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RESEARCH STUDIES ON
ANALYSIS OF IONIZED GASES

by

William R. Snow

FINAL REPORT

Contract DA-49-146-XZ-049
Defense Atomic Support Agency
Washington, D.C.

292 079
July 31, 1962

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DASA-1329

GENERAL ATOMIC
DIVISION OF
GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

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ANALYSIS OF IONIZED GASES

FINAL REPORT

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Contract DA-49-146-XZ-049
Defense Atomic Support Agency
Washington, D. C.
General Atomic Project 212

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I. INTRODUCTION

This report is a summary of the research done under contract DA-49-146-XZ-049 during the period June 20, 1961, to July 31, 1962. This work is being continued under contract DA-49-146-XZ-041. The experimental results reported here represent primarily the work completed in the last few months of the contract period since the majority of the experimental results obtained during this period have been published in the Discussions of the Faraday Society⁽¹⁾ and as General Atomic report GA-2824⁽¹⁾ and will not be reproduced in this summary. Work performed during the initial contract period (June 20, 1960 through June 19, 1961) was reported in the first annual Technical Summary Report⁽²⁾ for this contract

II. EXPERIMENTAL METHOD

The experimental apparatus consists basically of a conventional 60 degree mass spectrometer fitted with an afterglow ion source and is shown diagrammatically in Fig. 1. Considerable care was exercised in the construction of the spectrometer to keep it clean since minor contamination of the discharge by adsorbed gases was found to make large changes in the course of the afterglow. The machine was constructed of stainless steel, and demountable joints were sealed by soft copper gaskets. All electrical connections into the vacuum were made with bakeable, ceramic-to-metal seals. The entire vacuum system above the mercury diffusion pumps and liquid nitrogen traps can be baked at 400°C.

Gas was admitted to the discharge chamber through a leak valve which maintained operating pressures of 0.1 to 10 mm Hg in the chamber. Electrostatic lenses were located in the differentially pumped section which accelerated the charged particles to 400 ev and focused them on the entrance slit of the mass spectrometer. The ions passing through the exit slit after analysis were accelerated to the first dynode of the electron multiplier by an additional 2 kv. The multiplier with a cathode follower output was used to provide a fast response time -- about 2 μ sec. The polarity of all voltages was reversible so that both positive and negative ions could be studied.

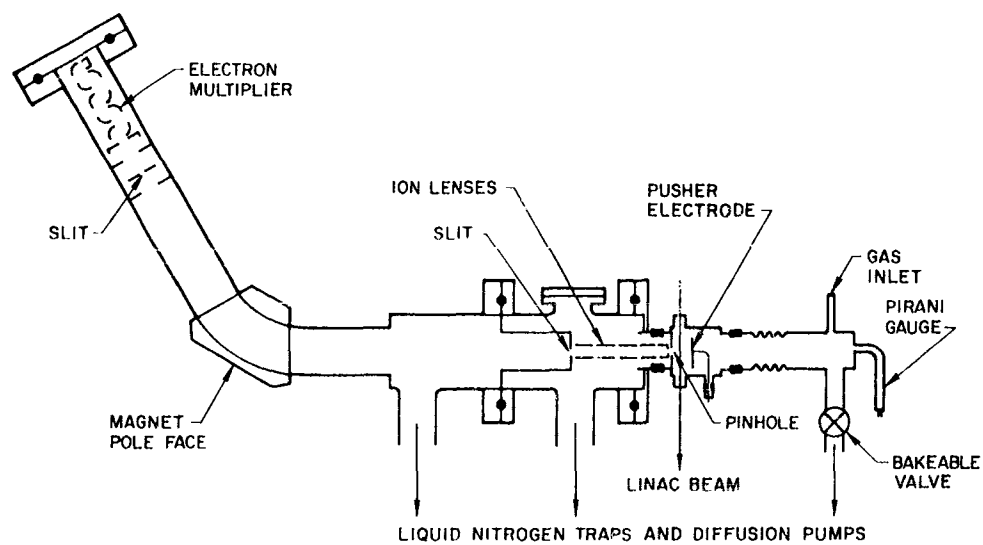


Fig. 1--Schematic diagram of apparatus for mass-spectrometric studies of afterglows

Figure 2 is a sketch of the source chamber. The radio-frequency power was applied between the plane wall containing the ion exit aperture and a plane "pusher" electrode. There was a three-to-one ratio between the diameter of the pusher and its distance from the plane of the aperture so that, to a crude approximation, the geometry was one-dimensional in the neighborhood of the exit aperture. The name "pusher" for this electrode was derived from the fact that it could be slightly biased, following cessation of an excitation pulse, to provide a drift field across the afterglow chamber. About 30 watts of rf power was provided to the discharge by a pulsed, 30 megacycle oscillator. The pulse length was variable from 0 - 10 μ sec. The source chamber has recently been modified to permit access to the chamber so that the electrode configuration could be changed. (Refer to the appendix).

Alternatively the gas could be ionized by a 5 μ sec pulse of 20 mev electrons, from the General Atomic Linear Accelerator (LINAC), which passed through thin stainless steel windows as shown in Fig. 2. The aperture for the source was a pinhole in a replacable platinum foil (typically a 0.006 in. hole in a 0.006 in. foil).

Radio-frequency excitation of the gas was found to be simpler and much less costly than LINAC excitation, and therefore was used wherever possible. However, there were two drawbacks to its use; first, it was found that, for reliable firing, the pulse repetition rate (prf) had to be fast enough that each pulse produced preionization for the next pulse; that is the prf must be of the order of a few hundred cps. This was a serious drawback in some gas mixtures because it was found that neutral impurities were built up which greatly influenced the course of the afterglow. Secondly, the mode of the rf oscillation appeared to change with pressure so that the pressure dependence of reactions could not be reliably determined.

The LINAC required no preionization, of course, so that the pulse rate could be slowed to prevent significant formation of impurities, and a reasonably good estimate of the ion density produced at any pressure could be made. Generally, the initial ion densities using the LINAC were 10^{11} cm^{-3} or less, and an order of magnitude less using the rf excitation.

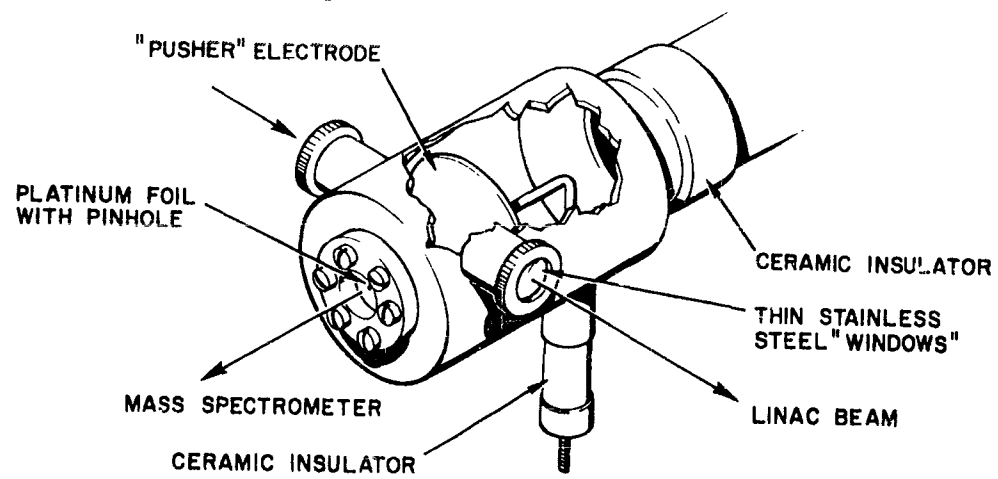


Fig 2--Source chamber

III. EXPERIMENTAL RESULTS

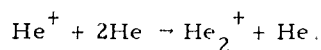
The appearance of a large mass 12 peak in pure helium afterglows prompted further investigations, from which it is believed that the mass 12 peak is carbon from a CO impurity, probably a result of outgassing of the walls of the discharge chamber. Mixtures of oxygen with helium and neon have been examined in an attempt to measure the O^+ to O_2 charge transfer rate. Afterglows in hydrogen, water vapor, and nitrogen-hydrogen mixtures have also been studied.

3.1 HELIUM

Samples of pure helium, prepared by allowing liquid helium to boil off into an evacuated container, have been examined in the mass spectrometer. The helium prepared in this way was found to contain negligible traces of argon and neon. Mass analysis of the ions in the afterglow showed that mass 12 was the major contaminant. Since this peak decreased in prominence as the helium pressure in the chamber was raised, it is felt that the contaminant is C^+ arising from contamination of the chamber walls. Lesser peaks of masses 16, 28, and 44, which behave in similar fashion, indicate that the source of the C^+ is CO and CO_2 , which have been found by many investigators to comprise the bulk of the gas evolved during high temperature outgassing of steel.

The experimental decays observed were found to be very similar in shape to those reported by Phelps and Brown.⁽³⁾ The ambipolar diffusion constant $D_{ap} = \Lambda^2 p / \tau$ for He_2^+ measured from the decay of He_2^+ is in substantial agreement with the value of $840 \text{ cm}^2\text{-mm Hg/sec}$ obtained by Phelps and Brown.

The ratio analysis described in GA-2824⁽¹⁾ was applied to the data over the range of pressure from 2 to 4.5 mm Hg, yielding a value of approximately $1.9 \times 10^{-31} \text{ cm}^6/\text{sec}$ for the 3 body rate constant for the reaction



At higher pressures the ratio He_2^+/He^+ was no longer small compared to one. It was found that above 4.5 mm Hg the pressure in the differentially pumped chamber where the ions are accelerated and focused became appreciable, and it is thought that the He^+ ions were lost from the beam by charge transfer while the He_2^+ ions were relatively unaffected. A cross section of $5 \times 10^{-15} \text{ cm}^2$ was estimated from the data

for the effect. This value compares favorably with the measured cross section for charge transfer of $1 \times 10^{-15} \text{ cm}^2$ at 200 ev. (4)

At pressures lower than 2 mm Hg, the decay of the He^+ was dominated by diffusion losses. The ambipolar diffusion constant D_{ap} for He^+ calculated from the decay of He^+ in the low pressure limit was essentially in agreement with the value of $540 \text{ cm}^2 \text{ -mm Hg/sec}$ obtained by Phelps and Brown.

Since the value for the 3-body rate constant, β , measured in the present experiment was about 4 times larger than that measured by Phelps and Brown, (3) the ratio analysis was applied to their published data. It was found that, when their theoretical curves were used, the ratio analysis gave their result; however, when their experimental data was used, the resultant β was essentially the same as obtained in the present experiment.

A simplified theory was used to attempt choosing β by curve fitting as Phelps and Brown did. (3) The production of He^+ by $\text{He}^* + \text{He}^* \rightarrow \text{He}^+ + \text{He} + e$ was neglected as was electron-ion recombination with He^+ . Under these conditions a reasonable fit with the experimental data was obtained for $\beta = 1.3 \times 10^{-31} \text{ cm}^6/\text{sec}$.

It would appear from these data that there is some process leading to the neutralization of the primary ion at early times which has not been considered in this simple picture, but which tends to make estimates of the rate coefficient too high.

3.2 HELIUM-OXYGEN MIXTURES

In 1960, Dickinson and Sayers reported a measurement of the transfer reaction $\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}$ using the decay of the mass analyzed O^+ ion density in the afterglow of a pulsed discharge in a mixture of helium and oxygen. (5) The rate reported was $2.5 (\pm .04) \times 10^{-11} \text{ cm}^3/\text{sec}$. Our early measurements reported in GA-2824 (1) indicated a value of about $10^{-10} \text{ cm}^3/\text{sec}$. Langstroth and Hasted have reported results of a similar experiment from which they obtained a value of $1.8 (\pm 0.2) \times 10^{-12} \text{ cm}^3/\text{sec}$. (6) Thus there is a disparity in the three measurements of almost two orders of magnitude.

A sample of helium with 0.4 percent oxygen was examined with the spectrometer in an attempt to refine our measurement of the transfer reaction. Even with this small concentration of O_2 , the He^+ lost

its charge in forming O^+ and O_2^+ in times of the order of the 5 μ sec time response of the cathode follower indicating a rate for these processes of the order of at least 10^{-9} cm³/sec. The data from the sample were analyzed by taking the ratio of $[O_2^+] / [O^+] = R$ at early times when R is small by taking the ratio of $[O^+] / [O_2^+] = R'$ at late times when R' is small, and by measurement of the decay of $[O^+]$. These results reproduced in Table i show that the β derived is not constant with pressure. The values are of the order of 10^{-10} cm³/sec, but the fact that these values vary with pressure casts doubt upon the validity of the assumption that the ion signals in electronegative gases accurately represent the ion densities in the bulk of the plasma.

Table i

Pressure (mm Hg)	β (from R) (cm ³ /sec)	β (from R') (cm ³ /sec)	β (from decay of O^+) (cm ³ /sec)
0.85	5.6×10^{-10}	1.7×10^{-10}	2.5×10^{-10}
1.4	1.2×10^{-10}	1.0×10^{-10}	1.1×10^{-10}
3.1	0.8×10^{-10}	0.31×10^{-10}	0.5×10^{-10}

It is particularly interesting to note that, when using any of the methods to determine β , the product βp appears to be approximately constant. Since determinations from measurements of R and R' compensate in large part for time variations in the extraction efficiencies of the ions from the plasma that arise from sheath formation, etc., it would appear that the experiments are observing a decay of O^+ in the bulk of the plasma itself. However, the pressure independence of the decay time argues against the decay being either by a collision process or by diffusion. The actual processes involved are not yet understood.

Further work will be done toward resolving the difficulties with He-O₂ mixtures. A neon-oxygen mixture has been used in the chamber in the hopes of reducing two unknown effects that is, (1) the increase of the O₂ content of the gas sample in the chamber by virtue of preferential flow of the much lighter He out of the pinhole under free molecular flow conditions, and (2), the production of O^+ by metastable He atoms (the Ne* atoms do not have enough energy to dissociatively ionize O₂). In the tests completed to date, the decay of the signals appears to be

strongly controlled by wall effects. Neon appears to be unsuitable for a "buffer" gas since very little O^+ is formed unless the pulse length and repetition rate are increased so that appreciable dissociated oxygen is present.

3.3 HELIUM-NITROGEN

Mixtures of approximately 100:1 and 10^4 to 1 of helium and nitrogen were examined in the spectrometer. The first sample was used to detect any HeN^+ if it were formed. There was no evidence of this ion at mass 18 above the relatively small H_2O^+ impurity signal. The latter sample was used in the hope of measuring the rate for charge transfer from He^+ to N_2 yielding either N_2^+ or N^+ . The signals due to N^+ and N_2^+ were surprisingly small. It is not clear whether the sample was not well mixed in the sample bottle so that the concentration of N_2 in the discharge chamber was lower than subsequently measured by analytical mass spectroscopy, or whether the rate for the reaction is not as high as expected, and the competing reaction to form He_2^+ became of greater importance. If the latter is the case, then the rate for the dissociative charge transfer must be of the order of $5 \times 10^{-11} \text{ cm}^3/\text{sec}$.

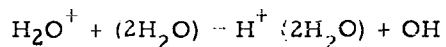
3.4 OXYGEN

The mass spectrometrically pure oxygen was found to have a slight N_2 impurity. This impurity produced an interesting mass spectrum of negative ions which showed masses up to about 230 amu. The peaks were grouped in such a manner that their identities are best fitted by combinations of nitrogen and oxygen. The positive spectrum on the other hand shows very little evidence of nitrogen-oxygen combination. NO^+ and NO_2^+ are the principal positive ions except for O^+ and O_2^+ . This indicates that oxygen and nitrogen readily combine to form rather large, stable negative ions.

3.5 WATER

Water is one of the most common contaminants in most vacuum systems and one of the hardest to entirely eliminate. A sample of water vapor from distilled water was examined in the source of the spectrometer to observe the clustering phenomenon often observed in this gas. The principal positive ions were identified as singly charged clusters of water molecules. Clustered ions with as many as 8 water molecules were observed at source pressures between 0.5 and 1.0 mm Hg. In this pressure range the cluster of 5 molecules gave

the largest signal. Trace amounts of water vapor in helium, nitrogen, and other gases used in the afterglow experiments consistently show a pattern of a rapidly decaying mass 18 peak and a mass 19 peak which apparently is fed by the reaction $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$ since it rises as the mass 18 decays and then decays very slowly (by diffusion to the walls). In pure water vapor, however, the signals for H_2O^+ , $\text{H}^+\text{H}_2\text{O}$ and $\text{H}^+\text{2H}_2\text{O}$ rose and decayed rapidly, whereas the signals for clusters of 3 to 8 molecules in size rose more slowly and decayed by diffusion. This behavior would suggest that under the conditions of the experiment a considerable amount of the water vapor was already in a di-mer state so that only a single collision with H_2O^+ would produce a 2 molecule cluster by the reaction,



In a future experiment it is hoped to raise the temperature of the water vapor in the chamber to see if these neutral di-mers can be broken up.

3.6 NITROGEN-HYDROGEN MIXTURES

It was found impossible to get pure hydrogen or deuterium with low enough water content to prevent the formation of H_3O^+ in quantities large enough to interfere with measurements of the rate for the reaction $\text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$. A palladium leak for the purification of H_2 was constructed and the hydrogen from the leak was admitted directly to the source chamber. In the early afterglow, H_3^+ was the principal ion as expected on the basis of the large rate for $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reported by Lampe, Franklin, and Field.⁽⁷⁾ In the late afterglow, however, this charge was transferred primarily to masses 17 and 29, presumably OH^+ and N_2H^+ .

A mixture of approximately 0.3 percent H_2 from the palladium leak with m. s. grade N_2 showed a very large water background signal, probably from the walls of the chamber.

A ceramic seal in the source failed during subsequent bake-out of the machine so that it has not yet been determined whether the sample or the chamber contained the water. It was found that, by cooling the chamber to about -100°C by pouring liquid N_2 over it, the water signal could be virtually eliminated. It should be possible to investigate the temperature dependence of the $\text{N}_2^+ + \text{H}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}$ reaction rate over the temperature range -190°C to $+300^\circ\text{C}$.

APPENDIX

NEW SOURCE CHAMBER

The source chamber has been modified to permit change of the electrode configuration in the chamber. This was done as shown in Fig. 3 by making the rear wall of the chamber a demountable flange sealed by a gold "O" ring. Four electrical connections were brought into the chamber by ceramic-to-metal seals.

Three electrode configurations have been studied as shown in Fig. 4. The first is similar to the one used previously with the bakeable machine. Operation with the rf applied between the plate and the can was similar to that obtained previously; however larger signals were observed when the rf was run between the rear electrodes and the can. In both cases a slight sweep field on the pusher plate was required to prevent cutoff of the signals after 50-100 μ sec. Diffusion length measurements, made using pure helium, showed an apparent shift in the effective diffusion length of the chamber with pressure. This apparent shift probably resulted from the presence of the pusher plate.

A coil electrode was found to give a uniform light density across the tube over most of the pressure region of interest, but the ion signals showed evidence of ringing in the LC coupling circuit from the pulser after the main pulse, and a sweep field was still required to prevent signal cutoff at late times.

The third arrangement operates the most reliably over the entire pressure range. The rf is applied to the 2 plates. A sweep field of 3 volts enhances the ion current at late times, but distorts measurement of diffusion length, presumably by increasing the drift velocity. Signals at late times can be seen in helium with no sweep field, but there is some mechanism operating in the source chamber which gives rise to a falsely-rapid decay of ion signals at early times (up to about 100 μ sec).

PULSED RF SOURCE

Figure 5 is a circuit diagram of a more powerful source of pulsed rf power which has been used for most of the past year. It was adapted from a circuit published in Electronic Design News, September 1958, p. 16. The output develops a 1 kv peak-to-peak rf voltage at about 30 Mc. Pulse repetition rate and pulse length are controlled by an external pulser and are variable over wide ranges.

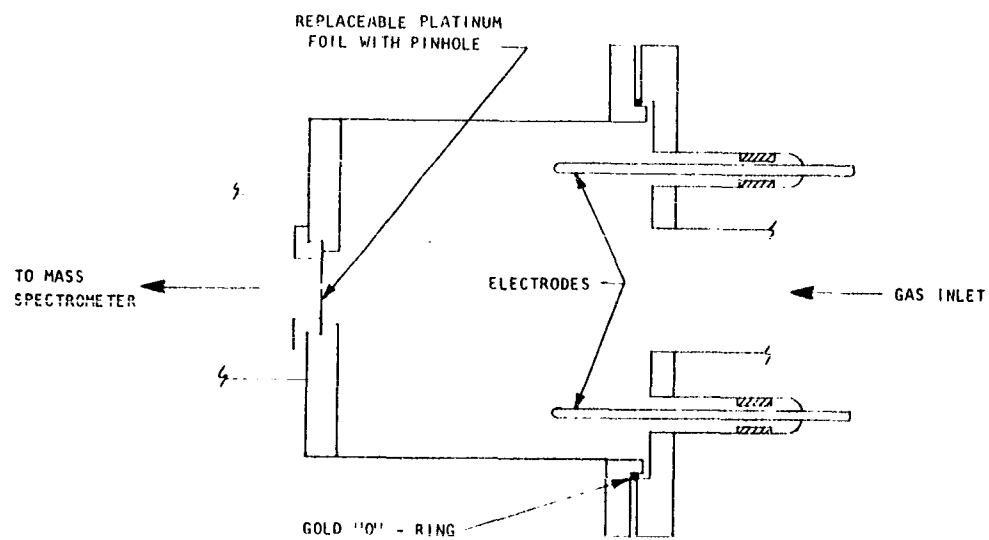


Fig. 3--Modified source chamber

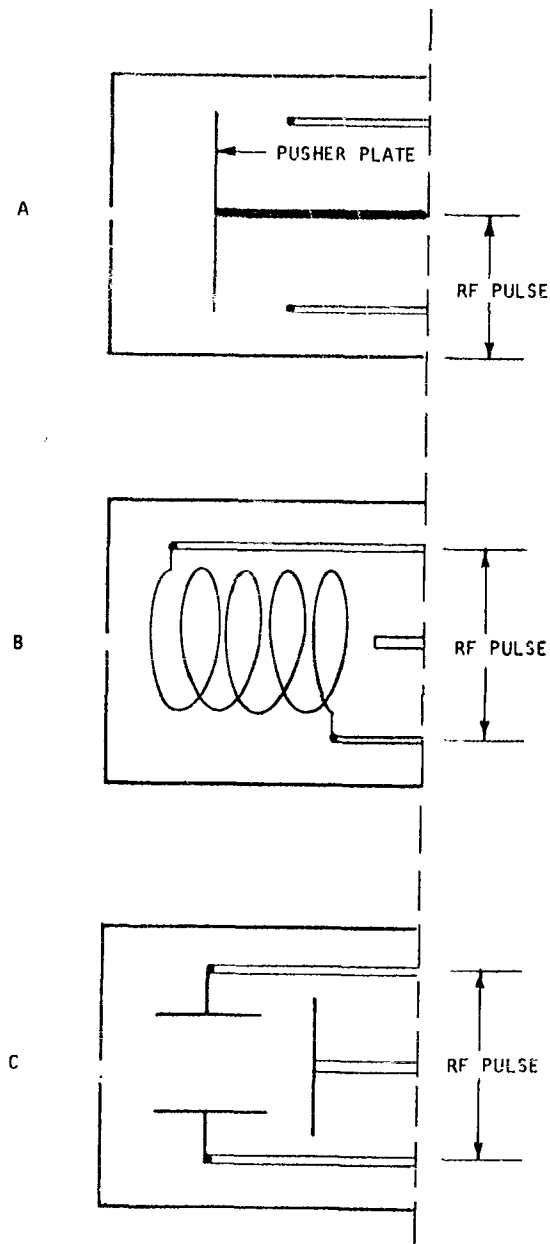


Fig. 4--Electrode configurations

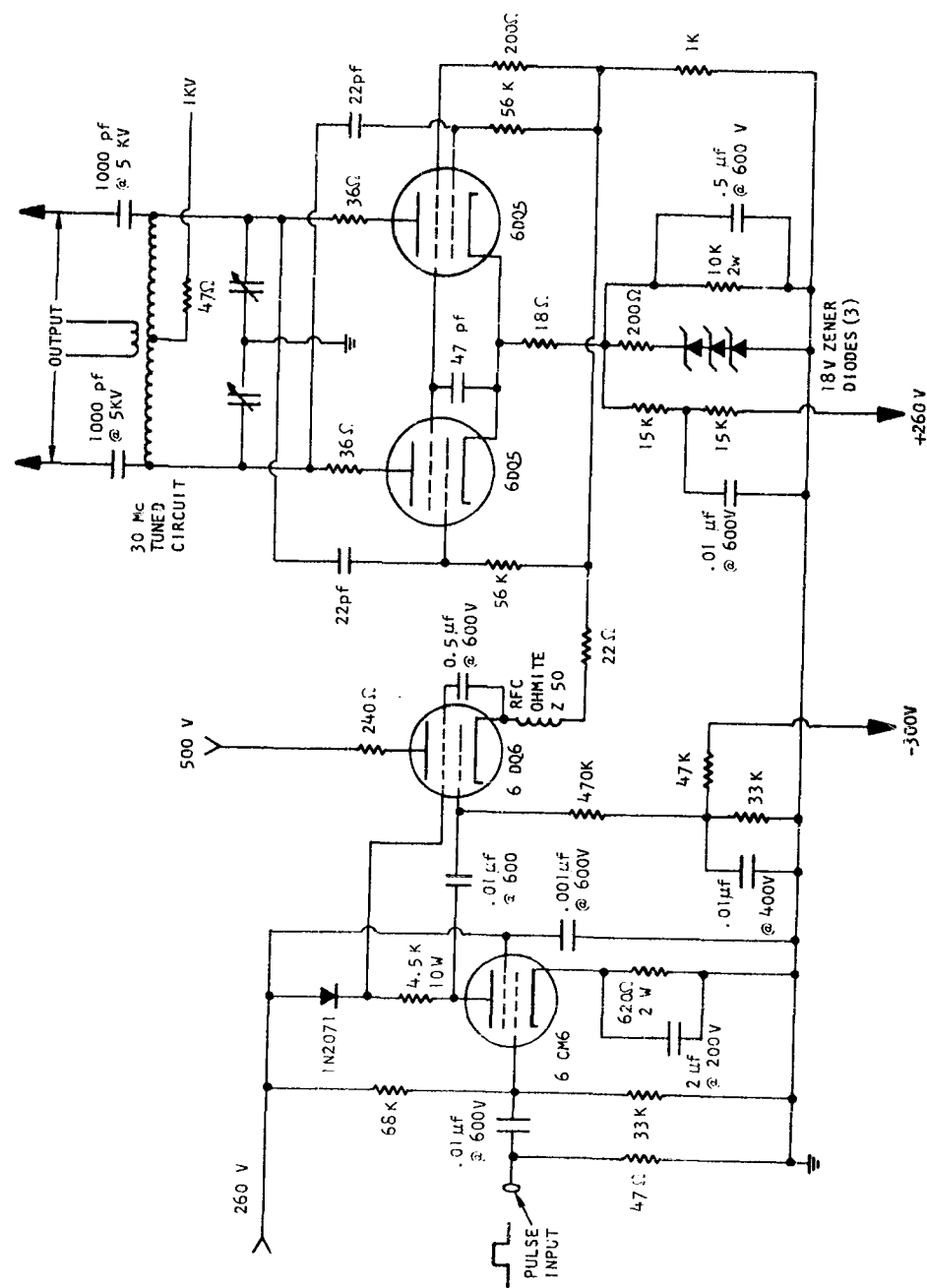


Fig. 5--Pulsed radio-frequency generator

AUTOMATIC LIQUID NITROGEN TRIP FILLER

It was necessary to have some means of automatically maintaining the level of liquid nitrogen in the traps during prolonged baking of the machine. It was found that some low-voltage, high-capacity ceramic capacitors had a leakage current, when subjected to an over-voltage, that was very sensitive to temperature in the region of liquid nitrogen temperature. An automatic filling system using a Sprague 3 v, 0.47 μ f "Hypercon" capacitor as the liquid level sensing element was built and has been in operation without failure for several months. Figure 6 shows the circuit used.

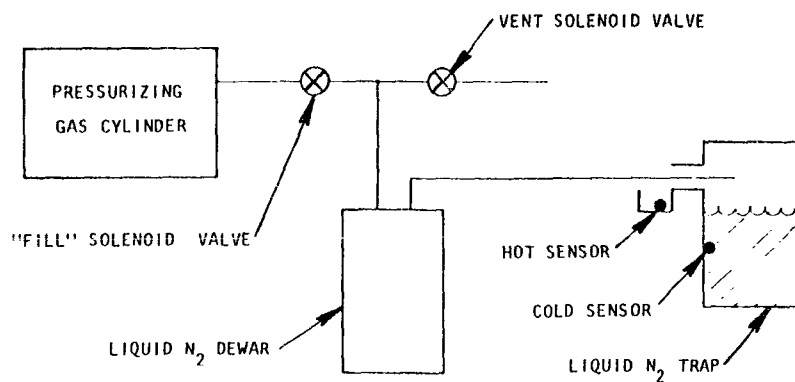
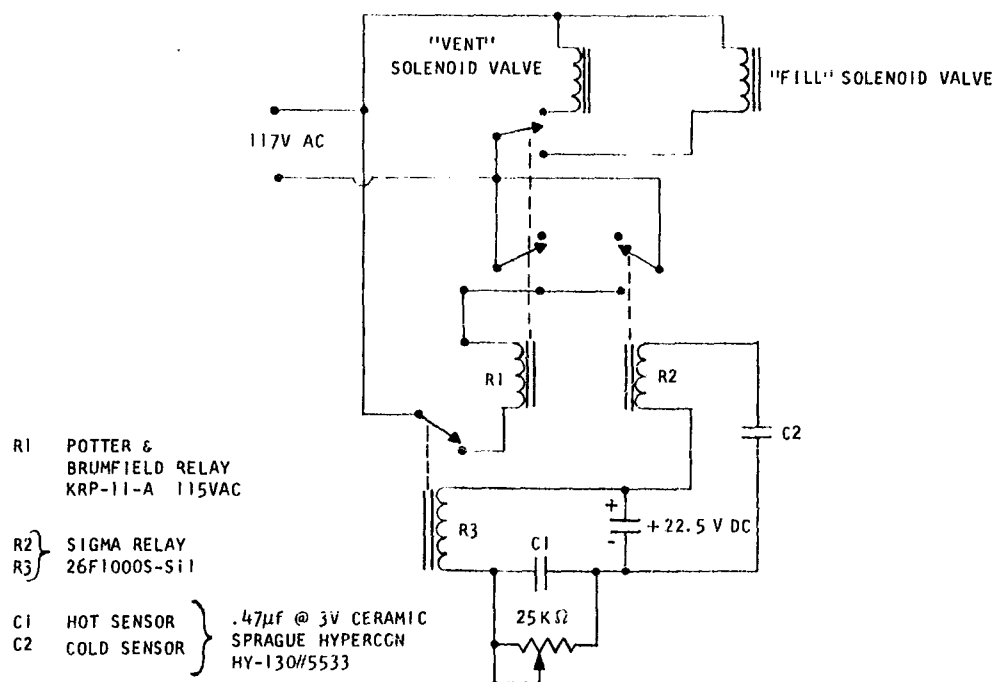


Fig. 6--Liquid nitrogen level controller

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