

PRECISION MEASUREMENTS OF THE TOWNSEND ENERGY RATIO FOR ELECTRON SWARMS IN HIGHLY UNIFORM ELECTRIC FIELDS

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Summary

A detailed account is given of the solution to the problems associated with the use of the Townsend-Huxley method of measuring the ratio of drift speed to diffusion coefficient for very low energy electron swarms. The elimination of radial components of the electric field within the diffusion chamber is shown to be the major experimental problem, especially in the case of the comparatively weak electric fields which must be used for some of the measurements in the near-thermal region. The experimental techniques and procedures, which are described in some detail, enable measurements to be made in this region with an accuracy comparable to that which has been achieved at higher electron energies.

I. INTRODUCTION

One of the methods of examining collision phenomena between low energy electrons and gas molecules is to measure the ratio of the drift velocity W to the diffusion coefficient D of an electron swarm moving under the influence of an electric field E in a gas at a pressure p . Since W/D is a pressure-dependent quantity, the experimental results are always given either in terms of D/μ , where μ is defined as the ratio W/E , or of k_1 , a parameter closely related to the Townsend energy factor, k_T , which is defined as the ratio of the mean energy of agitation of the electrons to the mean thermal energy of the molecules of the gas through which the electron swarm moves. These quantities are related by the expression

$$k_1 = \frac{D/\mu}{kT/e} = \frac{eE/kT}{W/D}, \quad (1)$$

where

k = Boltzmann's constant,

e = electronic charge,

T = absolute gas temperature.

Both k_1 and D/μ are functions of the ratio E/N and are also, in general, functions of the gas temperature.

An examination of a number of possible sources of error in the Townsend-Huxley method for measuring k_1 has been made by Crompton and Jory (1962), who showed that, by careful attention to the choice of experimental parameters and conditions, results with errors of less than 1% can be achieved for measurements of k_1 in hydrogen at 293°K over the range in E/p of 0.1–5.0 V cm⁻¹ torr⁻¹, for which the lowest value of k_1 is approximately 2. If the measurements are to be extended to lower values of E/p , the data lose much of their significance unless

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at least comparable accuracy is achieved in the face of increasing experimental difficulties. Improved accuracy is in fact desirable for the following reason. When the data from these experiments are used to investigate inelastic collision processes for quasi-thermal electrons in molecular gases (see, for example, Huxley 1959; Frost and Phelps 1962), the parameters which assume importance are not simply k_1 and D/μ but rather the difference terms (k_1-1) and $(D/\mu - kT/e)$, both of which approach zero as E/p approaches zero. Clearly, small errors in the determination of W/D can lead to serious errors in analyses which rely on these difference terms, and it is for this reason that an attempt has been made in the present work to achieve a high order of accuracy and to understand the factors that limit the accuracy of experiments of this type.

Although the results of a number of workers (Townsend and Bailey 1921; Crompton and Sutton 1952; Cochran and Forester 1962; Warren and Parker 1962; Rees 1964; Rees and Jory 1964) are in reasonable agreement when the mean energy of the electron swarm is in excess of about 0.5 eV, the agreement is not satisfactory when the electron energy approaches the energy of the gas molecules. Our own experience and that of Warren and Parker (1962) have shown that considerable difficulties exist in obtaining reliable, and therefore significant, data in this low energy region. In the recent extensive investigation carried out by Warren and Parker (1962), these difficulties were so severe that it was necessary to calibrate the apparatus empirically, the results obtained using the empirical calibration and those obtained from the mathematically derived calibration differing by up to 30%. Such a procedure is clearly undesirable where $k_1-1 \lesssim 0.10$, in view of the discussion above. In the present investigation no such procedure was necessary. In other investigations (e.g. Cochran and Forester 1962) it is apparent that large systematic errors were present but that it was not possible to take account of them.

In what follows, an account is given of the outcome of an extensive investigation into the factors that must be considered in order to obtain measurements of W/D at 293°K, to within 1%, down to a value of E/p of 0.006 where, for example in hydrogen, $(k_1-1) \approx 0.03$. The results from these investigations have been published previously in summary (Crompton and Elford 1963), and will be published in detail in due course together with an extension of the work to other gases and other temperatures.

II. PRINCIPLE OF THE METHOD

The method of measuring the ratio W/D has been described in detail elsewhere (e.g. Crompton and Jory 1962), and will be considered only briefly here.

Electrons enter the diffusion chamber (Fig. 1) through a small hole in the cathode, and diffuse and drift under the influence of the electric field E towards the anode. The anode is divided into a disk and annulus, and the ratio R of the electron currents received by these electrodes is measured.

The diffusion equation that describes the motion of an electron swarm is

$$\nabla^2 n = (W/D) \partial n / \partial z = 2\lambda \partial n / \partial z, \quad (2)$$

where n is the electron number density, and the z axis is parallel to the electric

field E . If the electrons originate from a point source, two solutions of equation (2) are (Huxley 1940):

$$n = A e^{\lambda z} \left(\frac{e^{-\lambda r}}{r} \right) \quad (3)$$

and

$$n = A e^{\lambda z} \frac{z}{r} \frac{d}{dr} \left(\frac{e^{-\lambda r}}{r} \right), \quad (4)$$

where r is the distance measured from the origin, and A is a constant.

The boundary conditions normally applied are that $n = 0$ everywhere at the cathode and anode except at the origin. No radial boundary condition need be imposed since it can be shown that, with the most widely divergent electron stream used in our experiments, less than 0.004% of the electron swarm is found outside

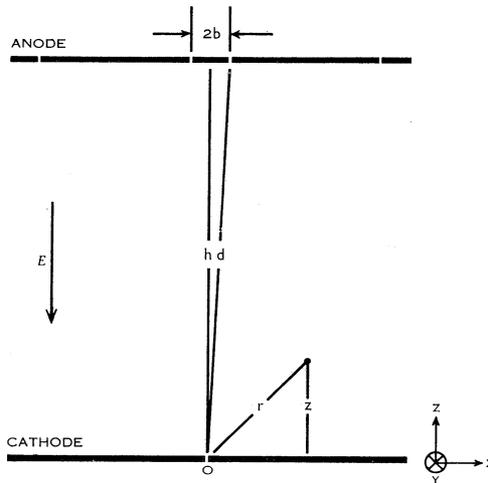


Fig. 1.—Geometry of diffusion chamber.

a radial distance of 4 cm. The electron concentration at the surface of the guard electrodes of the apparatus shown in Figure 2 is therefore negligible, and hence the presence of the guard electrodes cannot significantly affect the electron concentration elsewhere. Thus for this apparatus, and for others of the same type which have been used in this laboratory for similar experiments, it is unnecessary to take into account the effect of the walls of the diffusion chamber as has been suggested by Warren and Parker (1962). When the boundary conditions are imposed on the dipole solution (equation (4)), the ratio of the current i_b received by the disk of diameter $2b$ to the total current i arriving at the receiving electrode is given by

$$R = i_b/i = 1 - (h/d - 1/\lambda h + h/d^2\lambda)(h/d) e^{-\lambda(d-h)}, \quad (5)$$

where h is the distance between anode and cathode, and $d^2 = h^2 + b^2$.

It has been found that the experimental measurements do not always agree accurately with values calculated from equation (5), but that the expression

$$R = 1 - (h/d) e^{-\lambda(d-h)} \quad (6)$$

is consistent with experimental results over a wide range of experimental parameters. This expression follows from the use of the solution for n given in equation (3) together with the boundary conditions discussed by Huxley and Crompton (1955).

The expressions (5) and (6) for the ratio R have been discussed by Huxley and Crompton (1955) and by Crompton and Jory (1962), who show that, for certain experimental conditions, there is a negligible difference between the results obtained using these two expressions. These experimental conditions are certainly fulfilled where maximum accuracy is required in the experiments described in this paper.

III. THE CHOICE OF PARAMETERS IN THE DESIGN OF THE DIFFUSION APPARATUS

The design of the diffusion chamber that was finally adopted is shown in Figure 2. In choosing the dimensions of the chamber careful attention has to be paid to a number of parameters, although the final choice is in fact a compromise.

(a) Length of Chamber, h , and Radius of Collector Disk, b

The most obvious requirement that determines the choice of h and the ratio b/h is the need to measure the ratio of the currents received by the disk and annulus with adequate precision. The use of the current measuring equipment described in Section VIII(b) enables this to be done provided R lies between 0.2 and 0.9. The effect of this restriction on the choice of b and h can be seen by examining equation (6), which may be rewritten as

$$R = 1 - \{(b/h)^2 + 1\}^{-\frac{1}{2}} e^{-\lambda h} [\{(b/h)^2 + 1\}^{\frac{1}{2}} - 1], \quad (7)$$

where $\lambda = W/2D = (e/2kT)(E/k_1)$.

When k_1 is greater than about 5 it can be shown, with the aid of equation (7), that no great difficulty exists in choosing suitable values for b and h which will lead to current ratios in the centre of the prescribed range when field strengths of 10 V/cm or more are used. The pressure can then be chosen to obtain the value of E/p appropriate to the required value of k_1 . Cross checks can subsequently be made by either increasing or decreasing E and p , keeping E/p constant and the current ratio within the range.

The choice of parameters becomes more difficult, however, as k_1 approaches unity, and as the gas temperature is lowered. Calculations show that reasonable divergence of the electron stream can be obtained only with small values of the electric field; on the other hand, as will be discussed in Section V(b)(ii), significant experimental errors may arise from contact potential differences for values of E less than about 3 V/cm. The lower limit which must be placed on the value of E requires that small values of b and large values of h be used if a significant fraction of the electron stream is to arrive at the receiving electrode outside the central disk, but practical difficulties dictate a compromise in the choice of these two parameters. In practice it is difficult to achieve the required tolerance of $\pm 0.1\%$ in the effective diameter of the central disk for diameters less than about 1 cm, owing partly to difficulties in measurement but chiefly to the finite size of the air gap between disk and annulus (Section III(d)). Furthermore, errors resulting from the finite size of the

source hole (Section III(c)) become more significant as the diameter of the disk is reduced. The use of a diffusion chamber of length $h = 10$ cm in conjunction with a disk of radius $b = 0.5$ cm leads to a value of R as high as 0.5 for thermal electrons at room temperature (293°K) with $E = 3.0$ V/cm, still larger ratios resulting from

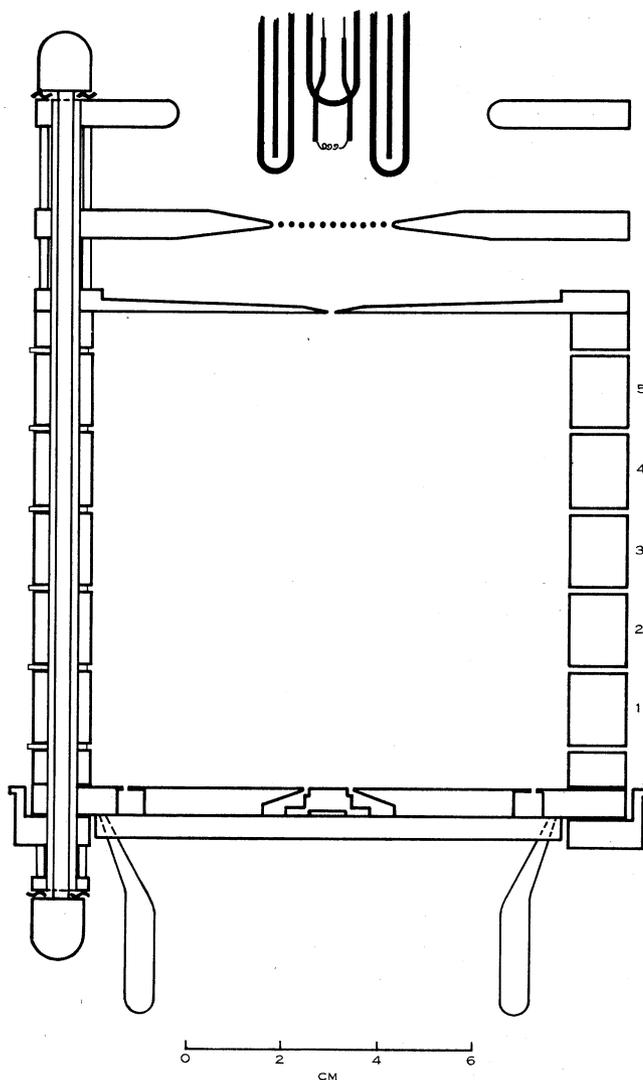


Fig. 2.—Cross section of diffusion chamber.

the use of lower gas temperatures or higher field strengths. If R is to remain within the prescribed range it is, in fact, impossible to use values of E higher than approximately 9.0 V/cm at 293°K or 2.5 V/cm at 78°K. Thus, even with this choice of the values of b and h , measurements can be made only at relatively low field strengths,

and this restriction leads to enhanced experimental difficulties and larger experimental errors, as will be discussed subsequently.

Some improvement to the situation can be achieved by increasing h , but there are factors which make such an increase undesirable. A significant improvement would be obtained only by a large increase in h , which would then add considerably to the difficulty of conducting the experiments at low temperatures. These difficulties result from the length of vacuum envelope to be immersed in the refrigerant and the increase in the already large quantity of gas of high purity required to perform the experiment at pressures of the order of 500 torr, such pressures being necessary to obtain the lowest values of E/p .

One further requirement governing the choice of b and h is already satisfied with this choice of dimensions, namely, the removal of a possible source of significant error in the interpretation of the experimental results in terms of the ratio W/D . Crompton and Jory (1962) have shown that with $h = 10$ cm and $b = 0.5$ cm, equations (5) and (6) lead to values of W/D that differ by less than 0.2% when $R > 0.5$. The discrepancy between theory and experiment, which is discussed fully in their paper, is therefore unimportant in the present work. Furthermore, uncertainty in the interpretation of the results arising from the spatial dependence of W/D , as discussed by Parker (1963), would also appear to be insignificant using the criterion suggested by Parker.

(b) Diameter of the Diffusion Chamber

The diameter of the diffusion chamber must be large enough to ensure that the electric field is uniform to the required tolerance (see Section VI(b)) over the volume of the chamber where the electron number density is significant. A diameter of 10 cm satisfies the requirements of field uniformity with the particular guard electrode structure used.

(c) Diameter of Source Hole

In obtaining a solution to the diffusion equation the assumption is made that the hole in the cathode acts as a point source of electrons. In practice there is a lower limit to the diameter of the hole set by the requirement that sufficient electron current be transmitted. The diameter chosen was 0.1 cm. Calculations made by Crompton and Jory (1962) indicate that, for a source hole of this diameter, the error in the value of W/D will be a function of R and will vary from 0.05% at $R = 0.1$ to 0.8% at $R = 0.8$. These calculations almost certainly overestimate the error, owing to the assumption which is made that the electron number density across the hole is constant. However, it is possible to observe the effect of this source of error in the experimental measurements, and its magnitude will be discussed in Section XI.

(d) Width of Annular Gap

Equation (7) may be used to show that an error of 0.0005 cm in b leads to an error of 0.2% in the determination of W/D , but a difficulty arises in the determination of b apart from that associated with measurement. The effective diameter of the central disk is normally taken as the actual diameter plus the width of the

gap between disk and annulus, on the assumption that the electrons arriving at the gap divide equally between disk and annulus. The accuracy of this assumption is difficult to assess, since the way in which electrons diffuse in the essentially field-free region within the gap is unknown. Any error arising from the incorrectness of this assumption may obviously be minimized by making the gap as narrow as possible.

The use of an extremely narrow gap leads to a high inter-electrode capacitance which may add to the difficulty of determining the current ratio R . The capacitance can be reduced by undercutting the edges of the electrodes, but there is a limit to the thinness of the edges set by the need to maintain a truly plane surface across the face of the whole electrode (Section V(b)(i)).

As a compromise, a gap width of 0.005 cm was used. The maximum error arising from the uncertainty in the effective diameter of the disk is therefore $\pm 1\%$, although experiments in which the gap width was varied indicate that this figure greatly overestimates the error from this cause. The width of the gap between the annulus and the outer earthed annular ring is not critical and was chosen to be 0.1 cm.

(e) *Preliminary Field Region*

In order to ensure that the energy distribution of the electrons entering the diffusion chamber approximates closely the equilibrium energy distribution throughout the chamber, the electrons are made to traverse a region 2 cm in length, immediately above the cathode, where the field is maintained at the same value as in the diffusion chamber (Fig. 2). To obtain some estimate of the distance required for an electron to reach its equilibrium energy the following expression was used (Loeb 1955):

$$x_{\eta} = \frac{1}{2a} \ln \frac{1+\eta}{1-\eta}, \quad (8)$$

where η is the fraction of its equilibrium energy attained by an electron in travelling a distance x_{η} in the direction of the electric field, and a is a parameter given by

$$a^2 = 5.32(m/M)(1/l^2),$$

where

- m = electronic mass,
- M = mass of the gas molecules,
- l = mean free path.

The factor 5.32 (m/M) is twice the mean fractional energy lost by electrons in elastic collisions. In the calculation which follows for the case of electrons in hydrogen this factor has been replaced by the value obtained experimentally, since inelastic collisions significantly alter its value.

If the following experimental conditions are assumed

$$\begin{aligned} E/p &= 1.0 \text{ V cm}^{-1} \text{ torr}^{-1}, \\ p &= 10 \text{ torr}, \\ \eta &= 0.99, \end{aligned}$$

then the value of x_{η} is approximately 0.1 cm.

Owing to the assumptions that have been made in the derivation of the expression for x_n , these calculations are approximate only. Nevertheless, they show that the length of the preliminary field region is adequate, and in any case no variation in the measured values of W/D could be found on varying the initial field over a wide range.

(f) *Diameter of Outer Collector*

The diameter of the outer annulus must be sufficiently large that only a negligible proportion of the electron current falls outside this electrode. In Section II it was stated that for the most divergent electron stream used (i.e. at the lowest values of E and p), less than 0.004% falls outside a diameter of 8 cm in a diffusion chamber 10 cm in length. The diameter chosen for the outer annulus was 8.5 cm.

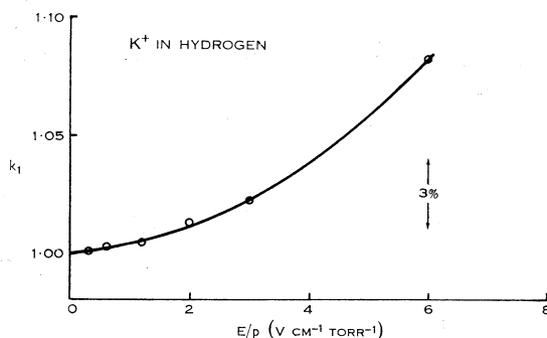


Fig. 3.—The variation of k_1 with E/p for K^+ ions in H_2 .

IV. TESTS FOR SOURCES OF SYSTEMATIC ERROR

There are two tests that can be made to detect the presence of systematic errors. In the first test, use is made of the fact that, at a constant temperature, k_1 is a function of E/p only, so that the same value of k_1 should be obtained at the same value of E/p regardless of the value of p . When experimental results are taken, both E and p are varied over the widest possible range and the results tabulated as a function of E/p and p . A pressure dependence of the experimental results at a fixed value of E/p indicates the presence of systematic errors.

The second and most stringent test that can be made is to determine the value of k_1 for positive alkali ions at values of E/p where the ions are virtually in thermal equilibrium with the gas molecules. At low values of E/p the value of k_1 increases very slowly as E/p increases. From Figure 3 it can be seen that, in the case of potassium ions in hydrogen, k_1 remains within approximately 0.2% of unity (corresponding to thermal equilibrium) for values of E/p less than 0.5. The procedure is, therefore, to take measurements with potassium ions in the range of values of E/p for which $k_1 = 1$ to within say 0.2%, that is, in the case of hydrogen, for $E/p < 0.5$. If the value of k_1 obtained differs significantly from unity then an error is present in the measurements.

When this second test employing positive ions was used with one of the early experimental tubes the results were found to be in error by 4%, and the cause of

this error was traced to distortion of the electric field. The type of field distortion responsible for errors of this magnitude was therefore investigated and the causes of such distortion determined.

V. DISTORTION OF THE ELECTRIC FIELD AS A SOURCE OF ERROR

(a) *Types of Field Distortion*

The distortion of an electric field that has cylindrical symmetry can take two forms. It is possible (for example, by applying non-equal potential differences to adjacent members of an infinite set of thin, equally-spaced guard electrodes) to produce an electric field that is everywhere axial but in which the field strength is not everywhere equal. The set of equipotential planes is then "bunched" in some regions and widely spaced in others. More often the distortion of the field arises from curvature of the equipotential planes so that the field lines are not everywhere axial. Thus, if the distortion results in a series of surfaces that are dished, the electric field at any point may be resolved into an axial and a radial component.

It has been found that the measured values of k_1 are sensitive to field distortion introduced, for example, through contact potential differences between the guard electrodes and the source and receiving electrodes. It is important to establish whether the divergence of the stream is affected by variations in the axial field strength, by the presence at some places within the diffusion chamber of radial fields, or by a combination of both effects.

In order to find out something about the relative importance of these effects the following experiments were performed. Considerable distortion was introduced by connecting the lowest full guard electrode in the electrode system shown in Figure 2 to the receiving electrode. The lead to this guard electrode was disconnected from the voltage divider so that each of the other guard electrodes had the correct potential applied to it. The total voltage applied to the diffusion chamber remained unaltered during the test.

The value of k_1 obtained for potassium ions in hydrogen when the electrodes were connected in this way was 16% higher than that obtained when the electrodes were correctly connected. A similar change (15%) was obtained for electrons in hydrogen at $E/p = 1$.

A qualitative and semi-quantitative estimate of the electric field within the diffusion chamber was made from a two-dimensional analogue, using conducting paper, for conditions equivalent to those used in the experiments described above. From the spacing of the equipotential lines along the axis of the system, the average value of the axial component of the field over intervals of 1 cm between source and receiving electrodes was found to be as follows:

Interval (cm)	1	2	3	4	5	6	7	8	9	10
Average field strength (V/cm)	9.33	9.73	9.80	10.0	10.2	10.42	10.4	10.4	10.37	10

Interval 1 began at the receiving electrode, and the nominal field strength was 10 V/cm.

From this table it can be seen that there are some regions in which the field is below the nominal value and some in which the field is above this value; furthermore, the lowest field strength is only 7% below the nominal value.

The effect of this variation in the axial component of the field can be estimated as follows. For positive ions near thermal equilibrium, as in this experiment, the value of W in each of the 10 regions will be proportional to the value of E in that region, whereas the diffusion coefficient will be practically independent of it. Thus, in region 1 the value of W/D , which determines the divergence of the stream, is smaller than the nominal value, while in region 7 it is larger. It might be expected, therefore, that the final divergence of the stream, and hence the value of k_1 determined from it, would be little affected. This is not so, and in fact the value of k_1 lies well outside the value it would have in the extreme case of the field being everywhere at the lowest value. If this were the case k_1 would be subject only to a 7% error and not the 15% error recorded. Furthermore, the regions of high field strength would reduce the 7% error, so that it appears that axial non-uniformity is not the main contributor to the spurious divergence.

Further evidence is afforded by the results for electrons. The value of $E/p = 1.0$ was purposely chosen to lie in the region where W/pD is largely independent of E/p . This was confirmed by altering the value of E/p , when it was found that a 7% change in E/p altered W/pD by about 1.5%. If non-uniformity of the axial field were to lead to the spurious divergence, then the error in k_1 would be expected to be far less for electrons at this value of E/p than for ions, for which a 7% change in E/p caused a 7% change in W/pD . Since the errors introduced are almost identical, the results of this experiment confirm the conclusions drawn from the experiment with positive ions.

It seems, therefore, that the results quoted above must be attributed to the introduction of radial field components. Further examination of the equipotential plot showed the lines to have very appreciable abnormal curvature towards the edges of the field, and just appreciable curvature in the region above the annular gap between the disk and the annular electrode, where any radial component of the field is likely to have the greatest effect in determining the distribution of current between these electrodes. It is necessary, therefore, to examine the ways in which radial components of the electric field could be introduced.

(b) Causes of Field Distortion

(i) *Field Distortion Introduced by Incorrect Geometry.*—Distortion of the electric field can be introduced by geometrical inaccuracy in the guard electrode structure, in the source electrode, or in the receiving electrode. Incorrect voltage division in the potential divider supplying the potentials to the guard electrodes is equivalent to a displacement of the guard electrodes and may therefore be included in this category.

The most serious error introduced by geometrical inaccuracy results from the surface of the collecting electrode not being a true geometrical plane. Radial fields arising from relatively abrupt changes in contour are more likely to occur in the

vicinity of the annular gap than elsewhere. Furthermore, this is the region where such fields would have maximum effect since they would cause a spurious distribution of current about the gap. For example, in a series of experiments with one particular apparatus a systematic error of the order of 1.5% was consistently observed. The cause of this error could not be traced to any of the other effects discussed in the present paper. When the region around the gap of the collecting electrode of this apparatus was examined it was found that a small lip of the order of 0.0004 cm in height existed at the inner edge of the outer annulus. This lip resulted from the extreme fragility of the inner edge of the annulus, which had been undercut to reduce interelectrode capacitance. Another electrode was constructed in which the thickness of the copper at the edge was increased. Optical tests showed that no lip existed after lapping and polishing. When this collecting electrode was inserted in the apparatus the 1.5% systematic error previously observed was no longer present.

If the distortion arises from either geometrical inaccuracy or insufficiently accurate division in the voltage divider feeding the guard electrodes, the percentage error in k_1 will be largely independent of both the divergence of the stream and the way in which W/D varies with E/p . This form of field distortion will therefore be characterized by an error which does not scale with E .

(ii) *Field Distortion Produced by Contact Potential Differences.*—Non-uniformity of the electric field can arise from contact potential differences either over a surface or between different surfaces. There may be contact potential differences between different parts of the anode or cathode surfaces, or between sections of the surface of the guard electrode structure. Furthermore, difficulty has been experienced in obtaining cathode and anode surfaces between which the average contact potential difference is zero even when vacuum coated simultaneously, and similar remarks apply to the guard electrodes. However, provided that the contact potential differences remain constant, the errors arising from field distortion introduced by them can always be recognized by the fact that the magnitude of the error is approximately inversely proportional to the magnitude of the applied field. For example, in experiments in which this type of field distortion has been simulated by imposing a constant additional potential, either on the guard electrodes or on the central disk, doubling the field has in each case approximately halved the error. Conversely, numerous tests have shown that the magnitude of the percentage error introduced is directly proportional to the magnitude of the potential applied at a given value of the main field.

Table 1 shows the additional potentials which, when applied to the respective electrodes of an apparatus of the form shown in Figure 2, lead to a 1% change in k_1 for a main field of 3 V/cm.

(c) *A Method of Distinguishing the Types of Error Caused by Field Distortion*

The magnitude and type of error can be found by measuring the variation of the error with increasing electric field strength E at one fixed value of E/p . From the discussion in the previous sections ($V(b)$, (i) and (ii)) it can be seen that errors arising from field distortion owing to geometrical inaccuracy (to be called type 1)

are independent of the magnitude of E , whereas those arising from contact potential differences (to be called type 2) are inversely proportional to E apart from second order effects due to the variation in R .

If, in measurements with electrons, errors of both type 1 and type 2 are present the variation of the error with E is as shown in curve (a) of Figure 4. If, instead of electrons, positive ions are used, errors of type 1 remain unchanged, while errors of type 2 reverse in sign but remain unchanged in magnitude at the same value of E (curve (b)). At high values of E errors of type 2 become negligible and the residual error (ϵ_1) arising from geometrical inaccuracy can therefore be found. This error can then be subtracted from the total error in order to obtain the magnitude of errors of type 2 at any given value of E . It should be noted that the signs of the errors shown in the figure are chosen only as an example.

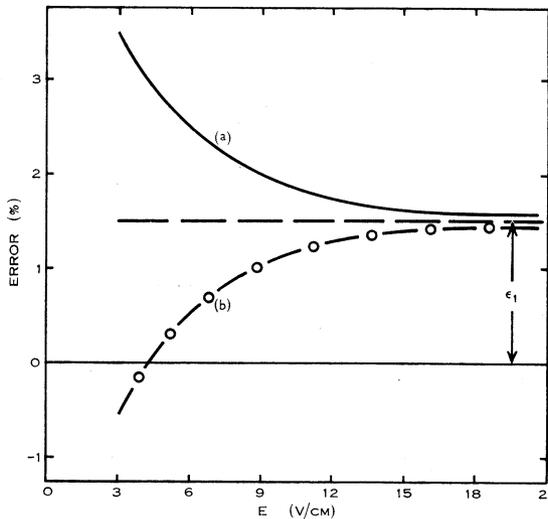


Fig. 4.—Variation of errors in k_1 with electric field strength (E/p fixed).

In practice the situation illustrated by Figure 4 is to some extent obscured by two other factors. The first is the variation with R of the errors from contact potential differences, which will be discussed in Section IX; the second arises from the effect of the finite size of the source hole and is also dependent on R (Sections III(c) and XI). Nevertheless, when used with care this method enables errors of both types to be identified and measured.

VI. PRODUCTION OF A UNIFORM ELECTRIC FIELD

(a) Alternative Methods of Producing a Uniform Electric Field

A longitudinal electric field is often held uniform by employing a series of guard electrodes maintained at voltages appropriate to their position along the length of the field. For diffusion chambers used in these experiments, it is also necessary to ensure that no penetration can occur through the guard electrodes of stray fields

outside the electrode structure. Although adequate shielding from wall effects was achieved in the apparatus described by Crompton and Jory (1962), more closely spaced guard electrodes had to be employed to give adequate shielding when an attempt was made to construct an apparatus of smaller diameter suitable for immersion in a refrigerant for measurements at low gas temperatures. In the latter apparatus the guard electrodes had an internal diameter of 3.7 cm and were spaced at 0.5 cm intervals. To avoid distortion caused by the finite thickness of the electrodes each was made 0.06 cm in thickness. The length of the diffusion chamber was 10 cm and the value of b/h was 0.05. When this apparatus was tested for systematic errors, as outlined in Section IV, using potassium ions in hydrogen, the measured values of k_1 were consistently less than unity by 2–3%. This error was thought to be due to the existence of field distortion in the diffusion chamber caused by warping of the thin guard electrodes.

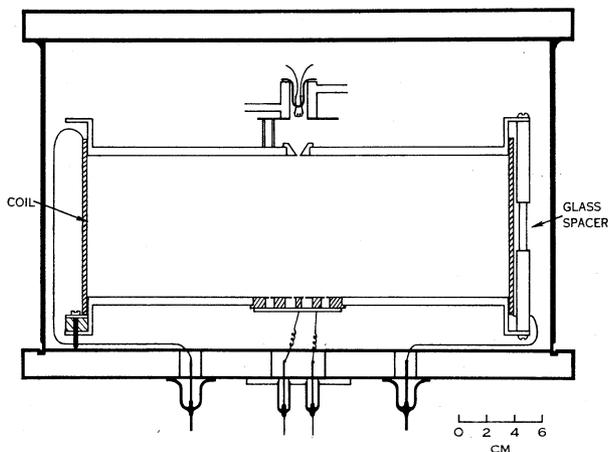


Fig. 5.—Apparatus designed to minimize field distortion produced by the guard electrode structure.

To test whether field distortion was in fact the cause of the incorrect values of k_1 a second apparatus (Fig. 5) was constructed in which the internal diameter of the diffusion chamber was increased from 3.7 to 25 cm. By increasing the ratio of diameter to length in this way the role of the guard electrode structure becomes less important. In addition an alternative form of guard electrode structure, theoretically superior to the more conventional type, was used, the design of which was based on the following considerations.

An electric field uniform over the entire volume of the diffusion chamber could be produced if it were possible to place the appropriate voltage across a uniform conducting surface forming the cylindrical wall of the diffusion chamber. In practice, there are a number of difficulties involved in producing a uniform field in this way. The conductivity of the surface must be uniform to a high degree and the current flowing through the conductor must be small to avoid ohmic heating. When high values of field are required these restrictions are such that no material

could be found which adequately met the requirements, and an alternative approach was adopted.

The ideal case of a continuous and linear variation of potential along a cylindrical wall parallel to its axis may be approximated by using a coil of fine wire. The resistance of the coil must be chosen to ensure that, at the maximum electric field strength used, the magnetic field and the ohmic heating produced by the current flowing through the coil will not significantly affect the results. The coil used in this second, large diameter apparatus (Fig. 5) consisted of 300 turns of nichrome wire wound on the inside of an epoxy resin former. The coil was placed inside a steel cylinder which formed the vacuum envelope. Measurements made with potassium ions in hydrogen gave values of k_1 which were within 0.25% of the true value of unity. The conclusion from the results of this and the previous experiment is, therefore, that a high degree of uniformity in the electric field is essential to obtain the required accuracy.

The epoxy resin used in the construction of this experimental tube resulted in the gas being contaminated to a level which would normally be regarded as unacceptable. However, gas purity cannot affect the values of k_1 for positive ions at low values of E/p , since the value of k_1 for any ion species in any gas approaches unity as E/p approaches zero. Because of the unacceptable impurity level and the size of the apparatus, it was considered to be unsuitable for measurements with electrons at room or low temperatures.

If the same degree of uniformity of electric field is to be maintained in an apparatus of reduced diameter, it is necessary to increase the number of turns in the coil. Another apparatus employing this guard system was constructed with the electric field held uniform by a coil of 10 cm diameter, consisting of 1000 turns of Karma wire which was both insulated and held in position by polyurethane. The coil was vacuum baked for 2 hr at 100°C before being assembled into the apparatus. Vapour pressure tests on the polyurethane indicated that it would not significantly add to the impurity level in the gas samples used. The resistance of the coil was 86 k Ω , and the variation from linearity in the potential drop along its length was less than 0.25%. The contact potential difference between Karma wire and a gold surface in air was measured as 0.22 V, and appropriate allowance was made when voltages were applied to the apparatus.

Measurements made using potassium ions in hydrogen were found to be alarmingly inaccurate (9% error at $E = 3$ V/cm), and the error was found to decrease as the electric field strength was increased. This behaviour is consistent with the presence of field distortion resulting from contact potential differences within the diffusion chamber (Section V(b)(ii)), and it was assumed that the distortion had been introduced as a result of incorrect compensation for the contact potential difference between the Karma wire and the gold surfaces of the anode and cathode. An apparatus employing the Kelvin method (Kelvin 1898) was constructed to measure the contact potential difference between the Karma wire and a gold surface under various atmospheres. It was found that changing the atmosphere from air to hydrogen caused a considerable change in the contact potential difference between these two metal surfaces. The inescapable conclusion would therefore seem to be that all

surfaces exposed to the diffusing electron swarm must be of the same material. Since gold had been chosen as the best material for coating the anode and cathode, this conclusion means that a coil cannot be used for the purpose of establishing a uniform electric field, as the resistance of a coil of gold wire or even gold-coated wire would be far too low.

The use of thin guard electrodes and of a coil to produce uniform electric fields were thus both unsuccessful, owing to insufficient mechanical rigidity in the first case and to the effects of contact potential differences in the second. Both these approaches were attempts to ensure that field distortion was made negligible throughout the

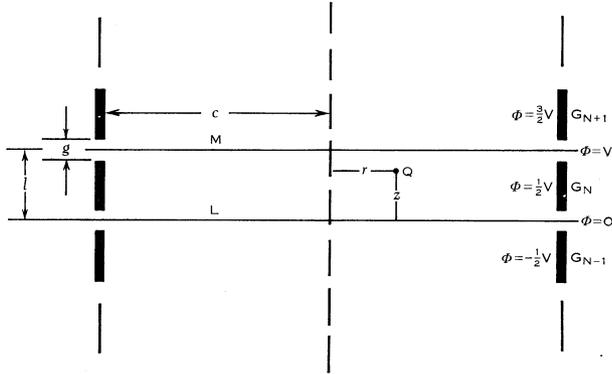


Fig. 6.—Geometry of guard electrode system whose electric potential distribution is as given by equation (9).

whole diffusion chamber. An alternative approach is to ensure that the amount of field distortion is made negligible in the region in which the electron or ion concentration is appreciable but to allow a certain known degree of distortion elsewhere. An electrode system that can be made to fulfil these requirements is one consisting of thick cylindrical guard electrodes. Such a system has the following advantages. First, each element of the system has a high degree of mechanical stability; secondly, this system shields the diffusion chamber completely from stray electrical fields exterior to it; and thirdly, the effects of dielectric soakage in the glass spacers separating the electrodes can be eliminated.* Since this electrode structure was used in the final apparatus the field produced by such a structure will be discussed more fully.

(b) An Analysis of the Field Produced by Guard Electrode Systems

The potential field generated by a system of identical guard electrodes spaced at regular intervals (Fig. 6) can be examined by considering the field within any module of the system. The planes L and M of the system shown in Figure 6 define such a module. If the potentials of the electrodes G_{N-1} , G_N , and G_{N+1} are $-\frac{1}{2}V$,

* A slow change of the current ratio R with time following a change of the electric field from a high to a low value was incorrectly attributed to surface effects at the receiving electrode (Crompton and Jory 1962). Subsequently it was shown that the effect was due to field distortion resulting from dielectric soakage in the glass spacers.

$\frac{1}{2}V$, and $\frac{3}{2}V$ respectively, the potentials of the planes L and M will be 0 and V respectively, and the solution to the Laplace equation with these boundary conditions is (Hurst 1960)

$$\phi = \frac{Vz}{l} + \sum_N \frac{2V}{N\pi} \frac{I_0(N\pi r/l)}{I_0(N\pi c/l)} \sin(N\pi z/l) \frac{\sin(N\pi g/2l)}{N\pi g/2l}, \quad (9)$$

where

ϕ = potential of the point Q at distances z from L and r from the axis of the system,

l = length of the module,

c = inner radius of the guard electrodes,

g = thickness of the gap between the guard electrodes,

I_0 = modified Bessel function of zero order,

N = summation index, the summation being carried out for all even values of N .

In the electrode structure of the apparatus described in Section VII, $l = 10/6$ cm and $c = 5$ cm, and the use of equation (9) shows that the potential at any point within an axial cylindrical volume of 6 cm diameter is within 0.05% of the value corresponding to a uniform field. From equation (6) it can be shown that for a current ratio R greater than 0.2, 99.9% of the electron stream arrives at the anode within a circular area of this diameter. It can be seen, therefore, that it is possible to obtain a high degree of uniformity within a volume of adequate dimensions without the use of a large number of electrodes or of a large diameter, even though there is considerable distortion in the vicinity of the electrodes. By contrast, the use of the more conventional guard electrode structure, while theoretically providing uniformity over a larger volume in an apparatus of the same dimensions, is unlikely to produce a high degree of uniformity anywhere because of geometrical distortion of the electrodes.

The use of equation (9) shows that the deviation from a linear variation of potential along a line parallel to the central axis of the guard electrodes, and at a radial distance r from it, is a periodic function whose amplitude depends on r and the ratio of the thickness of the module to the internal radius. As a check on calculations based on this formula, a series of plots was made using an electrolytic tank to measure the deviation from a linear variation of potential at a radial distance of 4.5 cm. This radial distance was chosen to ensure that the distortion was easily measurable. The deviations observed agreed with the predicted values to within the experimental error (approximately 2%).

(c) *Production of Surfaces of Sufficient Uniformity in Contact Potential Difference*

To obtain an electric field of adequate uniformity it is necessary not only to minimize distortion resulting from geometrical inaccuracy in the guard electrode structure and elsewhere, but also to minimize distortion produced by contact potential differences. Table 1 shows that contact potential differences will have the greatest effect if they occur over the surface of the collecting electrode. Since very small differences in potential between adjacent areas of the surface of the collecting electrode can lead to large errors in the measured current ratios, it is essential to

produce a gold surface for which these differences are reduced to a minimum. In order to test the uniformity of these surfaces an apparatus (Fig. 7) was built to measure contact potential differences. The surface to be examined is supported by insulating glass blocks on a table that can be rotated by a shaft passing through the baseplate. The probe can be raised and lowered by means of a sliding rod and can also be moved

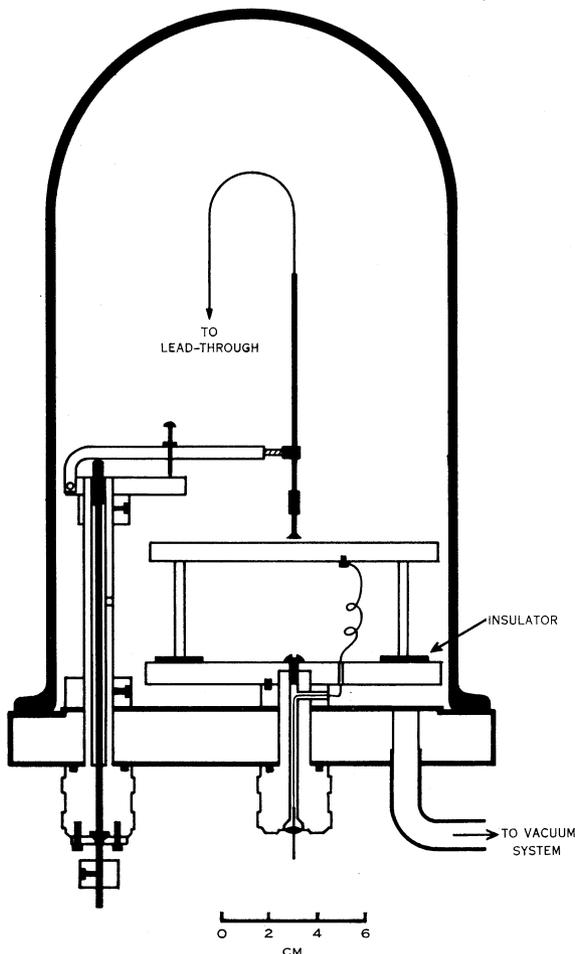


Fig. 7.—Apparatus used to measure contact potential differences.

through an arc of 45° . By the movement of the probe and turntable any small area 0.6 cm in diameter (the diameter of the probe) on a surface 10 cm in diameter can be examined. The contact potential difference between the probe and the surface could be determined to within approximately ± 1 mV. The vacuum conditions under which the apparatus was operated were chosen to approximate those of the diffusion apparatus. For this reason no attempt was made to outgas the contact potential apparatus or to obtain extremely clean surfaces by ion bombardment, etc.

The first measurements were made with electroplated gold surfaces. Large variations of up to 150 mV were found in the contact potential difference as the probe traversed the surface. In general the variation was randomly distributed over the surface. Parker and Warren (1962) have observed a similar behaviour for unbaked electroplated surfaces. Since it seemed impossible to make a significant improvement to the uniformity of electroplated gold surfaces, attention was turned to surfaces coated with gold by vacuum deposition.

The first of these surfaces was produced with either a short filament or a boat, and in general poor results were obtained. To improve the uniformity of the coating over the surface and within the gaps of the electrode, a triple-strand ring filament was later used which was placed below the surface and at a distance from it equal to the radius of the ring (Bond 1954; Holland 1961). Care was taken to ensure that the filament was still covered with gold when the evaporation was terminated.

Measurements made with the contact potential apparatus established that the vacuum coated surfaces were in general more uniform than the gold plated surfaces, but that a small potential gradient across the surface often occurred, the effect of which is clearly undesirable (Section V). It was also found that, when more than one surface was coated simultaneously with the same filament, the contact potential difference between the surfaces differed by 30–100 mV. Furthermore, the coating procedure was found to have a marked effect on the uniformity of the surfaces. Nevertheless, by careful attention to the conditions under which the vacuum deposition took place and after a large number of trials, a method was developed for producing surfaces of acceptable uniformity and stability. The maximum contact potential difference between any two areas of the collecting electrode used in the diffusion apparatus was 8 mV, with differences of only 3 mV occurring in the central region.

Measurements of k_1 made with this new surface confirmed the superiority of the gold anode and cathode surfaces prepared by vacuum deposition. Although a discrepancy of just over 1% existed between the results taken at extreme values of E for the same value of E/p , this represented a considerable improvement on the previous attempt to use surfaces prepared in this way, when discrepancies in excess of 5% were found. The results were now more reproducible than previously, showing little or no variation with time or the previous history of the apparatus. Because of this reproducibility, and of the uniformity of the surfaces as demonstrated by preliminary direct measurement, it was considered that the most likely cause of the 1% variation was a contact potential difference between the vacuum-deposited gold surfaces of the anode and cathode, and the electroplated surfaces of the guard electrodes. No attempt was made to gild the guard electrodes by vacuum deposition because of the risk of producing non-uniform surfaces with the techniques available.*

To allow for the contact potential difference between the guard rings and anode and cathode surfaces, a compensating potential of the order of 100 mV was placed between the set of guard electrodes and the anode and cathode. The procedure

* In order to eliminate contact potential differences arising from the position of the surface relative to the evaporating source it would have been necessary to rotate the guard electrodes about an axial filament to ensure adequate uniformity.

for determining the correct compensating potential and the magnitude of the errors involved is discussed in Section IX.

VII. THE CONSTRUCTION OF THE DIFFUSION APPARATUS

The final form of the experimental tube is shown in Figures 2 and 8. The main electrode structure was made of copper, the only other metals used being nonmagnetic stainless steel and nichrome. The use of

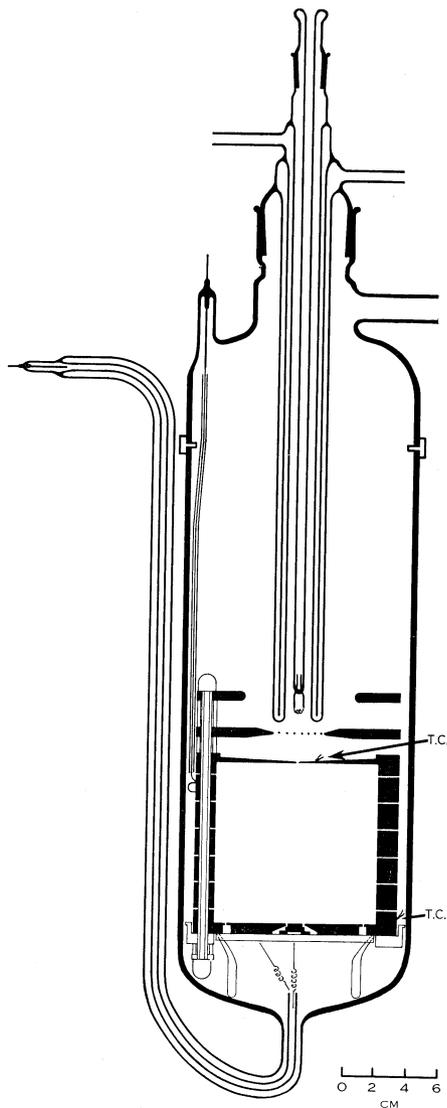


Fig. 8—The experimental tube.

nonmagnetic materials, together with other precautions, ensured that the magnetic field strength within the diffusion chamber was only that due to the Earth's field. The limits to the experimental parameters imposed by the other considerations discussed in this paper ensure that the effect of this field is negligible.

With the exception of the receiving electrode, the electrode structure is designed to withstand a temperature range of 80–520°K, while the arrangement of the electrometer leads enables measurements to be made at the lowest temperatures in this range. Since the principal aim of the experiments described in this paper was the precise determination of k_1 when k_1 approaches unity, no attempt was made to heat the experimental tube to accelerate outgassing because of the attendant risk of changing the contact potential differences within the chamber. Consequently, the use of Apiezon W 100 vacuum wax and Apiezon N grease was permissible for sealing the demountable joints. It is shown in Section X that the contamination of the gas samples from this procedure was negligible.

Two filaments are attached to the filament support. Electrons are produced from a platinum filament, and potassium ions from a heated potassium aluminosilicate bead (Blewett and Jones 1936). This arrangement enabled the change-over from measurements with electrons to those with ions to be made without changing the gas sample, thus avoiding any possibility of changes in contact potential differences within the apparatus. As a

control on the electron or ion current, the inner surface of the water jacket in the region of the filament was coated with a layer of platinum, the potential of which could be varied with respect to the filament.

The construction of the receiving electrode proved unsatisfactory below 90°K, when differential contraction of its components caused the disk and annulus to touch. This was not unexpected in view of the gap of only 0.005 cm between them. An alternative design employing concentric ceramic-metal seals successfully overcame this difficulty but introduced an equally serious one. As a result of the distortion of the annulus during cooling, a vertical displacement of the order of 0.005 cm occurred between the disk and the neighbouring section of the annulus. A solution has yet to be found to the problem of maintaining adequate mechanical stability over this temperature range to meet the requirements laid down in Section V(b)(i).

The dimensions of the apparatus are as follows:

length h of diffusion chamber	10 ± 0.005 cm
effective radius b of central collector disk	0.5 ± 0.002 cm
diameter of central collector disk	0.9955 ± 0.0005 cm
internal diameter of annulus of collector	1.0050 ± 0.0005 cm
width of gap between disk and annulus	0.005 cm
external diameter of annulus of collector	8.5 cm
internal diameter of guard electrodes	10 cm
diameter of source hole	0.1 ± 0.005 cm
thickness of full guard electrodes	1.616 ± 0.003 cm
thickness of glass spacers	0.051 ± 0.002 cm.

The tolerances to which the individual components of the apparatus are machined ensure adequate precision in the separation and parallelism of the cathode and anode, but considerable care has to be paid to the procedure of assembling the apparatus to obtain accurate alignment of the cathode and anode with respect to the principal axis of the diffusion chamber. In developing this procedure, it was necessary to recognize that the guard electrodes, rather than the cathode and anode, were principally responsible for generating the field and were therefore responsible for establishing the axis. The principal axis used for alignment was therefore taken as the axis originating from the centre of the receiving electrode whose direction was parallel to the axis of the guard electrodes rather than normal to the receiving electrode. In practice the difference in these directions is unimportant, apart from small anomalies which may be present in the plane surface of the electrode or which may arise from an accumulation of tolerances in the dimensions of the guard electrodes and spacers.

A Taylor-Hobson Micro-Alignment Telescope was used for the alignment. This instrument can be used to set up an axis normal to a plane surface and to measure deviations from this axis. In this instance the axis was parallel to the axis of the guard electrodes and incident on an indentation 0.01 cm in diameter marking the centre of the disk of the receiving electrode. When the cathode was placed in position it was moved laterally until the centre of the source hole coincided with

the principal axis, after which a final check on the position of the anode was made by sighting through the source hole. The maximum error in the alignment of the apparatus is less than 0.005 cm.

VIII. THE MEASUREMENT OF EXPERIMENTAL QUANTITIES

(a) *The Measurement of E/p*

The potentials of the electrodes were derived from a voltage divider in which the resistors were matched to better than 0.05%. The voltage to the divider was supplied by a Fluke 301 E power supply, the output of which is accurate to within 0.1%. Since the chamber length of 10 cm was known to within ± 0.005 cm, the value of the electric field strength E could be determined to within 0.15%.

The gas pressure was measured by means of two capsule gauges (Crompton and Elford 1957), which were calibrated against a C.E.C. type 6-201 primary pressure standard. The gas pressure can be measured with an error of less than 1% at 500 torr and 0.25% at 40 torr. The larger errors at high gas pressures are due to hysteresis effects in the capsules of the gauges. Fortunately, it is necessary to use high pressures only when measurements are being made at the lowest values of E/p , where small errors in the pressure measurement have little effect on the value of k_1 . This insensitivity to errors in pressure measurement is due to the value of k_1 varying only slowly with E/p ; for example, for electrons in hydrogen at $E/p = 0.006$, if the measurement of the gas pressure of 500 torr were in error by 5% the error in k_1 would be only 0.2%. At higher values of E/p , k_1 changes rapidly with E/p , but the lower pressures which are then used can be measured with adequate precision.

(b) *The Measurement of the Ratio R*

(i) *Double Induction Balance.*—In order to avoid the effects of Coulomb repulsion in electron or ion swarms it is necessary to ensure that the particle number density is very low. It may be necessary, therefore, for the total current arriving at the collector to be as small as 10^{-12} A. The ratio of the currents received by the disk and annulus must be determined with high accuracy if an error in this measurement is to contribute less than 1% to the error in the measured value of k_1 . Furthermore, in order to avoid effects similar to those described in Section V(b)(ii), arising from non-uniformity in potential over the collecting electrode, the potential of the disk and annulus must not depart significantly from earth potential in the course of the measurement.

The method adopted to measure the ratio is a modification of that used by Crompton and Sutton (1952). Their method employed a pair of integrating induction balances and was developed from the method originated by Townsend (1914). A simplified circuit diagram of the modified system is shown in Figure 9. The potentiometer P_1 is a 12 k Ω Colvern potentiometer, cam-corrected to give an output within $\pm 0.05\%$ of linear when loaded by the 450 k Ω 10-turn helipot P_2 . A voltage V , continuously variable from 1 to 10 V, is applied to P_1 from a highly stabilized d.c. power supply of low impedance. When P_1 is driven at a constant rate of 1 rev/min by a synchronous motor, a highly linear sweep voltage is generated at A while a similar

signal, the relative amplitude of which is determined by the setting of P_2 , appears at B. The two potentials are applied to the capacitors C_1 and C_2 , which have been designed to eliminate leakage currents from dielectric soakage (Crompton and Sutton 1952). Each capacitor has a capacitance of approximately 30 pf, and the pair is matched to within 0.01%. With this arrangement, two constant displacement currents i_1 and i_2 are generated, the ratio of which is determined simply by the setting of P_2 . Since the resolution and accuracy of the helipot is better than 1 part in 1000, the error incurred in k_1 due to this limit of resolution is 0.4% at $R = 0.2$ and 0.9, and 0.07% at $R = 0.5$.

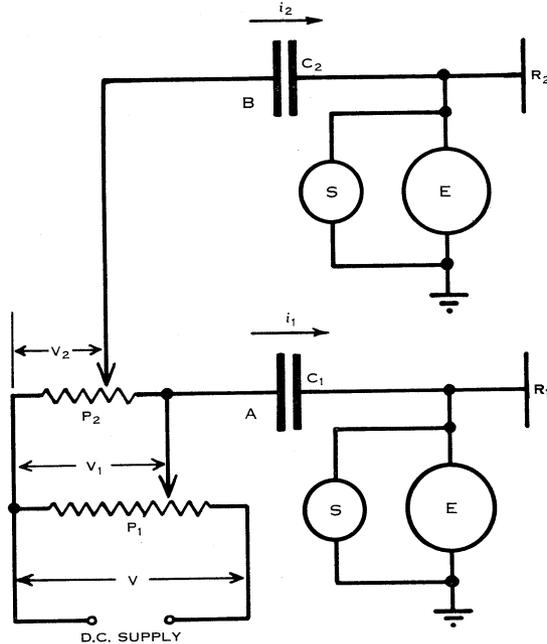


Fig. 9.—Simplified circuit of the double induction balance.

When measuring the ratio of the currents received by the segments R_1 and R_2 of the receiving electrode, the potential difference between each segment and earth is measured by the electrometers E. Adjustment of the voltage V , followed by adjustment of the potentiometer P_2 , is made until R_1 and R_2 are maintained at earth potential to within 0.2 mV. The ratio R is then the required ratio of the currents.

Full advantage can be taken of the method only by making it an integrating one, with the integration commencing when $V_1 = V_2 = 0$ and terminating just before $V_1 = V$. To effect this, a correctly phased cam operates a microswitch which in turn activates the electromagnetic earthing switches S (EIL type 33124C). The switches are designed to inject minimum charge into the electrometer circuits on opening as a result of contact potential differences between the moving contacts.

(ii) *Electrometers*.—To enable the ratio R to be measured to the required accuracy when currents of the order of 10^{-12} A are being compared, it is necessary to detect currents of the order of 10^{-15} – 10^{-16} A. The electrometers that are used as null indicators must therefore have a high order of stability over the period of integration, adequate sensitivity, and leakage currents less than 10^{-16} A. These requirements can be met by using selected double electrometer valves (Ferranti BDM 20) operated under closely specified and controlled conditions.

The grid current in the valve can be made vanishingly small by operating the valve at the grid voltage corresponding to the crossover point A in Figure 10, at the expense of greater difficulty in achieving stability in the grid current. One

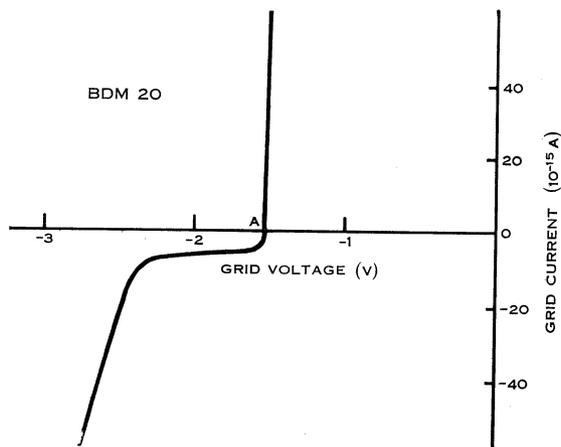


Fig. 10.—Typical grid current characteristic of the BDM 20 electrometer valve.

major advantage of using electrometer tubes in this way is that by suitable adjustments of the grid bias a leakage current of either sign can be introduced. Any small residual leakage current arising in either electrometer circuit, generated either internally or externally, can therefore be annulled. Before each measurement of the ratio R , one complete integration is taken with no current being received by the collecting electrode to ensure that the leakage currents in each electrometer circuit are negligible.

The circuit of the double electrometer unit is shown in simplified form in Figure 11. All resistors are high precision wire-wound types, and the cathode and plate voltages are supplied by a bank of 1.5 V dry cells. The sensitivity of the electrometers is such that an input of one millivolt causes a deflection of 5 mm of the galvanometer spot. By use of the procedure described above, the leakage rate for each of the electrometers can be made less than approximately 10^{-16} A over a period of several hours without adjustment of the grid bias controls. During the same period the zero drift is less than ± 0.2 mV.

(c) *Temperature Control and Measurement*

The temperature at which the measurements are made can affect the measured values of k_1 either directly (Section I) or indirectly through its effect on the gas number density N , since the gas pressure p rather than N is measured to determine E/N . In the region of low electron energy, that is as $E/p \rightarrow 0$ and $k_1 \rightarrow 1$, the error in the measured value of k_1 resulting from an uncertainty of 1 degC in the gas temperature may be as large as 0.3% when $T \approx 293^\circ\text{K}$, and in excess of 1% when $T \approx 80^\circ\text{K}$. By measuring the quantity D/μ it is not possible, of course, to avoid the consequences of errors of this magnitude when using these data in subsequent

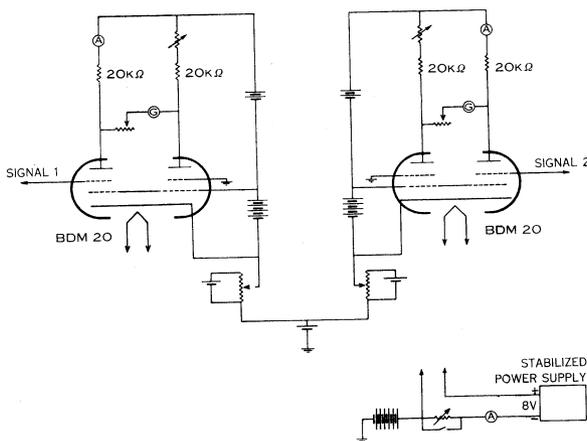


Fig. 11.—Simplified circuit of the electrometers.

analyses. Although D/μ can be determined accurately without knowledge of the gas temperature, the relevant quantity ($D/\mu - kT/e$), which expresses the energy excess, is subject to the same percentage error as its equivalent ($k_1 - 1$) through any error in the estimate of the temperature. Therefore, it is necessary to exercise considerable care in both the control and measurement of the gas temperature.

To assist in the maintenance of constant gas temperature, the temperature of the laboratory was controlled to ± 1 degC, and the experimental tube was surrounded by a 2-in. thick jacket of "Styrofoam". The heat generated by the platinum filament was removed by means of the cooling jacket, through which water was circulated in a closed system by a small pump.

To measure the gas temperature two copper-constantan fine-wire thermocouples were attached to the earthed ring of the collector electrode and to the cathode (Fig. 8). To avoid the danger of thermal e.m.f.'s being produced at conventional tungsten seals, hollow Kovar tube seals were used. The temperature as recorded by the two thermocouples showed a variation of the order of 0.1 degC over a period of 1 hr when measurements were being taken continuously.

IX. METHODS OF COMPENSATING FOR RESIDUAL ERRORS
DUE TO CONTACT POTENTIAL DIFFERENCES

When care has been taken to eliminate as far as possible all the sources of systematic error discussed in this paper, a residual error of the order of $\pm 1\%$ is usually present at the lowest value of E . This error results from the existence of contact potential differences within the diffusion chamber despite the attention given to this problem. A simple method of compensating for these contact potential differences has been used which largely removes this residual error. It has been shown in Section VI(c) that, with the present techniques for gilding the surfaces, the most likely place for large contact potential differences to occur is between the internal surface of the guard electrode structure and the surfaces of the anode and cathode. On the other hand, although contact potential differences across the

TABLE 1
VALUES OF ADDITIONAL POTENTIAL WHICH, WHEN APPLIED TO A GIVEN ELECTRODE,
CHANGE THE MEASURED VALUE OF k_1 BY 1%

Electrode	Potential Difference (mV)
Central disk (or annulus)	6
Central disk and annulus	100
Collecting electrode and adjacent half guard electrode	170
Source electrode and adjacent half guard electrode	500
Guard electrode 1	350
Guard electrode 2	500
Guard electrode 5	2500
Set of guard electrodes	130

surface of the anode are known to be small they have a much greater influence (see Table 1). The most exact method of compensation for these effects would therefore be to place compensating potentials between the guard electrode structure and the anode and cathode and between the disk and annulus of the collecting electrode. In practice the first of these methods is the simpler of the two, so that, if practicable, it is advantageous to compensate for contact potential differences occurring anywhere in the apparatus by this method alone. This procedure is adequate only if, for a given value of E , the percentage error in k_1 resulting from a contact potential difference of either type is either independent of R or varies with R in a similar way for each type.

In order to test the validity of this procedure, a potential difference of 10 mV was first placed between the disk and annulus and the change in the measured value of k_1 for electrons obtained when the potential was reversed, the value of E in this and subsequent tests being 3 V/cm. With $p = 500$ torr, R was approximately 0.5 and the change in k_1 was $3\frac{1}{2}\%$. On the other hand with $p = 10$ torr the ratio was approximately 0.2 and the change in k_1 was then $2\frac{1}{2}\%$, that is, the magnitude of the error is to some extent dependent on R .

The same experiments were repeated with a potential difference now applied between the guard electrodes and the cathode and anode. This time the percentage change was found to be independent of the value of R .

Finally, a comparison was made between the two experiments with quasi-thermal electrons ($p = 500$ torr, $E = 3.0$ V/cm, i.e. $E/p = 0.006$) and those performed using positive ions with $E = 3.0$ V/cm, the ratio R for the ions then being essentially the same as that for the electrons. The percentage change in k_1 was in each case found to be the same for the ions as for the electrons.

Two conclusions can be drawn from this set of experiments. First, the use of positive ions to adjust the value of the compensating potential is justified since, as might be expected, the measurements with ions and electrons are equally sensitive to contact potential differences provided the value of R is similar in each case. The use of positive ions takes obvious precedence since the value of k_1 is known. Secondly, regardless of where contact potential differences exist in the apparatus, they can be compensated for accurately when studying quasi-thermal electrons by applying a potential difference between the guard electrodes and the anode and cathode, the magnitude of this potential difference being adjusted by using positive ions. Furthermore, although the compensation using this method is less precise when the electrons are non-thermal it is still adequate. If, as in the present experiments, the residual error to be compensated for is only 1%, then the error resulting from the use of this method when non-thermal electrons are being studied is at most 0.3%.

X. EFFECT OF GASEOUS IMPURITIES

Some of the most commonly considered sources of error in experiments on electronic and atomic collision processes are those arising from the presence of gaseous impurities. While the effects of small traces of impurity may be significant in some swarm experiments, as for example the effect of molecular impurities in argon when the mean energy of the swarm is near the Ramsauer minimum (Bowe 1960; Uman 1964), it is necessary to recognize that in other circumstances larger errors may be introduced in reducing the impurity level than would be present if the impurity remained. The present investigation was aimed at obtaining maximum precision in the measurement of k_1 for quasi-thermal electrons in molecular gases. Calculations show that, for nitrogen and hydrogen, impurity levels of the order of 100 p.p.m. or less will have negligible effect on the results. Experience has shown that the level of impurity as a result of the outgassing of the tube can be kept well below this amount without baking. On the other hand, it seems highly probable that significant errors could be introduced through changes of the contact potential differences within the apparatus if the tube were subjected to elevated temperatures. The outgassing was therefore reduced to an insignificant level by employing long periods of pumping. Following pumping with a 5 l/s Vacion pump, isolation tests made without using liquid air traps showed that the rate of rise of pressure was of the order of 5×10^{-6} torr/hr, which corresponds to a gas influx rate of 8×10^{-8} torr-litres/s. When using samples at 500 torr the rate of rise of impurity level is therefore 1 part in 10^8 per hour. Measurements of k_1 taken over a period of 24 hr showed

no change with time, indicating that the background level of gaseous impurity had a negligible effect.

The gases for which results have been published to date using the techniques described in this paper are hydrogen and nitrogen (Crompton and Elford 1963). The hydrogen was obtained by diffusion through palladium using the apparatus and technique described by Crompton and Elford (1962). This method is capable of producing hydrogen with an impurity level which is certainly less than 0.1 p.p.m. (Young 1963). Nitrogen was obtained from a cylinder of Airco Reagent Grade gas.

TABLE 2
TYPICAL RESULTS FOR ELECTRONS IN HYDROGEN AT 293°K, SHOWING THE RESIDUAL VARIATION OF k_1 WITH GAS PRESSURE

p (torr)	500	400	300	200	150	100
E/p (V cm ⁻¹ torr ⁻¹)						
0.01	1.049	1.047	1.047			
0.02	1.131	1.129	1.130	1.128	1.125	
0.03			1.217	1.217	1.216	1.213
0.04				1.305	1.305	1.305

XI. RESIDUAL ERRORS DUE TO THE FINITE SIZE OF THE SOURCE HOLE

Part of a typical set of results for k_1 is shown in Table 2. These results were taken using a compensating potential of 100 mV between the guard electrodes and the cathode and anode. The use of this potential, the magnitude of which was set using the procedure discussed in Section IX, eliminates errors from contact potential differences of not more than 0.7% at the lowest field strengths used.

The table shows that the values of k_1 decrease slightly as the pressure is decreased at a fixed value of E/p . This variation is similar to that predicted when account is taken of the finite size of the source hole (Crompton and Jory 1962). However, as discussed in Section III(c), the magnitude of the variation of the results with pressure from this source of error cannot be accurately estimated, and for this reason the best estimate for k_1 at any given value of E/p was obtained by averaging the results taken over a range of pressures. The maximum error incurred using this procedure is less than 0.5%.

XII. ACKNOWLEDGMENTS

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XIII. REFERENCES

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