\circ$  may be obtained by the multiplication of  $k_0$  with the factor  $(760)(E/p)$ .  $k_0$  should therefore be expressible as well as  $v$  as a function of  $E/p$ , and a single curve should appear at all pressures. Instead, the curves for various pressures are spread out to an extent which becomes progressively worse as the molecular weight is increased. There is internal evidence, however, that the experimental values are meaningless at the lowest pressure. Thus a nearly twofold increase in  $H$  should accompany a decrease in  $\alpha$  to one-half. In argon at the lowest pressure and at the highest  $E/p$ , the factor of increase is only 1.53. The discrepancy may be attributed either to a strongly curved ion beam, whose deflection is proportional to  $H$ , or to a straight beam whose deflection is not proportional. The two alternatives are illustrated in Fig. 3 by the curves  $A$  and  $B$ , which are based on measurements with the filament at 6, 7, and 8 cm

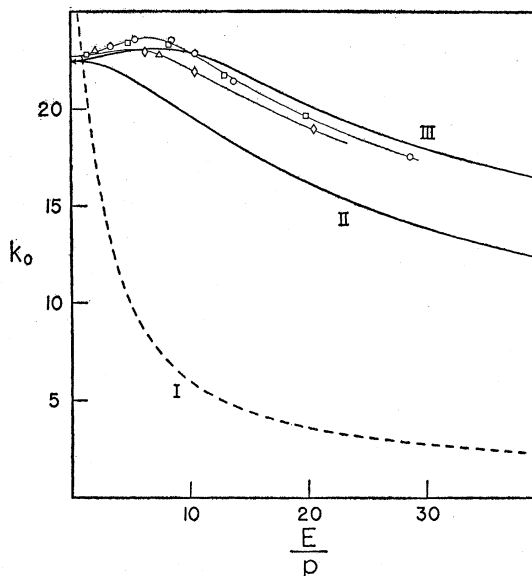


FIG. 5. The mobility of  $K^+$  in He.  $\diamond$ , 0.45 mm;  $\circ$ , 0.95 mm;  $\square$ , 1.95 mm;  $\Delta$ , 3.8 mm.

as well as at 5 and 10 cm. The discrepancy disappears as the pressure is increased, and inspection of Figs. 4 to 7 shows also that  $k_0$  approaches a limit. The conclusion may therefore be drawn safely that  $k_0$  is a function of  $E/p$ , and that it would be represented in the figures by curves which would lie slightly above the highest experimental points. The appearance of several curves cannot be ascribed to the formation of complex ions, because the mobility would then be lower at higher pressure. It probably arises from a failure of the ions to comply with Eq. (1).

At small values of  $E/p$  the results agree to within a few percent with the measurements by Tyndall and Powell,<sup>7</sup> and by Powell and Brata,<sup>8</sup> which are indicated for comparison in Figs. 4 to 7 by arrows at the border. As  $E/p$  is increased the mobility is at first constant. It then rises, passes through a peak, and finally falls. Pronounced peaks appear in the curves for  $H_2$ ,  $N_2$ , and  $A$ , but not for He. A constant mobility at low  $E/p$  has been observed by Loeb<sup>9</sup> and by Yen<sup>10</sup> with normal ions at atmospheric pressure. The rise in mobility with increase in  $E/p$  has been reported

<sup>7</sup> A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. **A136**, 145 (1932).

<sup>8</sup> C. F. Powell and L. Brata, Proc. Roy. Soc. **A138**, 117 (1932).

<sup>9</sup> L. B. Loeb, Phys. Rev. **8**, 633 (1916).

<sup>10</sup> K. L. Yen, Phys. Rev. **11**, 337 (1918).

for alkali ions in  $N_2$  by Mitchell and Ridler,<sup>11</sup> whose result with  $K^+$  is indicated in Fig. 6 by curve *a*. The subsequent decrease has been found by Townsend and Bailey<sup>2</sup> with electrons.

#### COMPARISON WITH THEORY

The variation of mobility with increase in  $E/p$  may be explained qualitatively in terms of the forces which act between the ions and molecules. At low field intensities the mobility would be two or three times higher if the ions and molecules were simple rigid elastic spheres. The mean free path, and hence also the mobility, are lowered by forces of attraction which arise from polarization of the molecule by the charged ions, and van der Waals interactions. As the speed is increased, the attractive forces have less time to act. The rise in mobility with increase in  $E/p$  may be interpreted as the result of the decrease in the effectiveness of the attractive forces. The presence of peaks in the curves for  $H_2$ ,  $N_2$ , and A may be associated with the greater polarizability of these gases.

Collisions with the molecules remove momentum from the ions as rapidly as they pick it up from the field. The momentum is transferred at a

rate which is proportional to the product of the momentum, the fractional loss of momentum per collision, and the frequency of collision. At low field intensities the collision frequency is determined primarily by the temperature, and is independent of the drift velocity. The rate of transfer of momentum is directly proportional to the velocity, and the mobility is independent of  $E/p$ . At high field intensities on the other hand, the drift velocity of the ions is greatly in excess of the thermal velocities of the molecules. The collision frequency is then proportional to the product of the collision cross section and the velocity. If the ions and molecules were rigid elastic spheres, the collision cross section would be constant. The rate of transfer of momentum would therefore be proportional to the square of the velocity, and the mobility would vary inversely with the square root of  $E/p$ . Actually the ions and molecules are not rigid. The collision cross section continues to diminish as the velocity is increased, and the mobility varies more slowly than inversely with the square root of  $E/p$ .

A formula has been derived by Compton and Langmuir<sup>12</sup> to express the transition from independence of  $E/p$  to inverse proportionality to

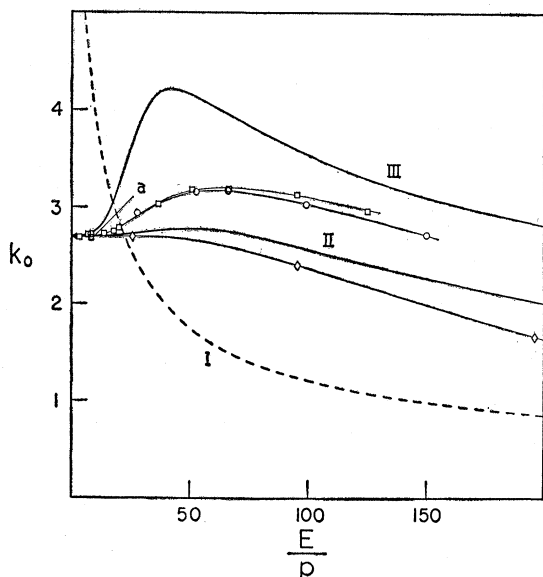


FIG. 6. The mobility of  $K^+$  in  $N_2$ .  $\diamond$ , 0.1 mm;  $\circ$ , 0.3 mm;  $\square$ , 0.7 mm.

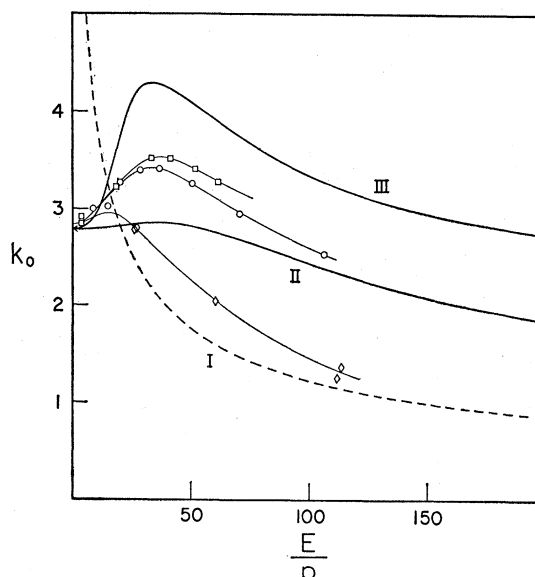


FIG. 7. The mobility of  $K^+$  in A.  $\diamond$ , 0.1 mm;  $\circ$ , 0.3 mm;  $\square$ , 0.7 mm.

<sup>11</sup> Mitchell and Ridler, Proc. Roy. Soc. **A146**, 911 (1934).

<sup>12</sup> K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 123 (1930).

the square root of  $E/p$ . It is given by the equation

$$k = \frac{(0.815)\lambda_0 e \left[ 1 + \frac{m_1/m_2}{2 + \left( \frac{1}{4} + \frac{\lambda_0^2 E^2 (m_1 + m_2)^2}{(6.57)\Omega^2 m_1 m_2} \right)^{\frac{1}{2}}} \right]^{\frac{3}{2}}}{(2em_1\Omega)^{\frac{1}{2}} \left[ \frac{1}{2} + \left( \frac{1}{4} + \frac{\lambda_0^2 E^2 (m_1 + m_2)^2}{(6.57)\Omega^2 m_1 m_2} \right)^{\frac{1}{2}} \right]^{\frac{3}{2}}}$$

in which  $m_1$  and  $m_2$  are the masses of the ion and molecule,  $\lambda_0$  is the mean free path, and  $e\Omega$  is the average thermal energy of a molecule. In Figs. 4 to 7 the curves labeled I are a plot of the formula. The curves are based on the kinetic theory radii given by Jeans.<sup>13</sup> A radius for the potassium ion was found by reducing the kinetic theory radius of the argon atom in the ratio between the radii calculated by Slater<sup>14</sup> from wave mechanics.

The formula of Compton and Langmuir does not take the attractive forces into account. Furthermore it is not applicable to heavy ions in light gases, since it is based on the assumption that the ions have a random energy which far exceeds the drift energy. On the contrary, the random energy is less than the drift energy. The formula gives too low a mobility since it assumes too high a collision frequency. The discrepancy between the formula and experiment amounts to a factor of nearly ten in  $H_2$ , but diminishes as the molecular weight of the gas is increased.

In Langevin's<sup>15</sup> theory of mobility, the ions and molecules are assumed to be rigid 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 molecules by the ions, and is expressed in terms of the dielectric constant of the gas. In Hassé and Cook's<sup>16</sup> theory, the rigid spheres are replaced by a repulsive force inversely proportional to the ninth power of the distance. Both theories are restricted to weak fields. Generalizations<sup>17</sup> of both to fields

of any strength have been developed, which not only express the transition from a constant mobility to a mobility which diminishes with increase in  $E/p$ , but also take into account the attractive forces, and the dependence of the random energy upon the relative masses of the ions and molecules. In Figs. 4 to 7, the curves labeled II are a plot of the theory for the model with rigid spheres, and the curves labeled III, for the model with an inverse ninth power law of repulsion. The curves are based on molecular force data from the equation of state. Fowler's<sup>18</sup> calculations of intermolecular and interionic energies were extended to ion-molecule combinations. He has correlated the equations of state of gases and crystals in terms of a model with a repulsive energy inversely proportional to the ninth power of the distance, and a van der Waals energy inversely proportional to the sixth power. These correspond respectively to an inverse tenth power law of force, and to an inverse seventh power law. The combined potential energy  $V$  between two molecules may be expressed in terms of the distance  $r$  by the equation

$$V = \lambda/r^9 - \mu/r^6.$$

Fowler has adopted the rule suggested by Lennard-Jones and Taylor<sup>19</sup> for estimating the coefficient  $\lambda_{12}$  in the repulsive energy of two unlike molecules from the coefficients  $\lambda_{11}$  and  $\lambda_{22}$  for the two corresponding combinations of like molecules. The rule is given by the equation

$$\lambda_{12}^{1/9} = \frac{1}{2}(\lambda_{11}^{1/9} + \lambda_{22}^{1/9}).$$

He has expressed the coefficient  $\mu_{12}$  in the van der Waals energy of two unlike molecules in terms of the coefficients  $\mu_{11}$  and  $\mu_{22}$  for like molecules by the equation

$$\mu_{12} = \frac{2(\mu_{11}^2 \mu_{22}^2 / Z_1 Z_2)^{\frac{1}{3}}}{(\mu_{11} / Z_1^2)^{\frac{1}{3}} + (\mu_{22} / Z_2^2)^{\frac{1}{3}}}$$

which is derived from formulae proposed by Slater and Kirkwood<sup>20</sup> for the van der Waals

<sup>13</sup> J. H. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, third edition, 1921), p. 327.

<sup>14</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

<sup>15</sup> Langevin, *Ann. de Chimie et de Physique* **8**, 245 (1905).

<sup>16</sup> H. R. Hassé and W. R. Cook, *Proc. Roy. Soc.* **A125**, 196 (1929); *Phil. Mag.* **12**, 554 (1931).

<sup>17</sup> A. V. Hershey, following paper.

<sup>18</sup> R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, second edition, 1936), Chapter X.

<sup>19</sup> J. E. Lennard-Jones and P. A. Taylor, *Proc. Roy. Soc.* **109**, 476 (1925).

<sup>20</sup> J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931); *J. G. Kirkwood, Physik. Zeits.* **33**, 57 (1932).

energy.  $Z_1$  and  $Z_2$  are the numbers of extranuclear electrons in the molecules.

For ion-molecule combinations a polarization energy was added to the intermolecular energies. The total energy  $V$  is expressed by the equation

$$V = -\frac{(\epsilon-1)e^2}{8\pi n} \frac{1}{r^4} + \frac{\lambda}{r^9} - \frac{\mu}{r^6},$$

in which  $n$  is the number of molecules per unit volume, and  $\epsilon$  is the dielectric constant of the gas. Values of  $\epsilon$  at 0°C and 760 mm were selected from the recent literature. They are 1.000270 for  $H_2$ ,<sup>21</sup> 1.000072 for He,<sup>21</sup> 1.000585 for  $N_2$ ,<sup>23</sup> and 1.000553 for A.<sup>21, 24</sup> The energy in electron volts is plotted with heavy lines in Fig. 8 as a function of the distance in Å. It is zero at a distance  $\sigma_{12}$  of separation. The calculated values of  $\sigma_{12}$  in Å are 2.39 for  $K^+$  in  $H_2$ , 2.48 in He, 2.77 in  $N_2$ , and 2.63 in A. They were retained in the subsequent selection of coefficients for the two models which are available to mobility calculations. Representation of the polarized molecule by an electric doublet of infinitesimal dimensions is basic to the calculation of polarization energy. Error arises from the finite distribution of charge which is induced by the powerful divergent field of the ion. Since, therefore, the energies plotted in Fig. 8 are not strictly accurate, the assumed magnitudes of the forces were freely adjusted to bring the calculated mobility into coincidence with the measurements by the Tyndall and Powell method. The energy which was selected for the model with

<sup>21</sup> Watson, Rao and Ramaswamy, Proc. Roy. Soc. **A132**, 569 (1931).

<sup>22</sup> Michels, Sanders and Schipper, Physica **2**, 753 (1935).

<sup>23</sup> H. L. Andrews, Physics **1**, 366 (1931); Michels, Jaspers and Sanders, Physica **1**, 627 (1934); C. E. Bennett, Phys. Rev. **45**, 200 (1934).

<sup>24</sup> G. Damköhler, Zeits. f. physik. Chemie **B27**, 130 (1934).

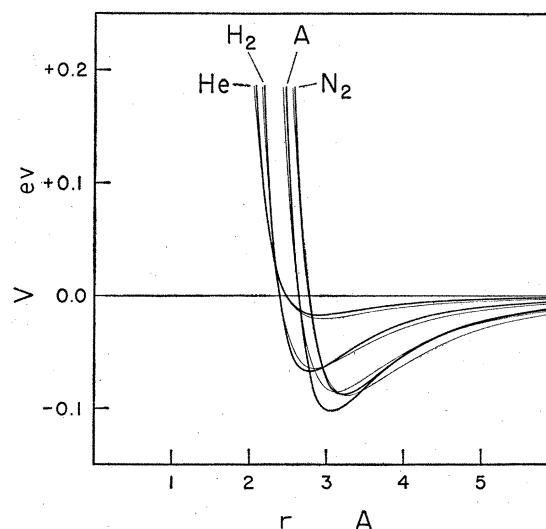


FIG. 8. The interaction energy between  $K^+$  and  $H_2$ , He,  $N_2$ , and A.

an inverse ninth power law of repulsion is plotted in Fig. 8 with light lines.

The experimental results are bracketed by the two theories of mobility. The repulsive force, therefore, varies with distance to a higher power than nine, and, indeed, the crystal data<sup>25</sup> call for a tenth-power law. The same conclusion has been reached by Pearce<sup>26</sup> from a study of the temperature dependence of mobility. It is hoped that the theory will eventually be extended to a model in better agreement with experiment.

The writer gratefully acknowledges his indebtedness to Professor Leonard B. Loeb, at whose suggestion this problem was undertaken, and without whose continued encouragement it could not have been completed. It is a pleasure to thank Mr. Edward H. Guyon, for his able assistance in the construction of the chamber.

<sup>25</sup> M. Born, Ann. d. Physik **61**, 87 (1920).

<sup>26</sup> A. F. Pearce, Proc. Roy. Soc. **A155**, 490 (1936).