Drift Velocity of Electrons in Mercury Vapor and Mercury Vapor—CO<sub>2</sub> Mixtures

C. W. MCCUTCHEN Cavendish Laboratory, University of Cambridge, Cambridge, England (Received July 25, 1958)

The drift velocity of electrons in mercury vapor has been measured with an apparatus of the type used by Klema and Allen. The effect of added CO2 has been investigated. The results are used to calculate the electron mean free path in mercury vapor. It is found that mercury vapor has a mean free path maximum (Ramsauer effect) at low electron energy.

## INTRODUCTION

HE drift velocity of electrons in mercury vapor has not previously been measured. Beside the obvious engineering value of this information, it can be used to throw some light on the mean free path of electrons in mercury vapor at very low electron energies.

With two exceptions, the data on the mean free path of electrons in mercury vapor do not extend to electron energies much below 1 volt. Most of the experiments have been transmission measurements following the method of Ramsauer.<sup>1</sup> Most of these, for example, the most recent data of Brode<sup>2</sup> shown in Fig. 1, show that the atomic collision cross section is still rising as the electron velocity decreases to 1  $(volt)^{\frac{1}{2}}$ .

The region right around 1  $(volt)^{\frac{1}{2}}$  has also been studied by Adler and Margenau<sup>3</sup> who observed the rf properties of ionized mercury vapor. Figure 1 shows that their results are in disagreement with those of the transmission experiments.

Very low electron energies were studied by Minkow-



VELOCITY-VOLTS

FIG. 1. The collision cross section of electrons in mercury vapor as a function of electron velocity.

ski.<sup>4</sup> He observed the effect of mercury vapor on spacecharge-limited thermionic emission and concluded that at very low velocities the collision cross section falls again. This experiment is very difficult to interpret as the geometry is complex. The results may not be contradictory with those of the transmission experiments if the rise in free path occurs at energies lower than those studied by the transmission experimenters.

In the experiments here described, the electron free paths are inferred from measurements of the drift velocity of electrons as a function of the applied electric field.

## EXPERIMENTAL PROCEDURE AND RESULTS

The method followed that of Klema and Allen<sup>5</sup> except that the apparatus was compressed into a small container (Fig. 2). To produce pulses of ionization,  $\alpha$ particles are collimated to travel parallel to the cathode and the drift of the resulting ionization electrons across the chamber is observed by a broad-band amplifier and oscilloscope connected to the anode. The field in the drift space is undoubtedly not quite constant, but the resulting smearing of the drift velocity vs field curve was not considered serious as the nature of a diffusion process eliminates the possibility of any fine detail. The problems and pitfalls of this method have been well described by Klema and Allen.

The chamber was heated in an oven and its temperature was measured with a thermocouple. The procedure was first to bake the chamber under vacuum for several hours at a temperature higher than the operating temperature and then to force mercury up the pumping tube by gas pressure. The mercury vaporized in the hot chamber, producing a meniscus between the chamber and the water-cooled section of the filling line. With the position of this interface known, the pressure was determined from the head of liquid mercury in the filling tube and the gas pressure behind it. This, together with the known temperature of the chamber, gave the density of the vapor. (Deviations from perfect gas behavior are minute.)

Figure 3 shows the results of two runs at different pressures. The drift velocity is plotted as a function of (X/P)(T/293), where X is the field in volts/cm and

 <sup>&</sup>lt;sup>1</sup> C. Ramsauer, Ann. Physik 66, 545 (1921); 72, 345 (1923).
<sup>2</sup> R. B. Brode, Proc. Roy. Soc. (London) A125, 134 (1929).
<sup>3</sup> F. P. Adler, J. Appl. Phys. 20, 1125 (1949); F. P. Adler and H. Margenau, Phys. Rev. 79, 970 (1950).

<sup>&</sup>lt;sup>4</sup> R. Minkowski, Z. Physik 18, 258 (1923).

<sup>&</sup>lt;sup>5</sup> E. D. Klema and J. S. Allen, Phys. Rev. 77, 661 (1950).



FIG. 2. The drift velocity apparatus used to obtain the data shown in Fig. 3 and Fig. 4.

P is the pressure in mm Hg. This allows direct comparison on a molecular density basis with data plotted against X/P from experiments performed at room temperature. Figure 3 is typical of many runs which were all quite consistent.

 $CO_2$ -mercury mixtures were then investigated by letting  $CO_2$  into the chamber before pushing the mercury up the filling tube. The results are shown in Fig. 4.

As will be seen later, the plateau in the drift velocity *vs* field curve is very interesting. In the case of argon such behavior has been shown to result from impurities.<sup>6</sup> The mercury used in these experiments was triple distilled and then refluxed under vacuum before use; however there were short lengths of neoprene in the filling system so the purity was not above suspicion (though the consistency of the results from run to run and for different pressures suggests that any impurity must have been present in remarkably constant proportion to the mercury density).

Therefore, an all-glass chamber was baked and filled

<sup>6</sup> W. N. English and G. C. Hanna, Can. J. Phys. 31, 768 (1953).

by distillation with triple-distilled mercury. This should contain little impurity and that small amount should be constant. The electrode system was the one used in the previous chamber. With all the mercury vaporized, the filling density was 0.004 g/cc. Figure 5 shows the results. The runs at lower than saturation density were made by lowering the temperature. No attempt was made to measure the temperature as the actual value of the density is not required for the argument.

The results show that reducing the pressure simply compresses the curve along the voltage axis. The diffusion theory shows that the drift velocity vs X/Pcurve should be the same shape whatever the pressure, provided that the gas composition is constant. The results of this experiment indicate that the gas composition is effectively constant. If impurities were determining the behavior of the electrons, then the curves at low density would be expected to have shapes different from those at high density as well as having the compression along the field axis, because lowering the mercury density should increase the relative concentration of impurity. It is concluded that impurities are not affecting the electron behavior.

The runs of Fig. 5 give consistently higher drift velocity than those taken with the original chamber. This suggests a systematic error, which is not surprising in the very cramped apparatus and imperfect geometry that had to be used in order to get the apparatus into the available high-temperature chamber. The best values are probably those of Fig. 3 because they were taken with larger plate spacing and are therefore less subject to errors arising from imperfect localization of the initial ionization.

## INTERPRETATION IN TERMS OF ELECTRON MEAN FREE PATH

By use of the standard diffusion theory<sup>7</sup> and assuming that all the collisions are elastic, the drift velocity vs



FIG. 3. The drift velocity of electrons in mercury vapor as determined by the apparatus of Fig. 2.

<sup>7</sup> L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955).



FIG. 4. Drift velocity of electrons in mercury vapor-CO<sub>2</sub> mixtures. The "quantized" appearance of the larger drift velocities results because the pulse rise times were measured only to the nearest half-µsec.

X/P data of Fig. 3 was used to derive the electron mean free path as a function of electron velocity. As there is some disagreement about some of the dimensionless constants the formulas used in these calculations are reproduced below:

$$h = (8m/3M)(1 - 3kT/mu^2),$$
 (1)

$$W = 0.815(h/2)^{\frac{1}{2}}u,$$
 (2)

$$\frac{X}{P}\left(\frac{T}{293}\right) = \left(\frac{h}{2}\right)^{\frac{1}{2}} \frac{u^2}{\Lambda} \frac{m}{e},\tag{3}$$

where h is the fractional energy less per collision, m is the electron mass, M is the molecular mass, u is the rms agitation speed of the electrons, W is the drift velocity, X is the field in volts/cm, P is the pressure in mm Hg,  $\Lambda$  is the electron free path at 1 mm Hg, e is the electronic charge, and T is the operating temperature.

In the actual calculations an arbitrary value of u would first be chosen. From Eq. (1) the value of h appropriate to this value of u was found. From Eq. (2) the value of W was next determined From the experi-

mental data the (X/P)(T/293) required to produce this W was next found and substituted, together with the value of u and h into Eq. (3) to find  $\Lambda$ . The results, plotted in terms of the collision cross section at 1 mm pressure (this is just the reciprocal of the mean free path at 1 mm pressure), are shown in Fig. 1. They agree quite well with the results of Brode and the other transmission experimenters over the velocity range covered, but at lower velocities the collision cross section again falls. It is this fall in cross section which is responsible for the plateau in the drift velocity vs field curve and it is because the plateau is so flat that the fall in  $\alpha$  at u=0.4 (volt)<sup>‡</sup> is so precipitous.

The values for  $\alpha$  obtained in this work must be taken with two reservations. It is assumed that all the collisions are elastic; however, if the electron distribution had a very small high-energy tail which reached 4.89 volts (the first excitation potential of mercury), the inelastic collisions thus produced would substantially raise *h*. The cross-section data are probably wrong at the high-velocity end. At what velocity the error becomes serious is not known, for the electron velocity distribution is not known. The Adler and Margenau

1850

results would suggest that ionizing collisions are occurring when the electron temperature is as low as 0.8 volt, for their experiments were performed in the positive column of a dc gas discharge. If this is true then excitations should occur at even lower electron temperatures so only the very bottom end of the data may be at all accurate.

The remaining reservation is that the diffusion theory of drift velocity is entirely too simplified. The variation of  $\Lambda$  with u, which from Brode's results should be extreme, is ignored in Eq. (3); so, even assuming that inelastic collisions are not occurring, the diffusion theory cannot be expected to yield very accurate results.

The variation of  $\Lambda$  with u can be expected to product a very strange electron energy distribution which mighd account for the disagreement between the Adler ann Margenau data and those of Brode and this paper. Ie their analysis Adler and Margenau assumed a Maxwellian distribution of electron energies.

In spite of all this uncertainty it seems clear that for very slow electrons  $\Lambda$  rises with decreasing energy. If Eqs. (2) and (3) are combined the result is

$$W = 0.815 \left( \Lambda \frac{e}{m} \frac{X}{P} \right)^{\frac{1}{2}} \left( \frac{h}{2} \right)^{\frac{1}{2}}.$$
 (4)

For W to be independent of X/P, that is, for the observed plateau to be produced,  $\Lambda$  must fall with increasing X/P since, in a pure gas, h can only rise with increasing X/P.

To my knowledge there has been no theoretical prediction of the collision cross section vs electron velocity relation for mercury; however, there has been one by Allis and Morse<sup>8</sup> for the chemically similar

<sup>8</sup> W. P. Allis and P. M. Morse, Z. Physik 70, 567 (1931).



FIG. 5. The drift velocity of electrons in mercury vapor as a function of electric field at various (unknown except for the highest) pressures. These data were taken with the sealed-off glass apparatus mentioned in the text.

element Zn. This predicts a fall in the cross section at energies less than 2 volts so to that extent these results may be considered as agreeing with theory.

No quantitative analysis of the mercury plus  $CO_2$  data has been undertaken; however, the effect of the  $CO_2$  in raising the drift velocity is the normal result when an inelastic gas is added to an elastic one.