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STUDIES OF ELECTRON TRANSPORT IN GASES, USING  
TIME-OF-FLIGHT SWARM METHODS  
(Thesis)

J. E. Parks  
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J. E. Parks and G. S. Hurst

Submitted as a thesis to the Graduate School of Vanderbilt  
University in partial fulfillment of the requirements for  
the degree of Master of Science

DECEMBER 1965

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## ABSTRACT

The method described earlier (Hurst, O'Kelly, Wagner, and Stockdale, 1963) for the determination of electron diffusion coefficients,  $D$ , and drift velocities,  $W$ , from time-of-flight studies of individual electron motion in gases has been improved in two essential ways. First, an accurate method of measuring all fluctuation in the time-of-flight distribution except that due to the diffusion process itself has been developed. Second, a data analysis procedure has been worked out in which the effects of instrumental fluctuations are removed and accurate values of the parameters  $D$  and  $W$  are found from a generalized least squares procedure making use of a digital computer. The previous assumption that single electron detection follows Poisson statistics was examined experimentally and found not to be in error. Distortions in the electron time-of-flight distributions arising out of electron losses during detector dead times were calculated.

Application of the improved method has been made to ethylene and ethylene-water vapor mixtures over the range of  $E/P$  from 0.1 to 1.0 ( $\text{volt cm}^{-1} \text{ torr}^{-1}$ ). Independent measurements of the quantities  $D$  and  $W$  were made; the ratios  $D/W$  were compared with theory in the region of thermal electron energies. The ratio of the momentum transfer cross sections for  $\text{H}_2\text{O}$  compared to ethylene was the same whether use was made of  $D(E/P)$  or  $W(E/P)$  data in the region of thermal energies. It was found that  $D/W$  for thermal electrons was 12 percent higher than theory. After

careful error analysis, it was suggested that infrequent long-duration collisions between electrons and ethylene may account for the larger D values.

## CHAPTER I

### INTRODUCTION

#### I. GENERAL PROPERTIES OF ELECTRON SWARMS

Information on the interaction of electrons with atoms and molecules is obtained from two general types of experiments—electron beam experiments and electron swarm experiments. Electron swarm experiments may be best defined by contrasting them with electron beam experiments. In a beam experiment, single collisions of the electrons with the gas are desired and the assumption is made that the energy distribution is that of the source. Hence a nearly monoenergetic beam of electrons is employed. Beam experiments are frequently performed because their results are more easily interpreted. However, beam experiments are limited to electron energies greater than one electron volt; another disadvantage in beam experiments arises from pressure limitations, thus reactions of low cross section and reactions that depend on collision processes are not easily observed.

In electron swarm experiments a large number of electrons diffuse through a gas, at a relatively high pressure, in the presence of a uniform electric field. Many collisions of electrons with the gas are desired, and the assumption is made that the energy distribution is independent of that of

the source. In an electron swarm, electrons collide frequently with the gas and an equilibrium energy is obtained where the energy gain from the electric field is balanced by the numerous but small fractional energy losses made by elastic or inelastic collisions. The energy distribution function depends upon the type of gas, the gas temperature, and ratio of the electric field to the gas pressure,  $E/P$ . Generally, the energy distribution function is not well known for electron swarms, and this is the main disadvantage of the swarm experiment. However, the electron energy distributions as functions of  $E/P$  are well known for several gases. For instance, the energy distributions for electrons diffusing through ethylene, nitrogen, and argon are known for the many different  $E/P$ 's that are of interest (Stockdale and Hurst, 1964). For ethylene the energy distribution is believed to be Maxwellian for  $E/P \leq 0.15 \text{ volt cm}^{-1} \text{ torr}^{-1}$ .

Large angle scattering has an important effect on the distance travelled by an electron in a swarm and thus the diffusion of the electrons through the gas. Consider the path of an electron moving through a gas in the presence of a uniform electric field. If  $S$  is the actual distance travelled, then  $S$  is much greater than  $x$ , the displacement of the electron in the  $x$  direction. An average velocity is reached as the electron undergoes the displacement,  $x$ , and the magnitude of this velocity is much less than the average random speed,  $\mu$ , of the electron. The average velocity in the field direction is called the drift velocity,  $W$ , and is a function of  $E/P$ . It can be shown that

$$S \approx \frac{\mu}{W} x \quad (1)$$

and that a typical value of the ratio  $\mu/W$  is of the order of several hundred.

Consider, as in Figure 1, a swarm of electrons diffusing through a gas in the presence of a uniform electric field. As the electrons drift toward the collecting plate, the swarm remains well defined in space about its center of mass although there is spreading out of the swarm due to diffusion. The velocity of the center of mass is the drift velocity of the swarm. The mean distance of separation,  $\delta x$ , of electrons in the swarm is directly proportional to the square root of the product of the diffusion coefficient,  $D$ , and the time of drift,  $t$ . Then  $\delta x$  is given by

$$\delta x = \sqrt{4Dt} \quad (2)$$

Data from swarm experiments are somewhat difficult to interpret, but satisfactory theory has been worked out which relates the measurable macroscopic quantities of the swarm experiment to the microscopic quantities of interest in the interactions of electrons with atoms and molecules. The parameters obtained from a swarm experiment can be related to the cross section for momentum transfer and other properties of molecules. For instance, the parameters  $D$  and  $W$  can be related to the momentum transfer cross section,  $\sigma(v)$ , with the equations (Allis, 1956)

$$W = \frac{4\pi}{3} \frac{e}{nm} \int_0^{\infty} f_0 \frac{d}{dv} \left( \frac{v^2}{\sigma(v)} \right) dv \times \frac{E}{P} \quad (3)$$

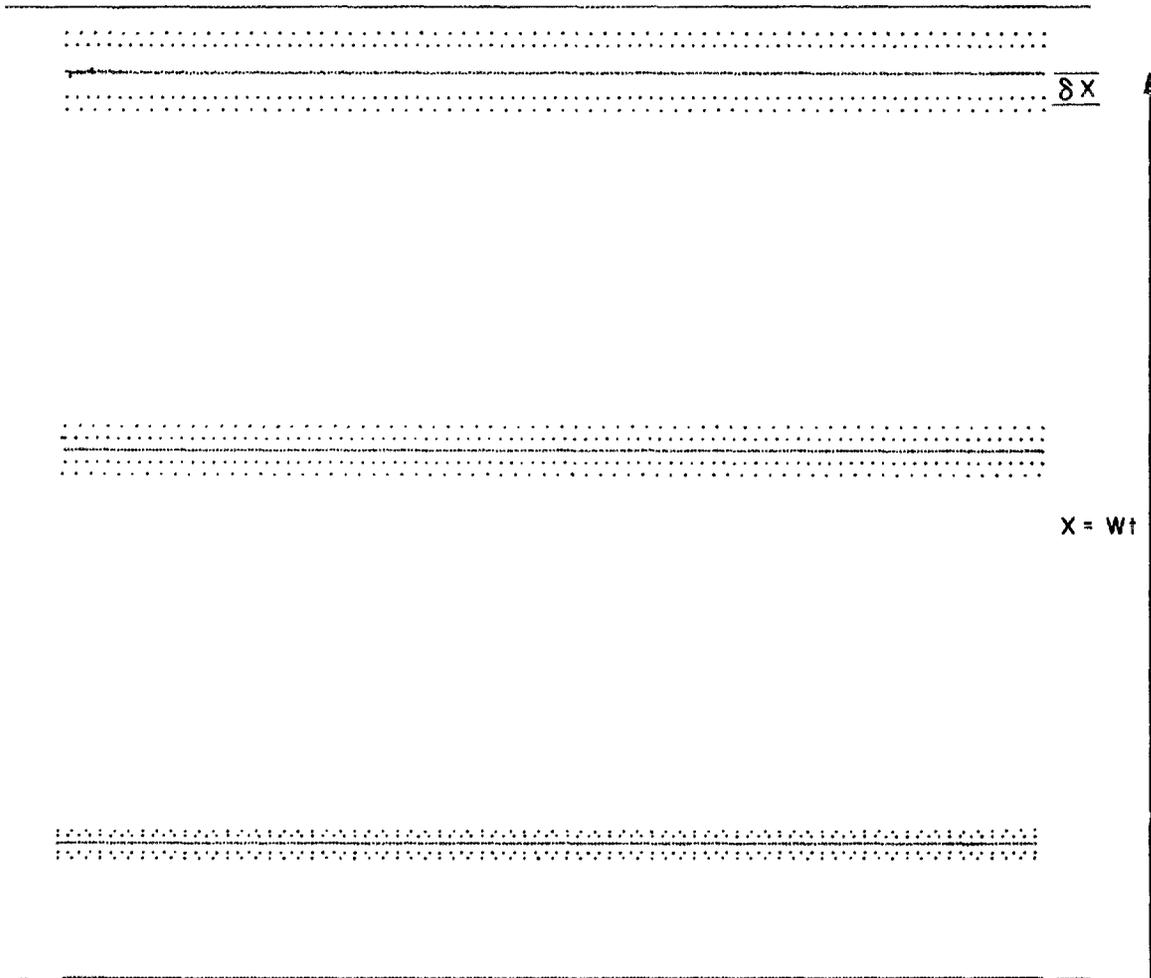


Figure 1. Schematic of electron swarm at constant E/P.

and

$$D = \frac{4\pi}{3} \frac{1}{n} \int_0^{\infty} f_0 \frac{v^3}{\sigma(v)} dv \quad (4)$$

where  $f_0$  is the spherically symmetric term in the expansion of the electron velocity distribution function,  $e/m$  is the charge to mass ratio of the electron,  $n$  is the number density of the gas at unit pressure, and  $v$  is the velocity of the electron.

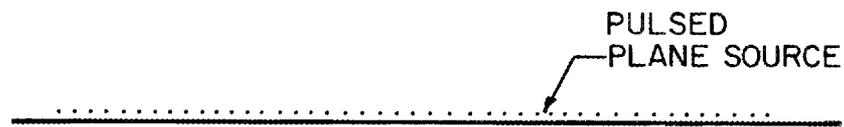
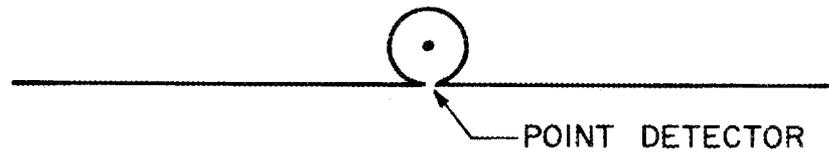
In addition to the intrinsic values of  $D$  and  $W$  (obtained from swarm experiments) these values are also valuable for the normalization of theoretical work and beam experiments. For example, theoretical values of elastic scattering cross sections can be checked by calculating  $D$  and  $W$  and comparing with experiment. In beam experiments one can seldom measure absolute cross sections as a function of energy. On the other hand, beam experiments do provide relative measurements of cross section and these can be normalized to swarm experiments by suitable analysis.

## II. SUMMARY OF WORK ON ELECTRON TRANSPORT IN GASES

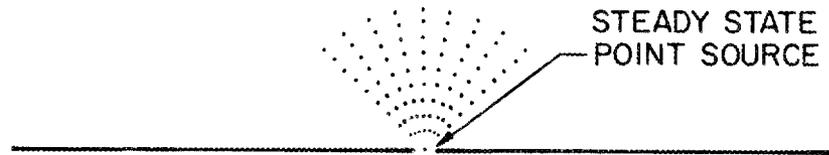
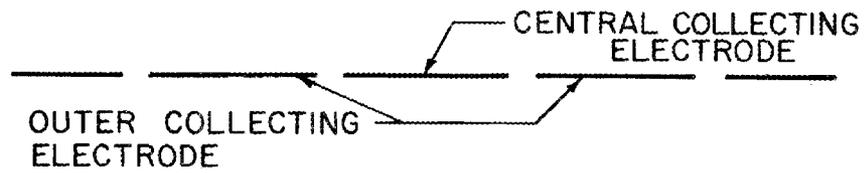
Until the present, almost all research on electron diffusion in gases has been based on the original method set forth by Townsend in the early 1900's. Early studies employing this method are summarized in Healey and Reed (1941). Some of the more recent studies have been made by Huxley (1940), Crompton and Sutton (1952), Crompton and Jory (1962), Cochran and Forester (1962), and by Warren and Parker (1962). A new approach to swarm experiments, which would measure independently  $D$  and  $W$ , was conceived by

Hurst, O'Kelly, Wagner, and Stockdale (1963), while considering the time-of-flight technique as a method of investigating long duration collisions of electrons with a gas. (Long duration collisions, sometimes referred to as temporary capture, are collisions in which the interaction time is long compared to the vibration time of a negative ion.) It was seen that this time-of-flight technique would provide a new method of determining the attachment coefficient,  $\alpha$ , of electrons in a contaminant gas. The promise of a better diffusion experiment temporarily overshadowed the originally sought ideas of measuring temporary capture cross sections,  $\sigma_c$ , and the lifetimes of negative ions,  $\tau$ , with a time-of-flight swarm experiment.

In describing the method of the time-of-transport swarm experiment, it would be well to contrast its features with those of the Townsend-Huxley method. The basic features of both the time-of-flight and Townsend-Huxley methods are illustrated in Figure 2. The time-of-flight technique makes use of a pulsed plane source of electrons (e. g., ultraviolet light activated photocathode), and a point detector (e. g., a small hole in the collecting electrode through which single electrons may enter into a Geiger-Mueller counter). Then using the assumption that the counting of these electrons obeys Poisson statistics, a time-of-arrival distribution function is constructed from which  $D$  and  $W$  are obtained. The Townsend method uses a plane detector, a central collecting electrode with a concentric outer collecting electrode, to measure the currents  $i_a$  and  $i_b$ , to the two collecting electrodes. From the ratio  $i_a/i_b$ , one obtains  $D/W$ .



(a) TIME OF FLIGHT GEOMETRY



(b) TOWNSEND-HUXLEY GEOMETRY

Figure 2. Comparison of time-of-flight and Townsend-Huxley diffusion geometries.

The transport equation for the time-of-flight method is a one-dimensional equation and can be solved in a straightforward manner to independently find  $D$  and  $W$ . The transport equation for the Townsend method is a three-dimensional equation which has not been solved satisfactorily by straightforward methods. Huxley (1940) has solved the three-dimensional transport equation by the method of images by assuming the ratio of  $W/D$  is independent of pressure and by making various trial assumptions on the boundary conditions. Warren and Parker (1962) have considered in more detail the effects of the boundary conditions, but there are still serious objections to the solution. One of these is that there is no direct way of testing the solution. The time-of-flight method does offer a verification of the one-dimensional solution, i. e., the measured time-of-flight distribution can be compared with theory.

The Townsend-Huxley method has a much more limited choice of independent variables in that it only measures two currents. From these, only the ratio of  $W/D$  is found and  $W$  has to be measured by some independent method in order to find  $D$ . On the other hand, the time-of-flight method has many independent variables in that a time distribution is measured with an arbitrarily large number of data points. From this distribution one may obtain independently  $D$ ,  $W$ , and the attachment coefficient,  $\alpha$ .

There are also certain geometrical problems with the Townsend-Huxley method. Centering of the source hole over the center electrode must be carefully made, otherwise appreciable errors will be introduced. The

collecting electrodes, although small, do have potential differences across their surfaces, even though they are of metal and are supposedly flat. This can produce a lateral electric field which causes appreciable change in the ratio  $i_a/i_b$ . Recently Crompton, Elford, and Cascoigne (1965) have evaluated these problems and have shown how some of the sources of errors may be eliminated.

While the time-of-flight method has advantages over the Townsend method, it does require a much more elaborate experimental setup. The most serious limitation to the time-of-flight method used here is that a common filling gas must be used for the Geiger-Mueller counter and the flight tube. Wagner and Davis (1965) have overcome this limitation through the use of an electron multiplier and a differential pumping system.

### III. STATEMENT OF PRESENT OBJECTIVES

The first pilot experiment, designed and developed by Hurst, O'Kelly, Wagner, and Stockdale (1963), successfully demonstrated the time-of-flight method for the study of electron transport. Their conclusions have provided the primary basis for the experiment reported here. As pointed out in Figure 2(b), the source for the time-of-flight method consists of a gold photocathode from which electrons are photoelectrically emitted by a pulse of ultraviolet light. This pulse of light has a finite time duration which leads to uncertainties in the time that the electron leaves the source. Also, as pointed out, the electron detector is a Geiger-Mueller counter

which has a characteristic time response. The time response of the detector has a finite width and this leads to uncertainties in the times of arrival of the electrons.

The source, detector, and associated electronics may then give rise to an error distribution function whose width may be comparable to that of the distribution being measured, particularly when gases with small diffusion coefficients are measured at the higher values of  $E/P$ . The effect of the error function is a general broadening of the measured time-of-flight distribution and as a result, measured diffusion coefficients are too large by an amount depending on pressure. This apparent pressure dependence was reported and shown by Hurst et al. for the data on  $C_2H_4$  and is reproduced in Figure 3.

It was felt that the experiment could be greatly improved even if basically the same types of apparatus were used again. Therefore, one goal of this experiment was to make general improvements of the method. Either or both of two types of improvements were considered. First, a substantial reduction in the error fluctuations was to be sought. The light pulse could be made to be of shorter duration and the electronics picking up the light signal could be made to be faster. Also, the Geiger-Mueller counter could be designed and more ideally operated and also the electronics following the detector signal could be made to be faster. Anticipating that the error fluctuations could not be reduced to the point that they would be negligible, the second improvement was contemplated. This improvement

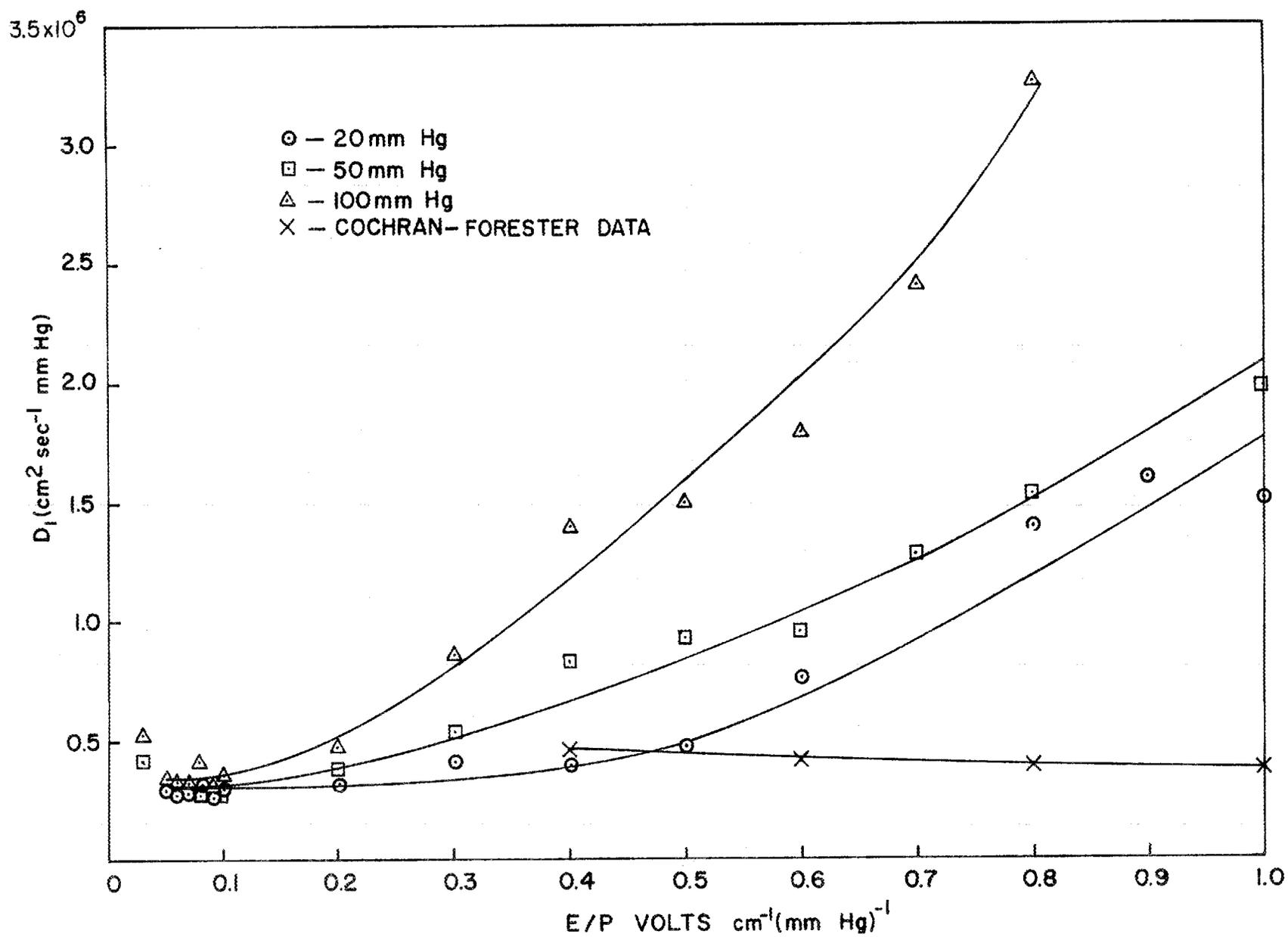


Figure 3. Preliminary diffusion data in ethylene.

would provide a means of correcting for the remaining error fluctuations. The procedure would consist of an experimental method of measuring the error distribution function, followed with an analysis of the errors which would involve the relationship of the measured distribution with the actual time-of-flight distribution and the measured error distribution. Therefore, the time-of-flight distribution could be unfolded from the experimental measurements.

The theory of measuring the time-of-flight distribution function assumes that the counting of single electrons follows Poisson statistics. This assumption had not been tested before this experiment. Therefore, it was another objective of this experiment to verify that this assumption is a valid one. The testing of this assumption would require a more detailed treatment of the theory involving the Poisson statistics. Another goal of this experiment was to obtain more accurate drift velocity and diffusion data for ethylene by using the improved time-of-flight method. It was hoped that the previous diffusion data on ethylene, as shown in Figure 3, could be resolved. In other words, it was anticipated that by using the improved time-of-flight method diffusion coefficients which would be independent of pressure could be taken at the higher  $E/P$ 's.

A careful set of data on mixtures of ethylene and water was also desired. This would demonstrate the applicability of the time-of-flight method to mixtures of gases and would provide an additional method for the measurement of the ratio of momentum transfer cross sections. As

mentioned before, the idea for the time-of-flight method as a diffusion experiment first originated from ideas on experiments for temporary capture or long duration collisions. Therefore, it was hoped that this experiment could also successfully demonstrate long duration collisions. No more than the demonstration of the existence of long duration collisions was to be sought, as a complete investigation would be beyond the scope of this thesis.

## CHAPTER II

### DESCRIPTION AND THEORY OF TIME-OF-TRANSPORT METHOD

#### I. JUSTIFICATION OF TRANSPORT EQUATION AND ITS SOLUTION

The time of transport of electrons moving through a gas of uniform pressure and constant electric field is not the same for all electrons, but is influenced by the diffusion of the electrons through the gas. This diffusion can be attributed to elastic scattering of the electrons and can be treated by elementary methods. Consider, then, the motion of a swarm of electrons through a carrier gas of uniform pressure with no external electric field present. If it is assumed that the electron density is small, so that the mutual repulsion of the electrons can be neglected, then it can be shown [ see, for example, Present (1958)] by mean free path methods that, due to diffusion, the electron transport across a surface is proportional to the space rate of change of the electron density at right angles to the surface. The constant of proportionality is known as the diffusion coefficient. If the electron transport is given in number of electrons per unit area per unit time, and if it is represented by  $\vec{G}$ , then the expression for electron transport is given by

$$\vec{G} = - D \nabla n \quad (5)$$

where  $n$  is the volume density of electrons and  $D$  is the coefficient of diffusion. The minus sign indicates that the transport is in the opposite direction to the density gradient.

Consider the diffusion through a gas of a swarm of electrons which originated from a plane source lying in the plane  $x = 0$  and which at time  $t = 0$  had a uniform area density  $N$ . If a uniform electric field is applied in the negative  $x$  direction, there will be a net transport of electrons in the positive  $x$  direction. This general drift in the  $x$  direction of all the electrons results in a mean drift velocity  $W$ . The electron transport  $G(x)$  across a plane at  $x$  is given by

$$G(x, t) = -D \frac{\partial n(x, t)}{\partial x} + Wn(x, t) \quad (6)$$

where the transport due to diffusion is reduced to one dimension since the density gradient in the plane is zero. Then the transport across a plane at  $x + dx$  is given by

$$G(x + dx, t) = G(x, t) + \frac{\partial G}{\partial x} dx \quad (7)$$

which is a Taylor's expansion of  $G$ . The net inflow of electrons per unit time into the region located between the two planes at  $x$  and  $x + dx$  is given by

$$G(x, t) - G(x + dx, t) = -\frac{\partial G}{\partial x} dx \quad (8)$$

and

$$G(x, t) - G(x + dx, t) = \left[ D \frac{\partial^2 n}{\partial x^2} - W \frac{\partial n}{\partial x} \right] dx . \quad (9)$$

Some gases form negative ions by attachment of electrons. Such a gas, if present, acts as a sink to remove electrons from the swarm. If an attachment coefficient,  $\beta$ , is defined as the probability of an electron being captured in traveling unit distance in the direction of drift, then the inflow of electrons per unit area per unit time into the region between the two planes at  $x$  and  $x + dx$  is given by

$$G(x, t) - G(x + dx, t) - \beta Wn(x, t) dx , \quad (10)$$

assuming no electron detachment.

If there are no sources within the gas, then from the conservation of free electrons, expression (10) must be equal to the time rate of increase of electrons per unit area into the region which is given by  $\frac{\partial(ndx)}{\partial t}$ . Hence,

$$\frac{\partial n(x, t)}{\partial t} dx = G(x, t) - G(x + dx, t) - \beta Wn(x, t) dx \quad (11)$$

and

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} - W \frac{\partial n(x, t)}{\partial x} - \beta Wn(x, t) . \quad (12)$$

It is easy to show that a time dependent solution to Equation (12) is

$$n(x, t) = A t^{-1/2} e^{-\left\{ \frac{(x-Wt)^2}{4Dt} + \beta Wt \right\}} \quad (13)$$

where

$$A = N(4\pi D)^{-1/2}, \quad (14)$$

and  $N$  is the area density of electrons when  $x = 0$  and  $t = 0$ . Then,  $n(x, t)$  is the volume density of electrons at any point  $0 \leq x \leq L$  as a function of time.

If a detector is placed at  $D$  a distance  $L$  away from the source and if the detector has an aperture of area  $a$ , then the number of electrons,  $\epsilon(t)$ , entering the detector between times  $t$  and  $t + \Delta t$  is given by

$$\epsilon(t) = n(L, t) aW \Delta t \quad (15)$$

or

$$\epsilon(t) = \frac{NaW\Delta t}{(4\pi Dt)^{1/2}} e^{-\frac{(L-Wt)^2}{4Dt} - \beta Wt} \quad (16)$$

We define  $E(t)$  as

$$E(t) \equiv \frac{\epsilon(t)}{\Delta t}, \quad (17)$$

thus

$$E(t) = \frac{NaW}{(4\pi Dt)^{1/2}} e^{-\frac{(L-Wt)^2}{4Dt} - \beta Wt} \quad (18)$$

It will now be shown that by measuring  $E(t)$  the parameters  $D$  and  $W$  may be approximated from  $t_m$ , the time which maximizes  $E(t)$  and from  $\delta t$ , related to the distribution half width. Hence,  $t_m$  and  $\delta t$  are defined by

$$\left. \frac{\partial E(t)}{\partial t} \right|_{t = t_m} = 0 \quad (19)$$

and

$$\delta t \equiv |t_1 - t_m| \quad (20)$$

where  $t_1$  is determined from

$$E(t_1) \equiv \frac{1}{e} E(t_m). \quad (21)$$

From Equations (18) and (19) it can be shown that

$$t_m = \frac{-2D + [4D^2 + 4L^2 (W^2 + 4D\beta W)]^{1/2}}{2(W^2 + 4D\beta W)}. \quad (22)$$

Using the inequalities  $\frac{4D\beta}{W} \ll 1$  and  $\frac{D}{LW} \ll 1$ , Equation (22) may be solved to approximate the drift velocity by

$$W \approx \frac{L}{t_m}. \quad (23)$$

Hence, as one might guess, the drift velocity is just the distance traveled divided by the most probable time of arrival of the electron.

The dependence of  $D$  upon the width of the electron time of arrival distribution will now be shown. By direct substitution into Equations (18) and (21) and by using the condition that  $2(D/LW)^{1/2} \ll 1$ , it may be shown that

$$t_1 = \frac{L}{W} \left[ 1 \pm 2(D/WL)^{1/2} \right]. \quad (24)$$

Then from the definition of  $\delta t$  given in Equation (20),

$$\delta t \approx 2(LD/W^3)^{1/2} \quad (25)$$

from which D may be approximated by

$$D \approx \frac{L^2(\delta t)^2}{4t_m^3}. \quad (26)$$

An approximation for the third parameter,  $\beta$ , is not so easily obtained from a single measurement of  $E(t)$ . The reason for this is that it is not experimentally feasible to measure the absolute number,  $N$ , of electrons emitted per unit area from a pulsed source. This means that the estimates (23) and (26) cannot be inserted into Equation (18) to obtain an estimate of  $\beta$ . Therefore, it is desirable to have an approximation for  $\beta$  which is independent of  $N$ . This is achieved by finding the ratio of the total number of electrons,  $C_\beta$ , arriving when  $\beta \geq 0$  and the total number,  $C_0$ , arriving when  $\beta = 0$ .

The total number of electrons,  $C_\beta$ , detected in any given swarm may be found by integrating Equation (18) over all time. Thus

$$C_\beta = \int_0^\infty E(t) dt, \quad (27)$$

and we may show that

$$C_\beta = \frac{NaW}{(W^2 + 4D\beta W)^{1/2}} e^{\frac{LW}{2D} \left[ 1 - \left( 1 + \frac{4D\beta}{W} \right)^{1/2} \right]} \quad (28)$$

by making use of the definite integral

$$\int_0^\infty e^{(-y^2 - a^2/y^2)} dy = \frac{e^{-2a} \pi^{1/2}}{2}. \quad (29)$$

If the first two terms of the expansion of  $[1 + (4D\beta/W)]^{1/2}$  are retained by using the approximation of  $(4D\beta/W) \ll 1$  and neglecting the higher order terms, Equation (28) will reduce to

$$C_{\beta} \approx Na e^{-\beta L}. \quad (30)$$

Clearly for  $\beta = 0$ ,  $C_{\beta} = C_o$ ,

$$C_o = Na \quad (31)$$

and

$$\frac{C_{\beta}}{C_o} \approx e^{-\beta L}. \quad (32)$$

Thus  $\beta$  may be approximated from the ratio of  $C_{\beta}/C_o$  and the distance  $L$  that the electrons travel.

## II. THEORY OF MEASURING THE DISTRIBUTION FUNCTION

It was shown above that  $D$ ,  $W$ , and  $\beta$  may be approximated from a measurement of  $E(t)$ . The theory of making this measurement must now be considered. The manner of measuring  $E(t)$  depends largely upon the detector and the time analyzing devices incorporated into the experiment. This experiment utilized a Geiger-Mueller counter to detect single electrons entering the aperture in the collecting electrode. Geiger-Mueller counters nominally have dead times of the order of several hundred microseconds, and in this case the dead time is many times longer due to resistor quenching of the counter. Since the arrival time distributions have widths of a few tens of microseconds, much less than the counter dead times, only the first

electron arrival time is analyzed. Therefore, there is clearly a need for some procedure of randomly picking out of a swarm a single electron and measuring its arrival time. Otherwise, if the electron were not randomly selected, there would be preferential counting of the electrons which reach the collecting electrode first or those in the first part of the distribution. Since only one electron may be counted per swarm, many swarms must be produced in order to measure a good distribution.

Suppose that  $E(t)$  is determined by the repeated measurement of  $F$  swarms of electrons where each swarm is released from the photocathode with an intensity of  $n_i$  electrons per unit area. Then  $N$  in Equation (18) may be replaced by

$$N = \sum_{i=1}^F n_i. \quad (33)$$

If the product  $an_i$  is kept small such that the counting efficiency  $C/F$  is much less than one, the probability is small that an electron will enter the detector hole and be counted after a given release of electrons from the source. This probability is namely  $C/F$  and  $C$  may be interpreted as the total number of electrons detected in  $F$  swarms. Therefore, if  $C/F \ll 1$ , from the Poisson distribution, it is seen that the probability that two or more electrons will enter the aperture is small compared to  $C/F$ . This, then, is a randomizing procedure for selecting a single electron and measuring its arrival time function,  $E(t)$ .

In order to obtain a criterion for the smallness of  $C/F$ , additional

considerations must be given. Recalling that  $E(t)\Delta t$  is the number of electrons arriving at the detector hole between times  $t$  and  $t + \Delta t$ , the number of these electrons which are detected,  $E''(t)\Delta t$ , is equal to  $E(t)\Delta t$  times the probability,  $P_s(t)$ , that the counter is sensitive at time  $t$ . In other words,

$$E''(t)\Delta t = E(t)\Delta t \times P_s(t), \quad (34)$$

or

$$E''(t) = E(t) P_s(t). \quad (35)$$

For the fortuitously simple case where the detector allows only one electron out of a given swarm to be counted (i. e., the counter dead time,  $t_D \gg \delta t$ ),  $P_s(t)$  is just equal to the probability,  $P_o(t)$ , that the detector has made no counts at time  $t$  or

$$P_s(t) = P_o(t), \quad (36)$$

and

$$E''(t) = E(t) P_o(t). \quad (37)$$

The probability that no counts have occurred,  $P_o(t)$ , must be found. Certainly  $P_o(t)$  will depend on the number of electrons emitted per swarm from the source and the time of arrival distribution  $E(t)$ . This probability function,  $P_o(t)$ , is found by first generalizing to a probability function,  $P_n(t)$ , for  $n(t)$  electrons, out of any swarm  $i$ , having entered the detector hole by some time  $t$ . At some time  $t$ , after any swarm  $i$  is produced,  $N_i(t)$  electrons, given by

$$N_i(t) = \int_0^t A n_i \frac{E(t)}{Na} dt, \quad (38)$$

have crossed a plane of area  $A$  at the collector. Here it was assumed that the number of electrons found in the region was independent of the number already present. Similarly, at time  $t$ , after the formation of any swarm  $i$ ,  $n(t)$  electrons will have moved across a plane of area  $a$  at the detector.

Then for  $F$  swarms of electrons the number  $n(t)$  will fluctuate about a mean number  $\bar{n}(t)$  given by

$$\bar{n}(t) = \frac{a}{A} \frac{\sum_{i=1}^F N_i(t)}{F}. \quad (39)$$

Thus,

$$\bar{n}(t) = \frac{a}{A} \frac{\sum_{i=1}^F \int_0^t \frac{A}{a} \frac{n_i}{N} E(t) dt}{F} \quad (40)$$

and

$$\bar{n}(t) = \int_0^t \frac{\sum_{i=1}^F n_i a}{F} \frac{E(t)}{Na} dt. \quad (41)$$

The geometric probability of finding  $n(t)$  electrons in a region and  $N_i(t) - n(t)$  electrons outside the region is given by  $(a/A)^{n(t)} (1-a/A)^{N_i(t)-n(t)}$ . Then the probability  $P_{n(t)}$  that  $n(t)$  electrons will be found in the region at time  $t$  is given by the product of the geometric probability and the number of ways in which  $N_i(t)$  electrons can be divided into two groups of  $n(t)$  and  $N_i(t) - n(t)$  electrons. Hence,

$$P_{n(t)} = \frac{N_i(t)!}{n(t)! [N_i(t) - n(t)]!} \left(\frac{a}{A}\right)^{n(t)} \left(1 - \frac{a}{A}\right)^{N_i(t) - n(t)}. \quad (42)$$

For cases where  $a/A \ll 1$  and where  $N_i(t)$  is sufficiently large that we can replace  $N_i$  with its average, it can be shown that Equation (42) will reduce to

$$P_n(t) = \frac{\bar{n}(t)^{n(t)} e^{-\bar{n}(t)}}{n(t)!} \quad (43)$$

which applies only when  $n(t) \ll N_i(t)$ . Hence this is the Poisson formula which applies for small samplings out of large numbers when the probability of getting a sample is small. (See Present, 1958).

From the generalized probability function given by  $P_n(t)$  in Equation (43), the particular probability function  $P_o(t)$  for no electrons entering the detector hole may be derived. Substituting  $n(t) = 0$  in Equation (43) results in

$$P_o(t) = e^{-\bar{n}(t)} \quad (44)$$

and

$$P_o(t) = e^{-\int_0^t \sum_{i=1}^F n_i^a \frac{E(t)}{Na} dt} \quad (45)$$

By defining  $\bar{Na} \equiv \frac{\sum_{i=1}^F n_i^a}{F}$ , the final result

$$E''(t) = E(t) e^{-\int_0^t \bar{Na} \frac{E(t)}{Na} dt} \quad (46)$$

is obtained by substituting Equation (45) into Equation (37). This equation will be used later to calculate  $E''(t)$  and a comparison with experiment will

be made.

The constant  $\bar{N}_a$  is not readily obtainable from experiment, hence we wish to obtain its connection with  $C/F$ . We will show that for  $C/F \ll 1$ ,

$$\bar{N}_a \approx \frac{C}{F} \quad (47)$$

and that

$$E(t) \approx E''(t) \text{ for } C/F \ll 1. \quad (48)$$

It is recalled that  $C/F$  is the probability  $P_c$ , that during any given swarm an electron will be counted. This is just equal to the sum of the probabilities that one, two, three, ..., and an infinite number of electrons will have passed into the detector region at time equal to infinity or

$$P_c = P_1 + P_2 + \dots + P_\infty. \quad (49)$$

From Equation (49) it is seen that

$$P_c = 1 - P_0, \quad (50)$$

and

$$P_c = 1 - e^{-\int_0^{\infty} \bar{N}_a \frac{E(t)}{N_a} dt} \quad (51)$$

follows from Equation (45). Thus, it is found that

$$\frac{C}{F} = 1 - e^{-\bar{N}_a}. \quad (52)$$

Therefore,

$$\bar{N}_a = \log_e \left( \frac{1}{1 - \frac{C}{F}} \right). \quad (53)$$

The quantity  $\bar{N}_a$  can be found by using Equation (53) and the theory can be tested. It is also evident from Equation (52) that for  $C/F \ll 1$  that  $\bar{N}_a \ll 1$  and the approximation given in Equation (47) is a good one. The quantity  $\bar{N}_a$  is an upper limit on the value of the integral in Equation (46) and if it is chosen small enough, the exponential in this equation will approach one and the approximation given by Equation (48) is valid.

In the foregoing discussion it has been shown that the measured distribution may differ from that given by transport theory because the electron detector does not have adequate time resolution. However, this distortion can be easily avoided by a proper sampling procedure in which  $C/F \ll 1$ . Another type of distortion, namely that due to instrument fluctuation is not easily eliminated and must be dealt with analytically. We show later that an accurate measurement of all fluctuations except those due to the diffusion process can be made. Call the unit normalized instrument fluctuation  $T_o(t)$ . Then the measured distribution function  $E'(\tau)$  is related to  $T_o(t)$  and  $E(t)$  through a convolution integral, i. e.,

$$E'(\tau) = \int_0^{\tau} E(t) T_o(\tau - t) dt \quad (54)$$

where  $E'(\tau)\Delta\tau$  represents the number of electrons recorded between the times  $\tau$  and  $\tau + \Delta\tau$ . A knowledge of  $E(t)$ , the actual arrival time distribution,

may then be gained by unfolding this convolution integral by suitable mathematical procedures.

## CHAPTER III

### EXPERIMENTAL METHOD

#### I. DESCRIPTION OF APPARATUS

The apparatus for this experiment consisted essentially of a swarm chamber, an electronics system for measuring the time-of-flight distributions, and a vacuum and gas purification system. The electronics system is shown in Figure 4 and the vacuum system is shown in Figure 5. A photograph of the apparatus is shown in Figure 6.

The swarm region was a stainless steel cylinder which was gold plated inside to cut down on the absorption and outgassing of certain molecules by the walls of the chamber. In particular, this was done because water vapor was to be introduced, and it is well known for being absorbed by container walls. A port with a quartz window intersects the chamber wall at an angle of  $30^\circ$  with the base of the chamber.

The flight path of the electrons was between two parallel plates, a photocathode and a collecting plate, spaced 27.03 cm apart. The photocathode was a gold plated brass disc 8 inches in diameter supported 1.25 inches off the base by three fluorothene insulating supports. A negative high voltage potential was put on the photocathode and the collector plate was placed at ground potential. A uniform electric field was maintained between the

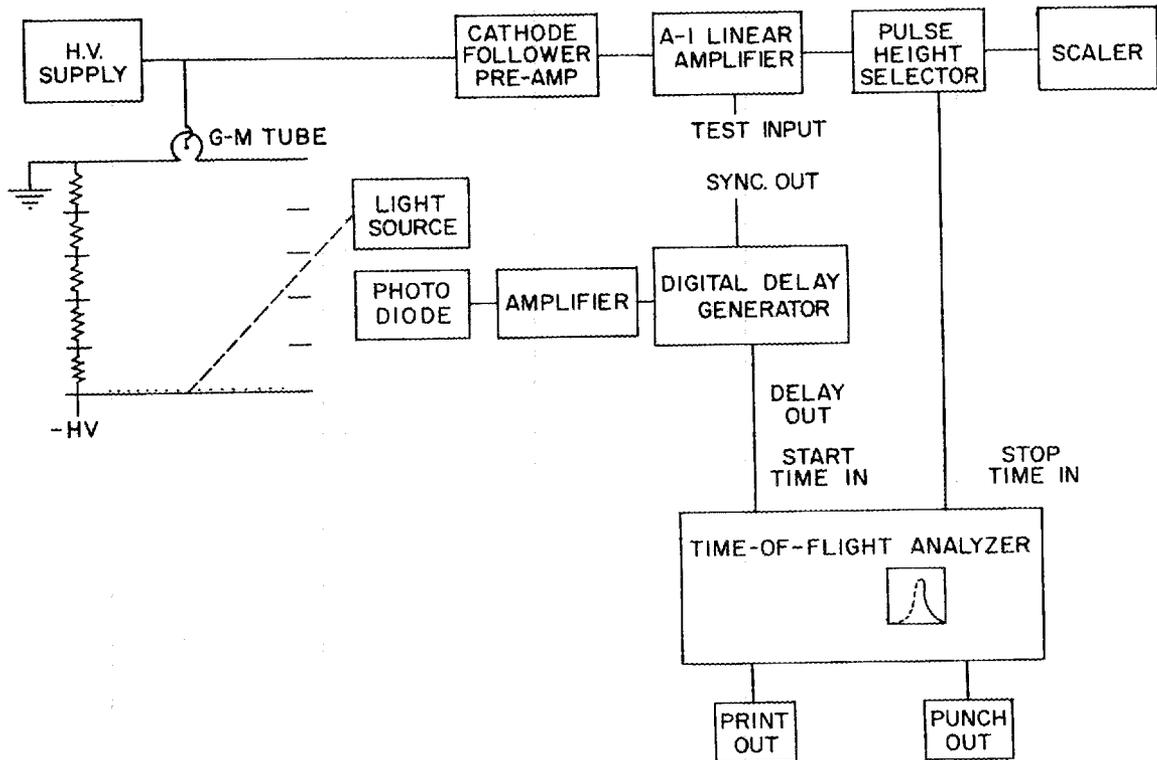


Figure 4. Electronics diagram for time-of-flight measurements.

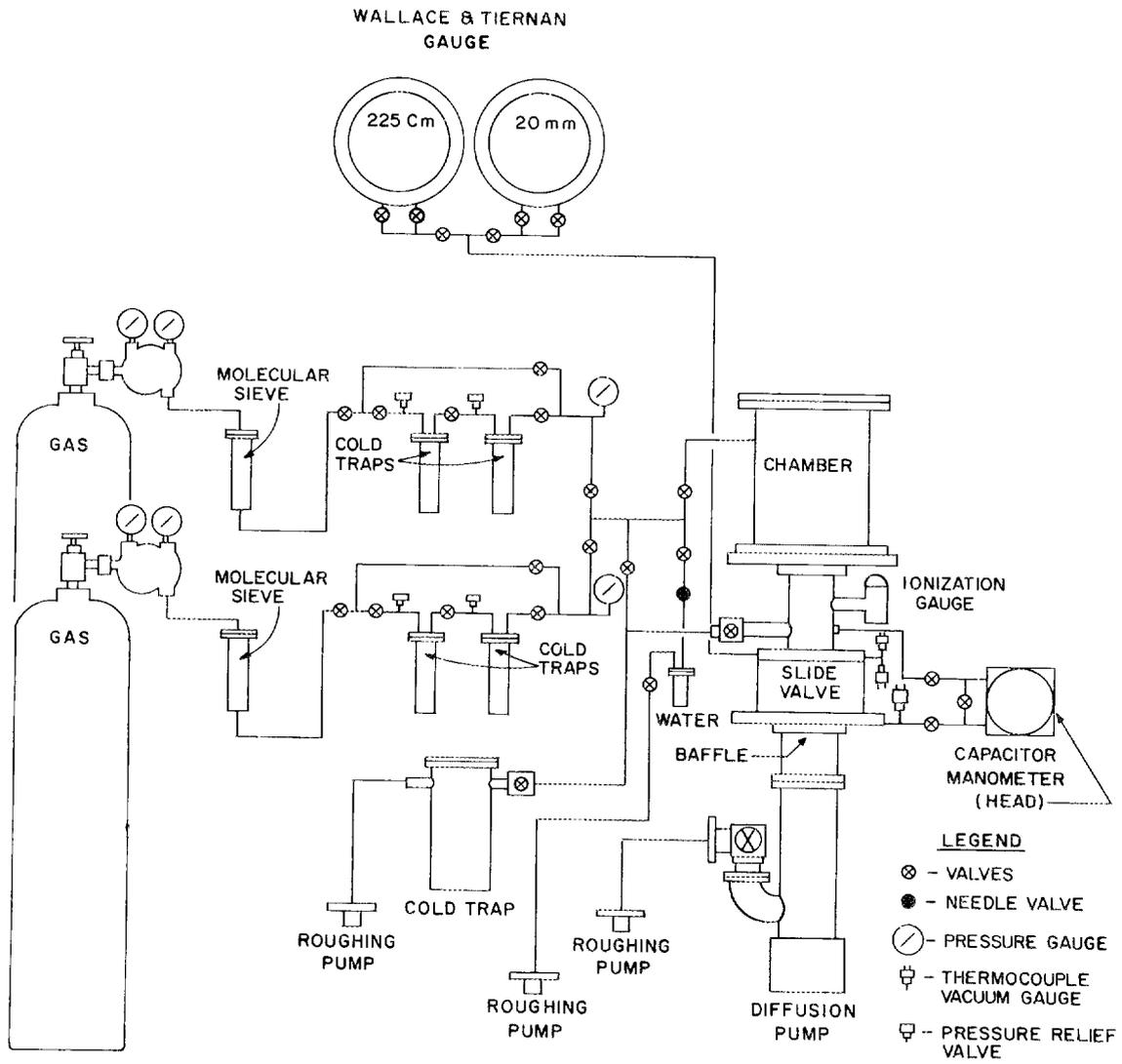


Figure 5. Gas purification and vacuum system diagram.

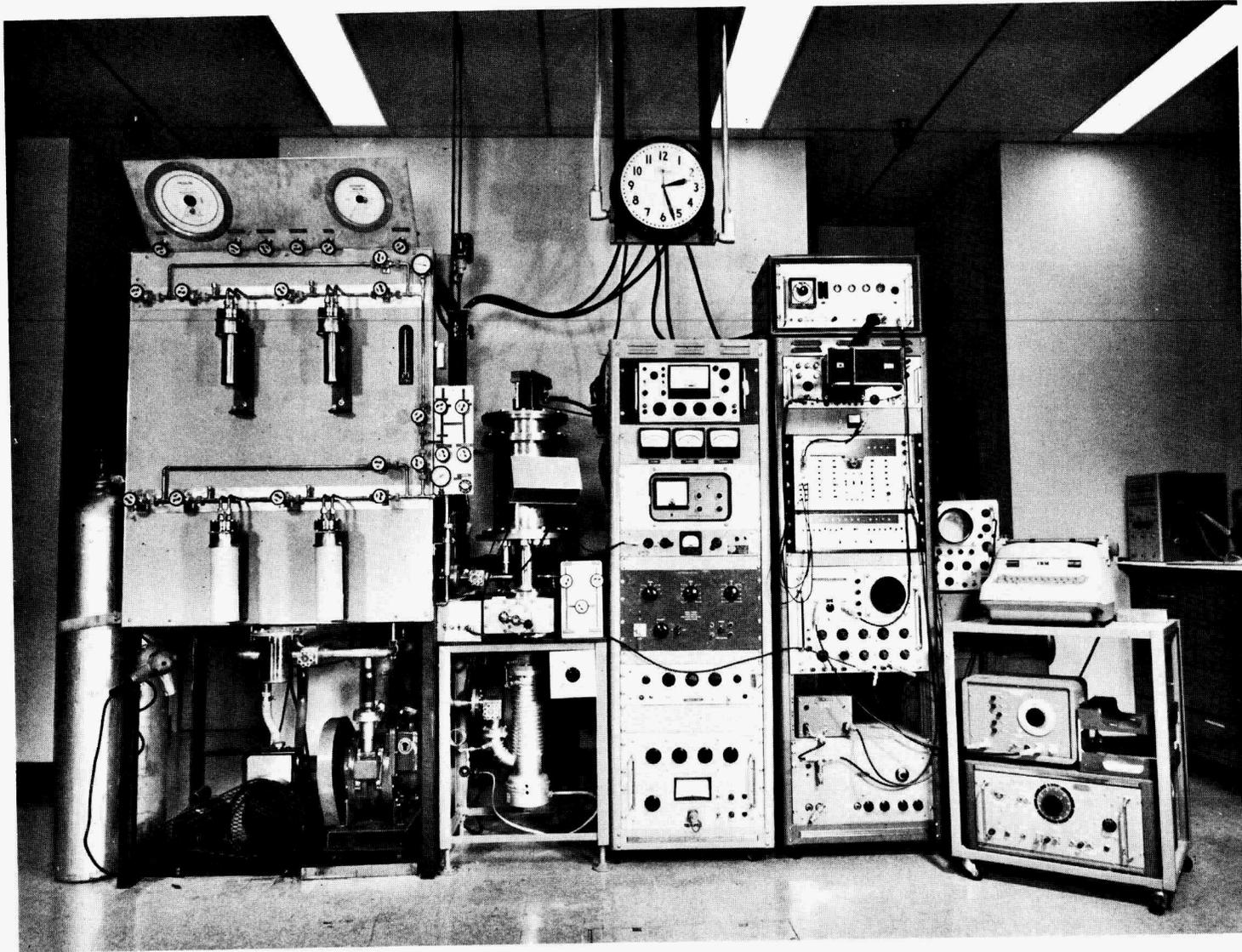


Figure 6. Photograph of apparatus.

photocathode and collector plates with the aid of four field rings. Field rings (6.125 inches inside diameter) were maintained at proper potential by a potential divider made up of five 10-megohm resistors. Hermetically sealed resistors were connected directly to the field rings and were located inside the chamber.

Swarms of electrons were initiated by a pulse of ultraviolet light passing through the quartz window onto the photocathode. The pulses of light were produced by an Edgerton, Germeshausen, and Grier xenon filled flash tube, type FX-31U with a quartz window. The tube was pulsed at a rate of 360 flashes per second. The light pulse had a peak rise time of approximately 350 nanoseconds as determined by an Edgerton, Germeshausen, and Grier photodiode No. SD-100. The flash tube produced a 2-volt pulse across the photodiode which served as the start pulse for the time-of-flight measurement.

The stop pulse for the time-of-flight measurement was produced by the detection of an electron by the Geiger-Mueller counter. The Geiger-Mueller counter was especially designed for this experiment to aid in verifying the theory of counting single electrons or what will be called the Poisson shift. The G-M tube was constructed of brass and was about 3.5 inches long and 0.687 inches in diameter. The center wire was 2.5 inches long and 0.003 inches in diameter. Instead of the usual one-hole opening in the tube, ten holes, each 0.031 inches in diameter, were equally spaced 0.125 inches apart along the tube. Thus more holes increased the

probability of an electron being counted. The wall thickness of the tube at the holes was 0.010 inches. A mechanism for selectively covering and uncovering each separate hole or any ordered sequence of holes was devised. This allowed control over the probability of an electron entering the counter. The covering mechanism added an additional 0.010 inches of thickness for the electron to travel to enter the tube. A calibrated mechanical bellows assembly provided a means of maneuvering the covering mechanism from outside the chamber without breaking the vacuum.

Since the gas used in the G-M counter had to be the same as the gas through which the electrons were diffusing, some electronic precautions had to be taken in order to prevent multiple pulsing or a continuous discharge from occurring when an electron initiated a discharge in the counter. Ordinarily G-M tubes are best quenched by the dissociation of some organic molecules when an avalanche has occurred. However, in this case, for obvious reasons, such an organic could not be used and some form of electronic quenching had to be employed. A simple form of electronic quenching was accomplished with a 100-megohm load resistor. The center wire of the G-M tube was at a positive potential with the outer cylinder at ground potential, as was the collecting electrode upon which it was attached. The tube operated nominally from 1500 to 2500 volts with the pressures of ethylene, hydrogen, and ethylene water mixtures used in this experiment.

Negative voltage pulses were developed across the G-M counter and were fed to a cathode follower preamp by a 50 $\mu$ f coupling capacitor. The

preamp had an amplification of 0.8 and was used as an impedance matching device. The preamp was located on top of the chamber and fed its pulses to an A-1 linear amplifier located a short distance away. The A-1 linear amplifier was adjusted for an amplification of 20 which was the maximum gain that could be used without overdriving the amplifier. With this amplification the G-M pulses were amplified to about 100 volts. As much gain as possible was desired in order to decrease the rise time of the pulses to some preset voltage level, which reduces the fluctuations in the time-of-flight measurement. The fast rise time in the A-1 linear amplifier helped to further decrease uncertainties in the time-of-flight measurements. The preset voltage level was set by a pulse height selector which gave a uniform output pulse. Since all Geiger pulses are the same size, the pulse height selector was set in the middle of the range well above the noise level and well below the level of maximum pulse height.

The time-of-flight measurements were first made with a modified version of the time-to-amplitude converter and the pulse height analyzer system used in the pilot experiment. This is the system that was photographed in Figure 6. Although this was a good system, its stability was not good enough for the sensitive diffusion measurements required in these experiments. Also, the system's non-zero time intercept required an additional delay line and an inverter amplifier for impedance matching. Any extra electronic equipment such as this is always undesirable since these increase error due to instrument fluctuations. A Technical Measurements

Corporation 1024-channel pulse analyzer system, Model TMC 1024-2, with a time-of-flight logic unit was used to measure the time-of-flight distributions. Two time-of-flight logic units were supplied with the system, Models 201 and 211. Model 211 measures time intervals of 250 nanoseconds per channel to 64 microseconds per channel. The Model 201 time-of-flight logic unit was used exclusively with this experiment. This unit had channel lengths (time interval per channel) equal to 31.25, 62.5, and 125 nanoseconds per channel. Data were analyzed and printed out on paper tape for permanent record and were punched out on paper tape for computer handling.

A Rutherford Electronics Company digital time delay generator, Model A11, was used to delay the starting pulse from the photodiode. This allowed the use of the smaller channel lengths in the time-of-flight analyzer. In other words, the time-of-flight distribution could be spread out over more channels and the resolution of the experiment be improved. This delay could be set from 0 to 1 second in 0.1-microsecond increments with an accuracy of 0.001 percent. The sync output was used for zero time delays. A Hewlett-Packard Model 450A amplifier was used to boost the 2-volt pulse output of the photodiode to an 8-volt pulse which would reliably trigger the delay generator. As mentioned later, this delay generator also served as a time calibration for the analyzer.

As it was known that small traces of impurities such as water vapor in a carrier gas such as ethylene could cause drastic changes in drift velocity and diffusion coefficients, it was desirable to have an effective

gas purification system and an efficient vacuum system. A gas manifold system was designed for purifying the gas and filling the chamber. The system actually contained two manifolds and was capable of handling two gases separately, although in this experiment only one was used. The gas was first run through a trap filled with Linde Type 13X molecular sieve to aid in the removal of water vapor. The gas then could be run through two cold traps or could be distilled several times. Both the molecular sieve and the cold traps could be heated to a high temperature as they were sealed with metal "O" rings. Generally, liquid nitrogen was used in the cold traps. A pressure gauge and two pressure relief valves were also supplied to each manifold. A small container for adding condensable vapors or liquids such as water was paralleled with the gas manifold. A needle valve was used so that the vapor could be introduced into the chamber very slowly.

Upon filling the chamber with some gas the pressure could be read in either or both of two ways. First, two Wallace and Tiernan differential pressure gauges were used--one with a maximum range of 2250 torr and the other of 20 torr. The second and the primary gauge used to determine the pressures was a capacitance manometer (an MKS Baratron Type 77 pressure meter supplied with a Type 77H-1000 pressure head). This capacitance manometer is a differential pressure device and measures true pressure. A vacuum was used as the reference pressure. The capacitance manometer offered a wide range of pressures that could be measured. With the particular head used, full scale readings on the pressure meter were from

1000 torr to 0.03 torr. The utility of this instrument was clearly demonstrated in adding small amounts of vapors to the carrier gas and in monitoring pressure changes. By balancing the bridge, 3-micron pressure changes could be easily detected.

A medium size Model 1405 Welch Duo Seal vacuum pump was used to pump out the gas manifold. This same pump was used as a roughing pump to rough the chamber down to about 10 microns. The chamber was roughed to this low pressure because ethylene was found to deteriorate the diffusion pump oil. A cold trap was placed in line with the pump so that pump oil would not back-diffuse into the system. When filled with liquid nitrogen, this trap would pump out ethylene from the chamber to a 10-micron pressure in less than a minute.

After the chamber had been roughed down, an optimum vacuum was achieved by evacuating the chamber with a Consolidated Vacuum Corporation (CVC) Type MCF-300 four-inch, water-cooled oil diffusion pump, using a Model 1377B Welch Duo Seal forepump. A CVC Type VW-40 water-cooled baffle was used above the diffusion pump to prevent back diffusion of the pump oil. An ultimate vacuum of  $8 \times 10^{-7}$  torr was achieved as measured with a CVC Type GIC-110A ionization gauge. Several Hastings thermocouple vacuum gauges were placed at different points of interest as shown in Figure 5.

## II. EXPERIMENTAL PROCEDURES

As stated in the objectives of this experiment, careful measurements of drift velocity and diffusion coefficients were to be made for electrons in ethylene and ethylene water mixtures. A chemically pure grade of ethylene, as supplied in steel cylinders by the Matheson Company, Inc., was used. This grade of ethylene has a minimum purity of 99.5 percent and is quoted as being typically 99.72 percent pure with propylene, propane, butenes, butanes, and ethane making up the impurities. As it was already known that traces of water vapor have large effects on the drift velocity and on the diffusion coefficients, maximum precautions were taken to free the ethylene of water vapor. This was done with the molecular sieve and the distillation procedure as has been mentioned. A mass spectrometer analysis showed that the small traces of water were reduced by distillation—enough to warrant continuation of the process.

Later a research grade of ethylene was obtained and used. The research grade had a minimum purity of 99.9 percent with the 0.1 percent impurity being most probably propane. The same results were obtained with both supplies of ethylene. Hydrogen of an ultra-pure grade was used as an additional check on the results obtained with ethylene.

When the optimum vacuum was achieved in the chamber, distilled ethylene was introduced into the chamber and the pressure was read with the capacitance manometer. When ethylene and water vapor mixtures were

studied, the water vapor was first introduced and then the ethylene was introduced in the usual manner for introducing pure ethylene. When the water vapor was first introduced into the chamber at some initial pressure, the pressure was observed to fall substantially. This was attributed to the well known fact that water vapor will plate out on, or will be absorbed by, metal surfaces. Therefore, before adding the ethylene, more water vapor was added until the pressure reached an equilibrium.

After filling the chamber with the desired gas at the desired pressure, the electric field intensity was adjusted to the desired  $E/P$ . The voltage potential was supplied by two power supplies, a one-kilovolt supply and a 10-kilovolt supply. The one-kilovolt supply was a Keithley Model 240 regulated DC high voltage supply and could be continuously adjusted to read from 0 to 1000 volts with an accuracy of plus or minus one percent or 0.1 volt. The 10-kilovolt supply was a John Fluke Model 410A high voltage supply. This supply was continuously variable from 1000 volts to 10,000 volts with an accuracy of 0.25 percent. Therefore, quite a range of  $E/P$ 's could be covered for any given pressure. Generally the voltage settings ranged from 5.4 volts to 2700 volts.

Since the gas used in the G-M tube was the same as the gas being studied, the proper operating voltage for the tube had to be determined for each mixture of gas at the particular pressure being studied. Initially this was done by finding the G-M plateau with the aid of a scaler at the pulse height selector output. Most of the time the operating voltage was found more

easily by looking at the Geiger pulses and adjusting the voltage until all the pulses became uniform in size. The G-M voltage was supplied by a John Fluke Model 400 BDA 5-kilovolt DC regulated high voltage supply.

As pointed out in the theory of detecting single electrons, only one electron out of a minimum of ten flashes should be detected in order to minimize the Poisson shift. This could be achieved by controlling the number of photoelectrons emitted per unit area from the photocathode and by selecting the number of holes under the G-M tube. The light intensity could be controlled in either or both of two ways. First, the intensity could be varied by increasing or decreasing the high voltage to the flash tube—in other words, by changing the amount of energy dumped into the tube per flash. In order to minimize error due to light fluctuations, it was desirable to use the highest voltage as feasible (generally about 1100 volts). The use of various sizes of apertures was the primary method of controlling the light intensity. These apertures ranged from 0.040 to 0.250 inches in diameter. The light intensity had to be adjusted with change of gas, pressure, and E/P. The importance of keeping the ratio of electrons per flash reasonably low was recognized. Therefore, by using the scaler, close surveillance was kept on this ratio and the proper adjustments were made to keep this ratio at all times below one tenth.

The time-of-flight logic unit was calibrated using the digital delay generator as the standard, although both instruments were crystal oscillator controlled. The digital delay generator was checked against a third crystal

oscillator with which there was agreement. The sync out pulse was used as a start pulse for the time-of-flight analyzer and the delayed pulse, fed to the linear amplifier test input, was used to stop the analyzer. Calibration was then done by putting in known delays and recording the channel in which the pulses accumulated. Plotting the calibration data clearly indicated that the instrument was nearly ( $\pm 0.1$  percent) linear; however, the data was fitted by a least squares procedure to a quadratic equation. As was suspected, the squared term contributed very little to the fitted curve. The calibration was checked from time to time and was found to vary little or none at all. The channel lengths were found to be within 1 percent of the dial settings.

In order to verify the theory of counting single electrons, Equation (46) had to be verified. This required an accurate value of  $\bar{N}_a$  to be determined from the experiment with the aid of Equation (52). Equation (52) is an asymptotic equation such that as  $C/F$  approaches one,  $\bar{N}_a$  must get infinitely large. Taking into account experimental error, a good determination of  $\bar{N}_a$  should be calculated from a  $C/F$  value that is not very close to one; however, in order to see an appreciable Poisson shift,  $\bar{N}_a$  cannot be too small. The multi-hole counter was built to meet these restrictions. A value of  $\bar{N}_a$  for each separate hole could be calculated for a  $C/F$  less than one. Then by opening up all ten holes a new value of  $\bar{N}_a$  could be assumed which would be the sum of the  $\bar{N}_a$ 's for each separate hole. The new value of  $\bar{N}_a$  would be much larger than would be practical to calculate from a

measurement of  $C/F$  which would be very close to one. This method gave results which were in error. The error was found to be a field effect which allowed more electrons to enter each hole when all were uncovered. When all holes were uncovered, there was less metal around each hole and there was a smaller region with zero electric field. Removing some of the metal improved the results, but not sufficiently.

A compromise between a large  $\bar{N}_a$  and a  $C/F$  value less than one was used. All ten holes were used and this gave a  $C/F$  value close to one. In order to determine  $C/F$  accurately, two separate scalers, each started and stopped by the same clock, were used. The total counts,  $C$ , and the total flashes,  $F$ , were measured at the same time as the Poisson shifted distribution was measured. This proved to be satisfactory.

Errors due to fluctuations in instruments could be taken into consideration by finding a function  $T_o(t)$  for electrons which is not allowed to drift or diffuse in the swarm region. The detection of photoelectrons emitted from the inside of the G-M tube is subject to all delays and fluctuations except those due to drift and diffusion in the swarm region. Therefore, to measure an error function  $T_o(t)$  the time distribution of these photoelectrons was measured. A reverse field was applied to the swarm region to prevent electrons from entering from outside the tube. Usually all ten holes were opened to improve the probability of getting photons into the tube. The number of counts per flash,  $C/F$ , was also kept below 0.1 for these measurements.

## CHAPTER IV

### EXPERIMENTAL RESULTS AND DATA ANALYSIS

A sample set of data as taken from the time-of-flight analyzer is shown in Table I. It would be impractical to present all the raw data in this form as there were similar sets of data for each of the many E/P's for the gases studied. The raw data will be kept on file at all times for recall. For a particular gas filling and channel length setting on the analyzer, one error function served for several measured electron distributions. Along with the raw data, log sheets were kept on which extraneous data that did not enter into the calculations was recorded. Such data were G-M and light voltages, field voltages, and aperture settings. These are kept on file also.

Experimental results verifying the theory of counting of single electrons are shown in Figure 7. Curve  $E_1''(t)$  is a measured experimental distribution for  $C/F \ll 1$  where, according to Equation (48),  $E(t) \approx E''(t)$ . Curve  $E_2''(t)$  is a measured Poisson shifted distribution for an  $\bar{N}a$  value of 3.35. Curve  $E_3'''(t)$  is the theoretical distribution given by Equation (46). By Equation (48),  $E(t)$  could be approximated by  $E_1''(t)$ ;  $E_3'''(t)$  was then constructed by numerical integration. The agreement is quite good and is well within experimental error. This verifies Equation (46) and the theory of counting single electrons. The experiment was repeated with similar

TABLE I

SAMPLE SET OF DATA (100 TORR PURE ETHYLENE;  
E/P = 0.1 VOLTS CM<sup>-1</sup> TORR<sup>-1</sup>)

Error Function, $T_o(t_i)$			Electron Distribution $E'(t_i)$		
Delay Time = 0.0 $\mu$ sec			Delay Time = 27.0 $\mu$ sec		
$C_i$	$t_i(\mu$ sec)	$T_o(t_i)\Delta t$	$C_i$	$t_i(\mu$ sec)	$E'(t_i)\Delta t$
5	0.1732	0	14	27.741	0
6	0.2363	1	15	27.804	1
7	0.2995	2	16	27.867	1
8	0.3626	16	17	27.930	2
9	0.4257	404	18	27.994	3
10	0.4889	1622	19	28.057	3
11	0.5520	2500	20	28.120	6
12	0.6152	1939	21	28.183	6
13	0.6783	1041	22	28.246	14
14	0.7414	504	23	28.309	13
15	0.8046	212	24	28.372	24
16	0.8677	126	25	28.435	54
17	0.9308	106	26	28.499	51
18	0.9940	75	27	28.562	68
19	1.0571	60	28	28.625	94
20	1.1203	38	29	28.688	121
21	1.1834	30	30	28.751	143
22	1.2465	26	31	28.814	215
23	1.3097	15	32	28.877	265
24	1.3728	21	33	28.941	305

TABLE I (continued)

Error Function, $T_o(t_i)$			Electron Distribution $E'(t_i)$		
Delay Time = 0.0 $\mu\text{sec}$			Delay Time = 27.0 $\mu\text{sec}$		
$C_i$	$t_i(\mu\text{sec})$	$T_o(t_i)\Delta t$	$C_i$	$t_i(\mu\text{sec})$	$E'(t_i)\Delta t$
25	1.4359	27	34	29.004	396
26	1.4991	22	35	29.067	460
27	1.5622	14	36	29.130	501
28	1.6253	16	37	29.193	604
29	1.6884	21	38	29.256	525
30	1.7516	15	39	29.319	707
31	1.8147	16	40	29.382	686
32	1.8778	10	41	29.446	761
33	1.9410	5	42	29.509	762
34	2.0041	12	43	29.572	756
35	2.0672	7	44	29.635	701
36	2.1303	9	45	29.698	710
37	2.1935	4	46	29.761	667
38	2.2566	6	47	29.824	569
39	2.3197	8	48	29.887	548
40	2.3828	4	49	29.951	502
			50	30.014	458
			51	30.077	397
			52	30.140	384
			53	30.203	302
			54	30.266	279
			55	30.329	202
			56	30.392	181

TABLE I (continued)

Electron Distribution $E'(t_1)$		
Delay Time = 27.0 $\mu\text{sec}$		
$C_i$	$t_i(\mu\text{sec})$	$E'(t_i) \Delta t$
57	30.455	153
58	30.519	95
59	30.582	112
60	30.645	87
61	30.708	82
62	30.771	69
63	30.834	53
64	30.897	60
65	30.960	55
66	31.023	39
67	31.087	36
68	31.150	38
69	31.213	32
70	31.276	39
71	31.339	26
72	31.402	33
73	31.465	29
74	31.528	23
75	31.591	28
76	31.655	20
77	31.718	10
78	31.781	24
79	31.844	18

TABLE I (continued)

Electron Distribution $E'(t_i)$		
Delay Time = 27.0 $\mu$ sec		
$C_i$	$t_i$ ( $\mu$ sec)	$E'(t_i)\Delta t$
80	31.907	25
81	31.970	19
82	32.033	20
83	32.096	23
84	32.159	14
85	32.223	16
86	32.286	12
87	32.349	10
88	32.412	9
89	32.475	6
90	32.538	10
91	32.601	5
92	32.664	6
93	32.727	11
94	32.790	8
95	32.854	11
96	32.917	4
97	32.980	5
98	33.043	9
99	33.106	4
100	33.169	3

Channel No. =  $C_i$ ; Time =  $t_i$ .

$$t_i = \left[ -1.425 \times 10^{-1} + 6.314 \times 10^{-2} \times C_i - 2.456 \times 10^{-7} \times C_i^2 \right] + \text{Delay Time} .$$

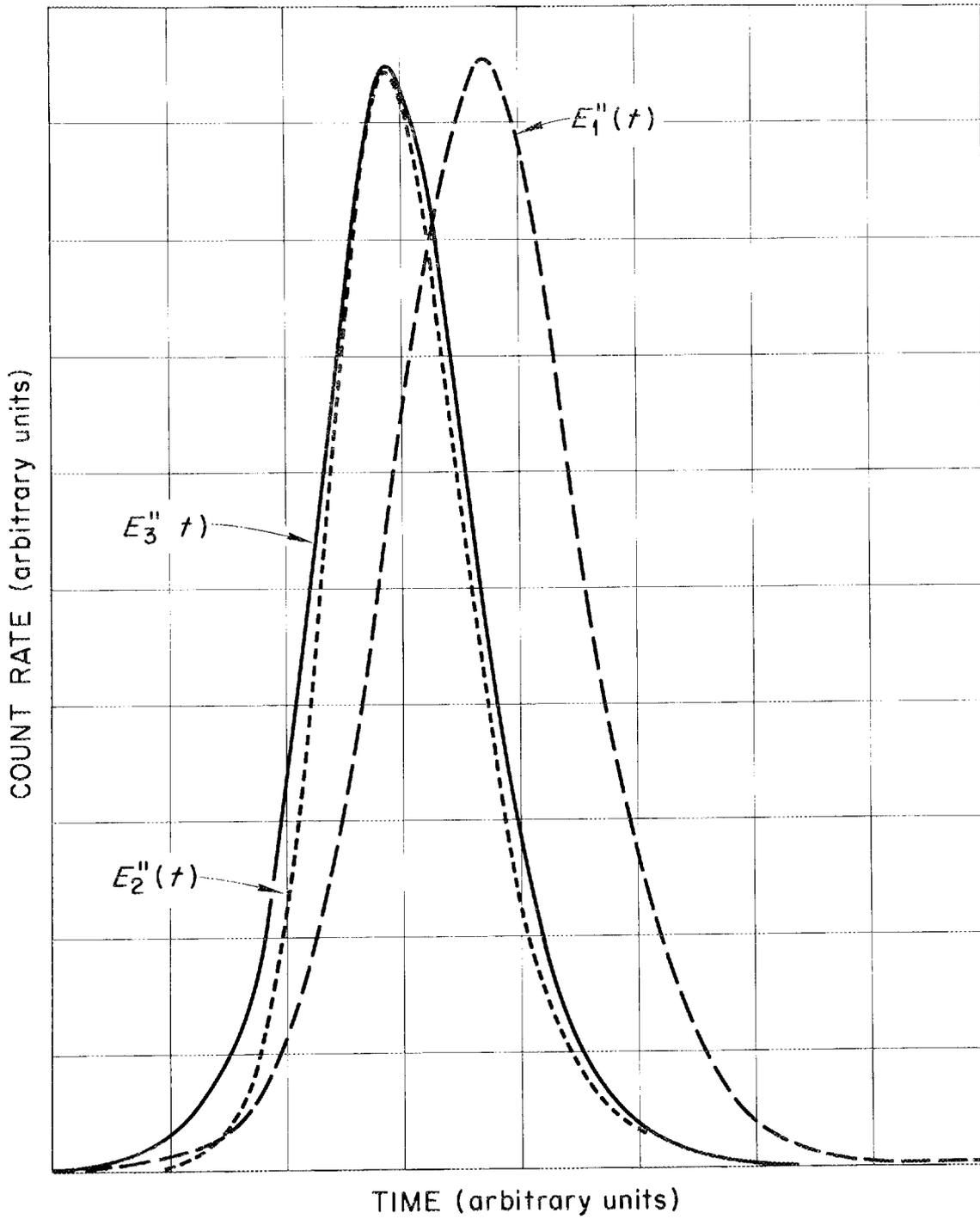


Figure 7. Experimental results of Poisson shift.

results and those results are kept on file.

A series of theoretical curves of Equation (46) were constructed as a function of  $\bar{N}a$  so that one might see the effect of the Poisson shift for different  $\bar{N}a$  values. These curves are shown in Figure 8. From these curves one can easily see that when  $C/F \ll 1$  that  $E''(t)$  is a very good approximation for  $E(t)$ . By using the estimates of Equation (23) and (26),  $D$  and  $W$  were calculated for each of these curves and are listed in Table II. For  $\bar{N}a$  less than 0.1, the change in  $W$  and  $D$  is insignificant, but for  $\bar{N}a$  equal to 100, the change in  $W$  is about 3 percent and the change in  $D$  is about a factor of 6.

Equation (54) provides the basis for the determination of  $D$  and  $W$  from the measured function  $T_0(t)$  and  $E'(t)$ . Equations (23) and (26) were used first to find estimates for  $W$  and  $D$ . Final values of  $W$  and  $D$  were found by a least squares data fitting procedure where  $E'(t)$  was data fitted to numerically integrated Equation (54). In this procedure  $E(t)$  is an analytical function and  $T_0(t)$  is a measured error distribution. A program was written which would take a minimum of twenty minutes computer (Control Data 1604) time to analyze a set of data for  $D$  and  $W$ . This straightforward method was considered too inefficient so another method of analyzing the data was sought.

An elegant method using Fourier transforms was derived and programmed by Ritchie and Anderson (1965). Basically the first step of this program was to take the Fourier transform,  $F$ , of both sides of Equation (54).

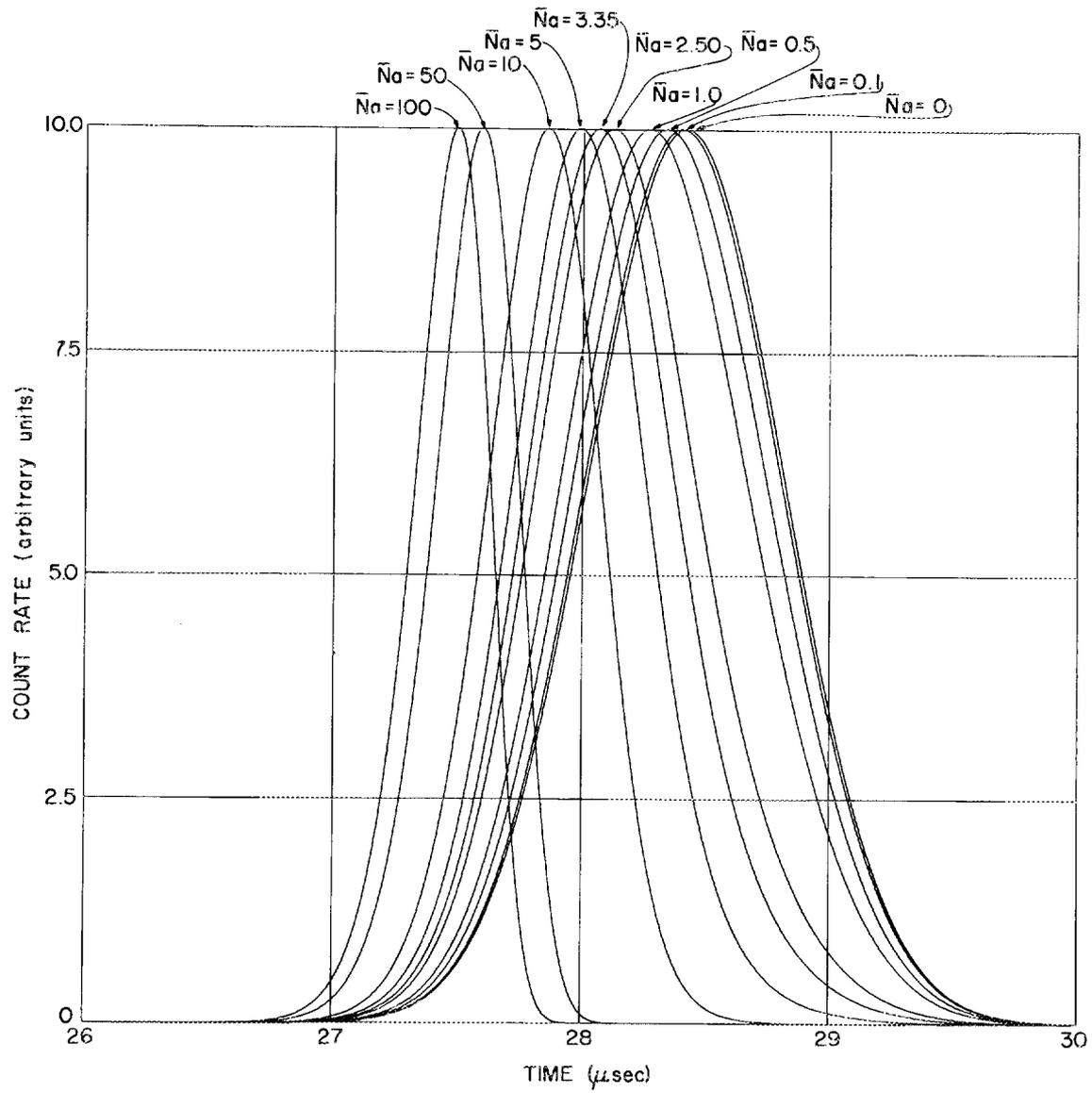


Figure 8. Theoretical distributions of Poisson shift.

TABLE II

DISTORTION OF D AND W DUE TO POISSON SHIFT

C/F	$\bar{N}_a$	$t_m$ ( $\mu\text{sec}$ )	$\delta t$ ( $\mu\text{sec}$ )	$W$ ( $\text{cm}\mu\text{sec}^{-1}$ )	$D \times 10^3$ ( $\text{cm}^2 \mu\text{sec}^{-1}$ )	$W/D \times 10^{-3}$ ( $\text{cm}^{-1}$ )
0	0	28.420	0.561	0.950	2.49	0.381
0.0488	0.05	28.410	0.561	0.950	2.49	0.381
0.0952	0.10	28.400	0.561	0.951	2.50	0.381
0.3935	0.50	28.340	0.554	0.953	2.46	0.388
0.6322	1.00	28.270	0.537	0.955	2.32	0.411
0.9180	2.50	28.120	0.465	0.960	1.77	0.543
0.9650	3.35	28.070	0.432	0.962	1.66	0.580
0.9930	5.00	27.990	0.387	0.965	1.24	0.777
1.0000	10.00	27.860	0.324	0.969	0.882	1.10
1.0000	50.00	27.590	0.239	0.976	0.477	2.05
1.0000	100.00	27.500	0.217	0.982	0.411	2.39

This gives

$$F[E'(\tau)] = F\left[\int_0^{\tau} E(t) T_0(\tau - t) dt\right]. \quad (55)$$

Then by the convolution theorem,

$$F[E'(\tau)] = F[E(\tau)] \times F[T_0(\tau)] \quad (56)$$

and

$$F[E(\tau)] = \frac{F[E'(\tau)]}{F[T_0(\tau)]}. \quad (57)$$

The Fourier transform of  $E(t)$  can be written by defining equations

$$F[E(t)] \equiv \bar{E}(\omega) \quad (58)$$

where  $\omega$  is frequency and

$$\bar{E}(\omega) = \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt. \quad (59)$$

For the special case where  $E(t)$  is identically zero for negative arguments,

Equation (59) becomes

$$\bar{E}(\omega) = \int_0^{\infty} E(t) e^{i\omega t} dt. \quad (60)$$

Replacing  $E(t)$  in Equation (60) with Equation (18) and with  $\beta = 0$ ,  $\bar{E}(\omega)$  is

found to be given by

$$\bar{E}(\omega) = \frac{e^{-b(\sqrt{1-i\omega a} - 1)}}{\sqrt{1-i\omega a}} \quad (61)$$

where

$$a = \frac{4D}{W^2} \quad (62)$$

and

$$b = \frac{WL}{2D} . \quad (63)$$

Therefore, the Fourier transform of  $E(t)$  can be found analytically so that on the left of Equation (57) there is an analytical expression. The Fourier transform of the measured distributions  $E'(\tau)$  and  $T_o(\tau)$  can be found by numerical integration. This integration process has to be done only once for as many least squares fitting iterations that have to be made. (The straightforward method had an integration process for each iteration.) The estimates for  $D$  and  $W$  were then used to data fit, by a least squares procedure, the analytical expression on the left of Equation (57) to the quotient of the transforms of the measured distributions on the right. This method works very efficiently and takes approximately one half minute of computer time to analyze a set of data for  $D$  and  $W$ .

Figure 9 shows a plot of a typical measured error function,  $T_o(t)$ , along with a plot of experimental values of  $E'(t)$ . The best fit of the convolution of the analytical function  $E(t)$  and the experimental  $T_o(t)$  is shown on the same graph. It can be seen that the fit is very good. The analytical function  $E(t)$  is also plotted so that one sees the actual electron time-of-flight distribution as compared to the measured distribution. This distribution is for electrons swarming through 100 torr of pure ethylene at an  $E/P$  of 0.4 volts/cm<sup>-1</sup>/torr<sup>-1</sup>. A diffusion coefficient,  $D$ , of  $2.9 \times 10^{-3}$  was calculated, and when normalized to unit pressure this gives a value of  $0.29 \text{ cm}^2\text{-torr}/(\mu\text{sec})^{-1}$  for  $D \times P$  or  $D_1$ . Comparing this to the preliminary

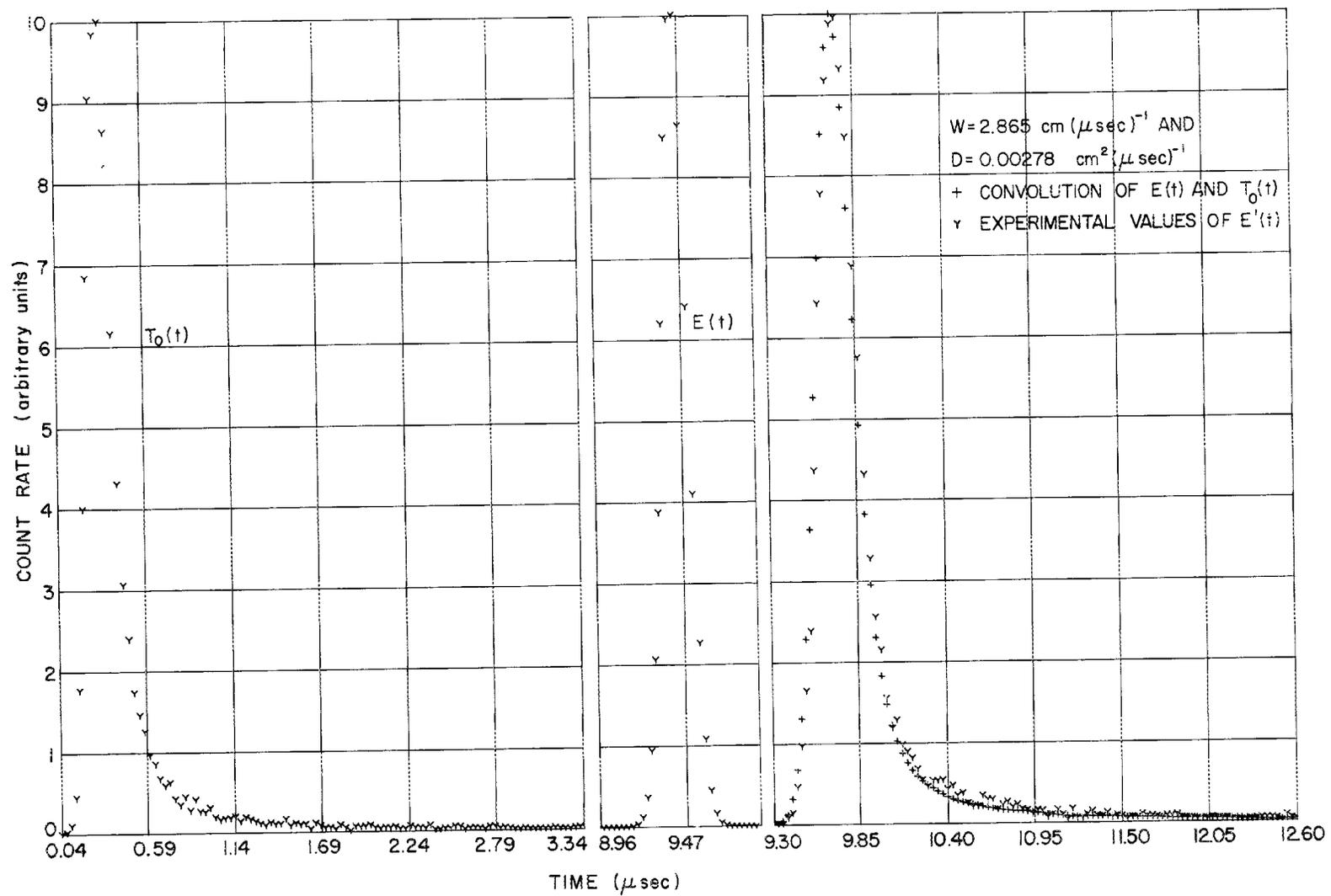


Figure 9. Error function, measured distribution, unfolded distribution, and convolution of unfolded distribution and error function.

diffusion data in Figure 3, a marked improvement is noted.

For further illustration the data were processed assuming that there were no error fluctuations. The measured distribution and the best fit of  $E(t)$  to this distribution is shown in Figure 10. It is very clear that the fit is not very good. The drift velocity remains unchanged while the diffusion coefficient is a factor of four larger. However, it should be noted that the diffusion coefficient is not as large as in the pilot experiment. This is an indication that basic improvements in the electronics system were made.

All data were taken over an  $E/P$  range of  $0.02 \text{ volts/cm}^{-1}/\text{torr}^{-1}$  to  $1.0 \text{ volts/cm}^{-1}/\text{torr}^{-1}$ . Drift velocity and diffusion coefficients were measured in pure ethylene at pressures of 100 and 50 torr. These data are listed in Tables III and IV. Data were taken for ethylene and water mixtures at a total pressure of 100 torr with the partial pressures of water ranging from 0.25 torr to 4 torr. These data are listed in Tables V through IX. Drift velocity data for pure ethylene and the ethylene water mixtures are shown on two graphs. In Figure 11 drift velocities are plotted as a function of  $E/P$  for the  $E/P$  range of 0 to  $0.1 \text{ volts/cm}^{-1}/\text{torr}^{-1}$ . In Figure 12 the drift velocities are plotted over the  $E/P$  range of 0 to  $1.0 \text{ volts/cm}^{-1}/\text{torr}^{-1}$ .

Diffusion coefficients normalized to pressure,  $DP$ , for 100 torr pure ethylene are shown graphed in Figure 13 for  $E/P$ 's of 0 to 0.1 volt.  $DP$  values for the ethylene water mixtures are shown on the same graph. The dotted lines are the average  $DP$  values at the  $E/P$ 's shown for each gas and gas mixture.

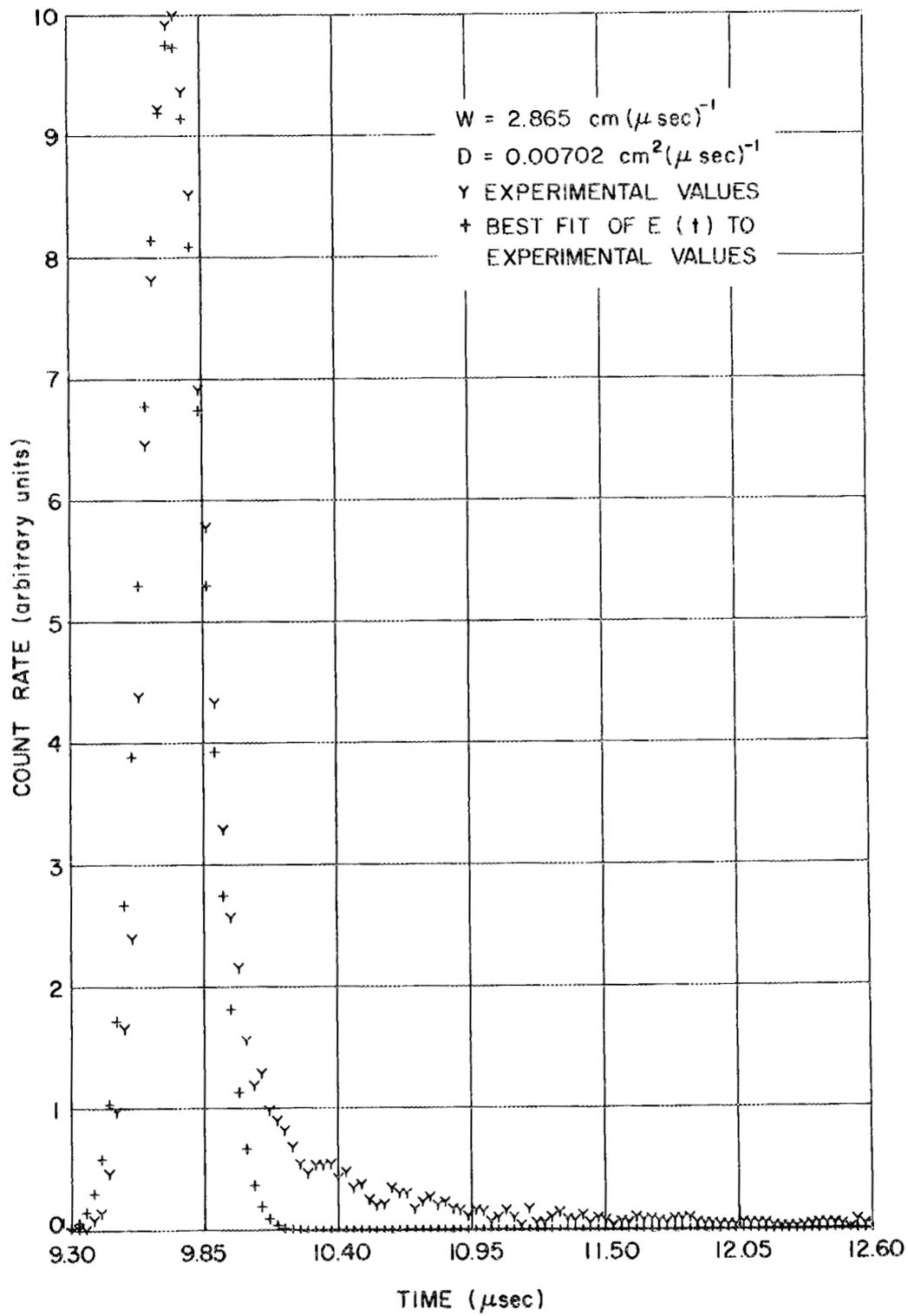


Figure 10. Misfit of data when no error correction is made.

TABLE III  
SUMMARY OF RESULTS FOR 100 TORR ETHYLENE

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.02	0.1957	3.2370	0.3237
0.03	0.2930	2.8739	0.2873
0.04	0.3884	2.9125	0.2912
0.05	0.4831	2.8204	0.2820
0.06	0.5755	2.8960	0.2896
0.07	0.6663	2.8742	0.2874
0.08	0.7553	2.9416	0.2941
0.09	0.8457	2.8557	0.2855
0.10	0.9320	3.0744	0.3074
0.20	1.6990	2.9651	0.2965
0.30	2.3335	2.9936	0.2993
0.40	2.8652	2.7840	0.2784
0.50	3.3088	3.0295	0.3029
0.60	3.6635	2.7541	0.2754
0.70	3.9699	4.0787	0.4078
0.80	4.1837	2.4994	0.2499
0.90	4.3766	2.2199	0.2219
1.00	4.5637	3.9065	0.3906

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE IV  
 SUMMARY OF RESULTS FOR 50 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.02	0.1944	6.9571	0.3478
0.03	0.2885	7.4879	0.3743
0.04	0.3856	7.1450	0.3572
0.05	0.4798	6.9813	0.3490
0.06	0.5723	6.7931	0.3396
0.07	0.6615	7.1357	0.3567
0.08	0.7510	6.9149	0.3457
0.09	0.8401	6.7500	0.3375
0.10	0.9280	6.5873	0.3293
0.20	1.7092	6.1045	0.3052
0.30	2.3273	6.4669	0.3233
0.40	2.8557	5.5507	0.2775
0.50	3.2835	4.8830	0.2441
0.60	3.6324	5.2318	0.2615
0.70	3.9154	6.6730	0.3336
0.80	4.1839	5.3367	0.2668
0.90	4.3768	5.3959	0.2697
1.00	4.5156	5.8121	0.2906

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE V

SUMMARY OF RESULTS FOR 0.25 TORR H<sub>2</sub>O PLUS 99.75 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.02	0.1516	2.3905	0.2390
0.03	0.2280	2.1972	0.2197
0.04	0.3047	2.2299	0.2229
0.05	0.3677	2.1972	0.2197
0.06	0.4410	2.1319	0.2131
0.07	0.5135	2.1949	0.2194
0.09	0.6573	2.1756	0.2175
0.10	0.7280	2.2175	0.2217
0.20	1.3976	2.4092	0.2409
0.30	1.9792	2.8195	0.2819
0.40	2.4946	2.5335	0.2533
0.50	2.9258	3.1330	0.3133
0.60	3.2961	2.8319	0.2831
0.70	3.5968	3.0900	0.3090
0.80	3.8674	2.1850	0.2185
0.90	4.0899	2.2204	0.2220
1.00	4.2744	2.3301	0.2330

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE VI

SUMMARY OF RESULTS FOR 0.5 TORR H<sub>2</sub>O PLUS 99.5 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.02	0.1197	1.6914	0.1691
0.03	0.1801	1.9610	0.1961
0.04	0.2433	1.9346	0.1934
0.05	0.3048	1.9033	0.1903
0.06	0.3594	1.7053	0.1705
0.07	0.4206	1.7689	0.1768
0.08	0.4809	1.7752	0.1775
0.09	0.5448	1.8703	0.1870
0.10	0.6259	2.0158	0.2015
0.20	1.1637	2.0221	0.2022
0.30	1.6945	2.5428	0.2542
0.40	2.1773	2.2757	0.2275
0.50	2.5958	2.1595	0.2159
0.60	2.9692	2.1809	0.2180
0.70	3.2783	2.7378	0.2737
0.80	3.5689	1.6728	0.1672
0.90	3.7956	1.8264	0.1826
1.00	4.0053	1.8425	0.1842

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE VII  
 SUMMARY OF RESULTS FOR 1 TORR H<sub>2</sub>O PLUS 99 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.03	0.1186	1.1595	0.1159
0.04	0.1580	1.1007	0.1100
0.05	0.1968	1.0854	0.1085
0.06	0.2350	1.1097	0.1109
0.07	0.2742	1.1422	0.1142
0.08	0.3114	1.1470	0.1147
0.09	0.3515	1.1304	0.1130
0.10	0.3934	1.1998	0.1199
0.20	0.7740	1.2312	0.1231
0.30	1.1539	1.2604	0.1260
0.40	1.5351	1.4034	0.1403
0.50	1.8925	1.4973	0.1497
0.60	2.2299	1.6977	0.1697
0.70	2.5468	1.2449	0.1244
0.80	2.8401	1.5048	0.1504

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE VIII  
 SUMMARY OF RESULTS FOR 2 TORR H<sub>2</sub>O PLUS 98 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.03	0.0802	0.8649	0.0864
0.04	0.1063	0.9230	0.0923
0.05	0.1337	0.8445	0.0844
0.06	0.1611	0.7759	0.0775
0.07	0.1882	0.7782	0.0778
0.08	0.2100	0.7137	0.0713
0.09	0.2325	0.7454	0.0745
0.10	0.2637	0.9413	0.0941
0.20	0.5272	0.8519	0.0851
0.30	0.7867	0.9123	0.0912
0.40	1.0589	1.0241	0.1024
0.50	1.3361	1.0573	0.1057
0.60	1.6006	1.1948	0.1194
0.70	1.8656	1.1522	0.1152
0.80	2.1197	1.4041	0.1404
0.90	2.3593	1.4006	0.1400
1.00	2.5877	1.5354	0.1535

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

TABLE IX  
 SUMMARY OF RESULTS FOR 4 TORR H<sub>2</sub>O PLUS 96 TORR C<sub>2</sub>H<sub>4</sub>

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )
0.06	0.0897	0.4337	0.0433
0.08	0.1194	0.4255	0.0425
0.10	0.1510	0.4757	0.0475
0.20	0.2953	0.4549	0.0454
0.30	0.4432	0.4814	0.0481
0.40	0.5966	0.5134	0.0513
0.50	0.7482	0.5548	0.0554
0.60	0.9053	0.5535	0.0553
0.70	1.0632	0.6336	0.0633
0.80	1.2247	0.6355	0.0635
0.90	1.3899	0.6626	0.0662
1.00	1.5523	0.8197	0.0819

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

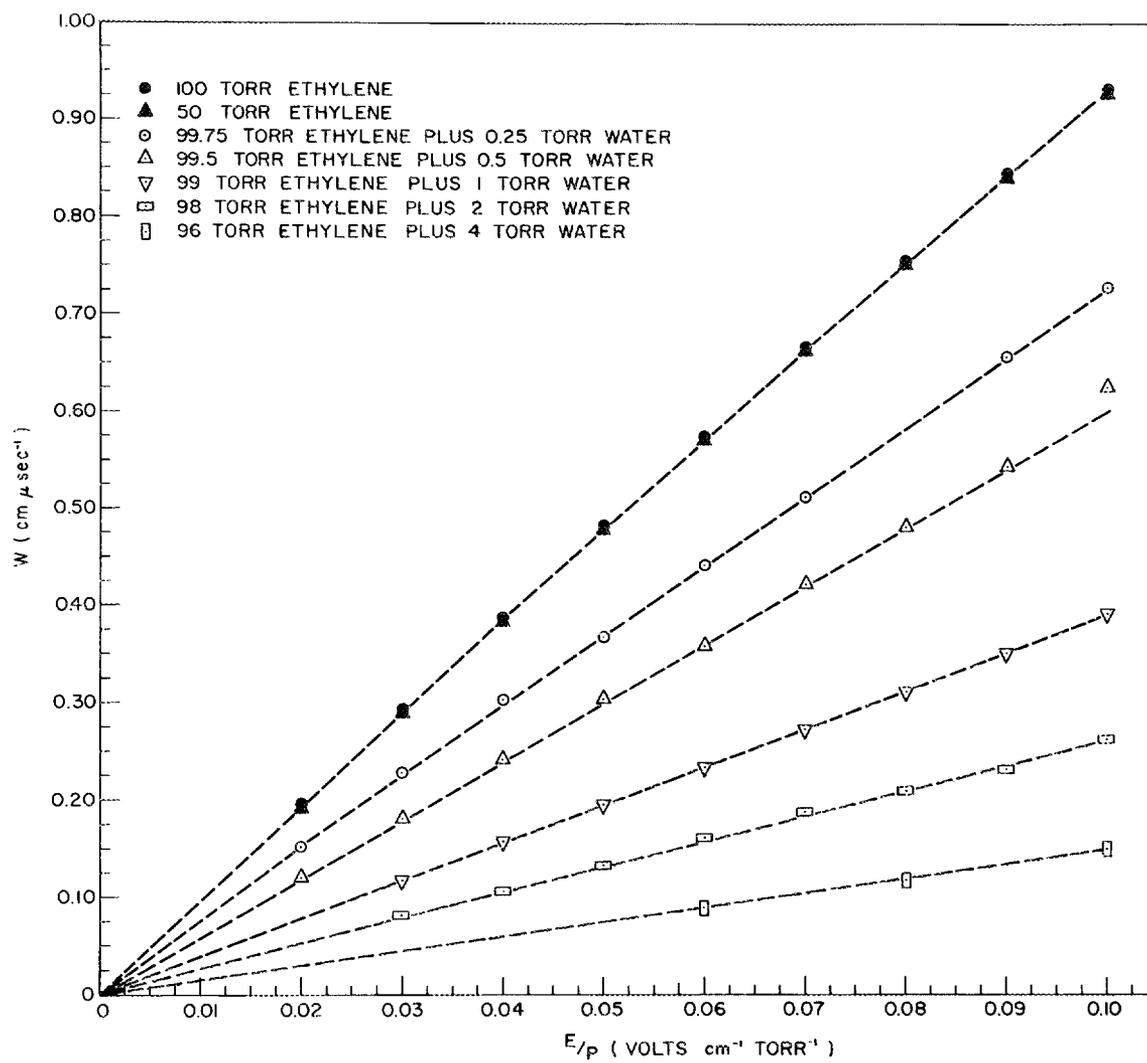


Figure 11. Drift velocity vs  $E/P$  for ethylene and ethylene-water mixtures (0 - 0.1 volt  $\text{cm}^{-1}$  torr $^{-1}$ ).

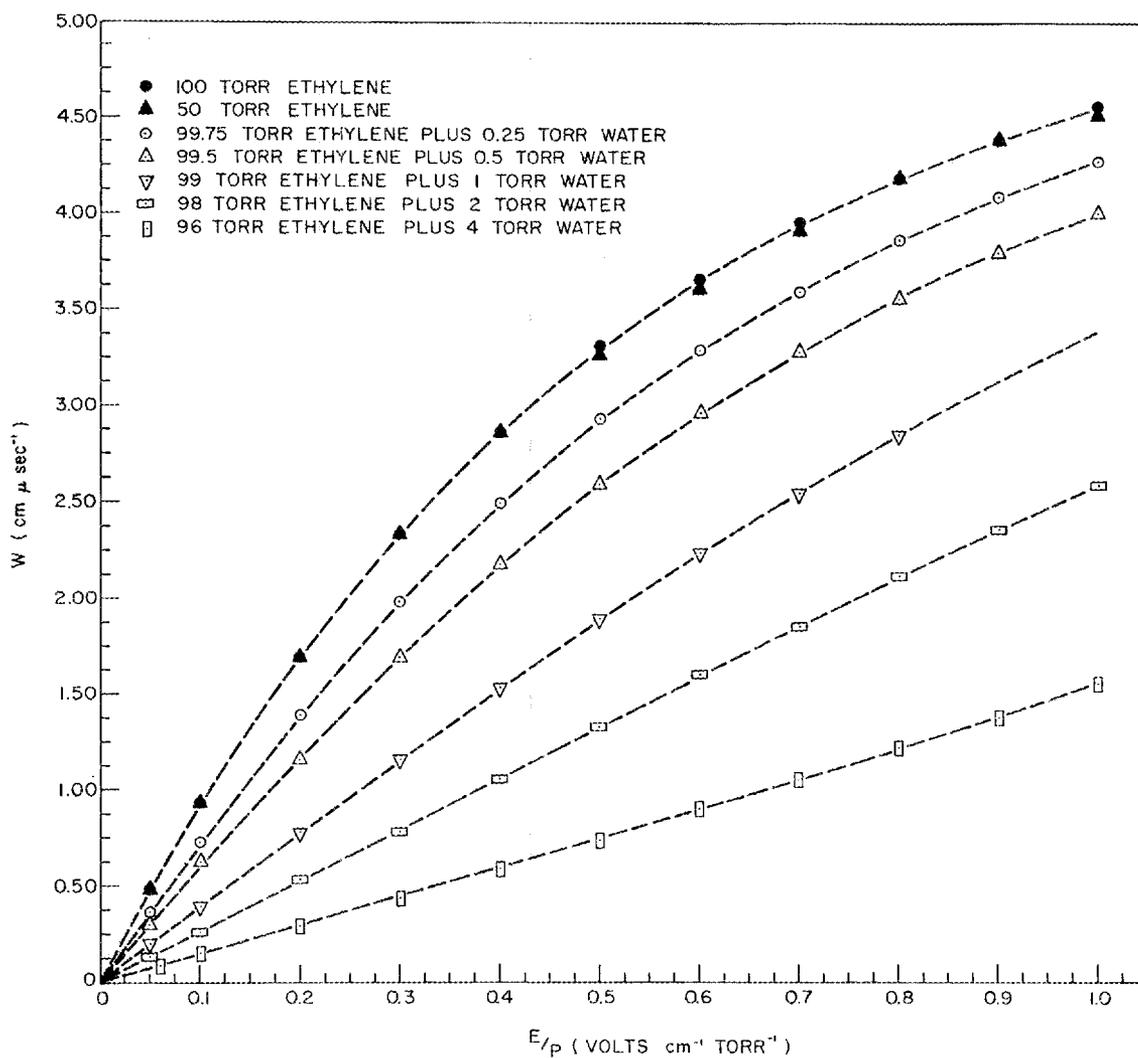


Figure 12. Drift velocity vs  $E/P$  for ethylene and ethylene-water mixtures ( $0 - 1.0 \text{ volt cm}^{-1} \text{ torr}^{-1}$ ).

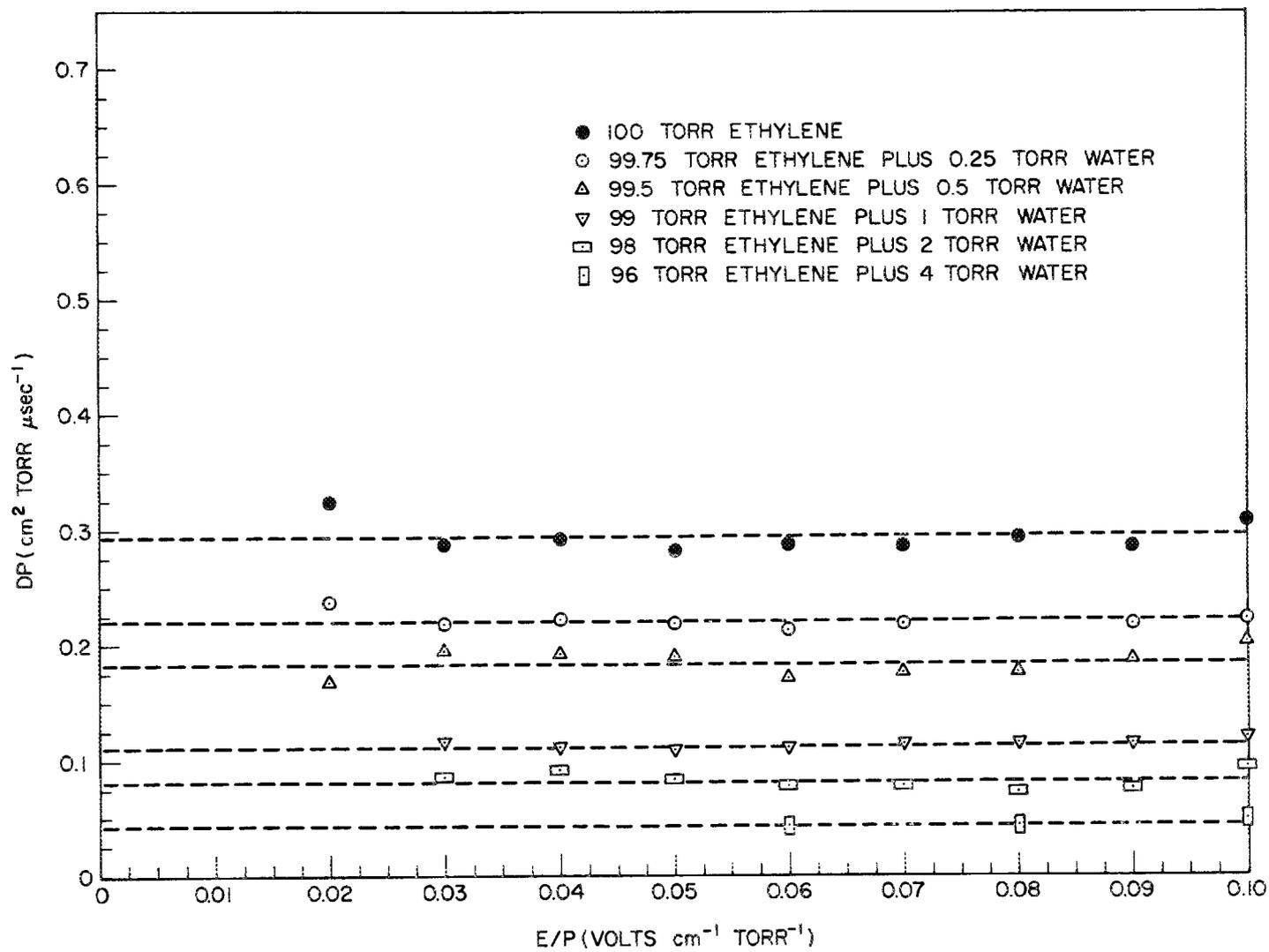


Figure 13. DP vs E/P for ethylene and ethylene-water mixtures.

## CHAPTER V

### DISCUSSION AND SUMMARY

#### I. DISCUSSION OF RESULTS

The time-of-flight swarm method is a very accurate method of measuring drift velocities. In pure ethylene the drift velocity could be reproduced within  $\pm 0.5$  percent. Comparing the drift velocities in ethylene for this experiment with those obtained by Bortner, Hurst, and Stone (1957), it is found that the present  $W$  values are about 10 percent higher. The  $W$  values of Hurst, Stockdale, and O'Kelly (1963) up to an  $E/P$  of 0.5 are also lower than those of the present experiment, but from an  $E/P$  of 0.5 to an  $E/P$  of 1.0, Stockdale's  $W$  values range up to 20 percent higher than the results of this experiment. The methods used by Bortner et al. and Hurst et al. both required reading drift times from an oscilloscope, thus making error more probable, especially at the high  $E/P$ 's where drift times are very short. The results on drift velocities in ethylene for the first pilot time-of-flight experiment are in fair agreement with those of this experiment.

The drift velocities for ethylene water mixtures were not found to be as repeatable as those of pure ethylene although the drift velocity can be found as accurately. The problem is not in repeated measurement, but in

the repeated gas filling with a partial pressure of water. This is understandable when it is realized that 0.05 percent water in ethylene makes a 1 percent change in the drift velocity. Therefore, in order to get a 1-percent repeatability the partial pressure of water has to be known within 0.05 percent. This sort of accuracy is very difficult to achieve with water as it is readily absorbed and outgassed from the walls of the chamber.

There are very few results for diffusion coefficients in ethylene for comparison. In Figure 14 the present values for DP for 100- and 50-torr pure ethylene are plotted on a graph as a function of E/P from 0 to 1.0 volts/cm<sup>-1</sup>/torr<sup>-1</sup>. The preliminary diffusion data from the first time-of-flight swarm experiment of Hurst *et al.* (1963), as shown in Figure 3, are shown plotted on this graph. There is obvious disagreement, but to improve those results was the purpose of this experiment. The data of Cochran and Forester (1962), which disagree with the present results, are shown also on the graph. The method used by Cochran and Forester was the Townsend-Huxley Method.

The diffusion coefficient can be checked for electrons at thermal energies by the Einstein equation (Healey and Reed, 1941) given by

$$\frac{W}{DP} = \frac{38.92}{k_T} \frac{E}{P} \quad (64)$$

where  $k_T$  is the Townsend energy factor and 38.92 is a constant based on the charge of the electron and Avagadro's number at a temperature of 25° C.

For thermal electrons  $k_T$  is equal to one, and drift velocity is a linear

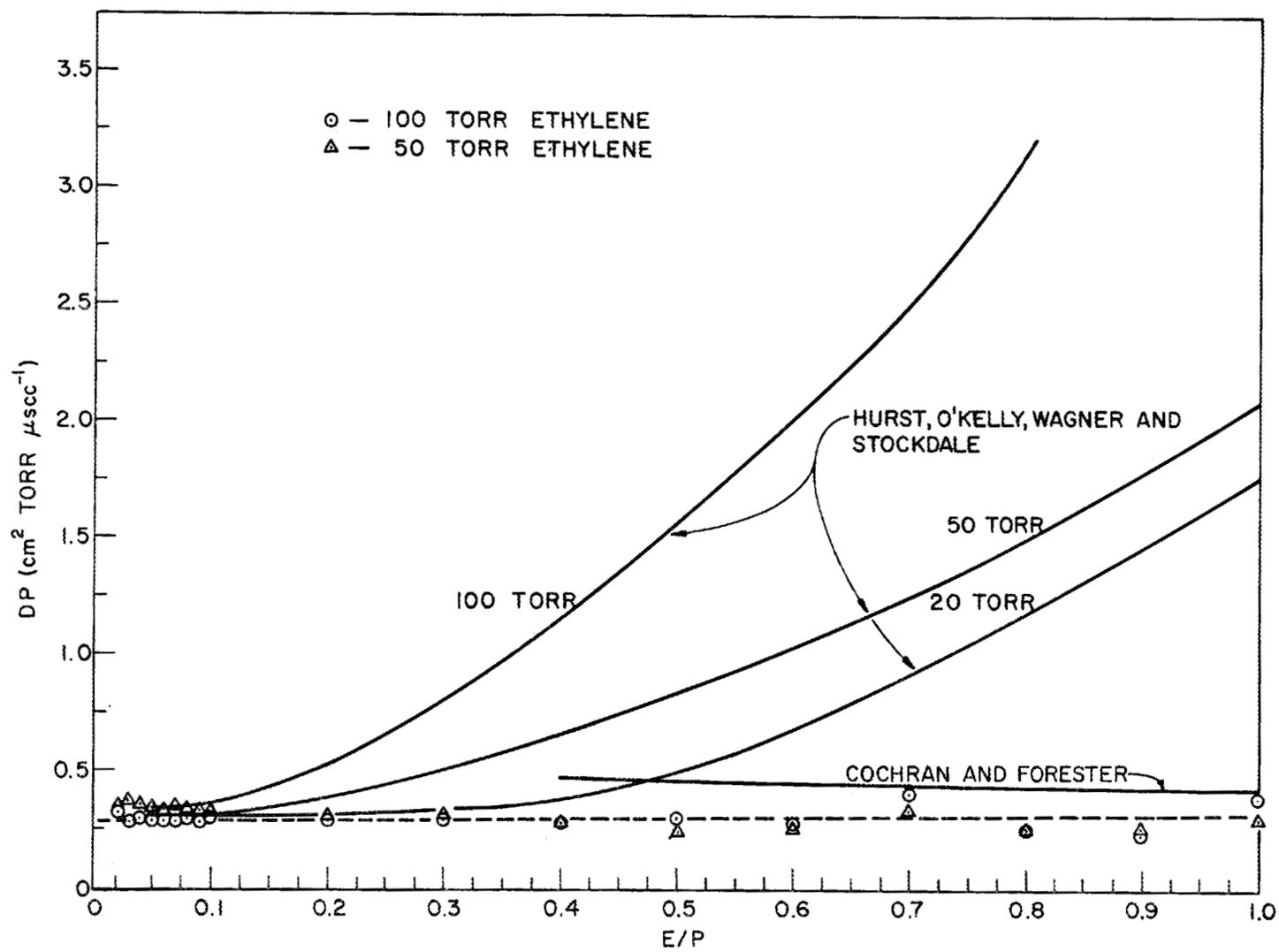


Figure 14. DP vs E/P for ethylene.

function of  $E/P$ . A check of the experimental results with the Einstein equation shows a disagreement of about 12 percent. Instead of a DP of  $0.25 \text{ cm}^2\text{-torr}/\mu\text{sec}^{-1}$  as calculated, a value of  $0.29 \text{ cm}^2\text{-torr}/\mu\text{sec}$  is measured. Consistently high diffusion coefficients were measured for the ethylene water mixtures also. The percentage that D was high remained about the same regardless of the amount of water present. A detailed analysis of this inconsistency will follow later in an error analysis.

The effect on the diffusion coefficients in ethylene when water vapor is added is clearly illustrated in Figure 13. From the Einstein equation (for thermal electrons) one expects this effect to be identical with the effect on drift velocities. When small concentrations of a dipolar gas, such as water vapor, is added, the changes in drift velocity and diffusion coefficients for thermal electrons may be analyzed in terms of the ratio of the momentum transfer cross sections,  $\sigma_1(v)$  for water and  $\sigma_2(v)$  for ethylene.

It is known from classical theory and from quantum mechanics that for molecules having strong permanent dipole moments the cross section for electron momentum transfer depends on the inverse square of the electron velocity,  $v$ . Assuming that for thermal electrons the momentum transfer cross section in ethylene also has this velocity dependence, it follows that

$$\sigma_1(v) = \frac{A_1}{v^2} \quad (65)$$

and

$$\sigma_2(v) = \frac{A_2}{v^2} \quad (66)$$

for water and ethylene, respectively.

The momentum transfer cross section,  $\sigma_m(v)$ , for a mixture of ethylene and water can then be expressed by

$$\sigma_m(v) = \frac{f_1 P}{f_1 P + f_2 P} \left( \frac{A_1}{v} \right) + \frac{f_2 P}{f_1 P + f_2 P} \left( \frac{A_2}{v} \right) \quad (67)$$

where  $f_1 P$  is the partial pressure of water and  $f_2 P$  is the partial pressure of ethylene. The diffusion coefficient,  $D_m$ , for a mixture of ethylene and water vapor can be expressed by

$$D_m = \frac{4\pi}{3} \frac{1}{n} \int_0^{\infty} f_o \frac{v^3}{\sigma_m(v)} dv. \quad (68)$$

By substituting Equation (67),  $D_m$  can then be expressed by

$$D_m = \frac{4\pi}{3} \frac{1}{n} \int_0^{\infty} f_o \frac{v^5 dv}{x_1 A_1 + x_2 A_2} \quad (69)$$

where the constants  $x_1$  and  $x_2$  are defined by

$$x_1 \equiv \frac{f_1 P}{f_1 P + f_2 P} \quad (70)$$

and

$$x_2 \equiv \frac{f_2 P}{f_1 P + f_2 P} = 1 - x_1. \quad (71)$$

Equation (69) can be rewritten such that

$$D_m = \frac{4\pi}{3} \frac{1}{n} \int_0^{\infty} f_o \frac{v^5}{A_2} dv \left[ \frac{A_2}{x_1 A_1 + (1 - x_1) A_2} \right]. \quad (72)$$

The diffusion coefficient of ethylene,  $D_e$ , can be written as

$$D_e = \frac{4\pi}{3} \frac{1}{n} \int_0^{\infty} f_o \frac{v^5}{A_2} dv. \quad (73)$$

The ratio  $D_e/D_m$  is therefore

$$\frac{D_e}{D_m} = 1 + x_1 \left( \frac{A_1}{A_2} - 1 \right) \quad (74)$$

and

$$\frac{D_e}{D_m} = 1 + \frac{f_1 P}{f_1 P + f_2 P} \left( \frac{A_1}{A_2} - 1 \right). \quad (75)$$

When  $A_1/A_2 \gg 1$  and  $f_1 P \ll f_2 P$ ,

$$\frac{D_e}{D_m} = 1 + \frac{f_1 P}{f_2 P} \frac{A_1}{A_2}. \quad (76)$$

A similar result for the drift velocities may be derived in the same manner and is reported by Hurst et al. (1963). This result is given by

$$\frac{W_e}{W_m} = 1 + \frac{f_1 P}{f_2 P} \frac{A_1}{A_2} \quad (77)$$

where  $W_e$  is the drift velocity for pure ethylene and  $W_m$  is the drift velocity for the ethylene water mixture.

Graphs of  $W_e/W_m$  vs  $f_1 P/f_2 P$  and  $D_e/D_m$  vs  $f_1 P/f_2 P$  are shown in Figures 15 and 16 for this experiment. The ratio  $W_e/W_m$  was found for each partial pressure at an E/P of 0.05 volts/cm<sup>-1</sup>/torr<sup>-1</sup>. The ratio  $D_e/D_m$  was

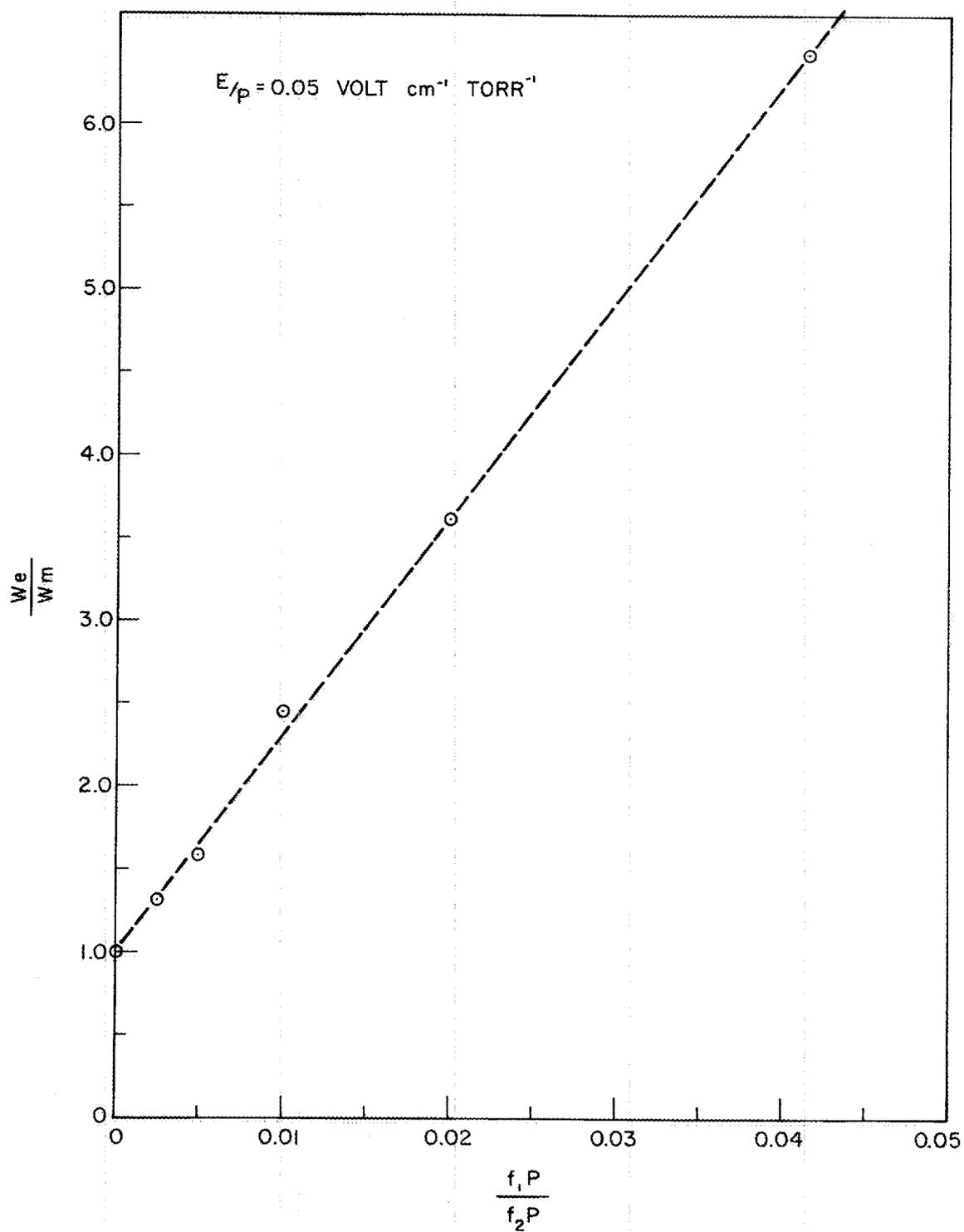


Figure 15.  $W_e/W_m$  vs  $f_1 P/f_2 P$  for ethylene and water mixtures.

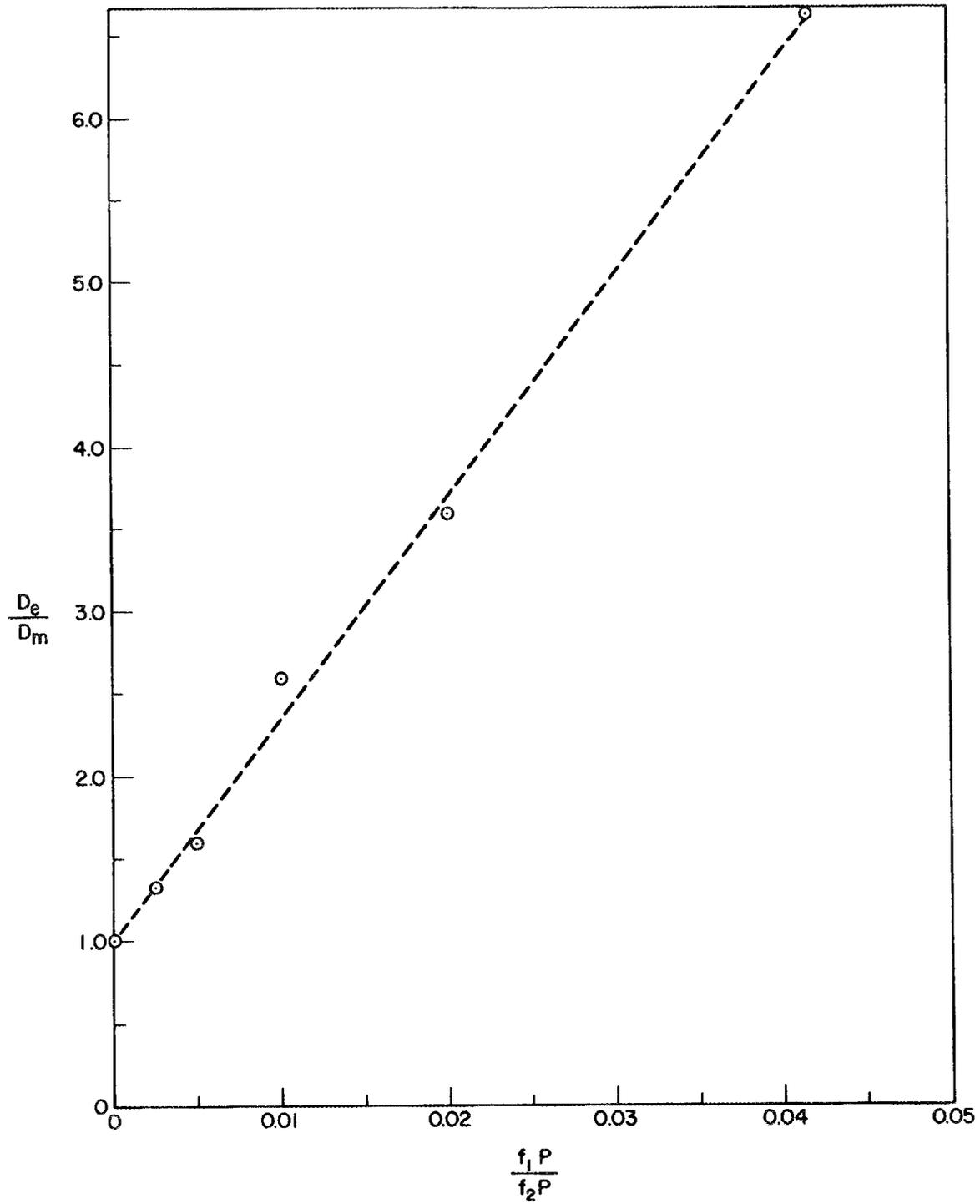


Figure 16.  $D_e/D_m$  vs  $f_1 P/f_2 P$  for ethylene and water mixtures.

found from all the DP's for each partial pressure averaged over the E/P's for 0 to 0.1 volt/cm<sup>-1</sup>/torr<sup>-1</sup> (the dotted lines in Figure 13 represent the average DP for the particular partial pressure of water). Over this range of E/P the electrons are thermal. The slopes of these two graphs represent two independent calculations of  $A_1/A_2$ . The ratio  $A_1/A_2$  for  $D_e/D_m$  was found to be 135 and for  $W_e/W_m$  was found to be 131. The ratio  $A_1/A_2$  for  $W_e/W_m$  as found by Stockdale was about 137.

## II. ERROR ANALYSIS

The discrepancy between the measured diffusion coefficient and that calculated from the Einstein equation has been carefully examined. Every detail of the experiment was scrutinized and an analysis was made for possible sources of error. Using the estimates for D and W given by Equations (23) and (26) and Equation (64), the Einstein equation with  $k_T$  equal to one, it is found that

$$\frac{4t_m^2}{L(\delta t)^2} = 38.92 E, \quad (78)$$

but the electric field, E, is the applied voltage  $V_0$  divided by the length L so that

$$\left( \frac{t_m}{\delta t} \right)^2 = 9.73 V_0. \quad (79)$$

Therefore, the 12 percent discrepancy in the diffusion coefficients may be due to error in the three parameters appearing in Equation (79).

Errors in  $t_m$  were minimized with the use of the crystal-controlled

digital delay generator. The time-of-flight analyzer was calibrated using this instrument. Its accuracy is quoted as being 0.001 percent and was checked with another crystal-controlled oscillator. The repeatability of drift velocity was within 0.5 percent, but these fluctuations could be well explained by differences in minute amounts of water vapor. These small uncertainties in  $t_m$  cannot explain the 12 percent difference in the measured and theoretical coefficients.

Errors in  $V_o$  were eliminated by monitoring the high voltage with a digital and a differential voltmeter. These instruments would measure the voltage with an accuracy of 0.05 percent and detect changes in voltage of 0.05 percent the input voltages. No error was found in the measurement of  $V_o$ .

Errors in  $t_m$  and  $V_o$  were completely eliminated and it is thought that these are not the cause of the discrepancy. Therefore, we considered errors which would increase  $\delta t$ . There are several effects that will broaden the distribution, probably the most important effect is a change in drift velocity occurring during a measurement.

In order to show how sensitive the experiment would be to this peak drift effect, consider an experimental measurement at some specific E/P. Equation (79) can then be written

$$\frac{t_m}{\delta t_o} = \psi \quad (80)$$

where  $\psi$  is a constant equal to the square root of  $9.73 V_o$  and  $\delta t_o$  is the

instantaneous width of a measured distribution when the peak occurs at time  $t_m$ . Suppose that during a measurement a drift in  $t_m$  has gradually occurred. A reasonable estimate of the width of the new distribution,  $\delta t_f$ , after the drift has occurred is

$$\delta t_f = \sqrt{\delta t_o^2 + \Delta t_m^2} \quad (81)$$

where  $\Delta t_m$  is the change in the peak time. Thus,

$$\frac{\delta t_f}{\delta t_o} = \sqrt{1 + \left(\frac{\Delta t_m}{\delta t_o}\right)^2} \quad (82)$$

Letting  $t_m$  change a factor of  $\phi$ ,

$$\Delta t_m = \phi \times t_m, \quad (83)$$

and it is seen from Equation (80) that

$$\Delta t_m = \phi \times \psi \times \delta t_o. \quad (84)$$

The ratio  $\delta t_f/\delta t_o$  is then expressed in the final result by

$$\frac{\delta t_f}{\delta t_o} = \sqrt{1 + (\phi\psi)^2} \quad (85)$$

It is clear that a factor of change in  $t_m$  is amplified to make a change in  $\delta t_o$ , e. g.,  $\psi$  is typically 40 so that a 1 percent change in  $t_m$  would produce an 8 percent change in  $\delta t_o$ . Since  $\delta t$  in Equation (79) is squared, the 8 percent change would produce about a 16 percent inequality.

One of the primary effects that would cause a peak drift is the

ingassing or outgassing of some impurity which would slowly change the drift velocity of the electrons. The peak time was monitored over a period of time which was long compared to the observation time for pure ethylene and no change was detected. A peak drift could be caused by a change in  $V_0$  during a measurement, but as has already been discussed, no change in  $V_0$  was detected. Another broadening effect connected with changes in  $V_0$  is that oscillations in  $V_0$  would cause the peak time to oscillate and broaden the distribution. However, no oscillations were observed in  $V_0$ . Pressure changes, other than those due to changes in temperatures, could change E/P and thus the peak time. The pressure was monitored with the MKS Baratron capacitance manometer at all times and no changes were observed.

Electronic drift was also considered as a possible broadening effect, but constant calibration checks indicated no changes whatsoever. Any electronic fluctuation should have been taken into account by measuring the error function. At the high E/P's the results are quite sensitive to the error function and the data indicate that the correct error function was measured.

None of the above effects were observed to broaden the distributions so that explanations, other than experimental difficulty, were sought. Interactions other than elastic and inelastic scattering collisions of the electrons with the gas molecules were considered. Such an interaction that would broaden the electron time-of-flight distribution would be a long

duration collision. In a long duration collision an electron would occasionally become temporarily attached to a gas molecule and a short time later be released. This type process would broaden the electron distribution and could explain the discrepancy.

Another gas was run in which the type of process just described would be very unlikely. Hydrogen was used as this gas and the results are listed in Table X and are graphs in Figures 17, 18, and 19. In Figure 17 the drift velocity in hydrogen is plotted as a function of  $E/P$ . The results are compared to Lowke (1962) and the agreement is very good, especially at the higher  $E/P$ 's. DP values of hydrogen are plotted in Figure 18. The diffusion coefficient divided by the mobility (the mobility,  $\mu$ , is the drift velocity divided by the electric field) is plotted as a function of  $E/P$ . It can be shown using the Einstein equation that for thermal electrons  $D/\mu$  converges to a constant equal to 0.025 volts. Electrons in hydrogen become thermalized only at the very low  $E/P$ 's. The  $D/\mu$  data are compared to the data of Cochran and Forester (1962), Townsend and Bailey (1921), and Crompton and Elford (1963). These sets of data were taken with the Townsend-Huxley method and are in serious disagreement with the time-of-flight results of this experiment. The data of Wagner and Davis (1965) are also compared to the present results. The method of Wagner and Davis is also a time-of-flight method and is more in agreement with the present results. It should be noted that the Wagner-Davis results were not corrected for error fluctuation which tends to make  $D/\mu$  larger. The  $D/\mu$  results of this

TABLE X  
SUMMARY OF RESULTS FOR 100 TORR HYDROGEN

E/P (V cm <sup>-1</sup> Torr <sup>-1</sup> )	W (cm μsec <sup>-1</sup> )	D × 10 <sup>3</sup> (cm <sup>2</sup> μsec <sup>-1</sup> )	DP (cm <sup>2</sup> Torr μsec <sup>-1</sup> )	D/μ (Volts)
0.04	0.1653	1.2266	0.1226	0.0296
0.05	0.1985	1.1174	0.1117	0.0281
0.06	0.2278	1.0696	0.1069	0.0281
0.07	0.2558	1.1000	0.1100	0.0301
0.08	0.2792	1.0749	0.1074	0.0307
0.09	0.3051	1.0475	0.1047	0.0308
0.10	0.3272	1.0203	0.1020	0.0311
0.20	0.4905	0.9392	0.0939	0.0382
0.30	0.5998	0.9087	0.0908	0.0454
0.40	0.6829	0.8930	0.0893	0.0523
0.50	0.7487	0.9064	0.0906	0.0605
0.60	0.8074	0.9988	0.0998	0.0743
0.70	0.8567	0.9873	0.0987	0.0806
0.80	0.9077	1.0506	0.1050	0.0925
1.00	0.9931	1.1409	0.1140	0.1147

Values of W and D are reported as found by machine computation. However, no more than three significant numbers can be claimed for W and no more than two for D.

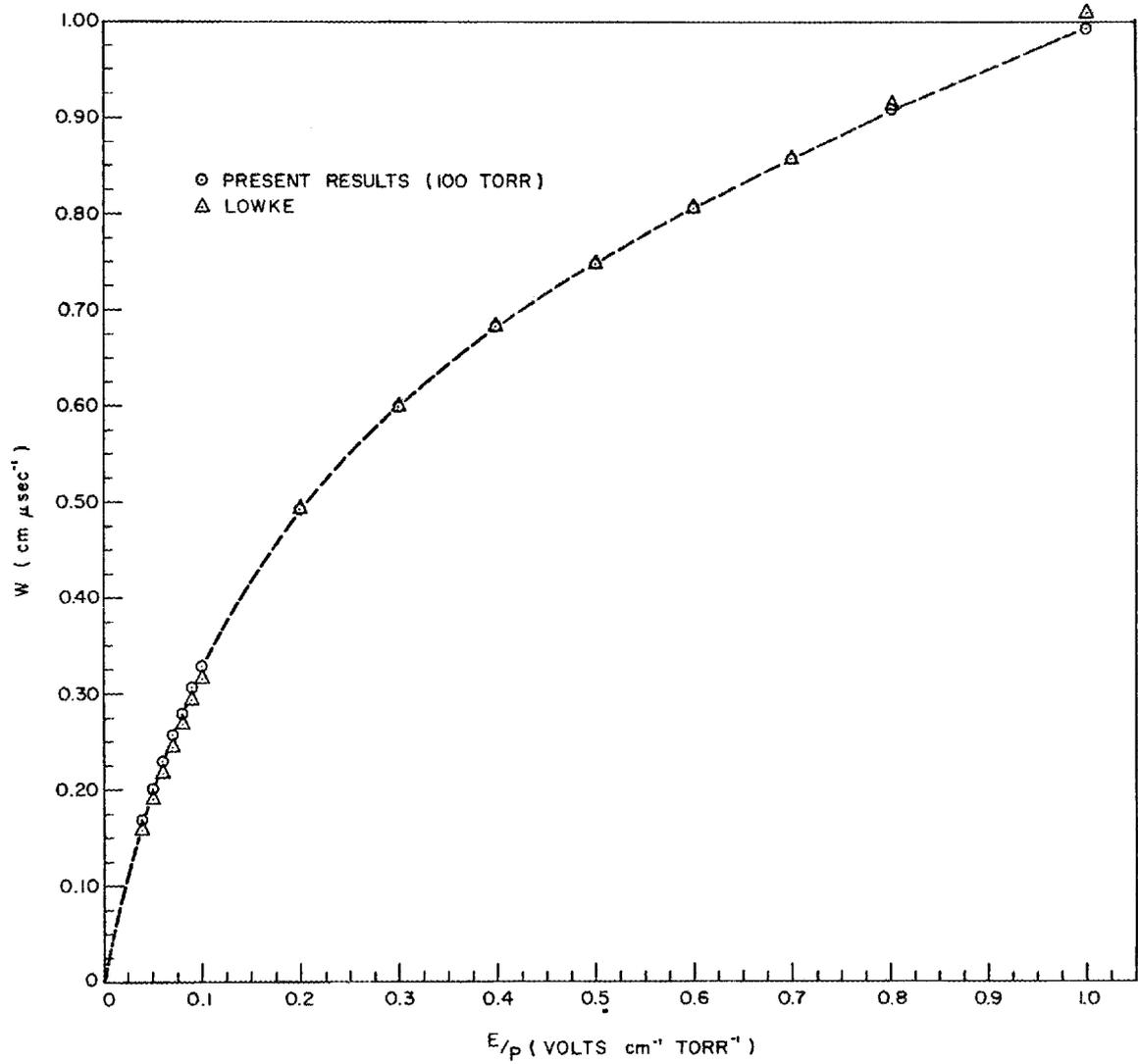


Figure 17.  $W$  vs  $E/P$  for hydrogen.

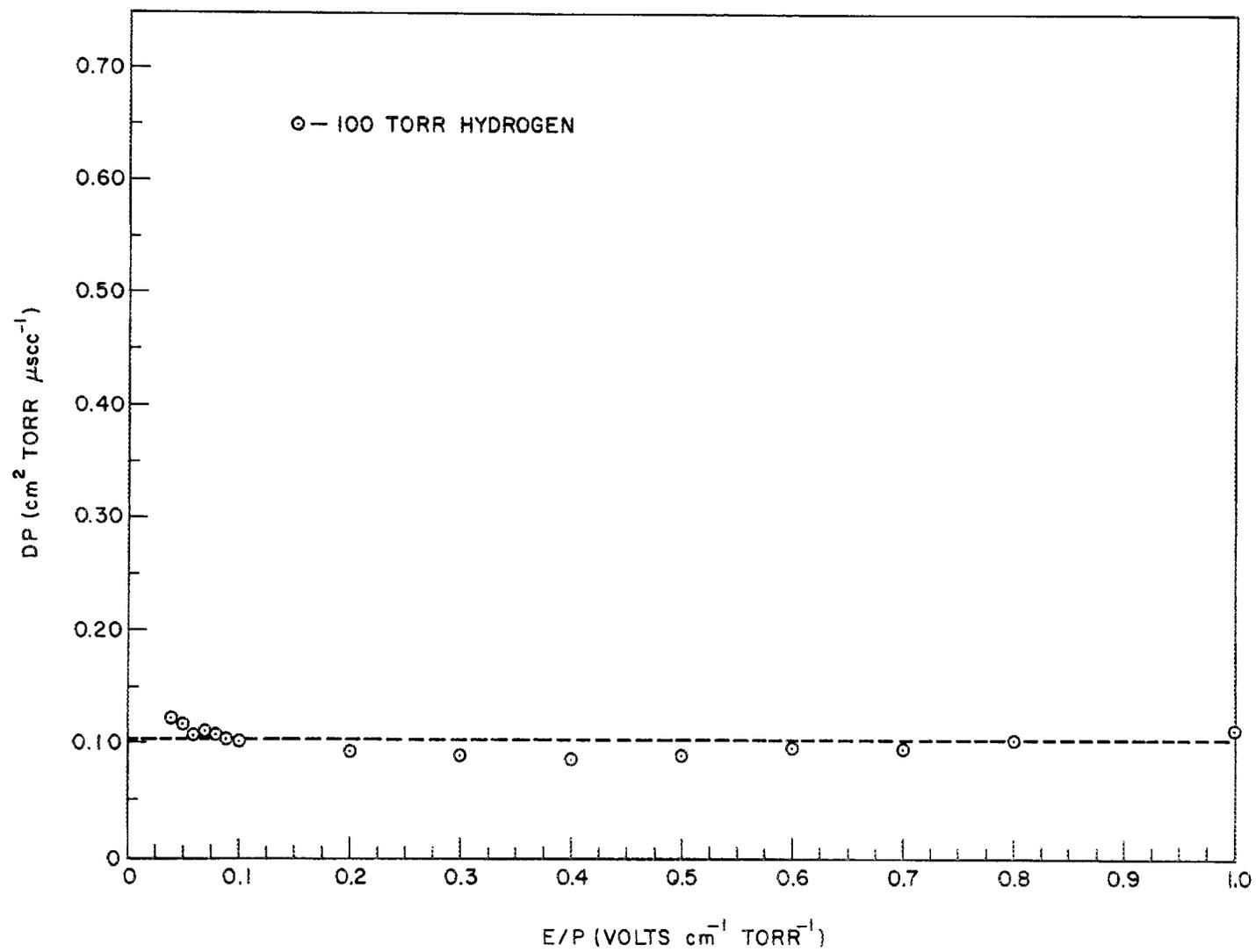


Figure 18. DP vs E/P for hydrogen.

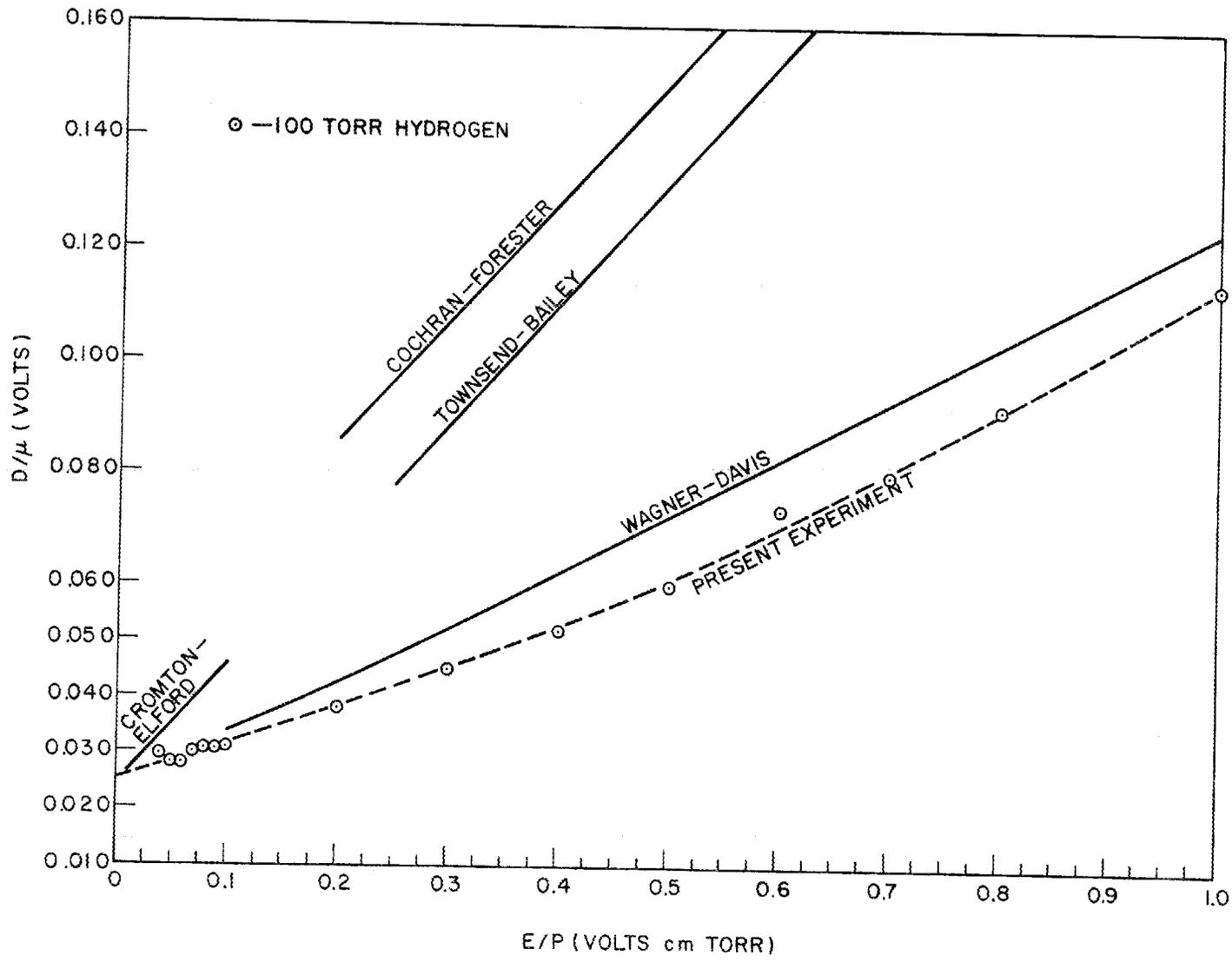


Figure 19.  $D/\mu$  vs  $E/P$  for hydrogen.

experiment seem to converge to the theoretical value of 0.025 which indicates that the apparatus was operating normally. This strongly implicates another process such as long duration collisions between electrons and ethylene.

### III. SUMMARY OF ACCOMPLISHMENTS

It is felt that the following accomplishments were attained in this experiment. Experimental techniques were refined and the time-of-flight apparatus improved for more precise measurements. A method of measuring error fluctuations was devised and proven, and a method of calculating the correction for these error fluctuations was devised. This method of calculating a correction can be applied to many other types of experiments where error fluctuations are present and can be measured. The applicability of Poisson statistics to single electron sampling have been experimentally demonstrated. The effect of the distortion of D and W due to the Poisson shift has been evaluated. Accurate measurements of drift velocity for electrons in ethylene and ethylene water mixtures have been made. For the first time accurate diffusion coefficients using a time-of-flight technique have been obtained for ethylene. Accurate diffusion coefficients for mixtures of ethylene and water have been obtained making possible an independent calculation of the ratio of the momentum transfer cross sections. The drift velocities and diffusion coefficients for electrons in hydrogen have been measured. The possibility of long duration collisions

has been considered and an experiment has been suggested to investigate, using the time-of-flight technique, the subject of temporary electron capture.



## BIBLIOGRAPHY

- Allis, W. P. In Handbuch der Physik, edited by S. Flugge. Berlin: Springer-Verlag, 1956. Vol. XXI, p. 413.
- Anderson, V. E. and R. H. Ritchie. Oak Ridge National Laboratory Report ORNL-TM-1261 (in press).
- Bortner, T. E., G. S. Hurst, and W. G. Stone. *Rev. Sci. Instr.* 28, 103 (1957).
- Cochran, L. W. and D. W. Forester. *Phys. Rev.* 126, 1785 (1962).
- Crompton, R. W. and D. J. Sutton. *Proc. Roy. Soc. (London)* A215, 467 (1952).
- Crompton, R. W. and R. L. Jory. *Australian J. Phys.* 15, 451 (1962).
- Crompton, R. W. and M. T. Elford. In Proceedings of the Sixth International Conference on Gaseous Ionization Phenomena, Paris, 1963. Amsterdam: North Holland Publishing Co., 1964.
- Crompton, R. W., M. T. Elford, and J. Gascoigne. Precision Measurements of the Townsend Energy Ratio for Electron Swarms in Highly Uniform Electric Fields. Report 65-2, Ion Diffusion Unit, The Australian National University, Canberra, June 1965.
- Healey, R. H. and J. W. Reed. The Behavior of Slow Electrons in Gases. Sydney: Amalgamated Wireless Ltd., 1941.
- Hurst, G. S., L. B. O'Kelly, E. B. Wagner, and J. A. Stockdale. *J. Chem. Phys.* 39, 1341 (1963).
- Hurst, G. S., J. A. Stockdale, and L. B. O'Kelly. *J. Chem. Phys.* 38, 2572 (1963).
- Huxley, L. G. H. *Phil. Mag.* 30, 396 (1940).
- Lowke, J. J. *Australian J. Phys.* 16, 115 (1963).
- Present, R. D. Kinetic Theory of Gases. New York: McGraw-Hill Book Co., Inc., 1958.

Stockdale, J. A. and G. S. Hurst. *J. Chem. Phys.* 41, 255 (1964).

Townsend, J. S. and V. A. Bailey. *Phil. Mag.* 42, 873 (1921).

Wagner, E. B. and F. J. Davis. Oak Ridge National Laboratory Report ORNL-3849 (in press).

Warren, R. W. and J. H. Parker, Jr. *Phys. Rev.* 128, 2661 (1962).

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