

Physical Processes in the Recovery of TR Tubes¹

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Gas-filled switching (TR) tubes are important components of a radar duplexer. The recovery of the tube, i.e., the elimination of ions on termination of the discharge, is of great interest because it determines the quality of radar reception. In the first part of this paper, techniques of measurement of the recovery of certain types of TR tubes are described and results are reported. In the second part, the physical processes responsible for recovery are discussed in connection with simple theoretical developments concerning recombination of electrons and positive ions, diffusion of electrons, and capture of electrons by gas molecules. The last of these processes is found to be of principal importance in removing electrons and producing a short recovery time.

INTRODUCTION

GAS-FILLED switching tubes, or transmit-receive tubes (TR tubes), make it possible to use the same antenna and transmission line for pulse radar transmission and reception. This duplexing is accomplished by a circuit in either wave guide or coaxial line in which the gas discharges in one or more TR tubes act as short circuits and accomplish the switching of the antenna to the transmitter for the duration of the emitted pulses and to the receiver during the periods between the pulses. The gas discharge takes place at pressures of from 5- to 20-mm Hg and is excited by the radiofrequency power from the transmitter. A TR switch usually consists of a TR tube, containing a gap across which the discharge takes place, and a resonant cavity into which the TR tube is inserted. When the discharge is formed across the gap, the large admittance of the ionized gas detunes the resonant cavity and effectively prevents transmission through it. At the power levels used for radar transmission (10 to 1000 kw) the discharge forms within a small fraction of a microsecond. After the transmission period, the TR tube recovers as electrons are removed from the neighborhood of the gap,

and the cavity is restored to resonance. The results to be presented here arise from a study of this period of recovery.

At the frequencies encountered in the microwave region (3000 to 25,000 mc/sec.) heavy positive ions have little effect on a traveling electromagnetic wave compared with that of the electrons. Hence only the free electrons need be removed from the TR-tube gap in order for the tube to recover. The processes of diffusion and recombination take much too long a time to be satisfactory for radar purposes. Certain gases, however, are known to capture free electrons, and, if heavy negative ions can be formed fast enough, a short recovery time can be obtained. After the transmission period, the free electrons in the gap lose energy rapidly by virtue of elastic collisions with the gas molecules and to a large extent the capture takes place at thermal energies.

The transmission through a TR switch during the recovery period is directly related to the density of free electrons present, and the rate of change of transmission is proportional to the electron-capture cross section. The cross section may thus be determined experimentally. It should be pointed out that the measurement of capture cross sections by this method is, in a sense, only a by-product of the effort in the development of many types of TR switches and duplexers. The results are, therefore, neither as complete nor as accurate as might be desired.

EXPERIMENTAL TECHNIQUES

The transmission through the TR tube as a function of time was measured by applying an

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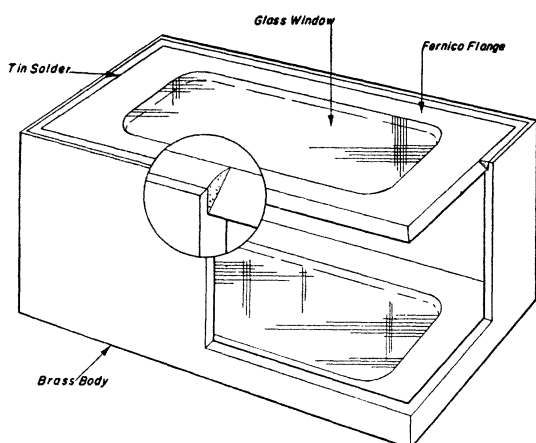


FIG. 1. Schematic diagram of A 1B38 pre-TR tube.

artificial signal, usually one microsecond long, to the switch. The strength of the signal could be altered by means of a calibrated attenuator, and the time of occurrence of the signal after the cessation of the high power pulse could be varied. A standard radar receiver was used to detect the signal. The data were presented on a cathode-ray tube so that the signal intensity was proportional to the spot deflection in one direction and time of occurrence proportional to the deflection in the perpendicular direction. The signal levels used were small, only a few decibels above the receiver noise after transmission through the TR switch.

The high power radiofrequency (r-f) source was a magnetron capable of delivering peak powers of about a megawatt at a wave-length of 10.7 cm. The magnetron was driven by a modulator capable of delivering microsecond pulses of 28,000 volts peak at a rate of 500 per sec. The peak r-f power used throughout this work was 700 kw unless it is specifically stated otherwise.

The tubes used were experimental models of the type 1B38 pre-TR tube. They consist of sections of wave guide of outside dimensions 1 in. by 3 in., one-quarter of a wave-length long, closed off by low- Q resonant glass windows sealed to Ferrico flanges. Figure 1 shows a schematic diagram of a tube. The tubes were attached to the wave guide so that one window of the tube formed a portion of the top surface of the wave guide. At high power, a discharge is formed

across the window and the wave guide acts as though the tube were not present and the top surface continuous. To protect the receiver from the power leaking through the pre-TR tube, a second TR tube, type 1B27, mounted in a cavity was used. The arrangement is shown in Fig. 2. To cause the low level signal to travel around the corner without excessive reflection, an ATR tube was placed at the correct distance from the T-junction. A block diagram of the whole apparatus is shown in Fig. 3.

It should be pointed out that the measured recovery times actually refer to the integrated effect of all three TR tubes in the duplexer. The TR tube between the pre-TR tube and the mixer contributes little since it is excited by only the relatively small leakage power from the pre-TR tube. Separate tests indicated that the ATR tube also had little influence. In any event, since the TR and the ATR tubes have a short time of recovery compared with the pre-TR tube, the presence of the other tubes may be neglected after a suitable interval. The estimates of electron-capture cross section which are made below are based only on the recovery rate after this suitable interval.

The results of numerous tests indicate that proper baking of the tubes before filling is highly important. Metal tubes that have not been

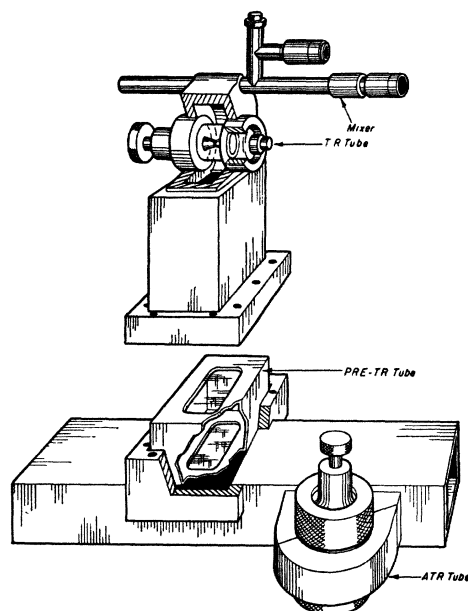


FIG. 2. Duplexer used for observations.

baked, but pumped to 10^{-6} mm or better, will yield large amounts of adsorbed gases under the conditions of the r-f discharge. One typical unbaked tube showed an increase of 15 percent in pressure during one hour of operation, another showed a pressure increase of over 38 percent in approximately 1000 hours of operation. A few pre-TR tubes were specially constructed from oxygen-free high conductivity copper with the windows attached with hard solder so that the tubes could be baked at 500°C while evacuated. These tubes were very fragile and their extensive use was not practical. Soft-soldered brass tubes could be baked at 150°C with little breakage and a series of tests on baking seemed to indicate that little was to be gained by baking at a higher temperature.

Some spectrographic analyses were made of several tubes filled with pure argon. Typical results are shown in Table I. The long time of recovery of the baked tubes should be taken as evidence of high purity of the gas filling.

RESULTS

Some of the experimental results will now be presented and the special significance of the data interpreted in a succeeding section. Figure 4 shows the effect of power level during the discharge on the recovery of the 1B27 TR tube which followed the pre-TR tube in the duplexer. The actual power level during the experiments was of the order of one kilowatt. The recovery time under this condition is evidently very short.

TABLE I. Spectrographic analysis of gas-filling of 1B38 tubes. *M*=major component; *m*=minor component; *tr*=trace.

| Components | Hard-soldered tube baked at 500°C | Soft-soldered tube baked at 150°C | Unbaked soft-soldered tube |
|---------------------------|---|---|----------------------------|
| A | <i>M</i> | <i>M</i> | <i>M</i> |
| CO | — | — | <i>M</i> |
| CH | — | <i>m</i> — | <i>M</i> |
| OH | — | — | <i>M</i> |
| N ₂ | — | — | <i>m</i> |
| C ₂ | — | — | <i>tr</i> |
| H | — | — | <i>m</i> |
| Sn | — | — | <i>tr</i> |
| O | — | — | — |
| Hg | <i>tr</i> | <i>tr</i> | — |
| CN | — | — | — |
| N | — | — | — |
| H ₂ | — | — | <i>m</i> + |
| Transmission 6 db down at | 710 $\mu\text{sec.}$ | 875 $\mu\text{sec.}$ | 13 $\mu\text{sec.}$ |

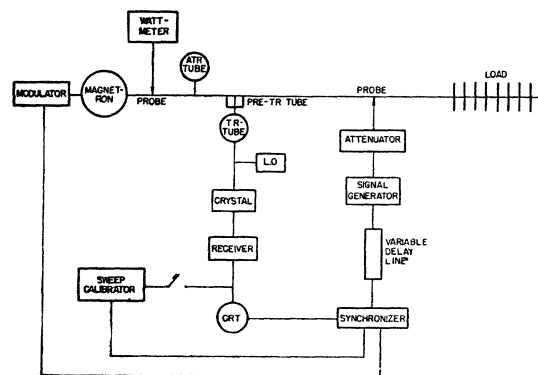


FIG. 3. Block diagram of experimental equipment.

Figure 5 shows the data taken with a hard-soldered tube, baked and filled with 5 mm of argon under the best conditions to maintain high purity of the gas. These data represent the slowest recovery that was possible to attain with the techniques available. Figures 6–8 show the effects of mixtures of argon and various captor gases, water vapor, pentene, and hydrogen sulfide, respectively. Figure 9 shows the recovery data for pure oxygen. The anomalous variation with pressure is to be noted.

THEORETICAL CONSIDERATIONS

Three physical mechanisms present themselves for consideration when an explanation of the recovery of a TR switch is sought: electrons can be removed by recombination with positive ions, by diffusion to the walls of the box, and by capture in the presence of captor molecules. Experimental evidence suggests that the last of these processes is the most important of the three. This is indeed borne out by numerical computation.

We first consider recombination. If the number of electrons per cc is *n*, their (mean) speed *v*, and the cross section for recombination *Q_r*, the rate of removal of electrons by recombination is governed by the equation

$$dn/dt = -vQ_r n^2, \tag{1}$$

which has the solution

$$n = n_0 / (1 + vQ_r n_0 t), \tag{2}$$

*n*₀ being the initial concentration of electrons. The half-value period of the process is

$$t_{1/2} = (vQ_r n_0)^{-1}. \tag{3}$$

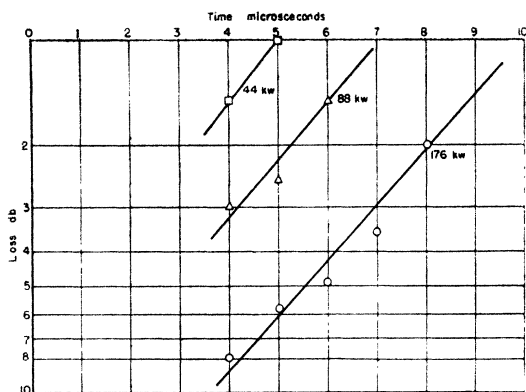


FIG. 4. Recovery of 1B27 TR tube as a function of line power.

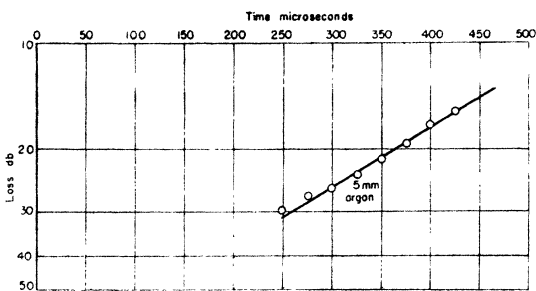


FIG. 5. Recovery of a hard-soldered tube filled with pure argon.

Now the speed of the electrons is approximately thermal, hence $v \approx 10^7$ cm. Recombination cross sections are not accurately known, but a typical value has been computed⁶ for H^+ ; it is 2×10^{-21} cm². As will be shown later in this report, n_0 is of the order 10^{14} cm⁻³. Hence, according to (3), t_1 is of the order of a second. Since recovery times are measured in microseconds, recombination may be ignored.

Diffusion and capture require more careful study. Both vary strongly with electron speed, and this circumstance makes an examination of the value of v and of the change in v during recovery time desirable. For clearly, while the discharge passes, v is great and diffusion proceeds rapidly. With the sudden stoppage of transmission the electrons will relax to smaller speeds until they have reached thermal velocities, which they then maintain even under the weak agitation of the reflected pulse.

The approach to thermal velocities takes place by the agency of electron collisions with gas

⁶ Cf. H. Bethe, *Handbuch der Physik*, Vol. XXV, 1.

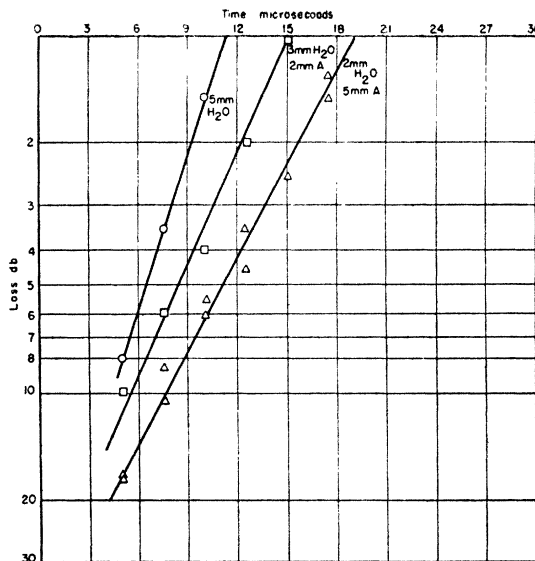


FIG. 6. Recovery of mixtures of argon and water vapor.

molecules which occur at the rate of v/λ per second. (λ =mean free path.) According to Cravath⁷ the mean energy loss of an electron at (equivalent) temperature T against atoms at temperature T_0 is

$$\Delta\epsilon = \frac{4m}{M}k(T - T_0).$$

The rate of loss of mean energy $3kT/2$ is therefore $\Delta\epsilon(v/\lambda)$, or

$$-\frac{d}{dt}\left(\frac{3}{2}kT\right) = \frac{4m}{M\lambda}k(T - T_0)\left(\frac{3kT}{m}\right)^{\frac{1}{2}}. \quad (4)$$

The solution of this equation is

$$\frac{S - S_0}{S + S_0} = \frac{S_1 - S_0}{S_1 + S_0} \exp(-gS_0t), \quad (5)$$

where $S = \sqrt{T}$, the indices 1 and 0 refer to initial and final values, and $g = (8/M\lambda)(km/3)^{\frac{1}{2}}$. From (5) it is seen that the time in which the speed will drop from its original value to α times its final value is

$$t_\alpha = \frac{1}{gS_0} \ln \frac{\alpha + 1}{\alpha - 1}$$

provided that $S_1 \gg S_0$, a condition satisfied in our applications. For $\alpha = 2$, this gives a relaxation

⁷ A. M. Cravath, *Phys. Rev.* 36, 248 (1930).

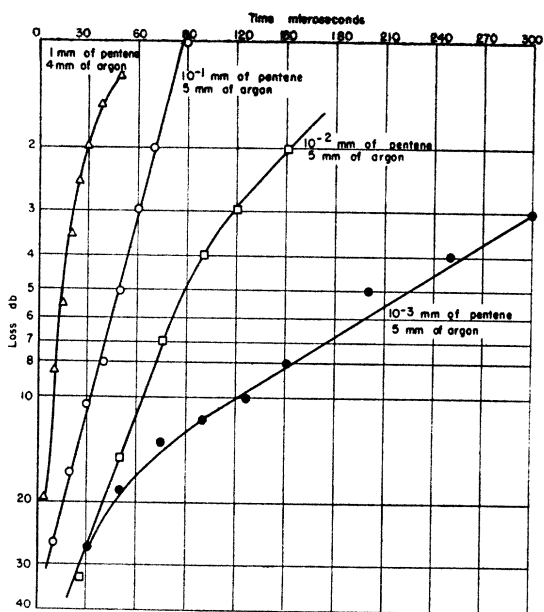


FIG. 7. Recovery of argon-pentene mixtures.

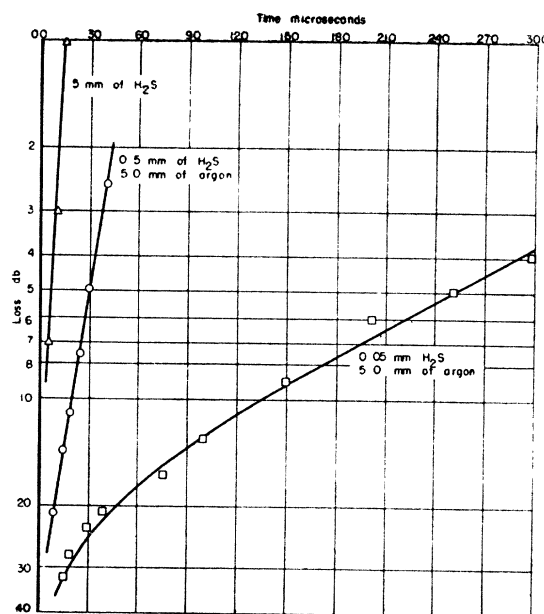


FIG. 8. Recovery of argon-H₂S mixtures.

period of a few microseconds for electrons in argon at 10-mm Hg pressure. Beyond that time, the approach to thermal speed is slow.

A similar result could have been obtained by a very simple argument. Since in one encounter an electron loses on an average the fraction $2m/M$ of its energy, it must make $M/2m$ impacts to lose a sizable part of its energy. The time between impacts is $\lambda/v \approx 10^{-10}$ sec. Hence the time in question is

$$\frac{M \lambda}{2m v} \approx 4 \times 10^{-6} \text{ sec.}$$

In our analysis we may assume, therefore, with reasonable safety that after about 10 μ sec. electron speeds are approximately thermal. The experimental data contain evidence of the relaxation phenomenon here described.

The theory of diffusion is well known. To solve the diffusion equation

$$\nabla^2 n - \frac{1}{D} \frac{\partial n}{\partial t} = 0, \quad (6)$$

for the geometrical condition of the pre-TR tube is a simple boundary-value problem. If we assume the discharge to take place in a thin plane sheet of thickness d adjacent to the window, so that at the beginning of recovery

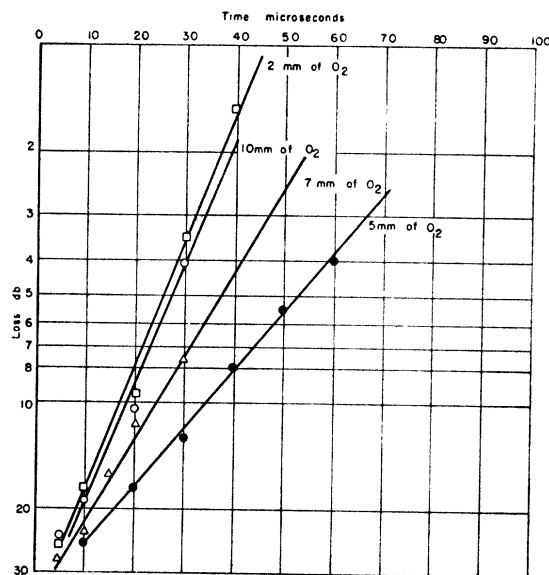


FIG. 9. Recovery of oxygen.

($t=0$) this region of space is uniformly filled with electrons of density n_0 , the solution of (6) may be shown to be

$$n = n_0 \left\{ \phi \left(\frac{x}{2(Dt)^{1/2}} \right) - \frac{1}{2} \left[\phi \left(\frac{d+x}{2(Dt)^{1/2}} \right) - \phi \left(\frac{d-x}{2(Dt)^{1/2}} \right) \right] \right\}, \quad (7)$$

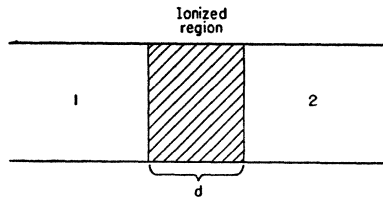


FIG. 10. Diagram for calculation of transmission.

where

$$\phi(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp(-x^2) dx.$$

We have here assumed that an electron hitting the glass window is absorbed, but have neglected absorption by the metal enclosure. More complicated geometrical conditions have also been treated, but the results do not modify the conclusions reached with this simpler picture and will not be included in this report. The coefficient of diffusion D requires comment. It is *not* the quantity $\frac{1}{3}v\lambda$ familiar from kinetic theory, for diffusion takes place in a manner sometimes called *ambipolar*. That is, the electrons do not diffuse outward like a free swarm of particles of velocity v ; they are held back by the positive ions because of the strong electric field called into action by incipient separation of the charges. Both types of ions diffuse simultaneously at a rate corresponding to the coefficient

$$D(\text{electrons}) = 2D(\text{ions}).$$

Under the conditions of the experiments, D has a value around $5 \text{ cm}^2 \text{ sec.}^{-1}$. From this a rough estimate of the times involved in diffusion can be made. The functions in (7) change appreciably when their arguments undergo changes of order 1. This occurs in times of order d^2/D . If $d \approx 1 \text{ mm}$ and $D \approx 5 \text{ cm}^2 \text{ sec.}^{-1}$, the time is several thousand $\mu\text{seconds}$. Few curves among those obtained involve times of that length. We conclude, therefore, that capture is mainly responsible for recovery. There is one case in which a gas of very great purity was employed (Fig. 5) and where the question as to the role of diffusion arises significantly. We return to it for special consideration when more fundamental things have been discussed.

First let us give an analysis of the capture process. As to symbols, we define:

n = concentration of electrons (number per cc),
 Y = concentration of neutral captor molecules,
 Y^- = concentration of negative molecular ions,
 M = concentration of total number of captor molecules, neutral, and negative,
 N = concentration of total number of negative charges,
 Q = gas-kinetic collision cross section for electrons (collisions between electrons will be neglected),
 h_{cap} = probability of capture per collision,
 h_{rel} = probability of release of electron on encounter with an electron with a negative ion, and
 v = electron velocity.

The subscript 0 indicates the values of quantities at $t=0$.

The equation for the rate of increase of negative ions is

$$dY^-/dt = vQn(h_{\text{cap}}Y - h_{\text{rel}}Y^-). \quad (8)$$

During the *discharge* the conditions to be imposed on (8) are

$$\begin{aligned} n &= \text{constant}, \\ Y + Y^- &= M = \text{constant}. \end{aligned}$$

The solution of Eq. (8) is then

$$Y^- = \frac{h_{\text{cap}}}{h_{\text{cap}} + h_{\text{rel}}} M \{1 - \exp[-vQn(h_{\text{cap}} + h_{\text{rel}})t]\}.$$

In general, h_{cap} and h_{rel} are functions of electron velocities. During the discharge v is great, corresponding to about 10 electron volts. In that case $h_{\text{rel}} \gg h_{\text{cap}}$,⁸ and the last equation may be simplified. The equilibrium value of Y^- , which results when $t \rightarrow \infty$, is given by

$$Y_{\infty}^- = h_{\text{cap}}M/h_{\text{rel}}. \quad (9)$$

For water⁸ as captor molecule, $h_{\text{cap}}/h_{\text{rel}} \approx 0.01$; this means that at the beginning of the recovery period about 1 percent of the water molecules are ionized. It is also possible to estimate the time of production of these negative ions during discharge: The exponential term in Y^- is reduced to e^{-1} in $(vQnh_{\text{rel}})^{-1}$ second.

For the *recovery* process the conditions to be imposed on Eq. (8) are different. Here n is no longer constant, but

$$n + Y^- = N = \text{constant},$$

and

$$Y + Y^- = M = \text{constant}.$$

⁸ See, for example, the values given by H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1938), for H_2O .

Hence Eq. (8) becomes

$$-dn/dt = vQ\{(h_{cap} + h_{rel})n^2 + [Mh_{cap} - N(h_{cap} + h_{rel})]n\}. \quad (10)$$

For the low electron velocities prevailing during recovery we may put $h_{rel} = 0$. The term proportional to n^2 on the right of (10) is interesting only in the initial stages of the process, during the first few microseconds, where it adds to the confusion arising from the relaxation of electron energies. Since our attention will be confined primarily to the terminal features of the experimental curves its neglect here is permissible.

Equation (10) may then be written in the form

$$dn/dt = -vQh_{cap}(Y_0 - n_0)n.$$

Capture will take place only when $Y_0 > n_0$. In those instances from which numerical conclusions can be drawn, $Y_0 \gg n_0$ as will be seen, and since only a small fraction of captor molecules is ionized, $Y_0 \approx M$. For many purposes the equation regulating capture may, therefore, be cast in the intuitively obvious form

$$dn/dt = -vQh_{cap}Mn. \quad (11)$$

When accurate data on recovery at small times are available, Eq. (10) should be used in their reduction. One effect which will be of concern to us is that according to Eq. (10) n goes down to $N - M$, not to zero as Eq. (11) predicts. This will be observed in some of the curves.

Figures 4 to 9 present graphs of "loss in decibels" vs. time. For the purpose of interpretation these must first be translated into graphs of n vs. t . To do this it is necessary to know the attenuation of microwaves caused by a region containing n electrons per cc. In a previous paper⁹ the complex conductivity $\sigma = \sigma_r - i\sigma_i$ has been derived as a function of frequency, gas pressure, and electron concentration. The results will here be applied. We first investigate, however, how the attenuation depends on σ .

Perhaps the simplest way of calculating the power loss of a signal passing through the TR tube in the present experimental arrangement is to regard the ionized sheet as being placed across a wave guide, after the manner of Fig. 10. One may then show that the amplitude attenuation

for waves going from region 1 to region 2 is

$$T = \left[\cos k'd - \frac{i}{2} \left(\frac{k'}{k} + \frac{k}{k'} \right) \sin k'd \right]^{-1}, \quad (12)$$

where

$$(k')^2 = \frac{\omega^2}{c^2} \left(\epsilon_0 + i \frac{4\pi}{\omega} \sigma \right) - \frac{\pi^2}{a^2}, \quad k^2 = \frac{\omega^2}{c^2} \epsilon_0 - \frac{\pi^2}{a^2},$$

ϵ_0 being the ordinary dielectric constant of the medium (here 1) and a the larger cross-sectional dimension of the wave guide. For σ the foregoing expression must be introduced. As an example we give the numerical data for some of the experiments (wave-length 10.7 cm, pressure of gas ≈ 5 mm Hg)

$$\begin{aligned} \sigma_r &= 1.68 \times 10^{-3}n, & \sigma_i &= 1.45 \times 10^{-2}n, \\ \omega &= 1.75 \times 10^{10}, & a &= 7.3 \text{ cm.} \end{aligned}$$

Very little is known about the magnitude of d , nor is it certain that this quantity is constant over the entire window. Under these circumstances it seems wise—and saves labor—to assume d to be very small compared to a wavelength and to evaluate (12) under this simplifying condition. More specifically, we let $d \rightarrow 0$ while σd and hence nd remain finite. We then obtain

$$T = \left[1 + \frac{2\pi\omega}{c^2 k} (\sigma_r + i\sigma_i)d \right]^{-1}.$$

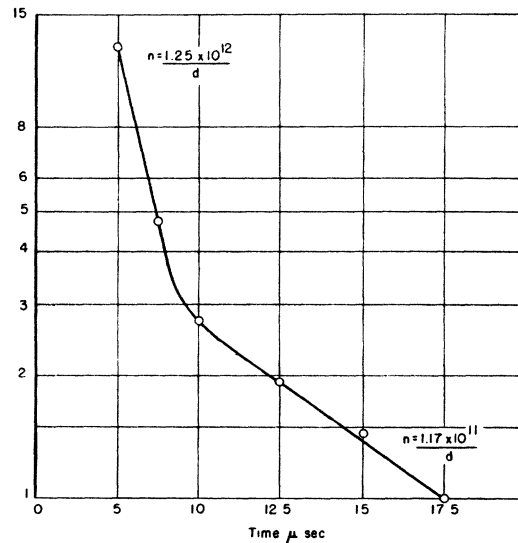


FIG. 11. Conversion of observed loss to electron density; $u = nd \times 10^{11}$.

⁹ H. Margenau, Phys. Rev. 69, 508 (1946).

The reduction in power is $|T|^2$. This provides a formula for the desired conversion:

$$\text{"loss in } db\text{"} = 10 \log_{10} |T|^2.$$

As an illustration of this procedure we show in Fig. 11 the result of translating¹⁰ Fig. 6 (2 mm H₂O) into a graph of n vs. t . The quantity u plotted there as ordinate is $10^{-11}nd$. If extrapolation to $t=0$ were permitted, n_0 would be 10^{14} to 10^{15} cm⁻³; this estimate is not likely to be far wrong. It is also interesting to note that the curve has a fairly constant terminal slope on a log u scale, which means that it satisfies Eq. (11) beyond 10 μ sec. The larger early slope is in qualitative agreement with the preceding conclusions. These features are rather typical of most "translated" graphs.

We shall not burden this report with a reproduction of all n vs. t -curves which were analyzed. To guide the reader we merely state that, while the n -curves have a greater initial slope, their terminal logarithmic slopes are on the whole equal to the logarithmic slopes of the db -curves. In particular, the n -curves also simulate and often exaggerate the curvature of the db -curves when curvature is present.

INTERPRETATION OF SPECIFIC RESULTS

It might seem that Fig. 5, obtained with very pure argon and showing unusually long recovery time, represents evidence for diffusion. To test this, Eq. (7) may be used. To be sure, the quantity of importance in this connection is not n but $(nd)_m$, the number of electrons at any time within a prism of 1 cm² base across the entire sheet of ions. This quantity is found by integration of (7) from $x=0$ to $x=\infty$; it is

$$N = N_0 \left\{ \phi \left(\frac{d}{2(Dt)^{\frac{1}{2}}} \right) - \frac{1}{\sqrt{\pi}} \frac{2(Dt)^{\frac{1}{2}}}{d} \times (1 - \exp[-d^2/4Dt]) \right\}.$$

If we put

$$\zeta = d/2(Dt)^{\frac{1}{2}},$$

it is easily seen that

$$-\frac{td \ln N}{dt} = \frac{1}{2\zeta\sqrt{\pi}} \frac{1 - \exp(-\zeta^2)}{\phi(\zeta) - \frac{1}{\sqrt{\pi}} \zeta^{-1}(1 - \exp(-\zeta^2))}.$$

¹⁰ The experimental points for the same t have been averaged.

Regardless of the value of ζ , the right-hand side can never be greater than $\frac{1}{2}$. But in the experimental curve, $-td \ln N/dt$ is about 3. Clearly, then, even in the purest filling of argon used here, diffusion is not the primary cause of electron disposal. Whether a very efficient captor substance is present in small quantities, or whether formation of unknown ions such as A_2^- (perhaps one A atom being excited) occurs, is difficult to say on the basis of the data. If the recovery in this case were caused by a substance as effective in capturing as H₂O, it would have to be present at a pressure of 0.18 mm Hg, which is, of course, out of question.

In all other curves selected for consideration here, capture of electrons by molecules is the process responsible for recovery. The capture probability can be computed from (11), which for that purpose may be written

$$h_{\text{cap}} = -vQMd/dt(\ln n). \quad (14)$$

Figure 4 shows three lines of nearly equal $d/dt(\ln n)$, indicating a unique capture probability for the gas (of uncertain composition) causing capture. The *displacement* of the lines relative to one another shows that n_0 has different values for different line powers, being larger for the greater power. This is quite in accord with expectation. If extrapolation is permitted, n_0 is found to be nearly proportional to line power.

Equation (14) further shows that, for a given captor gas, the logarithmic slopes should vary with M , hence with the pressure of the captor gas. This is illustrated in Fig. 6, showing the performance of water at 3 different pressures. In evaluating these we have taken Q to be 15×10^{-16} cm², and v corresponding to 300°K as $(3kt/m)^{\frac{1}{2}} = 1.2 \times 10^7$ cm/sec. One thus obtains for h_{cap}

$$\begin{aligned} &1.0 \times 10^{-4} \text{ from the 2 mm curve,} \\ &0.93 \times 10^{-4} \text{ from the 3 mm curve,} \\ &0.94 \times 10^{-4} \text{ from the 5 mm curve.} \end{aligned}$$

It should be remembered that these are capture probabilities for electrons at thermal velocities, which have not been obtained by any other means. They agree in order of magnitude with the measurements of Bradbury and Tatel,¹¹ who

¹¹ N. E. Bradbury and H. Tatel, J. Chem. Phys. 2, 835 (1934). See also Massey, reference 4.

list values running as high as 4×10^{-4} at somewhat greater energies. They, as well as Massey, believe capture at low energies to be an effect of molecular association. The constancy of h here found for different pressures seems rather to indicate the action of single molecules, though *why* an H_2O -molecule should capture slow electrons requires further elucidation.

Figure 7 is interesting because it shows the passage from conditions in which there are enough captors to eliminate all initial electrons to conditions where the number of captors is insufficient to effect complete removal. The curves corresponding to 1 mm and 0.1 mm pressure have straight terminal slopes, those for 0.01 and 0.001 mm show definite curvature, more marked on the n than on the db-graphs. Evidently, the last named curves are beginning to swing over into nearly horizontal slopes characteristic of diffusion.

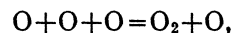
The transition from sufficiency to insufficiency of captors seems to occur between the pressures of 0.1 mm and 0.01 mm. This means that the initial concentration of electrons lies between $3.5 \times 10^{15} \text{ cm}^{-3}$ and $3.5 \times 10^{14} \text{ cm}^{-3}$, and this entirely confirms the estimate derived from extrapolation of logarithmic slopes.

If the capture possibility is computed by means of (14) from the 1-mm curve, it comes out to be $h_{\text{cap}} = 1.4 \times 10^{-4}$. But it is doubtful whether this value is to be ascribed to pentene; for this substance may dissociate during the discharge and its fragments may be the captors.

The transition just mentioned occurs again in Fig. 8 for H_2S . The data lead to the same estimate of n_0 . From the 5-mm curve one computes $h_{\text{cap}} = 5 \times 10^{-5}$. Again it is uncertain whether this value refers to hydrogen sulfide.

The data on oxygen (Fig. 9) are anomalous inasmuch as the slopes are not proportional to

the pressures. But with respect to oxygen we know that (1) the discharge causes the molecule to dissociate into atoms and (2) both atoms and molecules have electron affinities. Which has the larger capture cross section for thermal-energy electrons is not known. From the present data we suggest that it is the atom. For let us suppose that at the end of the discharge most of the gas is in atomic form. The atom can recombine into O_2 only by a three-particle mechanism such as



which leads to a recombination rate proportional to the *square* of the pressure.¹² Hence, O lasts longer at low pressures. At pressures above 5 mm, O_2 is the more active capturing agent, below it, presumably O. The several slopes with pressure at about 5 mm marks the condition in which atoms compete with molecules in capturing electrons. The 2-mm curve, on this interpretation, represents capture by 4 mm of atomic oxygen; it is about as effective as 10 mm of molecular oxygen. Numerically, we conclude that for O, $h_{\text{cap}} \approx 3.2 \times 10^{-4}$, for O_2 $h_{\text{cap}} \approx 1.5 \times 10^{-4}$ if the present interpretation holds. We are not prepared to suggest by what physical mechanism the attachment of electrons to O may occur.

In conclusion, one may be permitted to express the hope that methods for measuring attenuation of microwaves in gases will prove a useful tool in the study of molecular processes. Of this usefulness the present imperfect account gives only a meager indication.

We wish to express our gratitude to Mr. L. D. Smullin for his stimulating interest in these problems and to Dr. J. F. Carlson for specific help.

¹² Very little is known about the rate constant k_3 for this reaction. Calculation shows that if it is about $10^{19} (\text{cc}/\text{mole})^2/\text{sec.}$, the recombination times at pressures of millimeters is of the order of microseconds.