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TITLE

STUDY OF MICROWAVE GAS DISCHARGE - PHASE II*
Final Report

ABSTRACT

The material contained in this report supplements the results presented in an earlier report; TIS R58ELM 115. The principal topics considered are 1) the use of electron paramagnetic resonance (EPR) techniques for the quantitative measurement of the amount of atomic hydrogen produced in a microwave discharge in hydrogen, 2) the influence of water vapor on the production of atomic hydrogen, and 3) the measurement of electron density and collision frequency and the correlation of these factors with the production of atomic hydrogen.

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CONCLUSIONS

A satisfactory correlation was obtained between measurements of the concentration of atomic hydrogen in partially dissociated hydrogen by electron paramagnetic resonance (EPR) and recombination calorimetric methods.

Experimental evidence shows that electrons and excited atoms or molecules with a life time of 10^{-2} sec or more may be readily pumped from a hydrogen discharge containing water vapor.

Further work will be required to obtain accurate quantitative values of the electron density and collision frequency for a microwave discharge in hydrogen in the power and pressure ranges of interest for atomic hydrogen production.

By cutting out this rectangle and folding on the center line, the above information can be fitted into a standard card file. For list of contents—drawings, photos, etc. and for distribution see next page.

*Phase I of this work was reported in GEML TIS R58ELM 115

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TIS R60ELM 178

STUDIES OF MICROWAVE GAS DISCHARGE - PHASE II

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Contract DA 04-200-ORD-856

GEML Project 254-0401-2203

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MICROWAVE LABORATORY AT STANFORD

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GEML Project 264-0401-2203
GE TIS R60ELM 178

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Enclosed herewith are twenty-five (25) copies of the Final Report on Contract DA 04-200-ORD-856 on "Studies of Microwave Gas Discharge."

Our understanding of your policy for distribution (as stated by the letter from George B. Cox of OOR to Warren W. Chan of this laboratory, dated 3 October 1958) is that we can make distribution within the U.S.A. at our expense, and any foreign distribution at our expense, contingent upon OOR approval.

We have mailed the Phase I final report on this project (TIS R58ELM 115) to the following people outside of the U.S.A., with OOR permission.

Prof. J.C. Polanyi, University of Toronto, Canada
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We will look forward to hearing from you in regard to these questions.

Yours very truly,

C.G. Lob
Subsection Manager
Low Power TWT Subsection

CGL:eh
Enclosures

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STUDIES OF MICROWAVE GAS DISCHARGES - II

T. M. Shaw

I. INTRODUCTION

This report contains further results of a study of some of the factors that influence the production of atoms from simple diatomic gases in a gas discharge maintained with microwave power. The report also presents information concerning the measurement of atom concentrations by the application of electron paramagnetic resonance (EPR) techniques. Most of the material presented supplements the results contained in an earlier report (TIS R58ELM 115)[1] hereinafter referred to as I, which should be consulted for details of the earlier work.

The major topics considered in the present report are the following:

1) the use of electron paramagnetic resonance (EPR) techniques for the quantitative measurement of the number of atoms produced in a hydrogen discharge,

2) the influence of water vapor on the production of atoms in a microwave discharge in hydrogen,

3) the measurement of the density of electrons and the collision frequency of electrons in a hydrogen discharge, and the correlation of these factors with the production of hydrogen atoms.

II. THE APPLICATION OF ELECTRON PARAMAGNETIC RESONANCE (EPR) TO THE STUDY OF ATOM PRODUCTION IN A GAS DISCHARGE

In the previous work, I, EPR spectroscopy was used primarily as a means of establishing the absolute rate of production of hydrogen atoms in a microwave gas discharge. EPR and calorimetric measurements were performed simultaneously to make a direct comparison of atom density and thus to establish a calibration of the calorimeter which was used for the routine measurement of atom production.

As a result of the experience gained with the EPR method in I, the present program was directed toward three areas. 1) Improvement of accuracy was sought in the quantitative measurement of atom concentration based on the intensity of EPR signals. 2) A high frequency modulation spectrometer was applied to the problem of reducing the time required to achieve a satisfactory EPR signal. Such an improvement would permit the use of EPR techniques for the measurement of atom concentrations in situations where the atom concentration is changing rapidly. 3) EPR techniques were applied to the study of atom diffusion.

A. Quantitative Measurement of Atom Concentration

On the basis of the direct comparison between EPR measurements and calorimeter measurements discussed in I, it was concluded that the accuracy of the EPR measurements was poor because of some anomaly associated with the use of solid diphenyl picryl hydrazyl (DPH) as a reference standard of EPR intensity. It appeared that the number of unpaired electrons in the standard was approximately one-half of the expected amount. As a result, the atom concentration obtained from the EPR measurements was consistently about twice as large as the calorimetric result.

Although in principle it is not necessary to use a reference substance to make EPR intensity measurements, a reference material is usually employed because of the difficulty of making measurements of the microwave and related electrical parameters required for an independent determination of intensity.[2]

A survey of readily available solids which have properties such as an appropriate EPR line width and spin concentration which make them suitable for a permanent reference standard showed that none were well suited. Further consideration of the problem showed that standardization might be accomplished more readily by a calibrator similar to the Watkins-Pound calibrator[3] used at r-f frequencies for nuclear magnetic resonance measurements. Such a device would serve as a secondary intensity standard and, for narrow EPR lines at least, would allow intensity measurements to be made solely in terms of the pertinent microwave electrical parameters.

In a conventional microwave spectrometer of the type used in EPR spectroscopy, the signal observed arises from a change in the Q of a resonant cavity which, in turn, results from a change in χ'', the imaginary part of the complex magnetic susceptibility of the paramagnetic material.[2] In a spectrometer employing reflection type cavity, the change in Q is manifest by a change in the voltage reflected from the cavity.[4]

It was found that the EPR signal can be simulated in a number of ways. The scheme finally adopted utilizes a small rotating metal dipole to produce a reflected voltage in the spectrometer circuits synchronous with the voltage reflected from the EPR sample cavity. The dipole is rotated by a 1500 rpm motor driven by the 50 cps spectrometer modulator. The frequency of the reflected voltage corresponds to twice the frequency of rotation. The dipole signal is coupled into the

spectrometer microwave circuits by means of a calibrated directional coupler and may be used to place a calibration marker on the recorder chart at any time. This calibration marker is obtained under identical conditions of spectrometer operation as used in recording the unknown EPR signal. A detailed description of the calibration procedure is given in the appendix. As shown there, by means of a single graphical integration of the recorded derivative of the EPR absorption in conjunction with the calibration data from the calibrator, one obtains $\chi'' = \chi''(H)$, the imaginary part of the paramagnetic susceptibility as a function of the static magnetic field strength, H.

The number of paramagnetic molecules per unit volume in the sample, N_0, is obtained from χ'' by means of the relations,[2]

$$N_0 = 3kT\chi_0 / \gamma^2 \hbar^2 S(S+1) \qquad (1)$$

and

$$\chi_0 = (2\gamma/\pi\omega)\int_0^\infty \chi'' dH, \qquad (2)$$

where

χ_0 is the static susceptibility,
γ is the electron gyromagnetic ratio equal to $g\beta/\hbar$,
ω is the angular frequency of the linearly polarized microwave magnetic field,
$\hbar$ is Planck's constant divided by 2π,
k is Boltzmann constant,
S is spin quantum number,
T is absolute temperature.

Equation (2) which relates χ_o and χ'' can be derived from the Kramers-Kronig relation

$$\chi_o = \frac{2}{\pi}\int_0^\infty \frac{\chi''}{\omega}\, d\omega, \qquad (3)$$

subject to the restriction that the resonance is sufficiently narrow with respect to frequency that $(1/\omega)$ may be taken outside the integral.[5,6] Then, making use of the resonance relation $\omega = \gamma H$, equation (2) follows.

The use of equation (2) is also justifiable for magnetic resonances satisfying the Bloch equations.[6]

Application of equations (1) and (2) and the calibration procedure described in the appendix were made to obtain the density of hydrogen atoms in the gas stream flowing from a microwave discharge in hydrogen. The experimental arrangement used is shown schematically in Figure 1. This is basically the same arrangement used in I and provides for simultaneous determination of the rate of production of hydrogen atoms in the discharge from the hydrogen EPR resonance and by a calorimetric determination from the energy of recombination. Figure 2 shows a photograph of the spectrometer and calorimeter. Figure 3 is a closeup of the spectrometer showing the microwave components which make up the calibrator.

The calibration procedure used in making a determination of the density of hydrogen atoms by means of the EPR resonance is similar to that described in the appendix for the tests with manganous sulphate. After the discharge has reached steady running conditions, the curve representing the derivative of the EPR absorption is recorded on the chart recorder. A record is made of the spectrometer operating conditions, in particular ΔH_m, the modulation amplitude, and the rate of change of the magnetic sweep field. Immediately after recording the resonance, the motor-driven dipole is started and the attenuator ahead of the dipole is adjusted

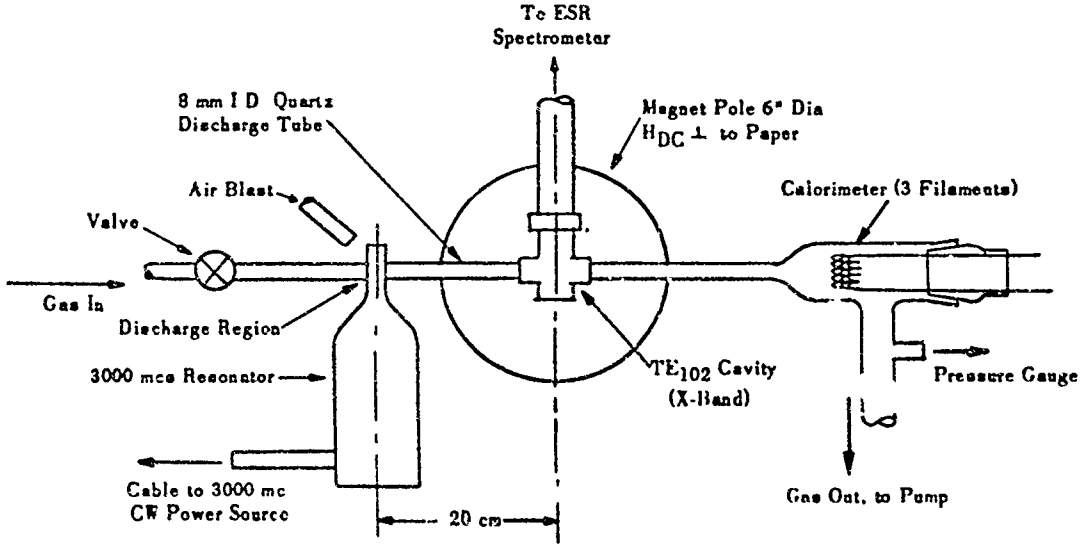


FIGURE 1. EXPERIMENTAL ARRANGEMENT USED TO STUDY CONCENTRATION OF ATOMIC HYDROGEN IN STREAM FLOWING FROM DISCHARGE TUBE.

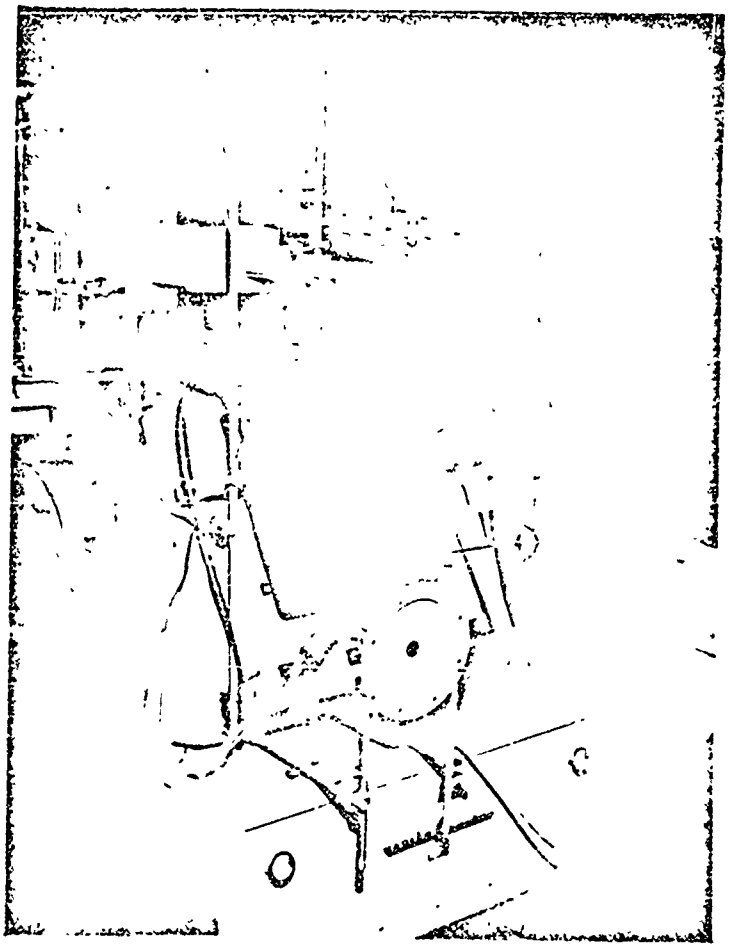


FIGURE 2. PHOTOGRAPH OF EPR SPECTROMETER AND RECOMBINATION CALORIMETER ARRANGEMENT

1. Microwave Bridge and Calibration Equipment
2. Gas Handling Equipment
3. Spectrometer Magnet
4. Calorimeter

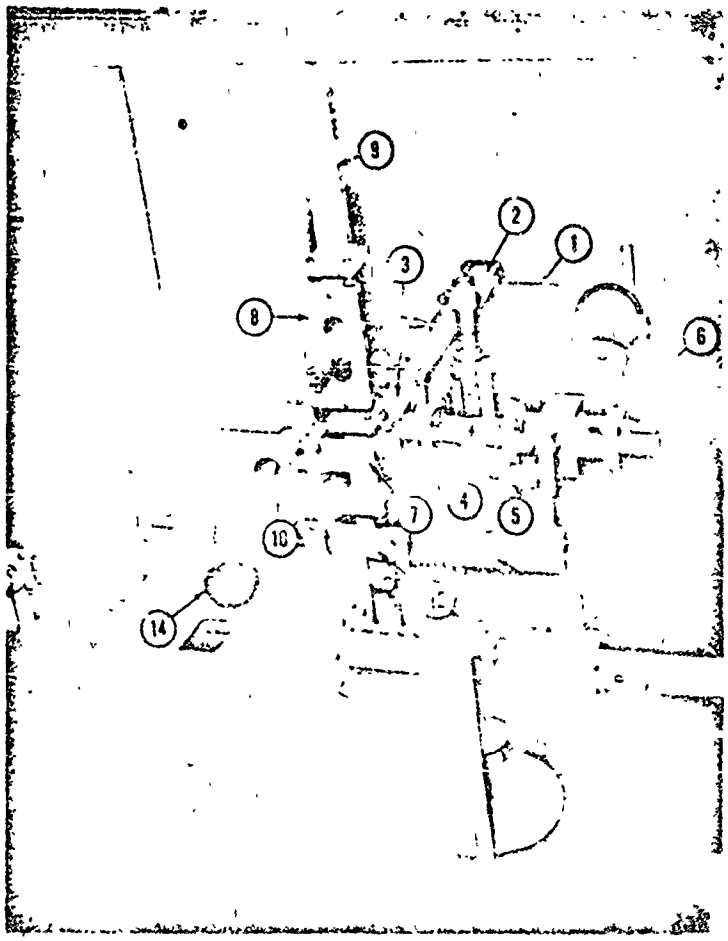


FIGURE 3. PHOTOGRAPH OF MICROWAVE BRIDGE AND CALIBRATION EQUIPMENT

1. Klystron
2. Uniline
3. 20 db Cross-Guide Coupler
4. Wavemeter
5. Waveguide Switch
6. Thermistor
7. Hybrid Tee
8. Slide-Screw Tuner
9. Matched Termination
10. Crystal Mount
11. Matched Termination
12. 20 db Cross-Guide Coupler
13. Adjustable Attenuator
14. Phase Shifter
15. Motor Driven Dipole
16. Matched Termination

to give a deflection of the recorder pen of roughly the same amplitude as the peak of the resonance signal. A final reading is taken after adjusting the phase shifters in both the dipole motor-drive circuit and the microwave circuit to achieve maximum deflection of the recorder pen. Figure 4 shows a typical chart recording of the EPR absorption derivative signal for hydrogen atoms and the calibrat record.

It is essential, of course, to establish that the EPR absorption signal is obtained for conditions of negligible r-f saturation. In the work done here, all data were obtained with not more than 0.5 milliwatt incident on the spectrometer cavity. At this power level, no evidence for r-f saturation was obtained.

All operating parameters for the spectrometer are maintained constant while recording the EPR and the calibration signals. For the measurements made here, a specially calibrated flap attenuator was used. For the highest accuracy, a precision attenuator of the rotating vane type is recommended. For this type of attenuator, the phase shift is negligible and the attenuator error is 0.1 db or less.

Table I summarizes the results obtained by an application of the procedure outlined above to obtain the density of hydrogen atoms in the gas flowing from a microwave discharge in hydrogen. A comparison is made between $(n_a)_{EPR}$ (the density of hydrogen atoms in the stream as determined by EPR measurements) and $(n_a)_C$ (the density derived from a calorimetric measurement of N_A, the number of hydrogen atoms recombining in the calorimeter per second, the pressure in the discharge tube p, and the flow rate, F.)

Comparison of the results presented in Table I with those obtained

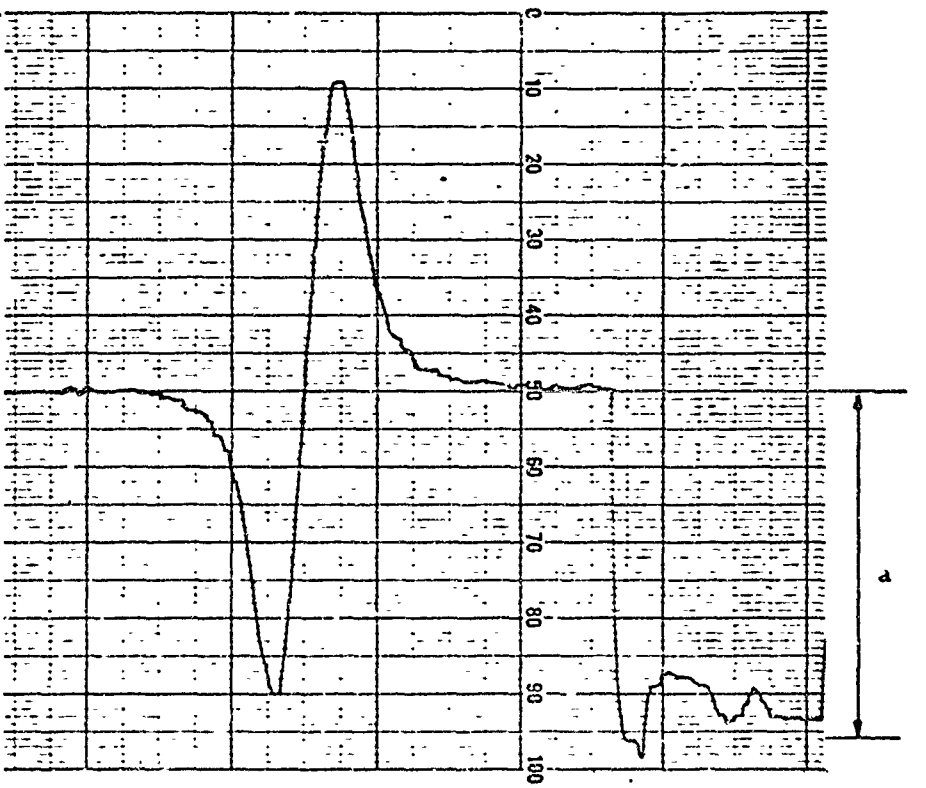


FIGURE 4. CHART RECORD OF π_1 LINE FOR ATOMIC HYDROGEN AND CALIBRATION DATA

(a = recorder pen deflection for calibrator attenuator setting of 8 db.)

TABLE I. SUMMARY OF EPR AND CALORIMETRIC DATA FOR HYDROGEN

Experiment Number	p mm Hg	F Moles/sec	N_A Moles/sec	$(n_a)_C$ Atoms/cc	$(n_a)_{EPR}$ Atoms/cc
c-10/1	0.60	49×10^{-6}	16.4×10^{-6}	0.65×10^{16}	0.59×10^{16}
d-10/2	0.40	49×10^{-6}	14.2×10^{-6}	0.38×10^{16}	0.38×10^{16}
e-10/2	0.40	49×10^{-6}	14.2×10^{-6}	0.38×10^{16}	0.37×10^{16}

earlier when DPH was used as an intensity standard (see Table V of I) shows a significant improvement in the correlation between the results of the EPR and the calorimetric measurements. However, the close agreement of the numerical values shown in some instances is probably fortuitous since no account was taken in the calculations of the loss of atoms due to recombination in the portion of the discharge tube between the EPR cavity and the calorimeter. Although this loss is probably less than ten per cent, in the absence of a specific correction for it, $(n_a)_C$ should be less than $(n_a)_{EPR}$.

The EPR results obtained with the aid of the calibrator permit a comparison of the EPR and calorimetric determinations of n_a for only a limited range of hydrogen pressure and flow. However, the good agreement shown in Table I between the values of n_a obtained by the two methods appears to show that the calibration procedure described in I is the source of the discrepancies reported earlier for the calorimetric and EPR methods (see Table V of I).

Further support for this conclusion was obtained by making, with the aid of the calibrator, an EPR determination of the number of unpaired electrons contained in a sample of DPH. The DPH was prepared according to the same procedure used in making up the standards used for EPR intensity measurements in the previous work. The results of this determination showed the number of unpaired electrons in the test sample to be only 43 per cent of the number expected on the basis of the amount of DPH used to prepare the benzene solution from which the test specimen was taken. In view of this result, it is concluded that the discrepancies in the earlier results can be attributed to a loss in paramagnetic activity of the DPH.

B. High Frequency Modulation Spectrometer

The EPR spectrometer which was used in I and for the measurements described in Section II-A of this report is of the low frequency modulation type. In this spectrometer, the magnetic field is modulated at a frequency of 50 cps and noise reduction is achieved by the use of a synchronous detector in conjunction with an integration time of a few seconds. Thus, to record a complete EPR signal such as that shown in Figure 4 requires a time of a few minutes.

For many potential applications of EPR, it would be highly desirable to reduce the time required to obtain a signal. For example, such a time reduction would make it possible to use EPR to follow rapid changes in atom concentration such as occur when discharge variables are adjusted or to measure the rapid decay of atom concentration in recombination reactions.

Recent developments have shown that in a high frequency modulation spectrometer[2,7] the time required to record a signal can be reduced to about 10^{-2} second. A brief investigation was made to determine the feasibility of using this type of spectrometer for measurement of the concentration of atoms in the gas phase.

For a test of high frequency modulation, the spectrometer described in I was modified as suggested by Bennett et al.[7] A block diagram of the principal components of the spectrometer is shown in Figure 5.

Probably the most critical component of the modified spectrometer is the sample cavity. The essential requirement for the cavity is that the walls must be thin to provide an adequate magnetic field at the modulation frequency (100 kc) at the sample. At the same time, the

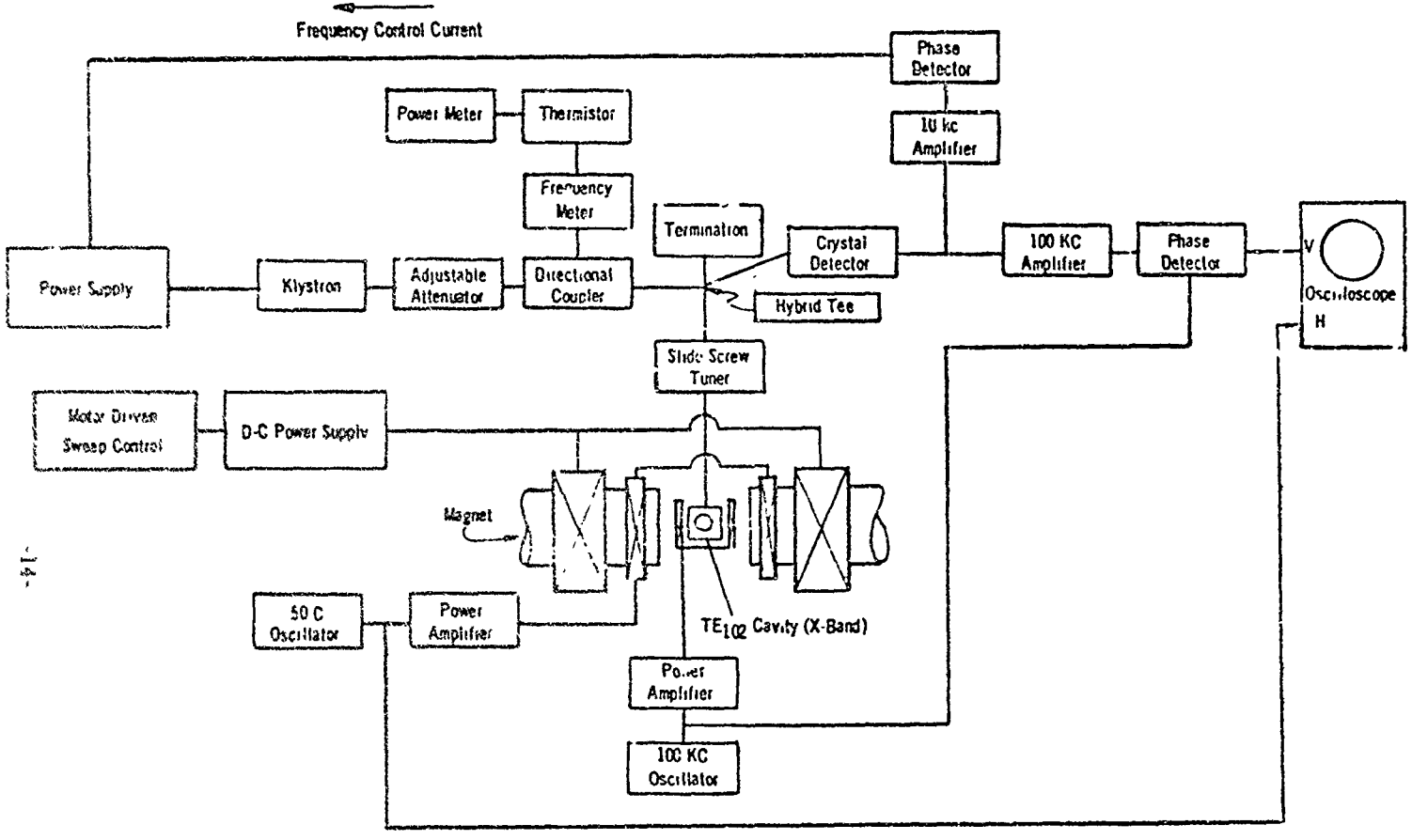


FIGURE 5. BLOCK DIAGRAM OF 100 kc MODULATION EPR SPECTROMETER.

wall thickness must be sufficient to provide a good conducting path for the microwave currents (9250 mc). This requirement has been met by various artifices.[7,8,9] For the experiments reported here, the cavity, Figure 6, was constructed of polystyrene with silver plated interior surfaces. The heavy polystyrene walls serve to avoid the microphonic effects observed with thin metal wall cavities. Unfortunately, the Q of the completed cavity was low (~200) owing to the difficulty of obtaining a continuous surface of silver on the polystyrene.

A test of the feasibility of the 100 kc modulation system was made by recording EPR spectra for hydrogen and nitrogen atoms produced in a microwave discharge. The arrangement of the discharge tube and EPR cavity was the same as shown in Figure 1.

The results obtained with the 100 kc modulation experiment are shown in Figures 7 and 8. Figure 7 shows the lines for the atomic hydrogen, together with a record of the signal obtained from a sample of DPH which was placed within the cavity for calibration purposes. The DPH was attached to the outer wall of the discharge tube and was contained within the EPR cavity during the entire experiment. Figure 8 shows similar data for nitrogen atoms exhibiting the characteristic triplet spectrum. Since the spectra for the hydrogen and nitrogen atoms and DPH were obtained for the same spectrometer conditions, an estimate of atom concentration can be made readily by comparing the integrated intensities of the spectra.

The results obtained with the 100 kc modulation system demonstrate the feasibility of making fast measurements of atom concentration in gases by EPR. Although the photographs shown in Figures 7 and 8 are records of multiple scans of the spectrum at a 50 cps rate, it is clear

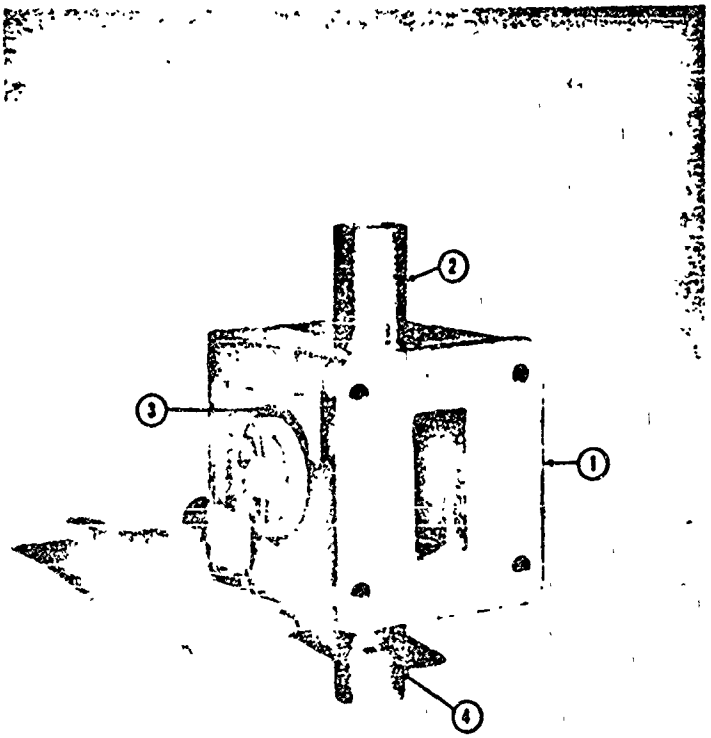


FIGURE 6. POLYSTYRENE CAVITY FOR 100 kc MODULATION EXPERIMENT

1. Standard X-band Flange
2, 4. 1.0 CM I.D. Openings To Accept Discharge Tube
3. Modulation Coils

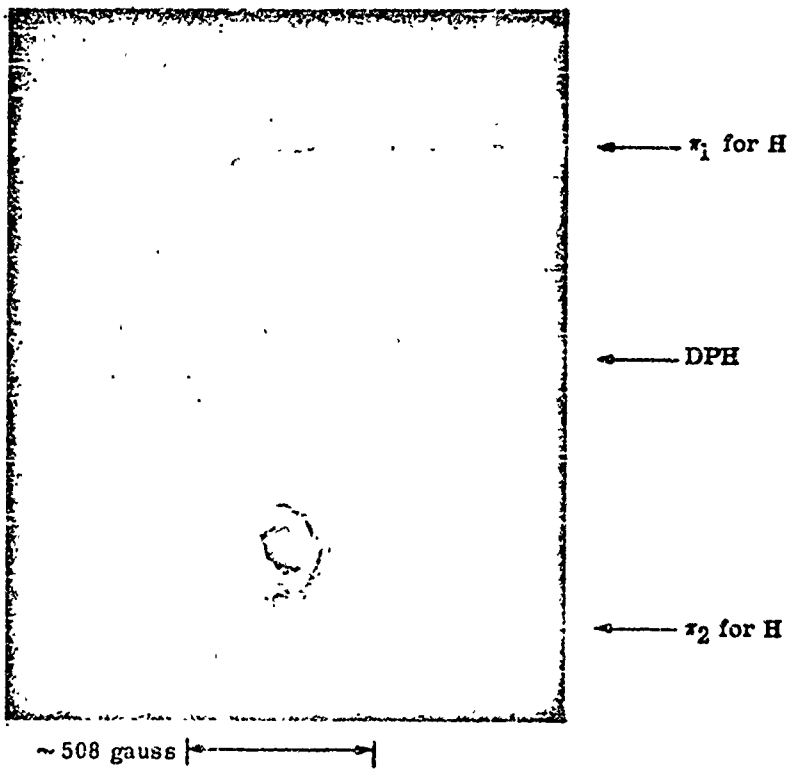


FIGURE 7. SPECTRA FOR ATOMIC HYDROGEN AND SOLID DPH OBTAINED WITH 100 kc MODULATION SPECTROMETER

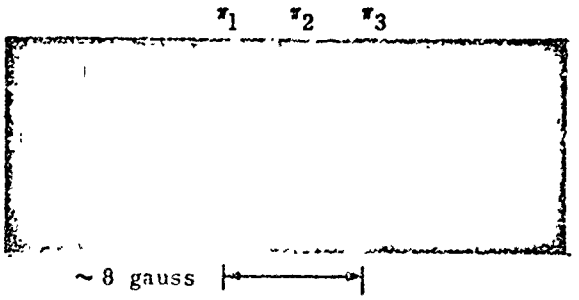


FIGURE 8. SPECTRA FOR ATOMIC NITROGEN OBTAINED WITH 100 kc MODULATION SPECTROMETER

that a record of a single trace could be used which would make it possible to distinguish changes in concentration occurring within about 10^{-2} second. Experience with hydrogen atoms in a flow system has shown that the lifetime of hydrogen atoms is sufficiently long that a resolution time of 10^{-2} second is adequate to follow details of the recombination process.

C. Diffusion Techniques

An important application of EPR spectroscopy is the study of the recombination of atoms on solid surfaces. The essential advantage of the use of EPR is that it provides for the measurement of the concentration of atoms without the need for disturbing the system under investigation, a problem which occurs, for example, through the use of thermocouple probes or other devices of a similar nature which may modify the local atom population. Previous experiments showed that EPR can be used to determine the concentration of radicals produced in discharge tubes.[10,11] In these experiments the gaseous products from the discharge are pumped through a glass or quartz tube which is passed through the cavity of an EPR spectrometer. Figure 1 shows a typical experimental arrangement that has been used for this purpose. The distance between the region where the atoms are produced and the EPR cavity is varied by moving the discharge cavity along the discharge tube. In a flow system of this type, the interpretation of the data is complicated by the fact that gradients in the atom population are produced both by the effects of atom diffusion and by effects due to mass flow. A desirable simplification would be achieved if flow effects could be eliminated.

An experiment was performed to determine if a sufficiently high concentration of hydrogen atoms for observation by EPR could be obtained by diffusion alone. The experimental arrangement used is shown in

Figure 9. Hydrogen atoms were produced in a discharge at a pressure of about one mm Hg and pumped through a 25 mm ID tube. At a distance of 35 mm from the discharge region, a 6 mm ID tube was attached to the larger tube. Both tubes were coated with Dri-film to reduce the loss of atoms due to wall collisions. The smaller tube passed through the cavity of the EPR spectrometer. Thus, the atoms observed by the EPR spectrometer were required to diffuse from the main tube an average distance of about 3.5 cm into the side tube. With this arrangement, EPR lines for atomic hydrogen were readily obtained with a signal-to-noise ratio of 50 or more. A typical record for a line is shown in Figure 10. The intensity of the line was varied by changing the power input to the discharge. The concentration of hydrogen atoms in the side tube at the position of the EPR cavity was estimated to be between 10^{15} and 10^{16} atoms/cm^3. No signals were observable in the same apparatus before application of the Dri-film coating. The experiment demonstrates the feasibility of using EPR with the diffusion technique to study the recombination of atoms on surfaces.[12,13] No attempt was made to determine the decay of hydrogen atom concentration as a function of the diffusion length, since the experimental arrangement used was not suitable for moving the diffusion tube relative to the EPR cavity.

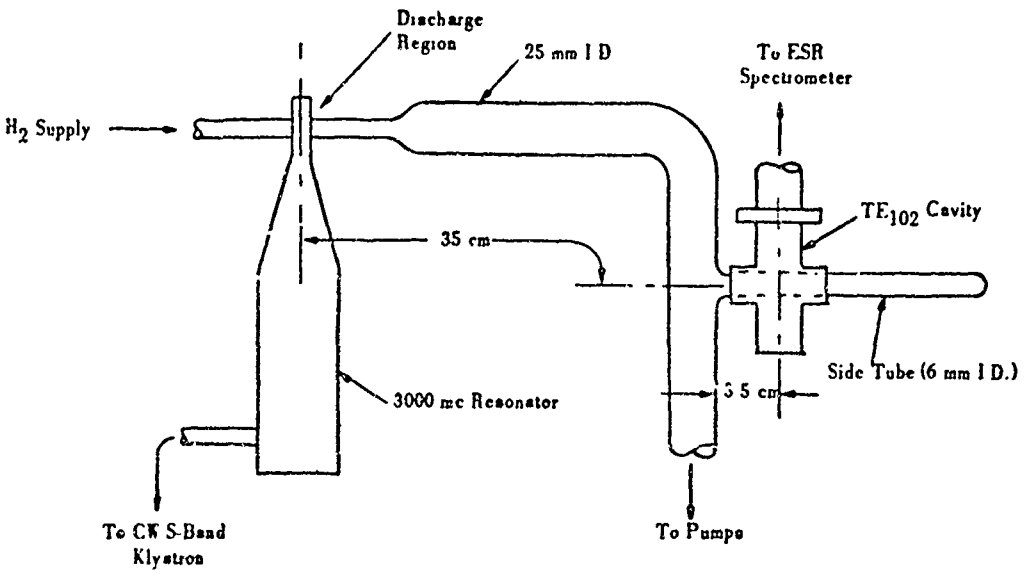


FIGURE 9. ARRANGEMENT OF DISCHARGE TUBE AND ESR APPARATUS FOR ATOM DIFFUSION EXPERIMENT

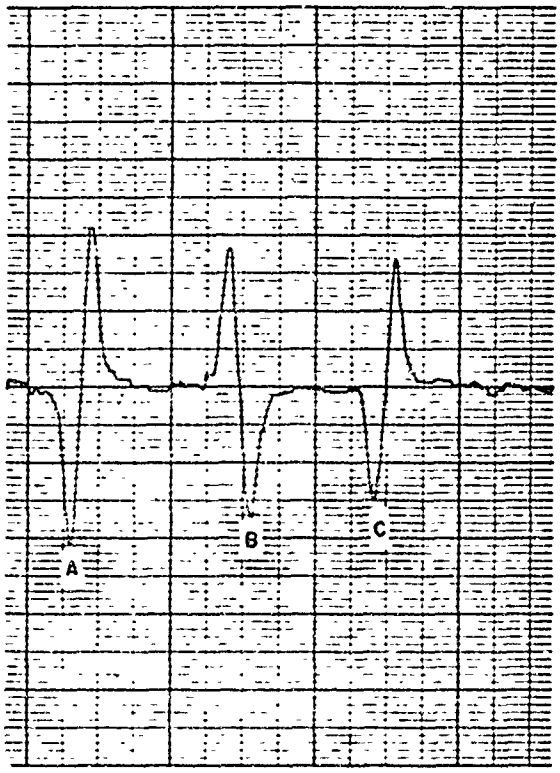


FIGURE 10. RESULTS OF DIFFUSION EXPERIMENT FOR ATOMIC HYDROGEN

(a, b, c are recordings of the π_1 line for atomic hydrogen obtained for a power input to the discharge of 95, 60 and 45 watts, respectively.)

III. WATER VAPOR AS A FACTOR IN THE PRODUCTION OF ATOMS IN A MICROWAVE DISCHARGE IN HYDROGEN

Since the early experiments of Wood,[14] it has been recognized that the dissociation of hydrogen in an electrical discharge is strongly influenced by the addition of small amounts of water vapor to the hydrogen. As described in I, a procedure which has been found to give a large and stable yield of hydrogen atoms consists of the use of a layer of Dri-film on the inner walls of the discharge tube, together with the addition of a few tenths of a per cent of water vapor to the hydrogen supplied to the discharge. With dry hydrogen, the yield of hydrogen atoms is only about 1/10 of that obtained when water vapor is present.[15] The experiments described below were performed in order to obtain more information concerning the role of water vapor in the dissociation process.

A. EPR Spectroscopic Observations on Hydrogen Discharge Products

A hydrogen discharge tube was arranged so that the discharge could be operated on 1) dry hydrogen, 2) hydrogen containing water vapor (H_2O or D_2O), or 3) water vapor (H_2O or D_2O). The experimental arrangement used is essentially the same as that shown in Figure 1 except for the addition of appropriate plumbing to facilitate operation on either or both hydrogen and water vapor.

In general, it was found that an intense EPR spectrum for hydrogen atoms was obtained when the discharge was operated on water vapor alone or on hydrogen containing a small amount (estimated to be of the order of 0.1 per cent) of either H_2O or D_2O. With dry hydrogen alone, the intensity of the hydrogen atom EPR spectrum was reduced by about 10-fold. When operating on dry hydrogen, the addition of a trace of either H_2O or D_2O resulted in an immediate increase in the intensity of the hydrogen atom

spectrum. Figure 11 contains spectra which illustrate some of the observations. Figure 11a shows the derivative of one of the EPR lines for atomic hydrogen obtained when the discharge was operated on dry hydrogen at a pressure of about 0.5 mm Hg. The sequence denoted b, c, d etc. in Figure 11 shows the changes in intensity of the atomic hydrogen line due to the addition of D_2O vapor to the hydrogen supplied to the discharge. To observe changes in intensity which occur with the addition of D_2O, the spectrometer was set on the peak of the signal for the hydrogen atom resonance. The discharge was operated on dry hydrogen and allowed to come to equilibrium. The addition of a small quantity of water vapor (the pressure change was not observable) resulted in an immediate increase in signal by about 10-fold. A few seconds later, the D_2O valve was closed and the signal decayed in a few minutes to the original value. The same change in intensity was obtained when H_2O was added to dry hydrogen. The agreement of the results for D_2O and H_2O shows that the increase in intensity is not to be ascribed to hydrogen atoms from H_2O.

B. Operation of Discharge on Water Vapor

When water vapor alone was used to operate the discharge, the hydrogen atom EPR spectrum was generally observed. However, under some conditions of pressure, flow rate, and power input to the discharge, a number of other EPR lines were observed. One group of lines was identified as due to oxygen atoms.[16] The other is believed to be due to a cyclotron resonance of electrons.[17]

C. Oxygen Spectra

As mentioned above, the lines for atomic oxygen were observed only under certain specific conditions of operation of the discharge. In general, at higher pressures (a few mm Hg) only the lines for atomic hydrogen were found. For pressures near 0.5 - 1.0 mm Hg, lines for both atomic hydrogen and oxygen were observed; the spectrum

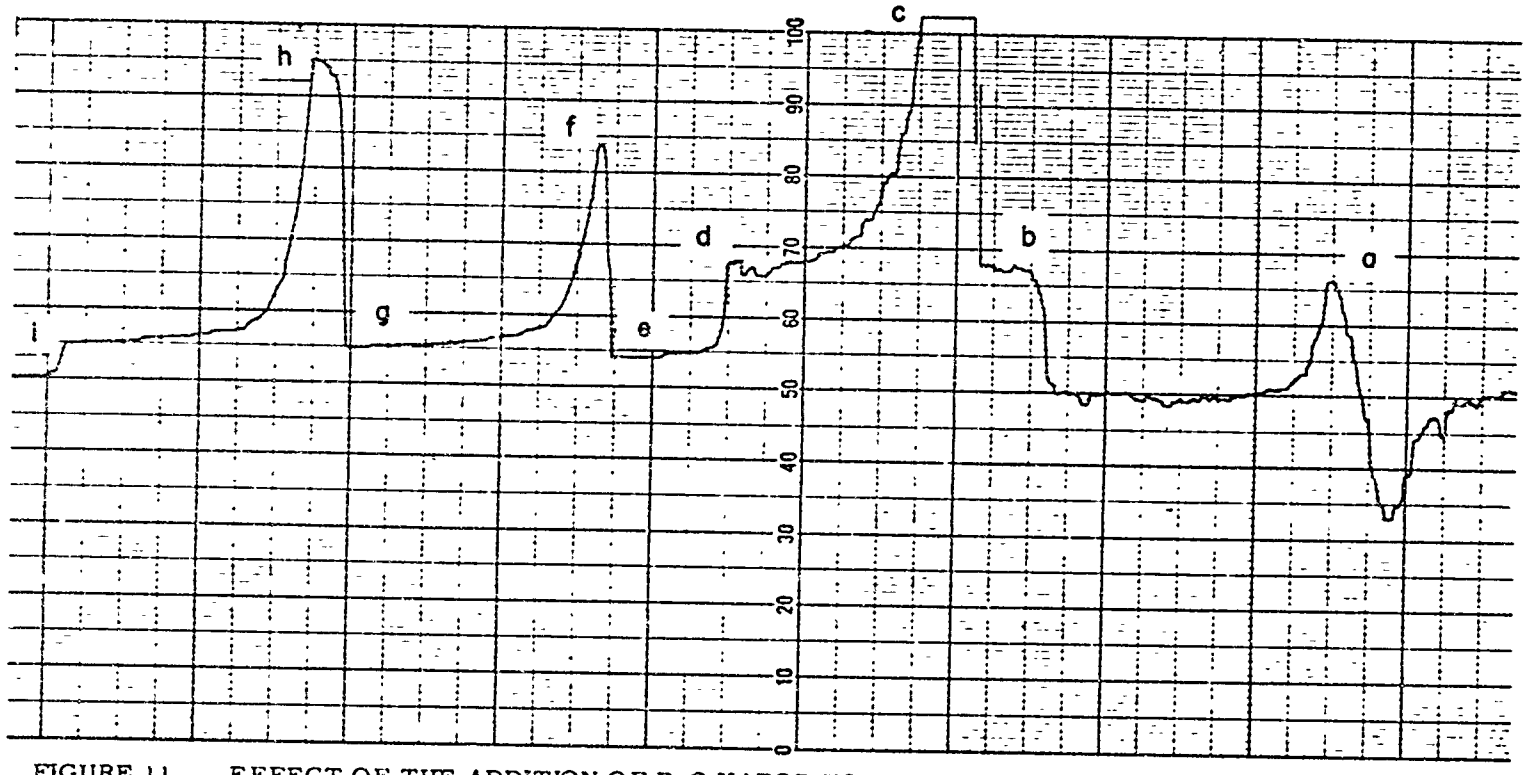


FIGURE 11. EFFECT OF THE ADDITION OF D_2O VAPOR TO HYDROGEN ON THE PRODUCTION OF ATOMIC HYDROGEN

a, EPR signal for atomic hydrogen, b, magnetic field set for peak of signal and valve opened to admit D_2O to discharge; c, valve closed; d, gain of signal amplifier reduced, e, and g, valve opened, f, and h, valve closed; i, discharge off.

for atomic oxygen consisted of only a single broad line. At lower pressures, the hydrogen lines disappeared and only the oxygen line was observed. Finally, at a pressure of about 0.1 mm Hg, the 6-line oxygen spectrum became resolved. These spectra are shown in Figure 12.

It is difficult to make a meaningful interpretation of the effects of pressure on the dissociation of water vapor in the discharge, as indicated by the spectra shown in Figure 12. In part, this is to be attributed to the fact that a number of phenomena determine whether or not a sufficiently high concentration of atoms is obtained in the EPR cavity. In addition to pressure-dependent dissociation processes in the discharge, there are recombination processes on the walls and in the gas phase which are also pressure dependent.

Under some conditions of pressure, flow rate, and power input to the discharge, a broad line shown in Figure 13 was observed at a value of the magnetic field appropriate to the $g = 2.0$ position. Since the line is not observed with hydrogen alone, but only with water vapor present in the discharge gases, consideration was given to three possible sources: 1) resonance due to OH radicals, 2) resonance due to O_2H radicals, as observed in solids by Jen[18] and by Livingston and Zeldes,[19] and 3) cyclotron resonance of electrons. As a result of the two series of experiments described below, it was concluded that the unknown resonance was due to cyclotron resonance of electrons.

D. Collision Experiments

In order to obtain O_2H for possible observation of the EPR spectrum, the discharge apparatus was modified to allow atomic hydrogen produced in the discharge tube to interact with molecular oxygen within

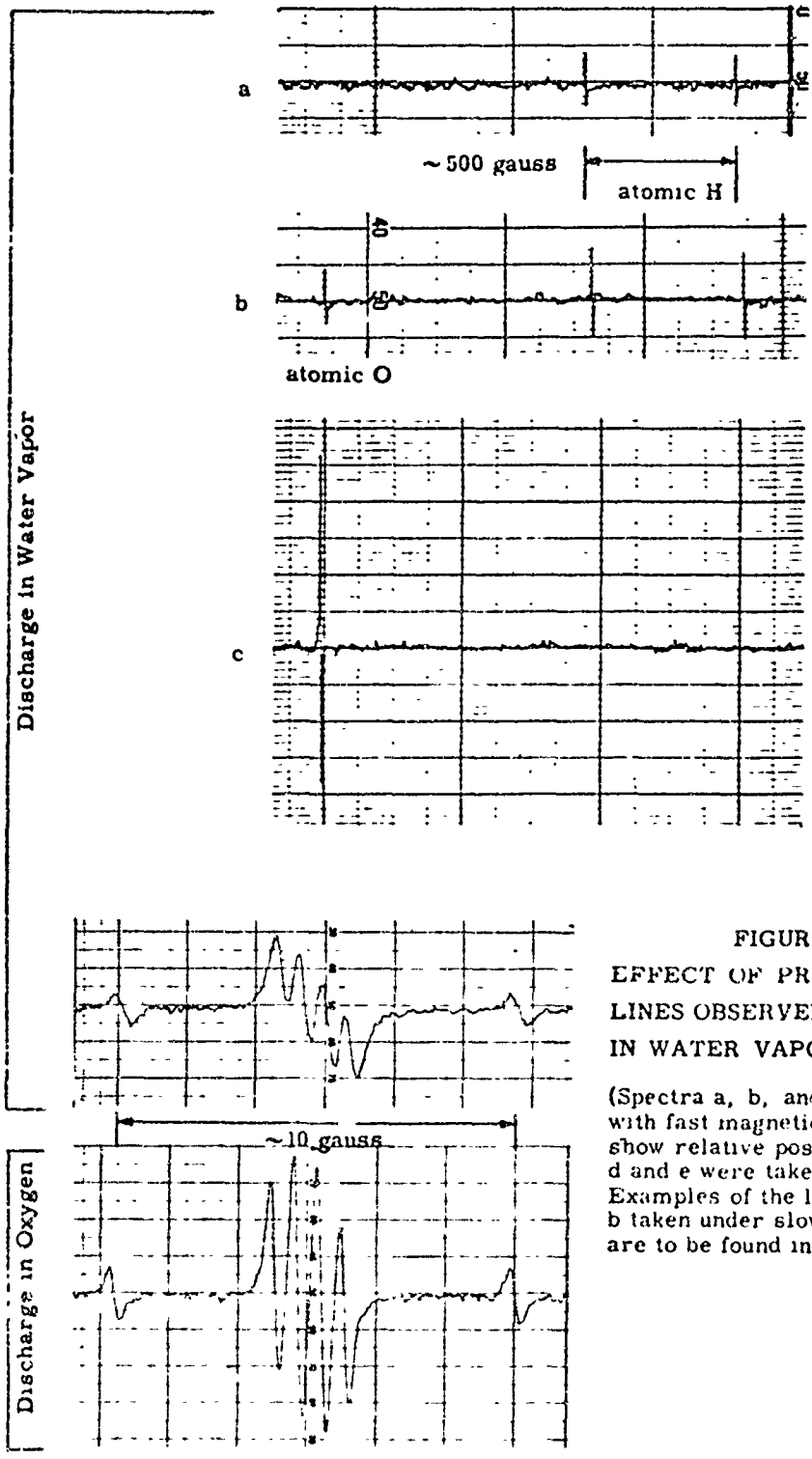


FIGURE 12

EFFECT OF PRESSURE ON EPR LINES OBSERVED FOR DISCHARGE IN WATER VAPOR

(Spectra a, b, and c were recorded with fast magnetic field sweep to show relative positions of lines only; d and e were taken with slow sweep. Examples of the lines shown in a and b taken under slow sweep conditions are to be found in reference 1.)

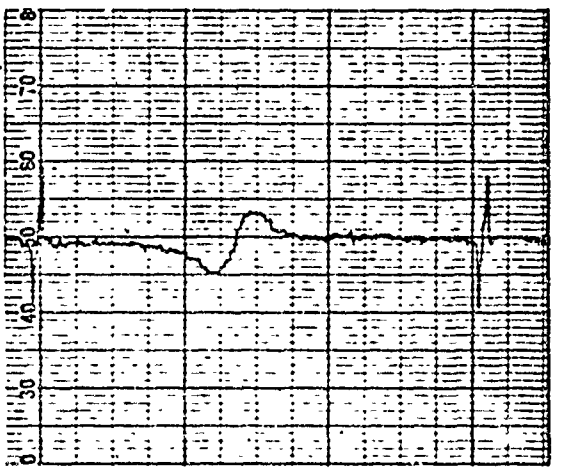


FIGURE 13. ESR SPECTRUM FOR PRODUCTS OF MICROWAVE DISCHARGE IN WATER VAPOR. THE SHARP LINES ARE DUE TO ATOMIC HYDROGEN

the EPR cavity. According to a study by Foner and Hudson,[20] the reaction of H and O_2 results in the production of sufficient O_2H to identify by a mass spectrometer.

The modified gas discharge apparatus is shown in Figure 14. The discharge is operated in the usual way, and the products of the discharge are pumped out of the discharge and through the EPR cavity. A small diameter tube allows a foreign gas to be mixed with the discharged gases just at the upstream end of the EPR cavity. Thus, any products of the reaction are immediately (within about one millisecond) swept into the EPR cavity for observation. The results of an experiment in which oxygen, nitrogen, and hydrogen were individually mixed with discharged hydrogen are shown in Figure 15. In all cases, EPR lines were observed for hydrogen atoms at roughly the same intensity, independent of the presence of a foreign gas. When oxygen is introduced, a broad resonance near the $g = 2.0$ position is observed. The position and width of this resonance is generally similar to that observed with water vapor in the discharge.

Measurement of the g-value of the broad line observed with water vapor and by reacting the products of the hydrogen discharge with oxygen gave in all cases a value slightly less than the value for an unperturbed electron ($g = 2.0023$). The measurements are summarized in Table II. The estimated limit of error for the g-value measurement is $\pm$ 0.0005. The g-values found for the broad resonance ranged from 2.000 to 2.001.

TABLE II. SUMMARY OF g-VALUES

H_2O	2.0012	$\pm$	0.0005
D_2O	2.0005	$\pm$	0.0005
$H + O_2$ reaction product	2.0003	$\pm$	0.0005

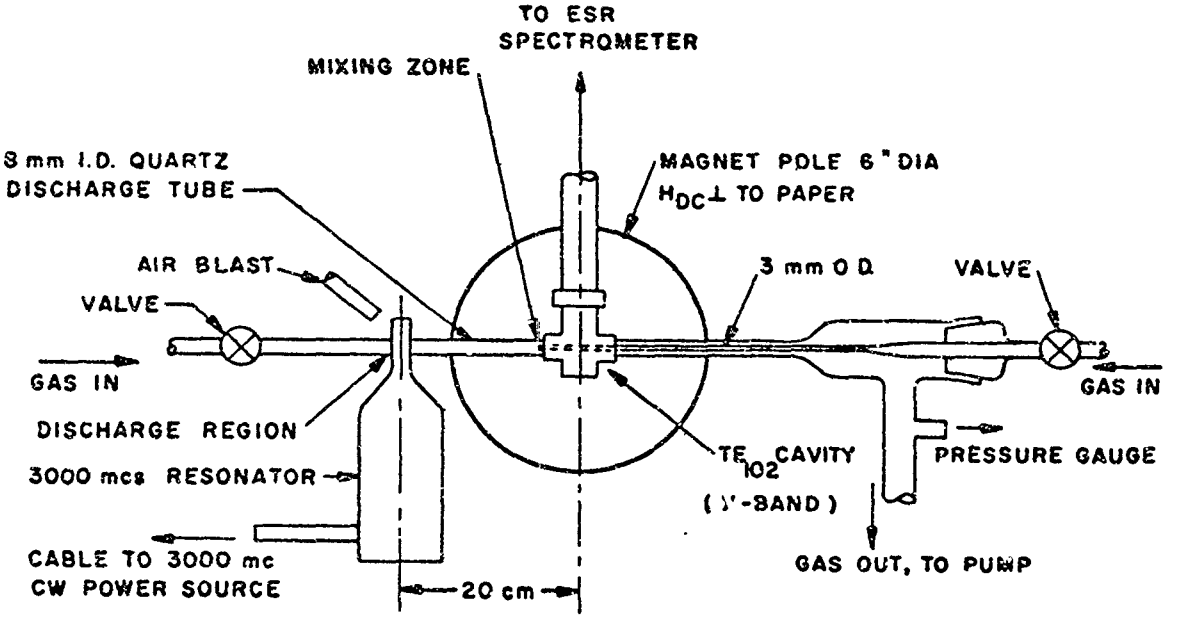
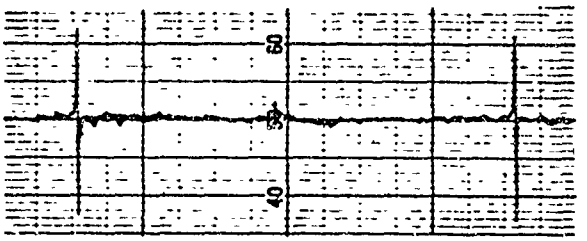
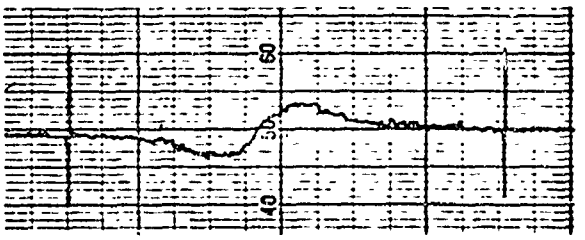


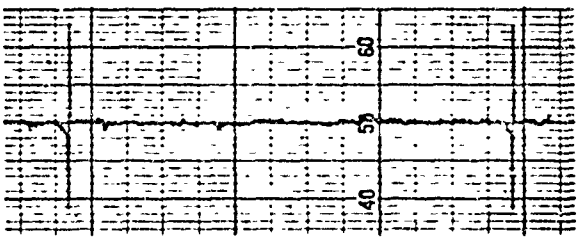
FIGURE 14. ARRANGEMENT USED TO OBSERVE EPR SPECTRA OF PRODUCTS OF REACTION OF ATOMIC HYDROGEN AND OTHER GASES.



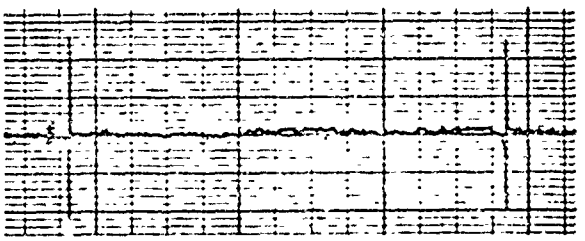
a. ESR spectrum for hydrogen at produced in microwave discharge hydrogen.



b. ESR spectrum obtained when p ducts of hydrogen discharge were mixed with molecular oxygen.



c. ESR spectrum obtained when p ducts of hydrogen discharge were mixed with molecular hydrogen.



d. ESR spectrum obtained when p ducts of hydrogen discharge were mixed with molecular nitrogen.

FIGURE 15. ESR SPECTRA

On the assumption that the broad resonance was due to electrons, it was apparent that they may originate in two ways. In one case, when the discharge is operated on water vapor, the electrons appear to be produced in the discharge and are transported or drift into the EPR cavity where they interact with the electric field and give rise to a broad cyclotron resonance. In the other case, interaction of discharged hydrogen with oxygen results in production of electrons. Further discussion of the electrons which appear to originate in the discharge will be presented later in Section III-E. The following discussion is concerned with the origin of the electrons which result from interaction of the discharged hydrogen and oxygen.

Although it is possible that electrons may be produced in this interaction by a number of different mechanisms, the most likely one appears to be ionization of molecular oxygen by hydrogen atoms or molecules excited by the discharge. The maximum excitation energy available for production of an oxygen ion and release of an electron would be less than the ionization potential of a hydrogen molecule, 15.6 ev.[21] Thus, it would be expected that electrons could result from collisions between excited hydrogen molecules and oxygen molecules, but not between excited hydrogen molecules and nitrogen, since the ionization potential of oxygen is only 12.5 volts while that of nitrogen is 15.7 volts. This expectation is in agreement with what was observed, as indicated in Figure 15.

To further confirm the suggestion that electrons (and the broad EPR lines) are due to ionization of neutral molecules by excited species

produced in the gas discharge, experiments were performed in which the products of a helium discharge interacted with hydrogen, oxygen, and nitrogen. Since the ionization potential of helium is 24.5 volts, the maximum energy available in excited helium atoms should be sufficient to ionize hydrogen, oxygen, and nitrogen because the ionization potentials of these molecules are all lower than 15.7 volts. This prediction was confirmed by the experiment, since in all cases a broad resonance at the g = 2.0 position was observed when the products of the helium discharge were mixed with the three gases mentioned.

In another experiment, the products of a discharge in oxygen were mixed with nitrogen and hydrogen. In this instance, for oxygen the maximum excitation energy available for ionization is only 12.2 ev. Since this is less energy than is required to ionize hydrogen or nitrogen, no electrons are to be expected as a result of mixing, and none were produced as demonstrated by the fact no broad resonances were observed at the g = 2.0 position. The results of the above experiments show that excited atoms or molecules which are produced in a microwave discharge have a lifetime of at least 10^{-2} seconds, since, at the flow rates employed in the experiments, a time of this order is required for the gas to flow from the discharge zone to the EPR cavity.

An experiment was performed with the hydrogen discharge to determine the depende the intensity of the broad resonance on the amount of oxygen m with the products of the hydrogen discharge. The results are shown in Figure 16. Since the line width was relatively constant, it is satisfactory to use the height of the derivative of the observed line as a measure of the intensity of the resonance. The curve of h versus the increase in total pressure is roughly linear for the initial 0.5 mm change in pressure. A similar result was

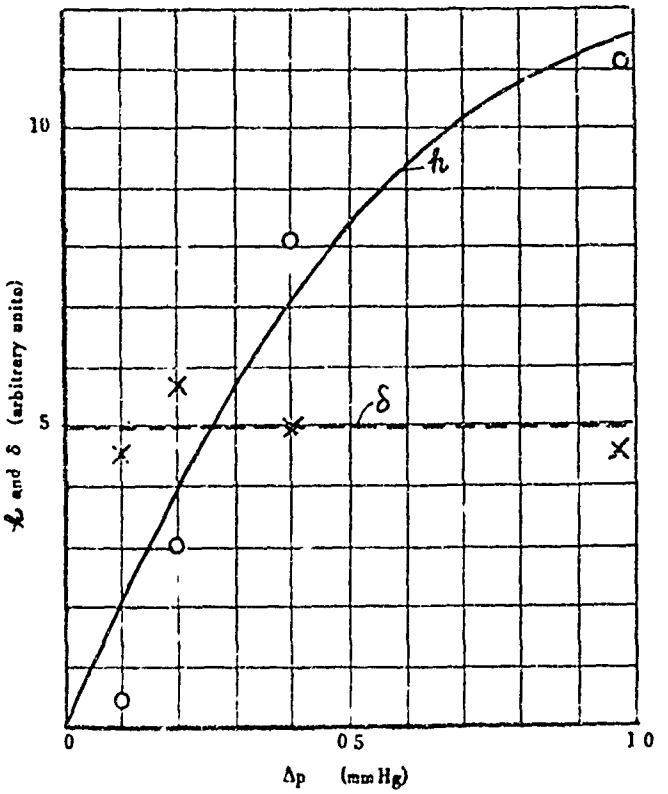


FIGURE 16 CHANGE IN PEAK AMPLITUDE (h) AND WIDTH (δ) OF $s = 2\,0$ LINE DUE TO ADDITION OF OXYGEN

obtained for a helium discharge upon the addition of oxygen to the discharge products.

E. Trapping Experiments

Some electrons appear to be produced in the discharge in water vapor and are transported or drift from the discharge region into the EPR cavity where they interact with the microwave electric field and give rise to a broad cyclotron resonance. Experiments showed that these electrons can be prevented from entering the EPR cavity by the application of an electric field placed between the discharge region and the EPR cavity. The arrangement used in the experiments is shown in Figure 17. This apparatus is the same as that shown in Figure 14, but with the addition of circuits and electrodes to apply a d-c field for trapping electrons. It was found that the intensity of the broad resonance at the $g = 2.0$ position could be influenced by the application of a d-c voltage. The minimum value which would eliminate the $g = 2.0$ line was 50 volts for a distance between the discharge and the electrode of 3 cm. When the distance between the discharge and the electrode was increased to 15 cm, about 2000 volts was required to eliminate the line. Other electrode arrangements were tried, but the one described was found to be the most effective. At no time was it found that the d-c voltage had an effect on the broad line (described in Section III-D) which resulted when gas from the discharge was mixed with other gases in the EPR cavity.

The following conclusions can be made from the experiments described.

1) With a discharge in water vapor or in hydrogen containing water vapor, electrons are produced which are able to drift into the EPR cavity where they give rise to a cyclotron resonance. These electrons can be trapped or prevented from entering the EPR cavity by an electrostatic field.

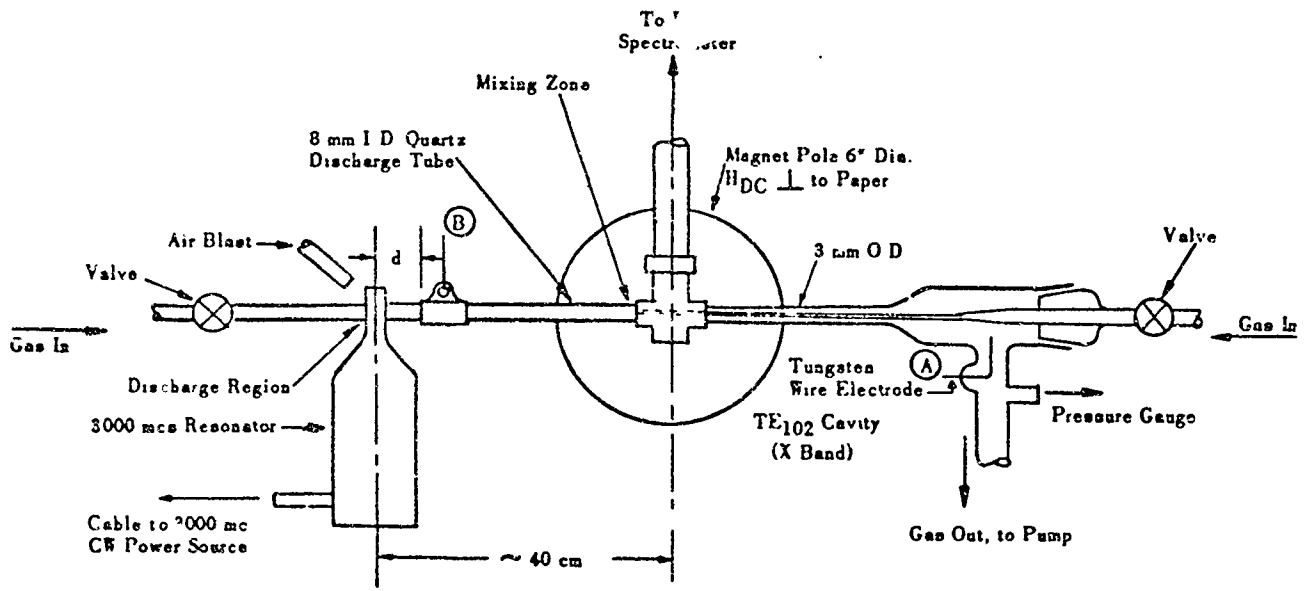


FIGURE 17. ARRANGEMENT OF GAS DISCHARGE TUBE FOR ESR MEASUREMENTS SHOWING ELECTRODE ARRANGEMENT. A d-c voltage was applied to the electrodes A, B.

2) An uncharged but excite species is produced in a discharge in hydrogen, helium, oxygen, and nitrogen, and probably in other gases which when mixed with other molecular gases can cause ionization. The lifetime of the excited species appears to be at least 10^{-2} seconds.

IV. ELECTRON DENSITY AND COLLISION FREQUENCY

The primary mechanism for the production of free radicals in an electrical discharge is the bombardment of gas molecules by electrons in the discharge plasma. There is, however, very little information available concerning the interaction between plasma electrons and the gas molecules for the discharge conditions under which free radicals are produced. For example, no information is available relating the number and energy of the electrons in a microwave discharge and the production of hydrogen atoms.

To obtain further information concerning these questions, experiments were conducted to determine the electron density and the collision frequency of electrons in a 3000 mcs discharge and to relate these quantities to the production of hydrogen atoms.

A. Experimental Techniques

The classical method for the determination of the electron density in a discharge utilizes a metallic probe in contact with the plasma of the discharge. It was expected that such a method would not be applicable for the present purposes since the introduction of a metallic surface would catalyze recombination of hydrogen atoms. A test with platinum and tungsten probes showed this expectation to be correct, since the yield of hydrogen atoms dropped essentially to zero when the metal probe was introduced into the plasma, as evidenced by inability to observe an EPR resonance for atomic hydrogen. This approach was abandoned and microwave techniques were used to obtain the desired information.

B. Transmission Along a Plasma Column

A number of studies have shown that the attenuation of a microwave signal in a discharge plasma is proportional to the electron density.[22,23] In

order to utilize this phenomena to determine the density of a discharge in hydrogen, the waveguide arrangement shown in Figure 18 was constructed. The structure was designed to provide an S-band signal to sustain the discharge and to utilize the transmission of an X-band signal by the plasma column as a measure of electron density. Use of this method assumes that microwave energy of one frequency (S-band) can be used to sustain a discharge while a second microwave signal at a different frequency (X-band) can be used as a probe to determine the electrical characteristics of the discharge. The basic problem to be solved was to provide a microwave structure in which the two microwave signals can interact with the discharge plasma without interfering with each other.

An experiment was performed in which terminals 2 and 4 of the X-band guides were short circuited, and the attenuation of an X-band signal by a cylinder of plasma between terminals 1 and 3 was measured as a function of the S-band power supplied to the discharge. The results are shown in Figure 19 for hydrogen at pressures of 0.3 and 1.0 mm Hg for a range of discharge power between 30 and 100 watts.

According to Figure 19, the attenuation of the X-band signal depends linearly on the power input to the discharge plasma. The attenuation at 0.3 mm Hg pressure is approximately 30 per cent larger than for 1.0 mm Hg.

A somewhat similar result has been obtained for the plasma of a d-c discharge, although in that case a more complex behavior was found. However, at the higher d-c power levels, increasing attenuation was observed with increasing power to the discharge.[22]

A simple interpretation of the results presented in Figure 19 may be made on the basis of the theory of Margenau[24] for a high frequency discharge. According to the theory, the conduction of the discharge is

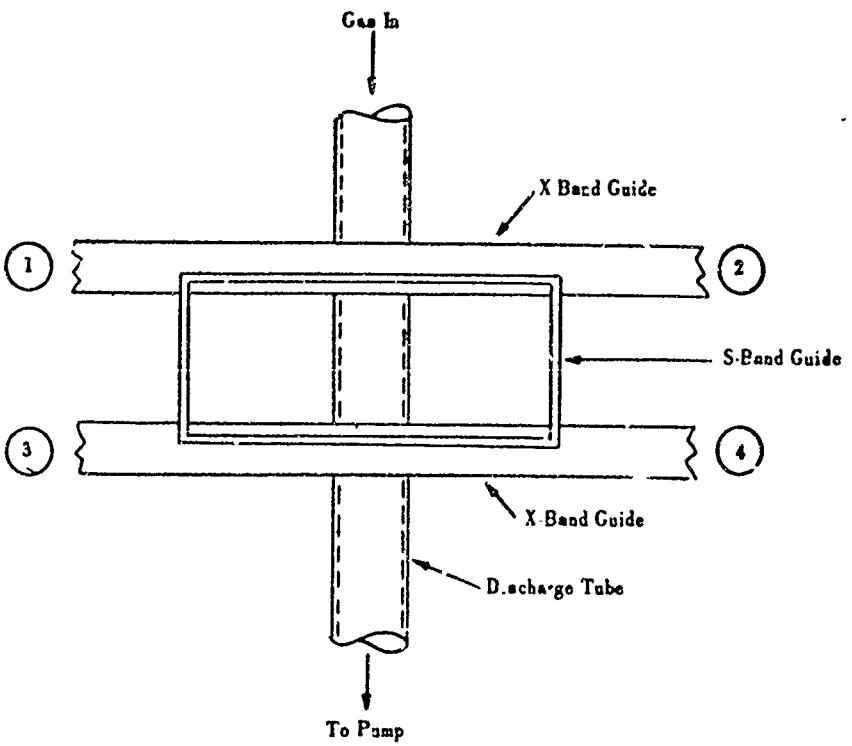


FIGURE 18 WAVEGUIDE STRUCTURE USED TO DETERMINE ATTENUATION OF PLASMA

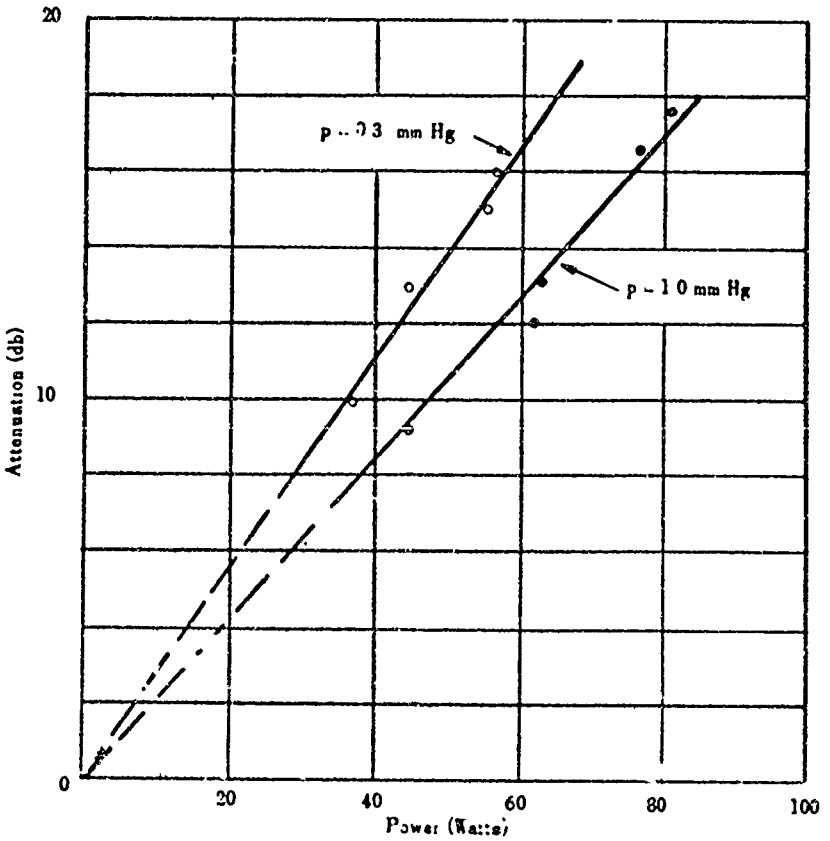


FIGURE 19 ATTENUATION OF 10 kmc SIGNAL BY PLASMA AS A FUNCTION OF POWER INPUT TO 3 kmc CW DISCHARGE IN HYDROGEN

proportional to the electron density for constant electron temperature and pressure. Since the attenuation of the X-band signal is directly proportional to the conductivity of the plasma, it follows from the observations that the relative electron density increases in direct proportion to the S-band power input to the discharge.

The problem remains to convert the data given in Figure 19 for the relative electron density to absolute values. To accomplish this, experiments were conducted with the resonant cavity method for the purpose of establishing the absolute density for at least one power level in the range covered in Figure 19.

C. Resonant Cavity Method

The resonant cavity method has been used widely to obtain the electrical characteristics of a gaseous discharge plasma. In most instances, the method has been applied to d-c discharge plasmas or to the decaying plasma produced by a pulsed microwave discharge. Only a limited use of the method has been made for measuring the properties of a CW microwave discharge of the type used for hydrogen atom production.

The theory and techniques of the cavity method are well known and have been described in detail.[25] For the present purpose, the discharge tube was passed through a rectangular resonator of the type shown schematically in Figure 20. The resonator was coupled to the S-band power source by means of an adjustable iris. Figure 21 is a block diagram of the cavity and test equipment. The discharge was operated on hydrogen at several pressures near 1 mm Hg and at power levels in the range 50 to 107 watts. The iris was adjusted to secure maximum power transfer to the discharge.

Measurements of VSWR in the input line to the cavity were made with and without the discharge. From these measurements were obtained the Q of

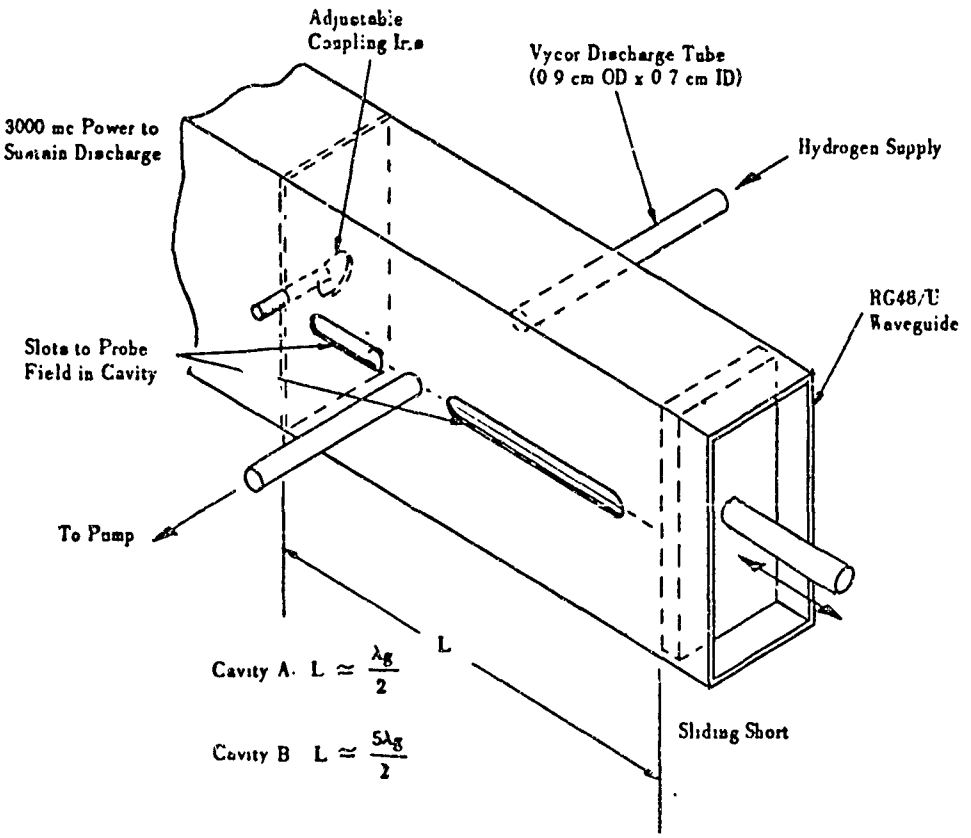


FIGURE 20. RESONANT CAVITY ARRANGEMENT USED FOR ELECTRON DENSITY MEASUREMENTS.

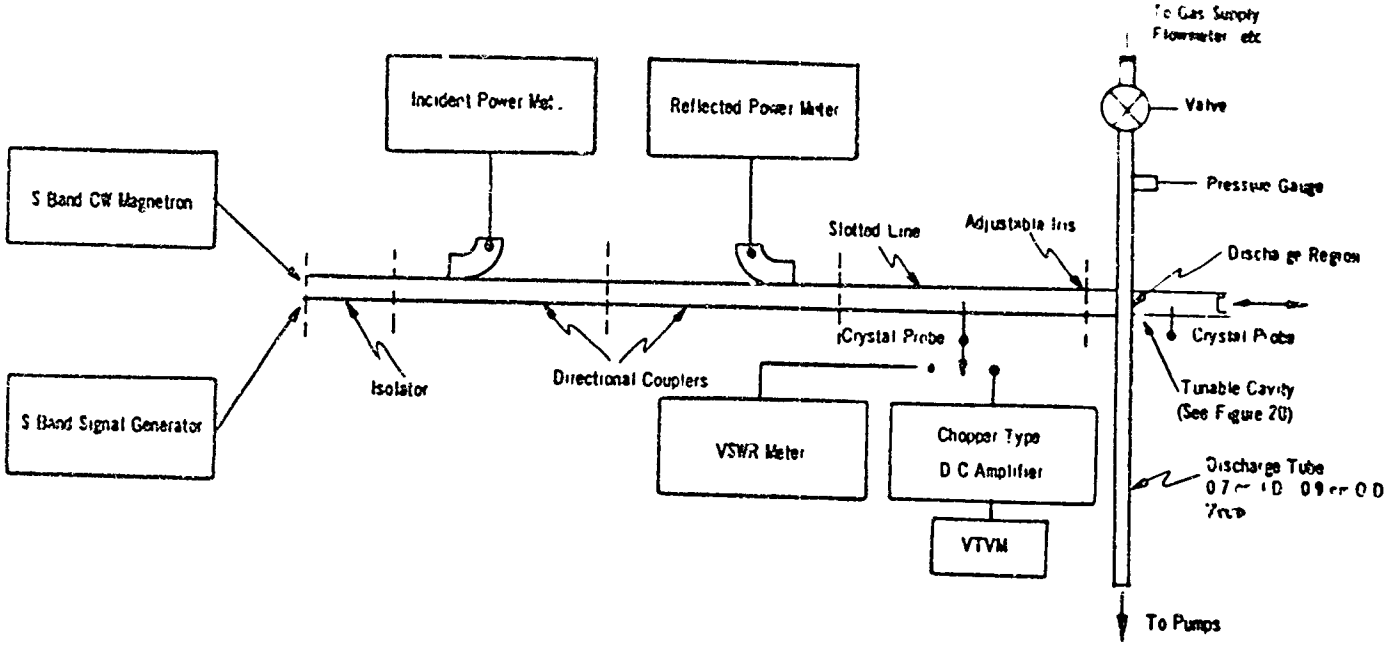


FIGURE 21. BLOCK DIAGRAM OF CAVITY AND TEST EQUIPMENT. FOR ELECTRON DENSITY MEASUREMENTS.

the cavity, Δf (the change in resonant frequency due to the discharge), and ΔVSWR (the change in the VSWR at resonance caused by the discharge). As shown by Udelson,[26] these quantities are related to the electron density, n_e, and collision frequency, ν_c, of the discharge according to the equations,

$$n_e = \left[\frac{4\pi\Delta f}{\omega}\right] \left[\frac{m\epsilon_o(\nu_c^2 + \omega^2)}{e^2}\right] \cdot F \qquad (4)$$

and

$$n_e = \left[\frac{\omega(\Delta \text{VSWR})}{\beta\nu_c}\right] \left[\frac{m\epsilon_o(\nu_c^2 + \omega^2)}{e^2}\right] \cdot F. \qquad (5)$$

Here e is the electron charge, m is the electron mass, n_e is the electron density, β is the coupling coefficient, and F is a factor related to the distribution of the electrons and the electric field in the discharge and the cavity.[25] From the ratio of equations (4) and (5),

$$\nu_c = \left(\frac{\pi f^2}{\beta}\right) \left(\frac{\Delta \text{VSWR}}{\Delta f}\right) \cdot \qquad (6)$$

The results of the measurements are summarized in Figure 22 and in Table III. Figure 22 shows Δf as a function of the power input to the discharge. Over the range of power investigated, Δf varies linearly with the power input. Measurements of Δf at lower levels could not be made because the discharge would not operate stably for less than about 50 watts input for pressures near 1 mm Hg.

A value of ν_c was calculated according to equation (6) from the experimental data for p = 1.0 mm Hg and the maximum power input to the dis-

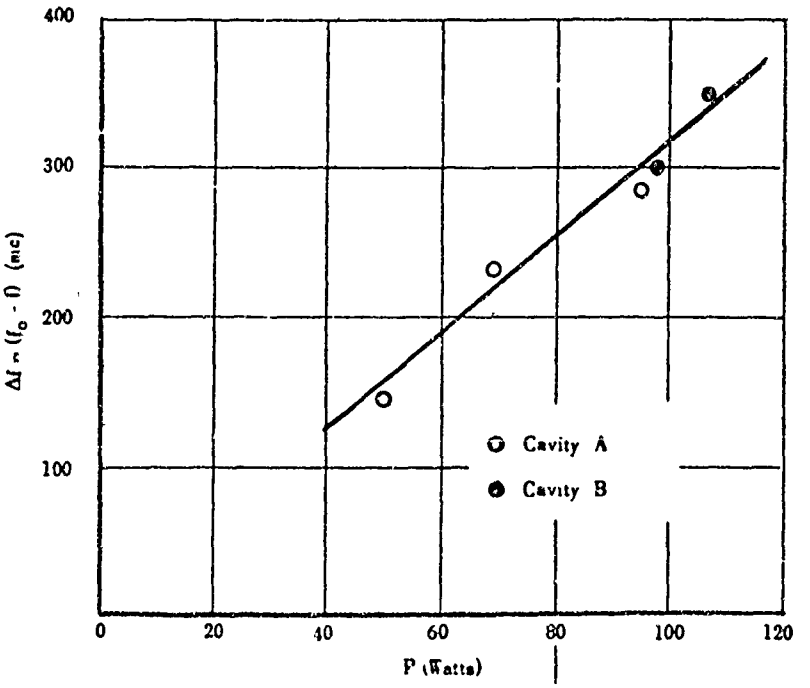


FIGURE 22 CHANGE IN RESONANT FREQUENCY OF CAVITY AS A FUNCTION OF POWER INPUT TO DISCHARGE

charge (107 watts). The value found, $\nu_c = 2.3 \times 10^9$ sec^{-1} is less than half of the value 5.9×10^9 which has been established for hydrogen for electrons with energies greater than 4 ev.[27] A second determination of ν_c for p = 0.5 mm Hg and a power input of 98 watts gave an almost identical value, $\nu_c = 2.2 \times 10^9$ sec^{-1}.

To obtain n_e from the experimental value of Δf given in Figure 22, it was assumed that the r-f field in the cavity was constant over the cross section of the discharge tube. With this assumption, a value of $n_e = 4 \times 10^{12}$ cm^{-3} was obtained for p = 1.0 mm Hg and a power input of 107 watts. Unfortunately, this result is of doubtful value because it is outside the range for which the resonant cavity method is applicable.[28] For a frequency of 3×10^9 sec^{-1} as used in the present measurements, the upper limit of electron density for which the method is applicable is somewhat less than 10^{11} cm^{-3}, the density required for plasma resonance. It is concluded that the resonant cavity method is not suitable for quantitative determination of the electron density or the collision frequency in a hydrogen discharge in the power and pressure range of interest.

TABLE III. CAVITY PARAMETERS

P = 107 watts, p = 1.0 mm Hg
VSWR (DISCHARGE ON) 1.5
VSWR (DISCHARGE OFF) 12
f = 3007 mc
Δf = 350 mc
β = 360

V. CONCLUSIONS AND RECOMMENDATIONS

A satisfactory correlation has been obtained in the measurement of the concentration of atomic hydrogen in partially dissociated hydrogen by electron paramagnetic resonance (EPR) and recombination calorimetric methods. The EPR measurements of atom concentration were performed by means of a microwave standardization procedure which is especially well adapted for measurements on gases. Time has permitted only a limited evaluation of the standardization procedure. A more extensive investigation of the technique will be required to determine the limits of error.

New information has been produced concerning the role of water in the production of hydrogen atoms in a microwave gaseous discharge. Evidence has been obtained to show that electrons and excited atoms or molecules may be readily pumped from a discharge containing water vapor. It is suggested that techniques utilizing cyclotron resonance may be profitably employed to obtain a quantitative estimate of the concentration of these species.

It was found that the conventional cavity method for measurement of electron density is unsuitable for use with a 100 watt, 3000 mc CW discharge in hydrogen because of the high electron density. It is suggested that in future work consideration be given to the low frequency solenoid method.[28]

VI. APPENDIX A: A TECHNIQUE FOR EPR INTENSITY STANDARDIZATION

C. Milazzo and T.M. Shaw

In principle, the determination of the absolute number of unpaired electrons can be evaluated directly from the observed EPR resonance and the electrical characteristics of the spectrometer.[2] In practice, this procedure is rarely followed, however, since it has been found more convenient and possibly more accurate to employ a reference material containing a known number of unpaired electrons. The lack of a convenient and stable reference standard for use in the determination of hydrogen atom concentrations by EPR led to the development of the procedure described herein.

The aim of the work was to develop a technique whereby the number of unpaired electrons in a sample of paramagnetic material might more readily be determined directly from measured electrical quantities. The usual microwave EPR spectrometer is a highly sensitive microwave receiver which amplifies an extremely small modulated signal reflected from the microwave cavity in which the paramagnetic substance is placed. This reflected signal is due to the change in the cavity Q caused by paramagnetic resonance. The magnitude of the signal is given by

$$\Delta V_{RS} = \frac{2V_0\beta}{(\beta+1)} \quad \frac{\Delta Q_0}{Q_0} \quad , \tag{7}$$

where V_0 is the microwave voltage applied to the cavity, β is the cavity coupling coefficient, Q_0 is the cavity unloaded Q, and ΔQ_0 the change in Q_0 caused by paramagnetic resonance.

Because of the field modulation technique used, see Figure 23, the change

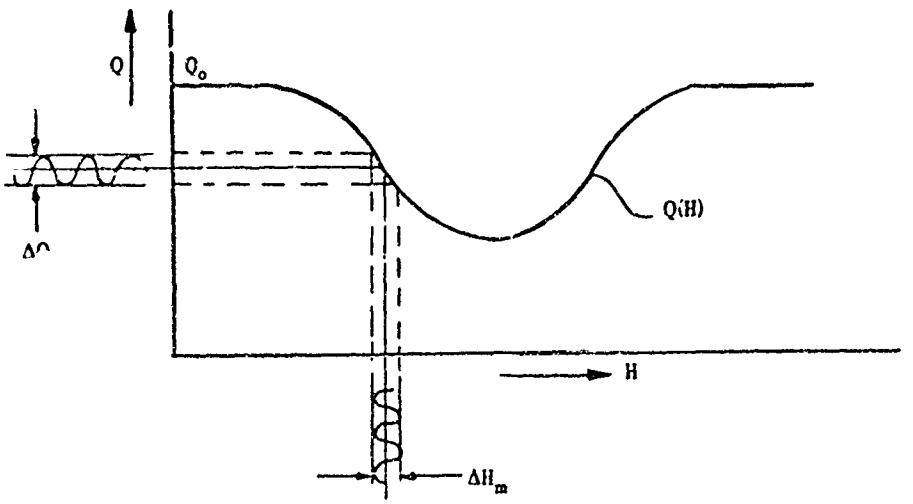


FIGURE 23 TO SHOW RELATIONSHIP BETWEEN ΔH_m AND ΔQ

in Q brought about by the modulation superimposed upon the slowly varying d-c magnetic field is,

$$\Delta Q(H) = \frac{dQ}{dH} \Delta H_m , \tag{8}$$

where ΔH_m is the peak-to-peak magnitude of the modulation and dQ/dH is the derivative of the paramagnetic resonance. Upon substitution of this relationship in equation (7), one obtains

$$\Delta V_{RS} = \frac{2V_o\beta}{(\beta + 1)^2} \quad \frac{1}{Q_o} \quad \frac{dQ}{dH} \quad \Delta H_m . \tag{9}$$

For linear detection and amplification in the spectrometer circuits, the recorder output is $E_{RS} = A \Delta V_{RS}$ where A is the total gain of the

spectrometer. To obtain χ'', the imaginary part of the paramagnetic susceptibility, it is necessary to perform a numerical integration of the recorder output with the use of equation (9) as follows.

From the relation $E_{RS} = A\Delta_{RS}$ and equation (9)

$$\frac{dQ}{dH} = \frac{(\beta + 1)^2}{\beta} \quad \frac{Q_o}{2V_o} \quad \frac{1}{\Delta H_m} \quad \frac{E_{RS}}{A} \tag{10}$$

Integrating over the absorption line, one finds

$$Q(H) = \frac{(\beta + 1)^2}{\beta} \quad \frac{Q_o}{2V_o} \quad \frac{1}{\Delta H_m} \int \frac{E_{RS}}{A} \quad dH + Q_o . \tag{11}$$

For small samples it is known

$$Q(H) = Q_o (1 - 4\pi\eta \quad \chi'' Q_o), \tag{12}$$

where η is the filling factor.

Equating (11) and (12), it follows

$$\chi''(H) = \frac{1}{4\pi\eta Q_o} \quad \frac{(\beta + 1)^2}{\beta} \quad \frac{1}{2V_o \Delta H_m} \int \frac{E_{RS}}{A} \quad dH. \tag{13}$$

In order to calculate χ'', it is necessary to know, in addition to the cavity parameters η, β and Q_o, the gain A of the system and the applied voltage, V_o. In the technique devised here, the gain of the system is measured by coupling a small fraction of the voltage, V_o, to an auxiliary waveguide containing a rotating metal dipole (see Figure 24). In the auxiliary guide,

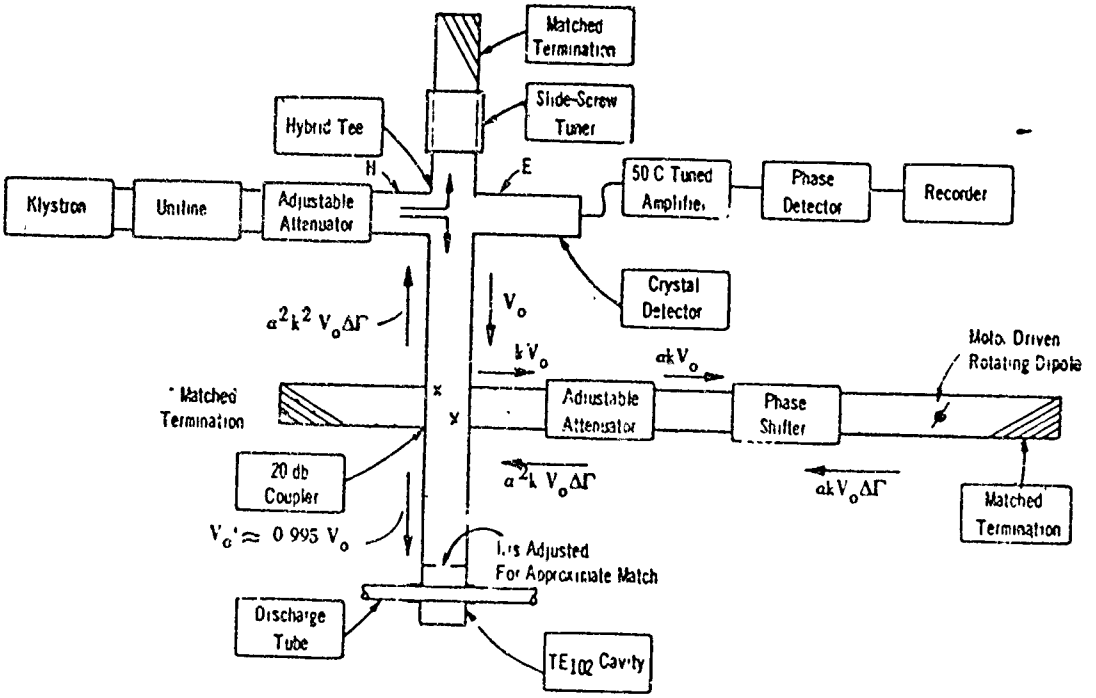


FIGURE 24 MICROWAVE BRIDGE AND CALIBRATION CIRCUIT

V_o is still further attenuated before it impinges on the dipole. The region beyond the dipole is terminated by a matched load. The dipole is driven by a synchronous motor from the magnetic field modulation source, and the rotating dipole induces a small reflection which varies at the modulation frequency.

For a directional coupler coefficient, k, attenuator loss, α, and dipole reflection coefficient, $\Delta\Gamma_m$ (peak-to-peak magnitude), see Figure 25, the

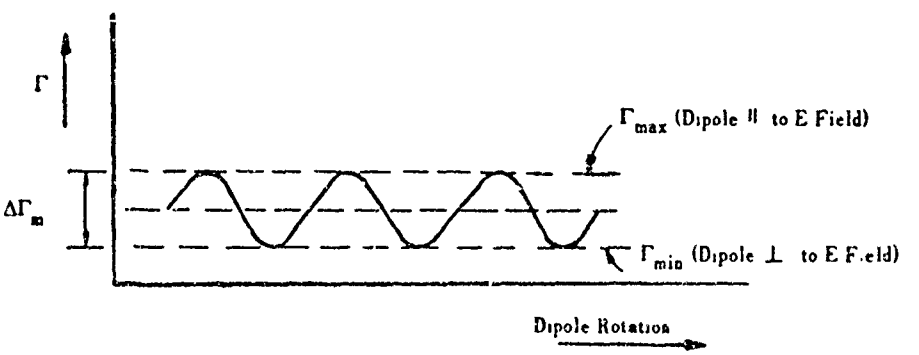


FIGURE 25. CHANGE IN Γ WITH DIPOLE ROTATION

recorder output is

$$E_{RO} = \alpha^2 k^2 \Delta\Gamma_m V_o A \quad (14)$$

Substituting the expression for the gain, A, from equation (14) into (13) yields,

$$\chi''(H) = \frac{1}{8\pi\eta Q_o} \frac{(\beta+1)^\beta}{\beta} \alpha^2 k^2 \frac{\Delta\Gamma_m}{\Delta H_m} \int \frac{E_{RS}}{E_{RC}} dH. \qquad (15)$$

or in terms of the loaded Q,

$$\chi''(H) = \frac{1}{8\pi\eta} (1+\frac{1}{\beta}) \frac{1}{Q_L} \alpha^2 k^2 \frac{\Delta\Gamma_m}{\Delta H_m} \int \frac{E_{RS}}{E_{RC}} dH. \qquad (16)$$

The application of this calibration technique to the measurement of hydrogen atom concentration is described in Section II-A. The system is well adapted for work with gases since a single evaluation of the parameters η, β, Q_L is sufficient. For work with gases such as has been performed here, these quantities need be evaluated only once for the particular experimental arrangement since they are not sensibly influenced by changes in gas pressure or atom concentration. The parameters for the spectrometer employed for the measurements described in Section II-A are tabulated below.

$k = 0.105$
$\beta = 0.734$
$Q_L = 1545$
$\eta = 0.175$
$\Delta\Gamma_m = 0.0343$

The performance of the calibrator was tested by measuring the EPR absorption in a material containing a known number of paramagnetic molecules. A series of samples was prepared, each containing a weighed amount of manganous sulphate ($MnSO_4 \cdot H_2O$) enclosed in a thin wall

Pyrex tube. To obtain the EPR absorption, each sample was placed on the axis of the discharge tube at the center of the EPR cavity. The volume of the samples was sufficiently small to ensure that the entire sample was exposed to essentially the maximum r-f magnetic field within the cavity and that the loaded Q of the cavity was unchanged from the value established with the discharge tube alone.

To make a determination of the number of paramagnetic molecules in the test samples, the EPR absorption derivative signal was recorded in the usual fashion for conditions of negligible r-f saturation. Following this, the calibrator attenuator and phase were adjusted to establish a calibration marker on the recorder chart. The number of paramagnetic molecules per cm^3 for each sample, N_o, was then obtained from the experimental data in accordance with equations (1) and (2) and the procedure outlined above.

The results of the test with manganous sulphate are presented in Table IV. It was found that the average value of N_o determined experimentally is approximately 20 per cent higher than the theoretical value. Examination of the individual determinations shows that the maximum error is associated with the smallest sample. Except for this sample, the maximum discrepancy is about 30 per cent. This is considered satisfactory, based on the relatively large possible errors involved in the microwave measurements and the graphical integration of the EPR derivative curves.

TABLE IV. RESULTS OF EPR MEASUREMENTS ON MANGANOUS SULPHATE

Experiment Number	Weight of $MnSO_4 . H_2O$ (Grams)	N_o (cm^{-3})
h-10/2	21.3×10^{-3}	0.98×10^{22}
i-10/2	48.6×10^{-3}	1.03×10^{22}
j-10/2	11.6×10^{-3}	1.46×10^{22}
k-10/2	1.4×10^{-3}	1.90×10^{22}
c-10/5 *	4.8×10^{-3}	1.12×10^{22}
	Average	1.30×10^{22} **

*Sample on outer face of discharge tube; field at sample position calculated and correction made to filling factor.

**$(N_o)_{Theory} = 1.05 \times 10^{22}$ cm^{-3} based on molecular weight of 169.0 and a density of 2.95 grams/cm^3.

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