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TRANSIENT PHENOMENA IN IONIZED GASES

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by

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Abstract

An electrodeless method of measuring electron attachment and ambipolar
diffusion in gases has been developed. An r-f field is used to break down a gas
in a glass bottle inside a cavity resonant at 3000 Mc. This field is applied for
1000 microseconds, then turned off for 4000 microseconds. The electrons produced
in the discharge then diffuse or attach depending on the gas used. If a small
c-w field is applied to the cavity, the free electrons will oscillate without
having their energy distribution disturbed. The electron oscillation causes a
shift of the resonant frequency of the cavity proportional to the number of free
electrons. Therefore by measuring the frequency shift in the cavity as a func-
tion of time, the change of electron density due to the various removal processes
is determined.

A MICROWAVE METHOD OF STUDYING TRANSIENT PHENOMENA IN IONIZED GASES

Over a period of years the processes of electron attachment and electron and ionic diffusion in gases have been investigated in many experiments. All methods, however, suffered from one principal disadvantage: metal surfaces were present in the measuring apparatus causing difficulty in maintaining high purity of gases and in some cases leading to undesired interaction between the metal electrodes and the charged particles. Also, in attachment measurements, the minimum electric field used confined measurements to medium and high electron energies.

By making use of recent developments in microwave techniques, a method has been developed for measuring electron attachment and ambipolar diffusion at thermal energies without the presence of electrodes in the gas. With this method a high degree of purity can be maintained. For attachment measurements the range of electron energies may be extended from the previous lower limit of about 0.2 ev to thermal energies (~ 0.04 ev). For diffusion measurements this method gives some of the first data on the relatively uninvestigated subject of ambipolar diffusion[1].

1. Theory and Experimental Method

If a gas-filled glass bottle is placed in a cavity resonant at 3000 Mc and ions and electrons are generated in the gas by a high-intensity r-f field, the properties of the cavity will be altered. At microwave frequencies the effect of the massive ions is negligible as compared to that of the electrons. Free electrons will oscillate in an applied r-f field, their motion being out of phase, drawing no power from the field, until they collide with a gas atom or ion. The electron orbit during collision has an in-phase component withdrawing, on the average, sufficient energy from the field to supply the energy lost in the collision. Therefore the electrons in the cavity have a complex conductivity, σ_c, whose real component, σ_r, is due to the in-phase motion during collision and whose imaginary component, σ_i, is due to the out-of-phase oscillation plus the out-of-phase component of the collision motion.

At thermal energies the energy distribution, f_0, of these electrons is very nearly Maxwellian:

$$f_0 = Ae^{-\frac{\epsilon}{kT}} \tag{1}$$

where A, as will be shown later, is proportional to the electron density, ϵ is the energy of the electrons, k is Boltzmann's constant, and T is the absolute temperature.

As has been shown by W. P. Allis, private communication, the complex conductivity of the medium may be written as:

$$\sigma_c = -\frac{8\pi}{3} \ell \frac{e^2}{m^2} \int_0^\infty \frac{\sqrt{\epsilon} - j\sqrt{\epsilon_2}}{\epsilon_2 + \epsilon} \epsilon^{3/2} \frac{df_0}{d\epsilon} d\epsilon \tag{2}$$

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1. Ambipolar diffusion is discussed in Sec. 3.2.

where ℓ = mean free path; e and m are electronic charge and mass, respectively; and $\epsilon_2 = \frac{1}{2} m \omega^2 \ell^2$, ω being the applied radian frequency; ϵ_2 represents the energy at which an electron makes collisions with gas atoms on the average at the same frequency as that of the applied r-f field. It defines a transition energy between energies at which an electron makes many oscillations in the applied field per collision with a gas atom and energies at which the electron makes many collisions per oscillation.

Since the integration of Eq. (2) is not readily performed, let us consider a region where $\epsilon_2 \gg \epsilon$; that is, a low pressure or low electron energy region[1]. Making the approximation:

$$\frac{1}{\epsilon_2 + \epsilon} \approx \frac{1}{\epsilon_2} (1 - \frac{\epsilon}{\epsilon_2})$$

and considering only the imaginary part of the integral:

$$\sigma_i = - \frac{8\pi}{3} \ell \frac{e^2}{m^2} \frac{A}{kT} \int_o^\infty \sqrt{\epsilon_2} \left(\frac{\epsilon^{3/2}}{\epsilon_2} - \frac{\epsilon^{5/2}}{\epsilon_2^2}\right) e^{-\frac{\epsilon}{kT}} d\epsilon. \qquad (3)$$

By separation and simplification, the integrals are reduced to the form of gamma functions. Therefore:

$$\sigma_i = - 2(\pi)^{3/2} \ell \frac{e^2}{m^2} \frac{(kT)^{3/2}}{\epsilon_2^{1/2}} (1 - \frac{5}{2} \frac{kT}{\epsilon_2}) A . \qquad (4)$$

A similar result is obtained for σ_r:

$$\sigma_r = \frac{16\pi}{3} \ell \frac{e^2}{m^2} \frac{(kT)^2}{\epsilon_2} (1 - \frac{3}{2} \frac{kT}{\epsilon_2}) A . \qquad (5)$$

The value of A may be obtained as follows: If the velocity distribution is Maxwellian, and the velocities are spherically symmetrical, we may write n, the electron density, as:

$$n = \int_o^\infty f_0(v) \, 4\pi \, v^2 \, dv = \int_o^\infty A e^{-\frac{\epsilon}{kT}} 4\pi \, v^2 \, dv. \qquad (6)$$

This integral may be reduced to the form of a gamma function. Therefore:

$$n = (2\pi \frac{kT}{m})^{3/2} A \qquad (7)$$

Therefore, both σ_r and σ_i are proportional to the electron density within the cavity. They simplify to the expressions:

$$\sigma_i = - \frac{e^2}{m\omega} \left[1 - \frac{5}{2} \frac{kT}{\epsilon_2}\right] n \qquad (8)$$

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1. For helium, pressures up to 50 mm satisfy this condition for thermal electrons. Experimental measurements rarely exceed pressures of 20 mm.

$$\sigma_r = \frac{8}{3} \sqrt{\frac{kT}{\epsilon_2}} \frac{e^2}{m\omega} \left[1 - \frac{3}{2} \frac{kT}{\epsilon_2} \right] n \qquad (9)$$

It can be shown that σ_r acts to lower the Q of the cavity while the shift of resonant frequency is proportional to σ_i.[1] In lumped constant analogy, the cavity would be considered as a parallel RLC tank circuit, with σ_r represented as an added shunt resistance and σ_i a shunt inductance.

The calculations of σ_r and σ_i for the high pressure or high energy case, where $\epsilon \gg \epsilon_2$ have also been done and the results are given below[2]; however, they do not apply to this experiment. A simple derivation involving the application of Newton's law to a free electron gas in which collisions are neglected gives a result for σ_i:

$$\sigma_i = - \frac{e^2 n}{m\omega} . \qquad (10)$$

Therefore the term $\left[- \frac{5}{2} \frac{kT}{\epsilon_2} \right]$ in Eq. (8) represents the correction of this simple theory for the effect of collisions. However, at thermal energies at pressures of the order of 10 mm, the correction term is only of the order of 10^{-9}, thus totally negligible. In the 10-mm pressure range this makes σ_i independent of electron energy over a range of 0 - 10 ev.

Let us relate these derivations to the physical problem. Consider a resonant cavity containing a glass bottle into which gas samples are introduced. If electrons are produced in the gas, they will change the cavity's resonant frequency and lower its Q in proportion to the electron density. By choosing suitable gas pressures and electron energies the decrease in Q can be made negligible compared to the resonant frequency shift of the cavity[3].

If a large number of electrons is initially produced in the gas inside the glass bottle, they will disappear with time principally on account of ambipolar diffusion, attachment (cf. Sec. 3), or volume recombination. Experimental data for the particular gases investigated in this experiment indicate that recombination is too slight to be an effective removal process. The time effect of these electrons will be to produce a large initial frequency shift in the cavity which will diminish with time as the electron density decreases. Therefore to study these transient processes it is sufficient to observe the resonant frequency shift of the cavity as a function of time.

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1. See J. C. Slater, Rev. Mod. Phys. **18**, 441 (1946).

2. If $\epsilon \gg \epsilon_2$:

$$\sigma_r = \frac{4}{3\sqrt{\pi}} \left(\frac{e^2}{m\omega} \right) \sqrt{\frac{\epsilon_2}{kT}} \left(1 - \frac{\epsilon_2}{kT} \right) n$$

$$\sigma_i = - \frac{2}{3} \left(\frac{e^2}{m\omega} \right) \frac{\epsilon_2}{kT} \left(1 - 2 \frac{\epsilon_2}{kT} \right) n$$

3. In the actual experiment the wall losses of the cavity are so large and σ_r so small compared to σ_i (see Eqs. (8) and (9), $\sigma_r / \sigma_i \approx 10^{-4}$) that only at large frequency shifts is the decrease in cavity response noticeable; that is, the Q of the cavity is primarily determined by the constant wall losses.

2. Experimental Arrangement

It has been pointed out /that σ_1 exceeds σ_r by a factor of 10^4, that is, that the frequency shift produced by electrons in a cavity is more easily detected, especially for low electron densities, than any attenuation of a transmitted signal which they might produce. Over a small frequency range the electrons produce a frequency shift proportional to their density [see Eq. (8)]. Also, so long as the condition $\epsilon_2 \gg \epsilon$ (the low pressure, low energy case) is valid, this frequency shift is independent of electron energies up to 10^3 ev. Of course, as soon as we deal with higher electron energies at a given pressure the condition might fail and the integral (3) would have to be solved for a new set of conditions. This is important since in helium typical pressures used experimentally are of the order of 10 mm. For thermal energy electrons in helium $\epsilon = \epsilon_2$ at about 100 mm so that the condition $\epsilon_2 \gg \epsilon$ is valid at 10 mm pressure; however, for 20-ev electrons such as are produced in a discharge in helium, $\epsilon = \epsilon_2$ at about 5 mm so that a transition solution must be used. Present investigations deal with measurements at thermal energies only. A simple calculation shows that the energy of electrons in helium will go from 20 ev to 0.04 ev, on account of elastic collisions, in about 50 μsec for pressures of the order of millimeters. Therefore if one waits 50 μsec after a discharge in helium has been terminated, the electrons remaining may be considered to be at thermal energy, so that the conditions leading to Eq. (8) are satisfied.

A block diagram of the apparatus used to measure the change of electron density with time is shown in Fig. 1.
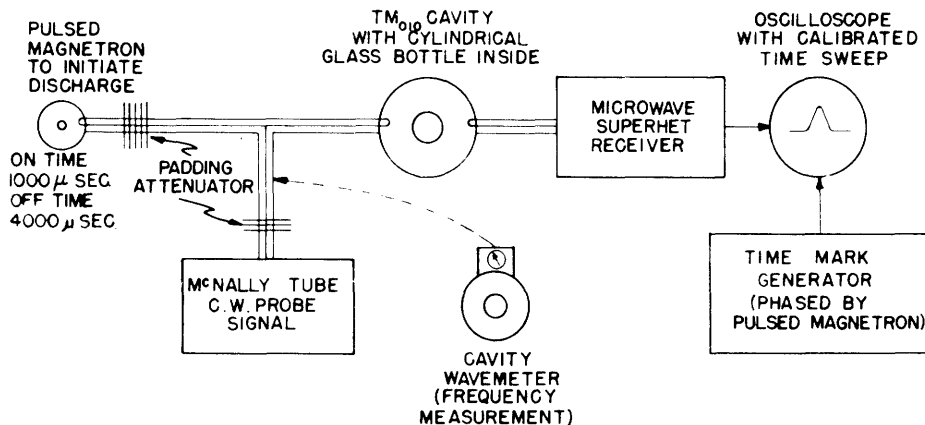

Figure 1. Simplified block diagram of apparatus.

A discharge is initiated in the gas-filled glass bottle for 1000 μsec by the pulsed magnetron, then turned off for 4000 μsec.[1] During this off time, observations are made. A small c-w signal from the McNally tube is used as the low-level probe signal. The cavity has a characteristic resonant frequency which is increased in proportion to the density of free electrons within the cavity. If we consider the cavity in the absence of free electrons, a probe signal whose frequency is set to the resonant fre-

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1. The discharge is maintained for this relatively long time in order to permit equilbrium conditions in the discharge to be reached.

quency of the "empty" cavity, f_{oe}, will undergo maximum transmission through the cavity. All probe signals having other frequencies will undergo reduced transmission.

If the probe signal is set to a higher frequency than f_{oe}, this signal will undergo maximum transmission through the cavity at the time at which the residual density of electrons remaining from the discharge and the cavity constants give a resulting resonant frequency, f_o, equal to that of the probe signal. The time of maximum transmission is measured by means of the calibrated time sweep of the oscilloscope. The origin of time measurements is the end of the magnetron pulse, when the discharge is terminated.

By varying the probe signal frequency in steps and measuring the time of maximum transmission corresponding to each frequency, one obtains a frequency shift versus time curve. This curve completely characterizes the change of electron density with time due to the various removal processes.

3. Physical Considerations of Attachment and Diffusion

3.1 Attachment. A few gases, principally oxygen, SO_2, H_2O vapor, and NO_2, exhibit the property of attachment. If electrons are produced in these gases there is a certain probability that on collision with a gas atom or molecule the electron will be captured to form a negative ion. This probability is known as the attachment probability, h, and may be expressed as the inverse of the average number of collisions with gas atoms per attaching collision. It is usually quite small, of the order of 10^{-3} attachments/collision or less.

Let us analyze the process of the removal of free electrons from the gas due to attachment. If we assume that the electrons have a Maxwellian energy distribution $f_0 = Ae^{-\epsilon/kT}$ [see Eq. (1)], which is a justifiable assumption at thermal energy, the electron density in a volume element between v and v + dv of velocity space is:

$$dn = Ae^{-\frac{\epsilon}{kT}} 4\pi v^2 dv. \tag{11}$$

In this element, the rate of removal due to attachment is:

$$d(-\frac{dn}{dt}) = Ae^{-\frac{\epsilon}{kT}} 4\pi v^2 dv \left(\frac{v}{\ell}\right) h \tag{12}$$

where ℓ is the electronic mean free path. If h is assumed to be independent of energy, the total rate of removal of electrons is:

$$-\frac{dn}{dt} = 4\pi \frac{h}{\ell} A \int_0^\infty 4\pi v^3 e^{-\frac{\epsilon}{kT}} dv \tag{13}$$

using $\epsilon = 1/2\ m\ v^2$, the integral can be reduced to the form of the gamma function. Therefore

$$-\frac{dn}{dt} = 8\pi \frac{h}{\ell} \frac{A}{m^2} (kT)^2. \tag{14}$$

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Using the value of A derived in Eq. (7), we obtain

$$-\frac{dn}{n} = -\frac{2h}{\ell}\sqrt{\frac{2}{\pi}\frac{kT}{m}}\; dt \tag{15}$$

Integrating:

$$n = n_0\, e^{-\frac{t}{\mathcal{T}}} \tag{16}$$

where $\mathcal{T}$, the time constant of this exponential process, is given by:

$$\mathcal{T} = \frac{\ell}{2h}\sqrt{\frac{\pi}{2}\frac{m}{kT}}\; . \tag{17}$$

We shall make use of this derivation in the section on experimental results.

3.2. Ambipolar Diffusion. The process of diffusion of electrons in the presence of a nearly equal number of positive ions takes place in a manner known as ambipolar, in which, on the average, an electron cannot diffuse out without taking along a positive ion; therefore, ambipolar diffusion is much slower than electron diffusion.

The migration of bodies due to a concentration gradient is expressed by:

$$\bar{v}_D = -D\frac{\nabla n}{n} = -D\nabla(\ln n) \tag{18}$$

where $\bar{v}_D$ is the average drift velocity; n is the particle density; and D the diffusion constant. For ambipolar diffusion we must also consider the mobility of the particles. The average velocity produced by an applied field E is:

$$\bar{v}_\mu = \mu\, E \tag{19}$$

where μ = mobility constant.

If we denote by N the positive ion density and by n the electron density:

$$\left.\begin{array}{l} v_+ = -D_+\nabla\ln N + \mu_+\, E \\[2mm] v_- = -D_-\nabla\ln n - \mu_-\, E \end{array}\right\} \quad \text{Equations governing diffusion.} \tag{20}$$

where v_+ and v_- are positive ion and electron average drift velocities, respectively,

           D_+ and D_- are positive ion and electron diffusion constants, respectively,

           μ_+ and μ_- are positive ion and electron mobilities, respectively.

In the steady state of ambipolar diffusion $v_+ = v_-$ so that when there is no field applied externally, E is the field set up by the system of positive ions and electrons to maintain ambipolar diffusion, i.e. $v_+ = v_- = v$.

Observing that $N \approx n$ in a gas discharge we solve Eq. (20) eliminating E:

$$v\left[\frac{1}{\mu_+} + \frac{1}{\mu_-}\right] = -\left[\frac{D_+}{\mu_+} + \frac{D_-}{\mu_-}\right]\nabla\ln n \tag{21}$$

or

$$v = -D_a\nabla\ln n \tag{22}$$

where D_a, the ambipolar diffusion constant is:

$$D_a = \frac{D_+ \mu_- + D_- \mu_+}{\mu_+ + \mu_-} \tag{23}$$

This expression may be simplified for the case of a Maxwellian distribution of energies. From kinetic theory[1] we find that

$$\frac{\mu_-}{D_-} = \frac{\mu_+}{D_+} = \frac{e}{kT} \tag{24}$$

where k is Boltzmann's constant, e the electronic charge and T is the temperature of the electrons and the ions (at thermal energy $T_+ \approx T_-$). Since the mobility of the electrons greatly exceeds that of the positive ions,

$$\frac{1}{\mu_-} \ll \frac{1}{\mu_+} \tag{25}$$

and
$$D_a \approx \frac{2kT}{e} \mu_+ .$$

The positive ion mobility μ_+ can be evaluated only approximately, but by using the type of derivation applied to electron mobilities where $m_{ion} \ll M_{atom}$, its order of magnitude is given by:

$$\mu_+ \sim \frac{\sqrt{2}}{3} \frac{2}{\sqrt{\pi}} e \, \ell_i \sqrt{\frac{1}{MkT}} \tag{26}$$

where ℓ_i is the positive ion mean free path and M is its mass.
Then

$$D_a \sim \frac{4\sqrt{2}}{3\sqrt{\pi}} \sqrt{\frac{kT}{M}} \, \ell_i \tag{27}$$

For the experiment considered here the gas bottle is cylindrical and therefore we must solve the diffusion equation for cylindrical coordinates; r, θ, z:

$$\nabla^2 n = \frac{1}{D_a} \frac{\partial n}{\partial t} . \tag{28}$$

By separating variables we obtain the elementary solutions:

$$n = e^{-\frac{t}{\tau}} \left[A \sin\left(\frac{k\pi}{L}z\right) + B \cos\left(\frac{k\pi}{L}z\right) \right] \left[C \sin(m\theta) + D \cos(m\theta) \right]$$

$$\times \left[E \, J_m\left(\sqrt{\frac{1}{D_a \tau} - \left(\frac{k\pi}{L}\right)^2} \, r\right) + F \, N_m\left(\sqrt{\frac{1}{D_a \tau} - \left(\frac{k\pi}{L}\right)^2} \, r\right) \right] \tag{29}$$

where τ is the time constant of the diffusion process; A, B, C, D, E, F are constants; k and m are integers; and L is the length. Since the differential equation is a homogeneous and linear equation, any sum of these solutions is also a solution.

Let us assume that the electron density goes to zero at the walls, r = R, Z = 0, and Z = L. Depending on the initial distribution of electrons and positive ions, the process may be a mixture of exponentials whose time constants, τ_p, are given by the zeroes of the Bessel functions:

$$J_m\left(\sqrt{\frac{1}{D_a \tau_p} - \left(\frac{k\pi}{L}\right)^2} \, R\right) = 0 \tag{30}$$

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1. L. B. Loeb, "Fundamental Processes of Electrical Discharges in Gases", John Wiley, New York, 1939, p. 166.

Note:

N_m, the Neumann functions are eliminated because all are infinite at the origin and thus cannot be used to represent an actual electron density inside a cylindrical container.

If proper precautions are taken, a discharge can be obtained inside the cylinder whose density distribution appears to be J_0 in form radially, half-sine in form axially, and symmetrical tangentially. Referring to Eq. (29) we then have k = 1, m = 0. This yields only one time constant, that given by the first J_0 root

$$\left(\sqrt{\frac{1}{D_a \tau} - \left(\frac{\pi}{L}\right)^2} \; R \right) = 2.405 \qquad (31)$$

which makes observation of the process relatively simple.

4. Experimental Results

4.1 Helium. Most of the development of the experimental method has been done with helium as the test gas. Since electrons were expected to diffuse ambipolarly in helium (which is a relatively slow process) it offered a means of accurate study of the linearity of frequency shift and electron density predicted by Eq. (8).

The time constant of a diffusion process should increase in proportion to the gas pressure. We see from Eq. (31) that for a given container the product $D_a \tau$ is constant. From Eq. (27) D_a is proportional to the ionic mean free path or $1/p$. Experimentally this was found to be true over an investigated range of 1 to 10 mm pressure. As the gas fillings were made purer by better vacuum technique and by out-gassing the walls of the glass bottle, the diffusion process became slower and slower until a terminal value of 450 μsec/mm of gas pressure was obtained for τ/p. This pure gas case is shown in Fig. 2.

If Eq. (27) is evaluated for helium and the value of D_a obtained is substituted in Eq. (31) along with the dimensions of the glass bottle, we find that

$$\frac{\tau}{p} = 315 \text{ μsec/mm of pressure.}$$

This theoretical result is about 30 per cent less than the experimental value. Qualitatively this is explained by the fact that the true value of μ_+ is smaller than that given by Eq. (26) which is at best an approximation. Therefore the calculated value of D_a is too large, and too fast a diffusion is predicted.

By using the value of τ/p = 450 μsec/mm obtained experimentally, D_a may be evaluated by Eq. (31). The result is

$$D_a = 710 \text{ cm}^2/\text{sec at 1 mm pressure.}$$

4.2. Oxygen. On the basis of the behavior of oxygen at higher energies and the results of Margenau, McMillan, Dearnley, and Pearsall[1] for thermal energy, it was expected that oxygen would attach with a probability of the order of h = 10^{-4} attachments/collision.

In the present investigation oxygen has been studied in some detail. The data are not good enough to enable us to classify oxygen's behavior, but it is clear
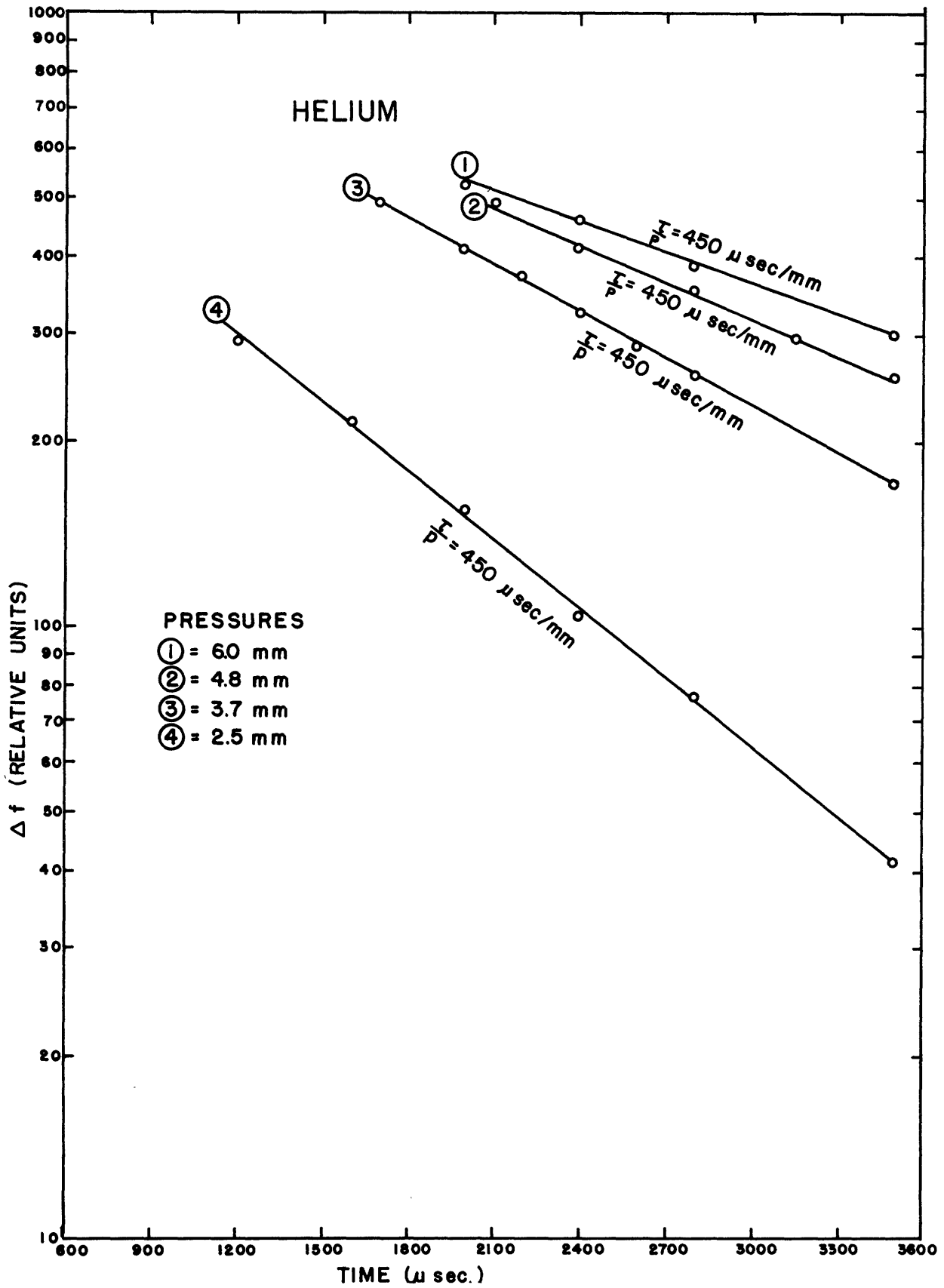
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1. Phys. Rev., 70, 349 (1946)

Figure 2. Ambipolar diffusion in helium.

that unlike previous results the cleanup of electrons in oxygen is slow at thermal energies. Whether this slow cleanup is due to a low attachment probability (10^{-6} to 10^{-7} attachments/collision), or is due to diffusion or recombination, or some combination of these processes is not at present clear. It is planned to investigate oxygen in greater detail.

5. Summary

The range of electron densities which can be observed by this method can be estimated. A simple calculation in which the effects of collisions of the electrons in the gas are neglected gives an equation for the resonant frequency shift of the cavity for a given electron density:

$$\Delta\omega = \frac{1}{2\epsilon_0} \left(\frac{e^2}{m\omega}\right) \left(\frac{V'}{V}\right) (K) \, n \qquad (32)$$

where ω is the applied radian frequency; e and m are the charge and mass of the electron, respectively; ϵ_0 is the permittivity of free space; V' is the volume of the gas-filled bottle and V the volume of the cavity; n is the electron density; K is a number accounting for the non-uniform E field within the cavity, and its value lie between 0.2 and 0.4.

The maximum detectable frequency shift at 3000 Mc is at present about 100 Mc. The minimum is about 0.1 Mc. These values correspond to initial concentrations of the order of 10^{10} electrons/cc and a minimum detectable density of about 10^7 electrons/cc. Therefore this method is supplementary to that of Margenau and his associates,[1] since it is sensitive to smaller electron densities.

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1. Phys. Rev., 70, 349 (1946).